High Pressure Superionic Ice Phase Diagram

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Abstract

Water is one of the most common substances in the universe and is found in many different phases. At extremely high temperature and pressure, water ice forms a superionic phase (SI) in which the water molecules dissociate into ions, with the oxygen ions forming a crystal lattice structure and the hydrogen ions flowing through the lattice like a liquid. Due to the extreme conditions, superionic ice has very different physical and chemical properties compared to water and ice at ambient condition. Moreover, the nuclear quantum effects at this pressure are significant and may change the phase diagram dramatically. Theoretical studies indicated that superionic ice may exist in the mantle of ice-rich planets such as Uranus and Neptune, and play a crucial role to explain the unusual non-dipolar, non-axisymmetric, magnetic fields on those planets. Despite the importance of the superionic phase, its properties are largely unknown. In this thesis, we present a first-principle study of the high pressure superionic ice phase, with an emphasis on important physical and chemical properties, such as electronic structure and conductivity. Our goal in this research is to understand the superionic phase diagram over a wide range of pressures and temperature, and provide important inputs for the interior model of ice-rich planets.

This thesis contains three main results. Firstly, we systematically explore the superionic phase diagram and carefully study its physical and chemical properties. As a result of this investigation, we find that superionic ice exists in three different phases differentiating from each other in the structure of the oxygen sublattice. One phase is the BCC-SI phase, which has BCC oxygen sublattice and has been predicted
by several groups[1, 2]. We find the BCC-SI phase is stable up to about 250 GPa. At higher pressure, BCC-SI transforms via a first order transition to the CP-SI phase. The oxygens form close-packed structures in this phase. CP-SI has also been predicted by other authors [3], though our predicted transition pressure is significantly higher. Finally, we find a third SI phase, P21/c-SI, which would exist at even higher pressure and it is predicted here for the first time. Superionic phases have also been found in other substances, and three types of crystal to superionic phase transition can be classified by the ionic conductivity. AgI, for example, has type-I transition, in which the ionic conductivity changes abruptly during the phase transition [4]. On the other hand, the type-II transition, such as in CaF$_2$, has a gradually changing ionic conductivity. There is also a type-III transition which is characterized by Arrhenius behavior but we do not consider it here. We found that superionic ice can have both types of crystal to superionic transition. The ice-X to BCC-SI and $P21/c$ to $P21/c - SI$ transitions are type-II transitions, while the crystal to CP-SI transition is a type-I transition. Our findings result from ab-initio molecular dynamics simulations in which the potential energy surface for the ions is derived from the electronic ground state within DFT theory. This is important because in DFT theory, molecular dissociation is not assumed a priori but may result from the minimization of the electronic energy. Thus DFT has predictive power across a vast range of temperatures and pressures.

The second main result is associated to the nuclear quantum effects (NQE). Due to the high pressure and the light mass of hydrogen, the zero-point energy (ZPE) in high pressure ice is rather large. Previous studies showed that the excess kinetic energy due to quantum fluctuation can be as large as 1eV per water molecule in high pressure ice phases, compared to about 150meV ZPE in normal ice. High pressure ice phase’s ZPE is significantly larger than the latent heat associated to the phase change, which is around 0.2eV per molecule. Therefore it is interesting to study how nuclear quantum effects affect the phase diagram. Here we use the imaginary-time path integral technique to study the nuclear quantum effects. We find the NQE
changes the SI ice phase boundaries significantly. Compared to the classical results, NQE make CP-SI phase more stable and increases the transition pressure from 1.4-1.6TPa to 1.6-1.75TPa. Meanwhile, NQE reduces the melting temperature of the hydrogen sublattice by about 200 K in CP-like solid phases, but has little impact on the melting temperature of P21/c. Although the impact from NQE is significant, it does not change the phase diagram qualitatively. In addition, we show that the NQE on the SI phase boundary can be explained by thermodynamic perturbation theory to the lowest order. Lastly, the difference in the transition pressure estimate between PIMD and quasi-harmonic theory suggests that the anharmonicity is strong in SI phases and impacts significantly on the phase boundaries.

The third main result is the change in chemical bonds and the band structure, and the approach to metalization due to pressure. We studied the chemical bonding and the electronic structures of high pressure superionic phases. We computed the distribution of maximally localized Wannier functions centers and showed evidence that the chemical bonding in high pressure ice phases is dominated by ionic interactions. This is very different from the low pressure phases, where the water molecules are intact and the intermolecular interactions are dominated by hydrogen bonds. In addition, we found the band gap decreases from BCC-SI to CP-SI, but increases from CP-SI to P21/c-SI. This is likely due to the $sp$ hybridization in high pressure superionic phases. In all of our simulations, we found the superionic ice phases are always electronically insulating.

The thesis is organized as follows. In Chapter 1, we briefly recall some important physical and chemical properties of water and ice and other related substances that are relevant to our research. In Chapter 2, we review previous studies on high pressure ionic ice phases. In Chapter 3, we present our classical simulation results and give a detailed analysis of the superionic phase diagram. In Chapter 4, we discuss the nuclear quantum effects and its impacts on superionic phases boundaries. In the last chapter we discuss the pressure effects on the chemical bonding and electronic
structure.
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Chapter 1

Introduction

Water is a very common substance in the universe. It has been found on many planets in the solar system. Besides its essential importance for life, water and related phases such as various forms of ice stand out for their atypical behavior and broad interest in many fields. In the field of high pressure physics, understanding the properties of ice under extreme pressure and temperature condition is particularly important for its impact on planetary science.

Water in condensed phase, either solid (ice) or liquid, is one of the simplest and most common substances on earth. It is transparent, odorless and tasteless, people usually think water is a very ordinary type of liquid. However, water is one of the most anomalous liquids. It has many special properties like a large heat capacity, a high boiling temperature, and exhibits a density maximum at 4 Celsius under standard pressure. In fact, these properties are crucial for life forms on earth. For example, the large heat capacity of the oceans makes them heat reservoirs, which reduce the temperature fluctuations. The density maximum at 4 Celsius, above the freezing temperature, is important to keep life forms survive below the frozen surface of oceans, lakes, and rivers.
Most of these unusual properties are due to the hydrogen bonds network (HBN) in water and ice. A hydrogen bond between two neighboring water molecules occurs when a positively charged hydrogen of one molecule is near a negatively charged oxygen of the other molecule. The hydrogen bond is relatively strong, and affects the structure of water significantly. One consequence is that water has an extremely complex phase diagram. As shown in Fig 1.1, there are more than ten different known phases for water and ice across a vast range of temperatures and pressures. At low pressure, all water and ice phases are characterized by the tetrahedral HBN. Due to the strong hydrogen bonding, the stability of the ice phase is largely determined by the formation of a regular tetrahedral network of hydrogen bonds. The local environment of water molecule obeys the so called ice rules, which state that each water molecule has four tetrahedrally arranged hydrogen-bonded neighbours, and for each oxygen atom, there are two near hydrogens and two far hydrogens. The large number of ice phases is due to the large number of different network topologies. All these different network topologies are still regular, tetrahedral and the hydrogens satisfy the ice rules.
Figure 1.1: The pressure-temperature phase diagram of water and ice [5] It summerizes the known water and ice phases up to 1000 K and 10 TPa. Note that the superionic phases exist at temperature higher than 1400 K and thus are not shown in this figure. Also, some of the newly found zero temperature phases such as $P3_{1}21$ and $P2\bar{1}/c$ are not shown in this figure.

The high pressure ice phases we considered in this thesis are very different from the phases characterized by the HBN. At sufficiently high pressure, as the distance between nearest oxygens are greatly compressed, the hydrogen will be halfway between two neighboring oxygens and the water molecules can no longer be identified. In these high pressure phases the covalently bonded molecular units and HBN are replaced by ionic bonds. As the pressure increases the first ice structure that undergoes the transition from HBN to ionic based structure is ice-X. In this phase the oxygen ions form a BCC lattice, and the hydrogen ions sit in the middle of two nearest oxygens.
The structure is shown in Fig 1.2. At even higher pressure there are plenty of other phases that had been predicted from theoretical simulations and are all characterized by ionic bonds. Ionic ice structures have many special properties and at sufficiently high temperature the hydrogen ions may become diffusive and form superionic phases.

Figure 1.2: The structure of ice-X The red and gray balls indicate oxygens and hydrogens, receptively. The stick indicates the ionic bond between oxygen and hydrogen ions. ice-X has an body-center cubic oxygen sublattic.

At high pressure, the phase diagram is even more complicated. In the past, several groups reported new ice structures at zero temperature and pressures higher than 50 GPa. These groups used DFT calculations to predict high pressure ice phase at zero K and have suggested a complex sequence of stable phases as one increases pressure with features such as the zero-point energy (ZPE) affecting the relative stability significantly. These phases have very different properties that do not exist in the low pressure water and ice phases. Here we list a few important properties that motivate our research. Firstly, when the pressure is higher than 50GPa, the behavior of the hydrogens is closer to that of bare ions than to that of neutral atoms. The water molecules do not exist any more and the hydrogen ions move midway between two
neighboring oxygen ions. At even higher pressure, as oxygen ions move closer to each other, the O-H-O linkage becomes more and more nonlinear at H. Due to the drastic change of the structure, it is important to understand how this affects the chemical and physical properties such as chemical bonding and electronic structure. Secondly, there is a clear pattern among these high pressure ice structures. Under increasing pressure the oxygen sublattice changes from BCC to distorted HCP/FCC, and to asymmetric structures like P21/c. At high pressure, the enthalpy is dominated by the pressure times volume term. As one increases the pressure, the enthalpy will favour the structures with higher density. It is clear that close packed structure like HCP and FCC are denser than BCC. But why does P21/c, a structure with lower symmetry, have lower enthalpy than HCP/FCC? In addition, at zero temperature there are many high pressure phases that have similar energies. And interestingly many of these structures have similar oxygen sublattice and their differences come mainly from the hydrogen sublattice. We want to understand whether these different zero temperature structures still exist at higher temperature and how does the phase diagram look like at higher temperature. Last but not least, at extremely high pressure, hydrogen atoms have large ZPE, whose magnitude is larger than the free energy deference between different structures. We want to investigate how does ZPE affect the phase diagram. None of these questions have been studied before and we try to answer some of them in this thesis.

The high pressure ice phase diagram has important implications in planetary physics. Besides Earth, water is abundant on other planets int the solar system like Uranus and Neptune. Planetary physicists observed that Uranus and Neptune have a very unusual magnetic field. Their magnetic field has a large tilt with respect to the rotational poles. The angle between the magnetic axis and the rotational axis is of 49 degrees in Uranus and of 47 degrees in Neptune. The magnetic field is also not centered on the core of the planet. Uranus and Neptune’s magnetic fields are centered away from the planet center by about 1/3 and 1/2 of the planet radius, respectively.
Simulation results [11] indicate that a possible explanation of this unusual magnetic field is due to the existence of two conductive layers in the mantle of these planets that have very different stability to convection. Water ice may play an important role in the formation of the two conductive layers. Simulation results indicate that at pressure higher than 50 GPa and temperature higher than 3500 K, water is dissociated and resembles a two-component ionic liquid [1], which is electronically insulating but ionically conducting. At a lower temperature between 2000 K to 3500 K, though hydrogen ions are still diffusive, oxygen ions form a lattice structure. This phase is known as the superionic (SI) phase. Owing to the liquid like hydrogen, SI phase is also ionically conducting. The conductive SI phase has similar conductivity than the ionic liquid water, however, SI phase has a lower heat absorption rate than ionic water. The different heat absorption rate helps the formation of a stably stratified conductive fluid regions in ice-giants, which may explain the formation of ice-giants’ unique non-dipolar, non-axisymmetric magnetic fields. Therefore, understanding the SI phases is crucial to understand the inner structure of ice-giants.

The nuclear quantum effect (NQE) of hydrogen and hydrides under extremely high pressure also attracts a lot of attentions. Under high pressure where the inter-atom space is largely compressed, light atoms such as hydrogens show very strong NQE that may change the physical properties of the material dramatically. Simulation results showed that in systems such as liquid hydrogen, the melting point of hydrogen are lower by about 100 K quantum mechanically than classically [12]. Similar results are also reported in other systems made by light elements such as dense lithium [13]. In the water ice system, several theoretical studies showed that at zero temperature NQE changed the relative stability of high pressure ice phases significantly [6]. Some phases such as the C2 and P21 that are stable in the classical limit no longer have regions of thermodynamic stability, while other unstable structures in the classical limit, such as P21/c, become stable phases when NQE is considered. However, there is not any study of NQE on the finite temperature phases. We want to understand how does
NQE affect high pressure ice phases at finite temperature. Another interesting topic related to high pressure hydrogen and hydrides systems is the possible metallization at high pressure. Metallic hydrogen was predicted to exist under high pressure by Eugene Winger and Hillard Bell Huntington in 1935. And various theoretical studies supported it although the predicted transition pressure with modern technology is much higher than the original one. Recently there has been some experimental evidence showing that metallic hydrogen may exist a pressure of around 495 GPa [14]. The metallic hydrogen may also be a high temperature superconductor due to the high frequency phonon and strong coupling between conduction electrons and lattice vibrations. Although the superconducting hydrogen has not been confirmed by experiments, a related hydrides, sulfur hydride, has been shown to be superconducting at about 90 GPa with a surprisingly high critical temperature of about 150 K. The critical temperature further increases to 190 K at 200 GPa [15]. Further studies showed the superconductivity is most likely due to $\text{H}_3\text{S}$, which is formed from $\text{H}_2\text{S}$ under high pressure. This raises an interesting question of whether water ice can also be metallic or even superconducting at high pressure. In our research we do not find any evidence of metallic ice. But since in our simulation we always assume homogeneous phases and did not consider different stoichiometries, our study does not eliminate the possibility that oxygen hydrides with different stoichiometry originating from the decomposition of $\text{H}_2\text{O}$ could be metallic or even superconducting. We leave this question to future studies.
Chapter 2

Review of Ionic Ice phases at High Pressure

In this section, we review previous studies on ionic ice phases at high pressures. Ionic ice phases exist at pressures higher than 50 GPa. Due to the difficulties to reach such high pressure experimentally, most studies of high pressure ice are based on first principles simulations. More than ten stable and meta stable zero temperature structures were predicted by several authors. At finite temperature, simulation results indicate that at pressure higher than 50 GPa and temperature higher than 2000 K, water ice transforms to BCC-SI. Recently, the existence of BCC-SI was confirmed experimentally [16].

2.1 Ionic ice phases at Zero temperature

Studying high pressure ice phases experimentally is difficult. A static diamond anvil cell can generate accurate data however, to date, no experiments have reached pressures beyond 190 GPa for water ice systems. Shock wave experiments can access higher pressures, but heat the sample significantly. Only recently, Marius Millot et al [16] used a combination of static precompression and laser-driven shock compression
to reach about 190 GPa at relatively low temperature. They documented evidences that confirm the existence of superionic ice phases. However, reaching an even higher pressure range has not been possible to date. Due to the lack of experimental data, most works have been based on ab initio, or first principles approaches. This type of ab initio approach is based on physical laws and does not need parameter fitting. Therefore, one could use this technique in absence of empirical data. More importantly, many studies in the past showed that ab initio studies could predict results in satisfactory agreement with experiment.

A lot of effort has been made on the understanding of the behaviour of high pressure water and ice. Several groups studied the zero temperature structure. Classically at zero temperature, finding the stable structure is equivalent to finding the configuration having minimum energy. Finding the global minimum of the enthalpy is a non-convex optimization problem, thus it cannot be solved with certainty. Many searching algorithms including variable cell molecular dynamics, simulated annealing, and genetic algorithm, have been proposed and more than 10 stable or meta-stable structures are found between 50 GPa and 5 TPa. The most recent and comprehensive zero temperature phase diagram is shown in Fig 2.1. In this figure the nuclear quantum effects are included via quasi-harmonic approximation. The stable structures from lowest pressure to highest pressure are ice-X, Pbcm, Pbca, P3121, Pcca, and P21/c. Among them, ice-X has a BCC oxygen sublattice. Pbcm, Pbca, P3121 and Pcca have similar oxygen sublattice, which are distorted close-packed structures. Lastly, P21c is a structure with lower symmetry, but interestingly, the density of P21c is higher than other close-packed structures.
Figure 2.1: Variation of the enthalpies with pressure of high-pressure water-ice structures. This figure summarizes the known zero temperature stable structures at pressures higher than 0.5 TPa [6].

### 2.2 High pressure superionic ice phases at finite temperature

At high pressure and temperature, ice transforms to superionic phases, in which the hydrogen ions become diffusive, while oxygen ions are still on lattice sites. In the superionic phase the system retains a large electronic energy gap, thus it is electronically insulating but ionically conducting. Planetary physics models suggest that superion-
inc ice may exist in the mantle of some large ice planets like Uranus and Neptune. The existence of conductive superionic phases may help to explain the non-dipolar and non-axisymmetric magnetic fields discovered by NASA’s Voyager 2 spacecraft in the 1980’s [17] in these planets. The first prediction of high pressure superionic ice was made by Demontis et al. [18] in 1988 with a simple ionic model. Later with ab-initio simulation technology and better predicitive power, Cavazzoni et al. [1] did a more careful research on the superionic ice phase diagram. They predicted a transition from ice-X to the BCC-SI phase at about 150 GPa and 2000 K. Recently, a group suggested that another superionic phase with FCC oxygen sublattice exists at pressures higher than 100 GPa [3]. At the same time, several groups also tried to prove the existence of superionic ice experimentally. Sugimura et al. [19] claimed an observed superionic conduction at about 50 GPa and 750 K in ice. However, they did not distinguish between electronic conductivity and ionic conductivity. More recently, Marius Millot et al. [16] proved the existence of BCC-SI phase experimentally. In their experiment the authors measured both of the total conductivity and the electronic conductivity and confirmed the ionic conductivity in superionic ice phases. Their transition pressure is also in agreement with Cavazzoni’s prediction. However, their result did not support the existence of FCC-SI phase at 190 GPa.

Most of the previous theoretical studies on superionic ice phases assumed a known oxygen sublattice and the system with a fixed supercell. However, this assumption imposed very strict constraints on the searching space and may bias to certain structures that fit to the super cell. To overcome this problem, we use the Parrinello-Rahman molecular dynamics (PRMD) technique that was not used for searching superionic ice phases before. PRMD allows both the volume and the shape of the supercell to change. It has been successfully applied to search for new crystalline structures [20, 21]. It is known that PRMD may have hysteresis effects so one may need to overpressurize the system to induce a structural transformation. However, we find that in the superionic phase the diffusive hydrogen ions help to alleviate this
kinetic effect and the uncertainty of transition pressure and temperature due to hysteresis effect is small and allows us to locate the phase boundaries with modest error bars.

With PRMD, we numerically mapped out the high pressure phase diagram of ice from 50 GPa to 2.5 TPa and up to 3500K. We report a comprehensive phase diagram of SI ice, with the numerical evidence for a new SI phase that is more stable than the FCC-SI phase at pressures higher than 1.6 TPa and which stays stable up to the highest pressures we consider (2.5 TPa). This new phase, which we call the P21/c-SI phase, has the P21/c monoclinic oxygen sublattice that is similar to the zero-temperature counterparts P21 and P21/c. We also suggest evidence that other less symmetrical close-packed structures such as double hexagonal close-packed (dHCP) may be competitive with the FCC-SI phase. We discover that higher pressure phases have lower transition temperatures. In addition, we measure the diffusivity and conductivity in these phases. The diffusive hydrogen in the P21/c-SI phase shows strong anisotropic behaviour and forms a quasi two-dimensional (2D) liquid-like structure. The sites occupied most frequently by the diffusing hydrogen do not coincide with the equilibrium sites in the crystalline regime, which indicates strong anharmonicity. The study of the variation of the conductivity with temperature indicates a very different nature of the solid to FCC-SI transition compared with the solid to P21/c-SI transition. The transition to superionic phase can be classified in three categories, "type-I, type-II, and type-III". The latter is characterized by Arrhenius behavior [22] and is not relevant here. Type-I transition are characterized by an abrupt change of the diffusion coefficient at the transition temperature. The diffusivity in superionic phase is several orders of magnitude higher than the diffusivity in solid phase. In type-II transitions the diffusivity changes continuously but second order derivatives such as the heat capacity have a shape change at the transition boundary [22]. In the past several superionic materials were found to be either type-I or type-II. For high pressure water ice, we find that depending on the thermodynamic
condition it can be either type-I or type-II. The ionic conductivity changes abruptly across the solid to FCC-SI phase boundary, while it changes continuously across the solid to P21/c-SI phase boundary.

In addition, we investigate the nuclear quantum effects in the SI phases of ice. NQE has been found to have influence on high pressure phase transitions. J Chen et al studied the NQE on high pressure hydrogen and found a considerably lower melting temperature of hydrogen when NQE is considered [12]. Y Feng et al found a similar result in dense lithium where the NQE also helps to reduce the melting temperature, but only by about 15K [13]. In our studied we focused on how does NQE affect the phase boundary between CP-SI phase and P21/c-SI phase, as well as whether it changes the melting temperature of the hydrogen sublattice in these two phases. We find the transition pressure from CP-SI to P21/c-SI is at about 200 GPa higher pressure when treated quantum mechanically than classically. This result is consistent with low temperature predictions with quasi-harmonic approximation by Pickard et al [6]. We also find the melting temperature of hydrogen sublattice in CP-SI phase is lower by about 200 K when NQE is considered. However, within our calculation accuracy, the melting temperature of P21/c-SI phase does not change.
Chapter 3

The Phase Diagram of High
Pressure Ice

In this chapter, we discuss the high pressure superionic ice phases and their properties in more details. First, we discuss the simulation results of the high pressure superionic ice phase transition. A new superionic phase, $P2_1/c$-SI phase, is identified. We discuss the physical properties of this new phase. The chemical properties and electronic structures are discussed in Chapter 5. In order to use a larger time step, we use the heavy water molecule (D$_2$O) in most of our classical simulations. In the classical limit, D$_2$O has the same static properties as H$_2$O. Due to the light weighted hydrogen/deuterium atoms in water molecule, it is known that the nuclear quantum effect (NQE) may affect the property of water and ice significantly. This effect is even more important under high pressure, since the structure is highly compressed and the distances between nearest atoms are greatly reduced. However, in this section I only discuss the phases in the classical limit. I leave the NQE to the next chapter.

In this chapter, we report a comprehensive phase diagram of superionic ice, with the numerical evidence for a new superionic phase that is more stable than the CP-like superionic phase at pressures higher than 1.6 TPa and which stays stable up to the highest pressures we considered ($\approx 2.5$ TPa). This new phase, which we call
the P2$_1$/c-SI phase, has the P2$_1$/c monoclinic oxygen sublattice which is similar to the zero-temperature counterparts P2$_1$ and P2$_1$/c [23, 6]. We discover that higher pressure phases have lower melting temperature of H sublattice. In addition, we measure the diffusivity and conductivity in these phases. Compared to other phases, the P2$_1$/c-SI phase has a smaller diffusion coefficient due to its higher packing fraction. The diffusive hydrogen in the P2$_1$/c superionic phase shows strong anisotropic behavior and forms a quasi-2D liquid-like system. The sites occupied most frequently by the diffusing D do not coincide with the equilibrium sites in the crystalline regime, which indicates strong anharmonicity. In addition to identifying the new stable sublattices, we find a number of unique properties of the superionic phases. In all of the superionic phases D and O appear as ions. To better quantify the charges on D and O, we compute the Born effective charges and find that they have average values close to +1.2 for D and -2.4 for O with minor fluctuations around the average in the CP-SI and P2$_1$/c-SI phases. The difference between the Born effective charges and the nominal charges originates from the electronic contribution. Via Nernst-Einstein relations, we estimate the average ionic conductivity of the superionic phases as $\sim$90 S/cm (BCC-SI, D$_2$O, 200 GPa, 2500 K), $\sim$120 S/cm (CP-SI, D$_2$O, 1.3 TPa, 2000 K) and $\sim$60 S/cm (P2$_1$/c-SI, D$_2$O, 1.9 TPa, 2500 K). The study of the variation of the conductivity with temperature indicates a very different nature of the solid to CP-SI transition compared to the solid to P2$_1$/c-SI transition. We find the ionic conductivity changes abruptly across the solid to CP-SI phase boundary, while it changes continuously across the solid to P2$_1$/c-SI phase boundary.

3.1 Simulation method

In this study, we apply first principles constant pressure molecular dynamics (NPT-AIMD) with the PBE density functional and norm conserving pseudo-potentials [24, 25] to study the superionic phases. The mathematical details of the simulation meth-
ods can be found in Appendix 1. We carefully checked that the adopted pseudopotentials for O and H work at high pressure. For O, the p channel is the local reference and the pseudopotential includes a nonlocal s channel. The H pseudopotential is local and regular at the origin. The transferability of these pseudopotentials can be gauged by comparing the ground-state radial atomic pseudowavefunction $u(r) = rR(r)$ ($\int_0^\infty u(r)^2 \, dr = 1$) and its corresponding all electron (AE) counterpart. For O, we find that the 2s and 2p radial atomic pseudowavefunctions coincide with their AE counterparts when $r$ is greater or equal to 1.1 Bohr, while for H the 1s radial pseudowavefunction is essentially indistinguishable from its non-pseudized counterpart all the way to the origin (where the pseudized $R(r)$ lacks the cusp of the non-pseudized $R(r)$). See Fig 3.1 for the details. The regions in which the pseudowavefunctions differ from their AE counterparts define the atomic cores. In our simulated structures, the minimum distance between two oxygens never goes below 2.8 Bohr, that between O and H never goes below 1.5 Bohr and that between two H never goes below 1.4 Bohr. We infer that the adopted pseudopotentials should be adequate since core overlap never occurs at the thermodynamic conditions of our simulations. As a further test we checked that with our adopted pseudopotentials the predicted phase boundaries between high pressure ices at zero T coincide with those reported in ref. [6], which used ultrasoft pseudopotentials, when ZPE is excluded.
Figure 3.1: **Validation of the pseudopotential.** This figure is taken from ref [7]. The dash lines indicate the wavefunction with true potential, while the solid lines indicate the pseudo wavefunction.

The temperature is controlled by a single Nose-Hoover thermostat. Since the anharmonicity is very strong in our system, we do not need to use the more complex Nose-Hoover chain thermostat. We used gamma point sampling and relatively large simulation boxes containing at least 108 molecules. We carefully checked that the relative phase stability does not change when we use more extensive k-point sampling. In order to use a larger time step, we used the heavy water molecule (D$_2$O) in most of our simulations. In the classical limit, D$_2$O has the same static properties as H$_2$O.

We use a plane wave energy cutoff of 1500 eV, with the effective constant energy cut-off technique [26] which adjusts the number of plane-waves used in the DFT calculation as the box size and shape changes. It has been shown that the total energy converges faster with constant energy cut-off than with constant number of plane waves [27]. Therefore, when the simulation box changes its shape, it is preferable to keep the energy cut-off constant. In the implementation, the electronic wave function is expanded with a fixed number of plane waves. Each plane wave function has a
variable weight that can vary between 1 and 0 in order to mimic constant energy cut-off. At the beginning, the number of plane waves is determined by a reference cell that is always larger than the real simulation box during the simulation, thus it can cover the Hilbert space up to the energy cut-off. During the simulation, the weight of plane waves that cross the energy cut-off drops rapidly but continuously to zero. To avoid wasting CPU time, one should choose the reference cell close to the real simulation box such that the total number of plane waves is not too large compared to the active number.

In the simulation, we prepared a BCC superionic phase at 200 GPa and 2200 K as our initial state. This temperature is high enough to keep the system in the superionic phase in the pressure range that we covered. The pressure is increased in increments of 40 GPa from 200 GPa to 400 GPa, and increased in increments of 100 GPa from 400 GPa to 1.3 TPa. Given the high diffusivity of the deuterium, the system reaches equilibrium rapidly; the potential energy of the system converges in less than 0.2 ps. At each step we wait for at least 1 ps to ensure equilibration. At 1.3 TPa, the size of the reference cell is almost twice as big as the real simulation box. For reasons of computational efficiency, we restart our simulation at 1.3 TPa and 1900 K with a smaller reference box. This simulation starts from the FCC superionic phase, which was suggested to be the most stable phase under this thermodynamic condition [3]. We increase 100 GPa each time from 1.3 TPa to 2.5 TPa and wait at least 2 ps to equilibrate at each step. Due to the kinetic effects, NPT-AIMD may skip some intermediate phases [20, 21]. Therefore, we also explored the superionic phase with different initial conditions to check for any intermediate states. We initialized our system to dHCP, which is a competing phase with FCC, as well as many of the previously suggested zero-temperature structures at different pressures including Pbcm, P3_{1}21 and Pcca [6]. We then heated the system at a fixed pressure until the hydrogen sublattice melted. The equilibrium phase boundary between different superionic phases and between the solid and superionic phases are estimated via
single-phase simulations: we vary either the temperature or the pressures such that the system can transform from one structure to another reversibly, while keeping other thermodynamic variables fixed. Our use of a flexible cell method minimizes the effects of hysteresis allowing for a more accurate identification of phase boundaries.

3.2 Results

3.2.1 Superionic ice phase diagram

We systematically investigate the superionic phase diagram of heavy ice (D$_2$O) from 200 GPa to 2.5 TPa. In the classical limit, D$_2$O has the same static properties as H$_2$O and thus we use H and D interchangeably. However when studying dynamic properties like the conductivity or the mobility H and D will behave differently. We estimated the conductivity and mobility with D in our study. We apply the constant pressure Parrinello-Rahman dynamics that allows the volume and the shape of the cell to vary with time [28]. Using single-phase simulations, we are able to map out the transitions between different superionic phases as well as the hydrogen melting curve in the comprehensive phase diagram. The transition pressure and temperature are represented as [$p_{low}$, $p_{high}$] and [$T_{low}$, $T_{high}$] respectively.

At 2200 K, we find a reversible transition from the BCC-SI phase to a superionic phase with the close-packed oxygen sublattice at [220 GPa, 280 GPa]. This transition pressure does not change appreciably at different temperatures. We find the transition pressure is [200 GPa, 260 GPa] at 3000 K. The pressure we find is close to the transition pressure from Ice-X to Pbcm [29] at zero K. At pressures higher than 280 GPa, we find that other less symmetrical close-packed structures may be competitive: the oxygen sublattice can interconvert between different close-packed structures, which include HCP (AB), dHCP (ABAC), and complex-HCP (ABABCA-CABCBC). The characters in the aforementioned parentheses indicate the stacking layer sequence of each structure, which is the only difference. Since these close-packed
structures are very similar and can transform from one structure to another in our simulations, we are not able to distinguish their relative stability. For that reason, we will not distinguish different close-packed structures and will refer to this superionic phase as the close-packed superionic phase (CP-SI).

A transition from BCC-SI to superionic phase with FCC oxygen sublattice (FCC-SI) was suggested to occur at significantly lower pressure of about 100 GPa by free-energy calculations in the NVT ensemble [3]. However, FCC-SI is not obtained spontaneously in any of our reversible transitions. In order to test the stability of the FCC-SI phase, we performed a simulation in which the system was initially placed in the FCC-SI phase. Figure 3.3 shows the simulation path we performed. Initially, at 1.5 TPa, the FCC-SI is in a metastable state. As the pressure is increased to 1.6 TPa, the system spontaneously transit to the P21/c-SI phase. However, when the pressure is reduced to 1.4 TPa, the system transit to the superionic phase with DHCP oxygen sublattice instead of FCC-SI. The occurrence of a transition between two SI structures at about 100 GPa does not seem to be confirmed in a recent experiment [16] neither. Free-energy calculations need prior knowledge of the two phases and uses a fixed simulation cell that may bias to certain structures. The suggested FCC-SI phase disagrees with our results, previous zero-K simulation results, and experimental results.

As one can see from Figure 3.3, the hysteresis effect is small, and the uncertainty of the transition pressure is less than 200 GPa. At 1900 K, the P21/c superionic phase is stable up to the highest pressure we considered. The simulations starting from the dHCP and other zero-temperature structures also converge to either the CP-SI phase or the P21/c-SI phase we found after the hydrogen sublattice melts. The details of the simulation results can be found in Fig 3.2.

At 1.6 TPa and 1900 K, the CP sublattice becomes mechanically unstable and it changes to a new superionic phase, which we call the P21/c-SI phase. The oxygen sublattice of the new P21/c-SI phase has higher symmetry than the oxygen sublattice
of the static (0 K) structures $P2_1$ and $P2_1/c$, to which it is very close. We also estimate the lower bound of the transition pressure, which is around 1.4 TPa by running the reverse process. The inset of Fig 3.2 summarizes the reversible process we performed. It is interesting to note that the reversible process returns to $d$HCP but not FCC.
Figure 3.2: **The detailed superionic phase diagram.** The hydrogen sublattice melting curves below 200 GPa (blue dots) are taken from [1]. The black triangles and solid red lines indicate the melting temperature of the H sublattice, ignoring quantum effects. The red dot-dash lines indicate the standard error of the melting temperature estimated by simulated annealing cycles. The gray area indicates the superionic phase boundary and the associated uncertainty. The solid blue lines show the transition starting from zero-temperature structures. The black dashed vertical lines indicate phase boundaries at zero K according to [6], where the ZPE is included. When the ZPE is ignored, the range of stability of P3\textsubscript{1}21 extends up to 2.0 TPa, followed by P\textsuperscript{c}c\textsubscript{a} up to 2.2 TPa. At higher pressure one has P\textsubscript{21} up to 2.7 TPa, followed by P\textsubscript{21}/c at even higher pressure [6]. Inset: The reversible transition between CP-SI and P\textsubscript{21}/c-SI.
Figure 3.3: A sample of the reversible transition between the CP-SI phase and the P21c-SI phase. The upper plot shows the dynamics of the cell tensor, while the underlying oxygen sublattice is identified via oxygen-oxygen pair correlation function. The lower plot tracks the stress tensor of the cell. At equilibrium, the average stress tensor equals the external pressure.

At 1.7 TPa and 1.9 TPa, we locate the transition temperature between the CP-SI and the P21/c-SI phase as [2700 K, 3000 K] and [3200 K, 3500 K], respectively. In addition, we estimate the melting temperature of the hydrogen sublattice. As we will discuss later, the solid to CP-SI phase transition has a sharp change in the conductivity at the melting temperature and thus we can use the conductivity to locate the transition temperature. However, the conductivity changes gradually in the solid to P21/c-SI phase transition. Therefore, it is not straightforward to locate a transition temperature. For that reason, we use a few order parameters, including the maximum peak value of the structure factor and a translational order metric [30], to locate approximately the transition temperature.
The solid to P21/c-SI transition is a type-II superionic phase transition, which does not have a sharp change in the conductivity. Therefore, we are not able to use the conductivity to locate the transition temperature. On the other hand, the structure factor, which is defined as $S(k) = \frac{1}{N} \sum_{jk} e^{-ik \cdot (R_j - R_k)}$, provides a better means to locate the transition temperature. We use the nonnegative scalar “order” metric $\tau$ introduced in Ref. [30], which is defined as $\tau = \frac{1}{N^2} \sum_k (S(k) - 1)^2$, where $N$ is the number of particles, as well as the intensity of $S(k \_\_{M-600})$, where $k \_\_{M-600}$ is the wave vector associated with highest peak of $S(k)$ at 600 K, to characterize the degree of disorder. For a spatially uncorrelated configuration of particles (ideal gas) in the infinite-volume limit, $S(k) = 1$ for all $k$ and hence $\tau$ takes on its minimum value of zero. When the system is correlated, then $S(k)$ will generally deviate from zero, and yield a positive value of $\tau$, providing a measure of the deviation from perfect disorder.

Figure 3.4 shows the two order parameters as a function of temperature at 1.9 TPa. Due to the finite-size of our system, we cannot locate the phase boundary very precisely. However, both of these two order parameters increase relatively rapidly in the temperature range from 1100 K to 1300 K. In addition, we show that with a fixed simulation box, the pressure as a function of temperature has an inflection point at [1100 K, 1200 K]. Since all of these three quantities consistently show that there is a relatively rapid change in slope in the temperature interval [1100 K, 1300 K], we conclude that at 1.9 TPa the transition temperature is [1100 K, 1300 K].
Figure 3.4: Order parameters used to local the melting temperature of P21/c solid phase. (a) Order metric $\tau$ of hydrogen in the P2$_1$/c-SI phase. (b) Highest peak of $S(k)$ of hydrogen in the P2$_1$/c-SI phase. (c) Pressure of the P2$_1$/c-SI phase as a function of temperature. All three measures indicate a transition temperature in the interval [1100 K, 1300 K], or inverse-temperature interval [0.77, 0.91] in the graph.
These order parameters consistently show that at 1.9 TPa, the transition occurs in the temperature interval [1100 K, 1300 K]; see the Fig 3.4 for additional details. Previous theoretical studies showed that the melting temperature of the H sublattice is around 1500 K at 50 GPa [1, 31] and then it rapidly increases to around 2000 K at 100 GPa - 200 GPa. At above 200 GPa, we find that though the melting temperature is roughly a constant within the same oxygen sublattice, the melting temperature changes when the oxygen sublattice changes. The melting temperature decreases from 2000 K to 1700 K when the oxygen sublattice changes from the BCC-SI to the CP-SI structure, and further decreases to 1200 K when it changes to the P21/c-SI. The new phase diagram is shown schematically in Fig3.5.

Figure 3.5: A schematic phase diagram of superionic ice from 50 GPa to 2.5 TPa. The blue, green and pink regions indicate the three superionic phases. The gray region indicates the crystalline regime. The yellow region represents the ionic liquid water phase [1]. The zero-temperature structures are taken from Ref. [6], which includes the contribution of the harmonic ZPE. The pressure range of the static structures is consistent with the superionic phase diagram, as discussed in the text.
The detailed simulation results are summarised in Figure 3.2. The hydrogen melting lines below 200 GPa are taken from [1]. We find they are in agreement with our predicted melting temperature at 200 GPa. We also estimated the melting temperatures of the H sublattice, ignoring the quantum effects, via single phase simulations at various pressures. The results are indicated by the black triangles in Fig 3.2. The melting temperatures do not change appreciably within the same oxygen sublattice, however they decrease across the superionic phase boundaries. The red dot-dash lines indicates the standard error of the melting temperatures. The phase boundaries between different superionic phases are also estimated via single phase simulations. The gray area indicates the uncertainty of the superionic phase boundaries. The inset of Fig 3.2 shows the reversible transition between the CP-SI and P2\textsubscript{1}/c-SI. The simulations starting from various zero-temperature structures are gradually heated until the H sublattice melt, while keeping the pressure fixed. The blue lines in Fig 3.2 summarize the simulation results. It is interesting to note that depending on the pressures, the final superionic phase starting from Pcca can be both CP-SI and P2\textsubscript{1}/c-SI. The simulation data indicate a likely negative slope of the BCC-SI to CP-SI boundary and positive slope of the CP-SI to P2\textsubscript{1}/c-SI boundary. It is very plausible that the slope of the melting line be negative in correspondence with the two sharp drops of the melting temperature.

### 3.2.2 The evolution of high pressure ice structures

Before we move to the physical and chemical properties of the superionic phases, it is interesting to revisit the zero temperature structures. The left panel of Figure 3.6 reports the OO pair correlation function and the corresponding coordination number for the sequence of static phases Pbcm, Pbca, P3\textsubscript{1}21, Pcca and P2\textsubscript{1}/c. This figure illustrates the systematic changes undergoing in the O sublattice with increasing pressure. The right panel of Figure 3.6 reports the OO pair correlation functions and the coordination numbers for CP-SI and P2\textsubscript{1}/c-SI. The static structures P2\textsubscript{1} and P2\textsubscript{1}/c
are also given for comparison together with corresponding quantities for the perfect FCC lattice.

When we cool down the system from the superionic phases, we find that the frozen crystalline structures are in agreement with previously found zero-temperature structures. In particular, starting from the CP-SI phase at 1.3 TPa and the P2\textsubscript{1}/c-SI phase at 1.9 TPa, the system freezes into static P3\textsubscript{1}21 and P2\textsubscript{1} structures respectively. Figure 3.7 shows the comparison of the OH and OO pair correlation functions and coordination number between the quenched structures and zero-temperature structures.

In the P2\textsubscript{1}/c-SI phase we report in this paper, the oxygen sublattice has P2\textsubscript{1}/c symmetry with 4 atoms in the unit cell. As shown in Figure 3.6, this oxygen sublattice is close to the oxygen sublattice in the zero-temperature P2\textsubscript{1} or P2\textsubscript{1}/c structures, which have, however, lower symmetry. In the zero-temperature P2\textsubscript{1}/c structure there are 8 O atoms in the unit cell, while the zero-temperature P2\textsubscript{1} structure has 4 O atoms in the unit cell but lacks the glide plane symmetry of the P2\textsubscript{1}/c structure. The hydrogen ions are diffusive. Figure 3.8 shows the isosurface of the density distribution of the hydrogen atoms in the P2\textsubscript{1}/c-SI phase. In the unit cell of the P2\textsubscript{1}/c-SI, we found ten sites with maximal hydrogen density. Among these ten sites, site 1 and 2 are the localized sites between the diffusion planes and the other 8 of them are located in the diffusion planes (also see Fig 3.8).

Our simulation results are very consistent with the previous zero temperature structures. The evolution of zero temperature structure has the same trend as the evolution of the change of superionic ice phases.
Figure 3.6: **Structural change in the solid high pressure ice phases.** (a) Pair correlation function for the static structures Pbcm, Pbca, P3$_121$, Pcca, and P2$_1$/c. (b) Coordination number for the static structures Pbcm, Pbca, P3$_121$, Pcca, and P2$_1$/c. (c) Pair correlation function for CP-SI and P2$_1$/c-SI. (d) Coordination number for CP-SI and P2$_1$/c-SI. The corresponding quantities for the static P2$_1$ and P2$_1$/c structures and the ideal FCC lattice are also given for comparison.
Figure 3.7: **Quenched structures from superionic phases.** The OH and OO pair correlation functions and the coordination numbers of the quenched structures from superionic phase at (T = 1900 K, P = 1.3 TPa) and (T = 1900 K, P = 1.9 TPa), respectively, compared with zero K $P3_{1}21$ and $P2_{1}$ structures. The minor differences between the quenched and the equilibrium 0 K structures reflect the accuracy of the final steepest descent minimization that we apply to the quenched structures at 200 K.
Figure 3.8: **Visualization of the P21/c-SI phase.** The oxygen sublattice (red balls) and the density distribution of hydrogen atoms (silver) in the P21/c-SI phase. The three axes are along [100](a), [010](b) and [101](a+c). The label from 1 – 10 indicates the density maxima. Site 1 and site 2 are the localized sites, and the rest are in the diffusion planes. Repeated sites reflect periodicity.

### 3.2.3 Ionic transport

Unlike the BCC-SI or CP-SI phase, the P21/c-SI has a monoclinic structure and it shows a large anisotropic effect in the diffusion coefficient tensor. Using the velocity auto-correlation function, we identify the principle diffusion axes along [201], [010] and [201] × [010] of the P21/c-SI. At 1.9 TPa and 1600 K, the diffusion coefficient ratio among these three axes is roughly 4 : 3 : 1. Thus the primary diffusion happens...
in a quasi two-dimensional layer, as shown in Fig. 3.9. Hermann et al. [8] suggested a diffusion path in the P2\textsubscript{1} crystalline structure at zero K via the Nudged Elastic Band (NEB) method. It is interesting to note that the most diffusive path at finite temperature is not following the lowest energy path at zero K. The transition path they found is along the [100] direction in the P2\textsubscript{1}/c-SI, which forms an angle of \(\sim 30\) degrees with the 2D diffusion layer. In the unit cell of P2\textsubscript{1}/c-SI, there are 6 out of 8 hydrogen ions in the quasi two-dimensional diffusion layer, but the other 2 hydrogen ions are more localized. In the two-dimensional diffusion layer there are four “sausage”-like high density regions which are indicated by the green lines in Fig. 3.9. These four “sausages” are indistinguishable in the P2\textsubscript{1}/c-SI phases. However, when the system freezes into the crystalline phases, two of the sausages are occupied by two hydrogen ions, while the other two only contain one hydrogen ion that stays in the center of the sausage, as shown in the right panel of Fig. 3.9. The fact that the most frequently occupied sites at high temperature do not coincide with the crystalline sites indicates strong anharmonicity.
Figure 3.9: The traces of the trajectories of D and O ions. The traces of the trajectories are accumulated over 8 ps in the P2$_1$/c-SI at 1400K and 1.9TPa. The three panels show projections on three different crystallographic planes defined by the principle vectors of the diffusion tensor. The red and grey regions are traces of the trajectories of each individual O and D ions, respectively. The solid black line indicates the unit cell of P2$_1$/c-SI. The O ions oscillate around the equilibrium positions, while the D ions are fully diffusive. The blue regions in panel (c) are traces of the trajectories of D ions at 400K and 1.9TPa, when the system is in the crystalline regime. The green dash lines indicate the “sausage”-like high density regions. The different distribution of blue and gray traces indicates strong anharmonicity. The three principle vectors of the diffusion tensor $a$, $b$ and $c$ are along [201], [010] and [201] $\times$ [010] of the P2$_1$/c-SI unit cell.

Compared to the BCC-SI and CP-SI phases, the average isotropic diffusion coefficient is smaller in the P2$_1$/c-SI phase. This is because there are less empty hydrogen sites in P2$_1$/c-SI unit cell. We define the hydrogen sites by locations of maximal hydrogen density. As shown in Fig 3.8, we find ten such sites in the P2$_1$/c-SI unit cell and there are eight hydrogen atoms. The fact that there are only two empty sites in the unit cell makes diffusion slow. Contrast this with the HCP sublattice where there are 2 empty sites per hydrogen atom.

We estimated the ionic conductivity of heavy ice at 1.3 TPa (CP-SI) and 1.9 TPa (P2$_1$/c-SI), and from 1100 K to 2500 K via Nernst-Einstein relations $\sigma_D = n_D \frac{D_D(Z_D e)^2}{k_B T}$, where
\( \sigma_D \) is the average isotropic ionic conductivity, which is defined as one-third of the trace of the conductivity tensor, \( n_D \) is the density of the mobile ions (D ions), \( D_D \) is the average isotropic diffusion coefficient of D estimated from the mean square displacement (MSD), and \( Z_D^* \) is the average isotropic Born effective charge of D. The average ionic conductivities of the superionic phases at different thermodynamic conditions are \( \sim 90 \) S/cm (BCC-SI, \( \text{D}_2\text{O} \), 200 GPa, 2500 K), \( \sim 120 \) S/cm (CP-SI, \( \text{D}_2\text{O} \), 1.3 TPa, 2000 K) and \( \sim 60 \) S/cm (P2\(_1\)/c-SI, \( \text{D}_2\text{O} \), 1.9 TPa, 2500 K). If we replace the D with H, we find the conductivity of H is roughly 1.2 \( \sim \) 1.3 times of the conductivity of D. The conductivity we found in the BCC-SI phase is in agreement with the result reported by French et al. [32]. The conductivity in the CP-SI phase is higher and that in the P2\(_1\)/c-SI phase is lower than in the BCC-SI phase. In all the three SI phases, however, the conductivity is in the range of the dissociated water phase in the outer shell of Uranus and Neptune (10-120 S/cm) [33]. The similar ionic conductivity of the superionic phase and the ionic water in the outer shell of Uranus and Neptune is consistent with the model suggested by Stanley et al. [11], which assumed equal conductivity across different phases.

Superionic phases can be classified into three types [22]. In type-I, the conductivity jumps at the transition temperature, while it gradually transforms in type-II and has Arrhenius behavior in type-III. We find the solid to CP-SI transition is consistent with a type-I transition. On the other hand, the solid to P2\(_1\)/c-SI transition is more continuous and is consistent with a type-II transition. Figure 3.10 shows the change of conductivity across the solid to superionic phase boundary. It is interesting to note the different behavior between the CP-SI and P2\(_1\)/c-SI. The discontinuity of the conductivity in the CP-SI phase indicates a type-I transition, while the conductivity of the P2\(_1\)/c-SI phase, which behaves similarly to the Ice-X to BCC-SI transition [31], is more continuous and belongs to type-II transition [22]. Type-I superionic transitions are known to be accompanied by a structural transition in the crystalline sublattice, but in type-II superionic conductors this structural transition is absent [22].
observe the same behavior here. When the hydrogen ions stop moving, the CP-SI phase freezes into the P3\(_1\)21 phase at 1.3 TPa. These two structures have different oxygen sublattices. On the contrary, despite the different symmetry, the P2\(_1\)/c-SI has a very similar oxygen sublattice to the solid P2\(_1\)/c (P2\(_1\)) phase. We confirmed this with the mean squared displacement (MSD) of oxygen ions in these two phases, which is shown in Fig. 3.10. There is a sudden change of the MSD as we cross the phase boundary between the CP-SI phase and P3\(_1\)21, while the MSD changes gradually as the phase changes from P2\(_1\) to P2\(_1\)/c-SI.
3.2.4 Near hyperuniformity

Although the hydrogen ions are highly diffusive in the SI phases, they are subject to the local charge neutrality due to the high energy cost from the Coulomb interaction. The local charge neutrality add a strong constraint on this diffusive system, and raise the question of whether there is any hidden order in the SI phases. We show evidence that the hydrogen ions in the SI phases may be a disordered near hyperuniform sys-
Hyperuniformity [34, 30] means that the number density fluctuation are greatly suppressed. This happens in crystals, but can also happen in disordered system [35]. Superionic ice would provide another example of disordered nearly hyperuniform system. In order to characterize hyperuniformity, we consider an arbitrary point pattern in a 3-dimensional Euclidean space $R^3$ and a window that lies in this $R^3$ space that centred at point $x$ and has a size of $\Omega$. Let use $N(x)$ to denote the number of points that are included in this window. If we vary the position of the window, then $N$ will fluctuate. Let $\text{Var}(N)$ and $E(N)$ be the variance and expectation of the number of points, respectively. For a Poisson point pattern, one can easily find that $\text{Var}(N) = E(N)$, the variance $\text{Var}(N)$ is proportional to $R^3$. Although the geometry of the windows is not essential for the argument we use here spherical windows with radius $R$. One can show that the variance $\text{Var}(N)$ can be written as [34]

$$\text{Var}(N) = E(N)\left[\frac{1}{(2\pi)^3} \int S(k)\tilde{\alpha}(k; R)dk\right]$$

where $S(k)$ is the structure factor of the point pattern, and $\tilde{\alpha}(k; R)$ is the Fourier transform of $\alpha(r; R)$, which is a non-negative function that purely depends on the separation between two spherical centers $r$ and the radius $R$.

$\alpha(r; R)$ is the ratio between the intersection of two windows that separates with $r$ and the volume of the window. As the size of the windows goes to infinity, $\lim_{R \to \infty} \alpha(r; R)$ converges to delta function as $(2\pi)^3 \delta(k)$. Then the variance of $N$ can be simplified as

$$\frac{\text{Var}(N)}{E(N)} = S(k = 0) = 1 + \rho \int_{R^3} h(r)dr$$

Thus, asymptotically, the ratio of the variance and the expectation of $N$ equals to the structure factor at $k = 0$. We will refer a system in which $S(k = 0) = 0$ as a hyperuniform system. In this system, the point patterns do not possess infinite-wavelength
fluctuations.

Since hyperuniformity can be quantified by the limit of the structure factor for $k \to 0$, we compute the $S(k)$ for two superionic phases, a low pressure BCC-SI phase at 100 GPa and 2200 K, and a high pressure P21c-SI phase at 1.9 TPa and 1600K. Since the minimum wave vector that is accessible in our simulation is inversely proportional to the size of the supercell, we should use a simulation with the largest cell. Although DFT is hard to apply on a system with very larger cell, we can work with force field that is faster to calculate. For the BCC-SI phase, there is a good force field that gives pair correlation functions in good agreement with those of DFT. This force field is an all-atom polarizable and dissociable force field, which was proposed by Pinilla et al[36], and it has been shown that it can generate satisfactory structures and dynamics over a vast range of thermodynamic condition. It involves a self-consistent iteration to find the dipole components on oxygen ions, but other than that, the computation is fast. With this force field, we can easily perform a simulation with several hundred molecules. The details of this force field will be explained in Appendix. We perform a simulation with 432 molecules for the BCC-SI phase. For the P21c-SI phase, the pressure is too high and the force field is no longer accurate. Thus we have to use CPMD to generate reliable dynamics. The simulation system we can afford is relatively small which only contains 64 molecules.

The calculated structure factor near $k = 0$ is shown in Fig 3.11. Due to the finite size of our simulation supercell, we cannot reach $k = 0$ in our simulation. To better estimate the structure factor at $k = 0$, we extrapolate the structure factor using the smallest 15 k points. We fit $S(k) = a + bk^2 + ck^4$ up to the fourth order of $k$. Note that due to the symmetry, both BCC-SI and P21/c-SI satisfy $S(\vec{k}) = S^*(-\vec{k})$ and thus after the spherical integration the coefficients of odd orders should equal to zero. The extrapolated line is also shown in Fig 3.11.
Figure 3.11: **Structure factors of superionic phases** The upper image shows the structure factor of hydrogen and oxygen in the BCC-SI phase. The lower image shows the structure factor of hydrogen and oxygen in the P21c-SI phase. The red square and blue square indicate the calculate $S(k)$ for hydrogen and oxygen, respectively. The red and blue solid line indicate the extrapolated $S(k)$ at $k=0$. See the text for more details.
A classical crystalline system at zero temperature is perfectly hyperuniform but when temperature and NQE are taken into account the system is nearly hyperuniform. For example, the oxygen sublattice which forms a crystal is a hyperuniform system and thus it should have zero structure factor at $k = 0$. As shown in these figures, the extrapolated structure factor of hydrogen is very close to the structure factor of oxygen. Both of them are of the order of $10^{-3}$. Therefore, the calculated $S(k)$ suggests that the diffusive hydrogen, though disordered, may actually have a hidden order and form hyperuniformity.

At the first glance one may feel surprised that the liquid like hydrogen is near hyperuniform. Where does the hidden order come from? Actually the diffusive hydrogen in superionic ice phases is not a normal liquid. Firstly, they are particles with positive charges, so they have strong Coulomb interaction with other hydrogens as well as the fixed oxygen sublattice. Secondly, the fixed oxygen sublattice provide a external field that prevents large fluctuation due to local charge neutrality. To some extent, the diffusive hydrogen can be viewed as an example of one component plasma, which is a well known hyperuniform system [30, 34]. The oxygen sublattice in SI phases generates a uniform background field while hydrogens can move almost freely. However, I need to point out in one component plasma the charged particles in the uniform background take any position with equal probability, whereas in the SI systems the H(D) do not exhibits uniform density.

### 3.2.5 Vibrational density of states in crystalline and superionic P21c phases

In nature, the cations in ice come in two isotopes - hydrogen and deuterium. Classically, any isotope effect manifests itself only in dynamic properties such as the vibrational spectra (Fig. 3.12), diffusivity and ionic conductivity. Quantum mechanically isotope effects manifest also in static properties. Such an effect has recently been seen for elemental material systems at high pressure such as Li [13] and H [12]. With the
possible exception of H at very high pressure, these nuclear quantum effects (NQE) were found to have only small effects on the classically calculated melting lines. Here we estimate the magnitude of this effect in superionic ice by looking at the vibrational frequency. Previous studies showed that at zero K [8], the vibrational frequency in P2$_1$ can be as high as 5000 cm$^{-1}$ for H, or 3000 cm$^{-1}$ for D. The corresponding ZPE is about 1.28 ev/mol for H$_2$O, or 0.99 eV/mol for D$_2$O. Using the power spectrum of the velocity autocorrelation function [37], we show the vibrational density of states (VDOS) in P2$_1$/c-SI in Fig. 3.12. In comparison with the zero-temperature spectrum, the H (D) ions have a diffusive mode at $f = 0$, which is characterized by the non-zero DOS at 0. And due to the molten hydrogen sublattice, the highest frequency mode, which is related to the stretching mode along the O-H ionic bond, becomes weaker in the superionic phase. We also find a softening of the vibrational modes for the oxygen sublattice in the superionic phase. The average vibrational frequency of the oxygen sublattice decreases from 1580 cm$^{-1}$ in the zero-temperature P2$_1$ structure to 1480 cm$^{-1}$ in P2$_1$/c-SI. The ZPE in the P2$_1$/c-SI phase is significantly higher than the energy necessary to melt the H sublattice and it could affect the phase diagram even at the temperature of the superionic transition. Therefore, we will explore the quantum effect in the next chapter.
Figure 3.12: **Vibrational DOS of crystalline P2\textsubscript{1} and P2\textsubscript{1}/c-SI.** (a) DOS of H\textsubscript{2}O. (b) DOS of D\textsubscript{2}O. The red and blue areas are the DOS of H/D and O of the zero-temperature P2\textsubscript{1} structure [8]. The dark line on top of it indicates the DOS of the P2\textsubscript{1}/c-SI phase at 2000 K. The non-zero DOS at zero frequency shows the diffusive nature of H/D.

### 3.3 Discussion

What drives the transition from CP-SI to P2\textsubscript{1}/c-SI? At extremely high pressure, the enthalpy is dominated by the PV term, which means that a more stable phase should have a higher density, and thus a larger packing fraction. Although the CP structures are the densest arrangements for a unary system, the presence of hydrogen makes denser structures possible. At 1900 K and 1.6 TPa, we find a 0.7% volume reduction, or 0.19 Bohr\textsuperscript{3}/mol when the oxygen sublattice changed from the CP-SI structure to P2\textsubscript{1}/c-SI. Due to the higher density, P2\textsubscript{1}/c-SI has a lower enthalpy than CP-SI, and thus it is more stable at higher pressure. Table 3.3 summarizes the enthalpy
difference between CP-SI and P2\textsubscript{1}/c-SI. When the CP-SI sublattice changes to the P2\textsubscript{1}/c-SI sublattice, the first shell of oxygen neighbors splits into two closely spaced shells. The readjustment of the oxygen positions allow one more oxygen to move closer. Figure 3.6 shows the O-O pair correlation functions and the coordination number of the oxygen sublattice for the CP-SI and P2\textsubscript{1}/c-SI phase, normalized to the same density. Compared to the CP-SI sublattice, which has 12 neighbors in the first shell, the P2\textsubscript{1}/c-SI sublattice does not have a well separated first and second shells. Instead, each oxygen has 13 neighbors within close distance. If one increases the temperature to \( \sim 3000 \) K at 1.7 TPa, the P2\textsubscript{1}/c-SI phase transforms back to the CP-SI phase. On the phase boundary at 3000 K, the P2\textsubscript{1}/c-SI phase still has a lower enthalpy of about 0.1 eV/mol. The fact that the P2\textsubscript{1}/c-SI phase spontaneously changes back to the CP-SI phase suggests a larger entropy in the CP-SI phase. This behavior is consistent with the larger diffusivity and hence a larger disorder in the H sublattice of the CP-SI phase, as discussed below.

| Change(CP-SI \( \rightarrow \) P2\textsubscript{1}/c-SI) |  \\
| \( \Delta H \) | -0.23 eV/mol |
| \( \Delta V \) | -0.19 Bohr\textsuperscript{4}/mol |
| \( P\Delta V \) | -0.28 eV/mol |
| \( \Delta U \) | +0.05 eV/mol |

Table 3.1: The change from CP-SI to P2\textsubscript{1}/c-SI at 1.6 TPa and 1900 K. The enthalpy difference is mainly due to the \( P\Delta V \) term, which in turn is due to the higher density in P2\textsubscript{1}/c-SI.

Compared to the zero-temperature stable structures, the superionic ice phase diagram in Fig. 3.5 is significantly simpler. We can understand this as follows. At zero K, as pressure is increased, the first stable structure after Ice-X is Pbcm [29], followed by Pbca [38] and by P3\textsubscript{1}21 [6]. Although these structures have different H sublattices, they all have a distorted CP O sublattice with the first 12 neighbors well separated from the next 6. In P2\textsubscript{1}/c a thirteenth O neighbor has moved to close
distance. In Pcca the thirteenth neighbor has only moved midway between the first and the second group of neighbors, characteristic of the CP-like structures. Thus Pcca can be seen as an intermediate structure between P3121 and P21/c. In Fig 3.6, we give more details to illustrate the systematic change with pressure in the O sublattice at zero K. Interestingly, harmonic ZPE affects significantly the zero-temperature phase diagram. Without ZPE the range of stability of P3121 would extend up to \( \sim 2 \) TPa, while P21 would be more stable than P21/c for pressure higher than \( \sim 2.4 \) TPa [6].

P21 and P21/c differ mainly in their H sublattices. As shown in Table 3.3, the centroid of oxygen atoms of the P21/c-SI phase has P21/c space group with 4 oxygen atoms in the unit cell, which is more symmetric than the P21/c structure at zero K which has 8 oxygen atoms per unit cell. It also has a higher symmetry than the P21 structure at absolute zero temperature because of the additional glide plane symmetry in P21/c. Obviously upon melting the H sublattice, the differences of the hydrogen sublattice disappear. Without the structure supplied by the extra hydrogen sublattice, the positions of oxygen ions change slightly with slightly different oxygen sublattices converging to a more symmetric structure. It is these more symmetric structures that appear in the superionic phase.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>P21/c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecules/unit cell</td>
<td>4</td>
</tr>
<tr>
<td>a(Å)</td>
<td>2.87</td>
</tr>
<tr>
<td>b(Å)</td>
<td>3.11</td>
</tr>
<tr>
<td>c(Å)</td>
<td>3.58</td>
</tr>
<tr>
<td>( \beta )(deg)</td>
<td>151</td>
</tr>
<tr>
<td>O atoms</td>
<td>(0.156, 0.636, -0.077)</td>
</tr>
</tbody>
</table>

Table 3.2: The structural parameters of the oxygen sublattice of P21/c-SI at 1.9 TPa and 1600 K.

Notice that the phase diagram indicates two additional novel effects. First, there are two crystalline phases which melt upon increasing the pressure; this is a result of the monotonic decrease in melting temperature as we move along the sequence BCC-
SI → CP-SI → P2\textsubscript{1}/c-SI. Secondly, the phase diagram has a number of regions where the phase boundary has a negative $dT/dP$ slope. This is true in the transition region between the solid and superionic phases where the negative slope must exist if the melting temperature decreases to avoid a superionic phase freezing upon an increase in temperature. Moreover, we can understand the sign of both these slopes as well as that of the superionic to superionic slopes using the Clausius-Clapeyron relation $dT/dP = \Delta v/\Delta s$, where $\Delta v$ and $\Delta s$ are the specific volume and entropy change of the phase transition, respectively. The slope of the coexistence line between two phases is negative if the denser phase has higher entropy while it is positive otherwise. Our calculated diffusivities suggest that under the considered thermodynamic conditions the CP-SI phase has higher entropy than either BCC-SI or P2\textsubscript{1}/c-SI. Thus the slope of the BCC-SI to CP-SI boundary should be negative, while that of the CP-SI to P2\textsubscript{1}/c-SI boundary should be positive, in agreement with our simulation results. Moreover, similar considerations suggest that the solid to CP-SI and the solid to P2\textsubscript{1}/c-SI transitions must be negative slope in the regions of melting temperature drop, as the entropy is likely to increase in a solid to SI transition. Finally, away from the regions where the melting temperature drops sharply (Fig. 3.5) the almost flat melting curves of CP-SI and of P2\textsubscript{1}/c-SI indicate a small volume change from the underlying solid to SI phases.

In summary, we provide a comprehensive superionic ice phase diagram from 200 GPa to 2.5 TPa and up to 3500 K in the classical limit. At 1900 K, we find a transition between the CP-SI phase and the P2\textsubscript{1}/c-SI phase at 1.4 TPa-1.6 TPa. This new superionic phase is stable up to 2.5 TPa. The melting temperature of the hydrogen sublattice has negative $dT/dP$ slope cross the superionic phase boundaries, and it decreases when the system changes to a high-pressure superionic phase. In all of the superionic phases, H and O are highly ionized. We evaluated the ionic conductivity of superionic ice and showed that the CP-SI and P2\textsubscript{1}/c-SI phases belong to different types of superionic phase. We also see a large anisotropic effect in the
new superionic phase in which the diffusion of hydrogen is mainly in a quasi 2D layer. Due to fewer hydrogen sites in the 2D plane, $\text{P2}_1/\text{c-SI}$ has a smaller diffusion coefficient. Finally, the large vibrational frequencies suggest the NQE in the superionic phase could be significant even at the transition temperature. It may affect the phase boundary and needs further studies.
Chapter 4

The Nuclear Quantum Effects on High Pressure Ice

The nuclei of hydrogen atoms play an important role in hydrogen bonded systems like water and ice. At ambient temperature and pressure, the physical and chemical properties of water and ice are largely determined by the hydrogen bond. Although hydrogen are usually treated as a classical particle in empirical force field and in first principle simulations, its behaviour is significantly affected by the quantum mechanics due to its light mass. With the recent development of experimental techniques such as deep inelastic neutron scattering, people were able to measure the proton and oxygen momentum distributions and quantum kinetic energies, providing intriguing new observations of these quantum properties of the nuclei under thermodynamic conditions ranging from supercooled to supercritical water and environments ranging from the bulk to hydrophobic confinement[39, 40, 41, 42, 43, 44, 45, 46].

In the previous chapter, we studied the high pressure superionic ice phases in the classical limit. When the nuclei are treated classically and the pressure is increased, the oxygen sublattice in the superionic state changes from BCC to close-packing, and then to lower symmetry P21/c. Although the phase diagram of high pressure superionic ice is clear and consistent with zero temperature structures, several questions
are still waiting to be answered. In particular, we notice that the phase boundary between crystalline CP-like phases and a P21c phase predicted using the quasi-harmonic approximation (QHA) in ref [6] is significantly higher than the phase boundary we predicted in the classical limit. The QHA explains part of the NQE by assuming the harmonic approximation applies for every lattice constant, but the phonon frequency is volume dependent. Since nuclear quantum effects typically become more important at high pressure, is this difference due to the NQE effect? If so, how does the NQE affect the phase boundary? In order to answer these questions, we need to take NQE into account and perform a more accurate, quantum mechanical simulation including fully anharmonic effects to determine the phase boundaries.

In this chapter, we discuss the nuclear quantum effect (NQE) in high pressure ice phases. First, I will briefly review the previous studies on NQE and high pressure physics. The results of NQE on zero temperature structures will be discussed. Next, I will introduce the imaginary time path integral method which we used to explore the NQE in superionic phases. With path integral molecular dynamics simulations, we study the nuclear quantum effect on high pressure water ice. We find evidence that nuclear quantum effects facilitate melting of the hydrogen sublattice, and that it stabilizes the close-packing superionic phase over the P21/c superionic phase. This result is consistent with previous theoretical calculations based on the QHA. We discuss the physics in more detail in the last section of this chapter.

4.1 Introduction

NQE, such as the zero-point motion energy (ZPE) and tunnelling effects, may play an important role in the static and dynamic properties of water and ice. The isotope effects of water under ambient condition are extensively studied both experimentally[39,
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40, 41, 42, 43, 44, 45, 46] and theoretically[47, 48, 49]. Isotope effects under ambient conditions, such as the change of bond energy and melting temperature, can often be attributed to the ZPE in the O–H stretch mode. The NQE becomes more important with increasing pressure, suggesting that effects such as proton tunneling and delocalization may become increasingly important. An important example of tunneling is the ice-VIII to ice-VII to ice-X transition [50]. In Ice-VIII the tunnel splitting is negligibly small so protons experience an effective asymmetric single well potential. As pressure increases, the oxygen-oxygen distance decreases and the tunnel splitting is comparable to the thermal energy. The quantum tunneling originates a bimodal distribution to the disordered ice-VII. At even higher density though the potential remains double welled but the hydrogen is unimodal distributed due to zero point energy and the system transits to ice-X. Since the NQE is stronger at higher pressure, we study how does it change the transition between CP-SI and P21c-SI, as well as the transition between crystalline phases to the superionic phases.

4.1.1 Nuclear quantum effects on high pressure zero temperature ice phases

Compared to the water and ice under ambient condition, high pressure ice phases are not well understood. One difficulty is that it is very hard to reach such high pressure experimentally. Thus most of the research on high pressure ice is based on first principle simulations. Several groups used various searching algorithms to find the stable phases for ice at pressures higher than 50 GPa. They found more than 10 different structures that are stable or meta-stable in this pressure range. However, most of them did not consider the NQE. Only recently, Pickard et.al.[6] considered ZPE with in the QHA, and a few more stable structures were reported when ZPE is included. As the pressure increases, the system becomes more and more compressed, the distances between atoms are greatly reduced and the motions of the particles are highly constrained. Therefore, it is not surprising that the ZPE is much stronger
in high pressure phases. In fact, Pickard et.al. found that in high pressure phases, the ZPE is so strong that it can change the boundaries between stable crystalline ice phases dramatically. Some phases such as the C2 and P21 phases that are stable in the classical limit no longer have regions of thermodynamic stability when NQE is included. At the same time other structures which were meta-stable in the classical limit become stable phases.

Since NQE is very strong at high pressure, one could expect even at temperatures above 1000 K, NQE is still not negligible. Strong NQE at finite temperature had been found for elemental material systems at high pressure such as Li and H [13, 12]. They show the NQE contributes significantly to the free energy and changes the phase boundaries. In water and ice system, under extremely high pressure and temperature, water forms a superionic phase(SI), in which water molecules break into oxygen and hydrogen ions. Although the oxygen ions still stay on lattice sites, the hydrogen ions become diffusive. We have shown that in the classical limit, there are three SI phases. From low pressure to high pressure, the stable phases are the Body Centered Cubic(BCC)-SI, the close-packed(CP)-SI and the P21/c-SI, respectively. The phase boundary between BCC-SI and CP-SI is [220 GPa, 280 GPa] and the boundary between CP-SI and P21/c-SI is [1.4 TPa, 1.6 TPa]. The melting temperature of the hydrogen sublattice is around 2200K, 1600K and 1200K in BCC-SI, CP-SI and P21/c-SI, respectively. With strong NQE, are the SI phase boundaries very different from the classical one? To answer this question, we study the quantum mechanical effects on the SI phase boundaries from first-principle calculations.

In order to understand how NQE affects the phase boundaries, we focused on two aspects: the phase boundary between different SI phases that is mostly dictated by pressure, and the phase boundaries between crystalline ice-phases and the SI phases that is mostly dictated by temperature. Since the NQE is more important
on high pressure phases, we focus on the CP-SI and P21/c-SI phase boundary. We find that NQE stabilizes CP-SI phase. The transition pressure between CP-SI and P21/c-SI is increased from [1.4 TPa, 1.6 TPa] to [1.6 TPa, 1.75 TPa] when NQE is included. In addition, we find that the quantum mechanical melting temperature of the hydrogen sublattice is lower than the one estimated in the classical limit for the CP-SI phase. Quantum mechanically, the melting temperature of the solid phase to CP-SI is [1300 K, 1500 K] which is about 200 K lower than the classical melting temperature. The change of the melting temperature between crystalline phase and the P21/c-SI phase is small and less than the numerical uncertainty of our simulation.

4.2 Simulation Methodology

4.2.1 The formulation of Imaginary time path integral

The formulation of quantum statistical mechanics introduced by Feynman greatly expand our ability to analyse the properties of many-body quantum systems at finite temperature. As we discuss below, the quantum statistics is not very important in the systems we considered. Thus in our study the effects due to quantum statistics are not included. Essentially the path integral formula shows that the average value of a physical quantity can be expressed as an integral over infinitely many paths in imaginary time. Efficient sampling methods such as molecular dynamics and Monte Carlo simulations can be used to estimate the integration. This so called imaginary time path integral is computationally tractable and perfectly suited for implementation on modern parallel computing architectures. Compared to other quantum simulation techniques, it provides an computationally efficient way to calculate equilibrium observable properties such as thermodynamic and structural quantities. In addition, it is easy to extend to other ensembles such as NVT and NPT, allowing a variety of external conditions to be investigated.
The Hamiltonian of the ionic system can be represented as \( \hat{H} = \hat{K} + \hat{\Phi} = \frac{\hat{p}^2}{2m} + \phi(x) \), where \( \hat{K} \) and \( \hat{\Phi} \) are the kinetic and potential operators. Substitute \( H = K + \Phi \) into the partition function, we can write it in the position eigenvector space

\[
Z(\beta) = Tr(e^{-\beta(K+\Phi)}) = \int dx <x|e^{K+\Phi}|x>
\]

Usually \( \Phi \) is diagonal in \(|x>\). However, in general, \( K \) does not commute with \( \Phi \). Thus \( <x|e^{-\beta H}|x> \), cannot be evaluated directly. In order to circumvent this issue, we could expand \( Z \) via Trotter theorem as

\[
Z(\beta) = \lim_{P \to \infty} \int dx_1 dx_2 ... dx_P <x_1|h|x_2><x_2|h|x_3> ... <x_P|h|x_1>
\]

where \( h = e^{-\beta \Phi} e^{-\beta K} e^{-\beta \Phi} \). Note that in the above formula, \( x_{P+1} = x_1 \), which forms a circle. With this expansion, operators \( K \) and \( \Phi \) are separate and the integration can be computed as

\[
<x_1|h|x_2> = <x_1|e^{-\beta \Phi} e^{-\beta K} e^{-\beta \Phi}|x_2>
\]

\[
= e^{-\frac{\beta}{2\pi} \Phi(x_1)} <x_1|e^{-\frac{\beta}{2\pi} K}|x_2> e^{-\frac{\beta}{2\pi} \Phi(x_2)} \tag{4.1}
\]

where the potential part is diagonalized in \(|x>\). Inserting \( I = |p><p| \), where \(|p>\) is the eigenvector of momentum operator, we can further simplify it as

\[
<x_1|h|x_2> = e^{-\frac{\beta}{2\pi} \Phi(x_1)} \int dp <x_1|p><p|e^{-\frac{\beta}{2\pi} K}|x_2> e^{-\frac{\beta}{2\pi} \Phi(x_2)} \tag{4.3}
\]

\[
= e^{-\frac{\beta}{2\pi} \Phi(x_1)} \int dp e^{-\frac{\beta}{2\pi} K(p)} <x_1|p><p|x_2> e^{-\frac{\beta}{2\pi} \Phi(x_2)} \tag{4.4}
\]

\[
= e^{-\frac{\beta}{2\pi} [\Phi(x_1)+\Phi(x_2)]} \int dp e^{-\frac{\beta}{2\pi} K(p)} <x_1|p><p|x_2> \tag{4.5}
\]

where \( K(p) = \frac{p^2}{2m} \), and \(<x|p>\) can be explicitly written as \(<x|p> = \frac{1}{\sqrt{2\pi \hbar}} e^{ipx/\hbar} \). Combining these formula, we can write down the element of the infinite small operator
\[ < x_1 | h | x_2 >= \frac{1}{2\pi \hbar} e^{-\frac{\beta}{\hbar^2}(\Phi(x_1) + \Phi(x_2))} \int dp e^{-\frac{\beta p^2}{2\hbar^2}} e^{ip(x_1 - x_2)/\hbar} \]  

(4.6)

\[ = \sqrt{\frac{mP}{2\beta \hbar^2}} \exp \left[ -\frac{mP}{2\beta \hbar^2} (x_2 - x_1)^2 - \frac{\beta}{2P} (\phi(x_1) + \phi(x_2)) \right] \]  

(4.7)

Once we have a analytical representation of the element of infinite small operator \( < x_1 | h | x_2 > \), we can write down the formula for the partition function \( Z \) as

\[ Z(\beta) = \lim_{P \to \infty} \left( \frac{mP}{2\pi \beta \hbar^2} \right)^2 \int dx_1 dx_2 ... dx_P \exp \left[ -\sum_{i=1}^{P} \left( \frac{mP}{2\beta \hbar^2} (x_{i+1} - x_i)^2 + \frac{\beta}{P} \phi(x_i) \right) \right] \]  

(4.8)

Note that this integration is over all possible close paths. In practice, the continuous path need to be discretized. We will refer those close paths as ”polymers”, and the discretized points as ”beads” or ”replicas”. Similarly, one can easily derive the formula for expected value of any observable operators \( \hat{O} \) as

\[ < O > = \frac{1}{Z} \lim_{P \to \infty} \left( \frac{mP}{2\pi \beta \hbar^2} \right)^2 \int dx_1 dx_2 ... dx_P \frac{1}{P} \sum_{i=1}^{P} \phi(x_i) \exp \left[ -\sum_{i=1}^{P} \left( \frac{mP}{2\beta \hbar^2} (x_{i+1} - x_i)^2 + \frac{\beta}{P} \phi(x_i) \right) \right] \]  

(4.9)

As one can see, the expected value of any observable variables can be estimated as the weighted average of value on each bead, where the weigh is defined by the path integral. This formula provides an elegant way to estimate any observable variable via sampling the close paths. In our simulation we neglect quantum statistics. We found even under the highest pressure we considered, the quantum statistics is not very important. In order to determine whether the quantum statistics is important, one could look at the thermal de Broglie wavelength, which is defined as

\[ \lambda_{th} = \frac{\hbar}{p} = \frac{\hbar}{\sqrt{2mE_k}} \]

where \( p \) is the momentum of the particle, \( m \) is the mass of the particle, and \( E_k \) is the kinetic energy of the particle. If the de Broglie wavelength is much less than the average distance between neighboring particles, then the quantum statistics can be
neglected. For hydrogen, if we replace $E_k = \frac{3}{2}k_B T$, we find $\lambda_{th} = \frac{h}{3mk_B T}$. For the superionic phases, the temperature is always above 1400 K. Thus the thermal de Broglie wavelength $\lambda_{th} = \frac{h}{3mk_B T} \approx 1.3 \text{au}$. As shown in Fig 4.2, at the highest pressure we considered, the closest distance between protons is more than 1.4 au, and the average distance is around 2 au, see Fig 4.2. The likelihood of finding two hydrogens in the same region is small. Therefore, the quantum statistics may have moderate effects on the properties of the system, but ignoring it should not change the qualitative picture.

### 4.2.2 Path integral via molecular dynamics

In the naive implementation, the path integral formulation can be simply discretized with $P$ beads. Then the quantum system can be mapped to a classical system with $P$ replicas, see Fig 4.1. For each particle, the replica $i$ is connected to the replica $j$ by a spring with frequency $\omega_P = \sqrt{P}\frac{\beta}{\hbar}$, and it feels a weakened potential which is $\frac{1}{P}$ of the original potential. This classical system recovers the quantum system as $P$ goes to infinity. Once we map it to the classical system, then any classical sampling techniques, such as molecular dynamics and Monte Carlo sampling, can be used.
Figure 4.1: Cartoon of the classical view and quantum path-integral view of a simple two-body system. (a) The classical view of the system. The green and red dots and the particles, and the blue line indicates the interaction between these two particles. (b) The quantum path-integral view of the system. Each particle is represented by $P = 5$ replicas. The yellow polymer represent the "spring" that connects replicas. Note the interaction (blue lines) are $\frac{1}{P}$ of the real potential.

Although the naive discretization is easy to understand, its convergence with $P$ may be slow, limiting practical applications. To reach convergence, the number of necessary fictitious classical particles is proportional to $\frac{\hbar \omega_{\text{max}}}{k_B T}$. For the liquid water at ambient condition, the naive implementation requires more than 32 replicas to converge [51]. For a system at much higher pressure, like SI phases, the structure is highly compressed and the maximum frequency is around $5000 \text{cm}^{-1}$ [ref]. Therefore, even if the temperature is in the range of 1000 K to 2000 K, it is necessary to use a large number of replicas to ensure convergence. Given that each replica need to be evaluated via a full DFT or CP, the total cost is too high to be applied on large system [51].

Therefore, we adopt a recent developed method, which is called the generalized Langevin dynamics with colored-noise thermostats (GLE) to reduce the number of
fictitious particles [52].

The GLE sampling was introduced by Ceriotti, Bussi, and Parrinello [51, 52, 53, 54]. It accelerates the convergence of PIMD with the number of beads $P$. Essentially the GLE generates a non-equilibrium steady state in which each vibrational mode is coupled with a thermostat. It has been shown that by tuning the correlated colored-noise, PI+GLE can yield exact quantum static properties for a harmonic system. The steady state has a distribution that follows the quantum mechanical distribution. Each vibrational mode has an effective temperature that includes the contribution of NQE. Thus, even with a single bead, the quantum mechanical system can be replicated in the harmonic limit. For a system like superionic phase that has strong anharmonicity, single bead GLE no longer gives exact quantum mechanical solution. We need to apply PIMD to handle the anharmonicity. However, since the harmonic part is already included in GLE and the Trotter expansion only contains the anharmonic part of the interaction, the convergence of PIMD+GLE is usually much faster.

To ensure convergence, we perform four different simulations under the same thermodynamic condition. These four simulations use classical simulation, PI+GLE with 2 replicas, PI+GLE with 4 replicas, and PI+GLE with 8 replicas, respectively. As shown in Fig4.2, the differences between quantum simulation and classical simulation are not negligible. In all of the O-O, O-H and H-H pair correlation functions, classical simulation has a sharper distribution than the quantum simulation, which indicates that NQE makes the system less structured. The height of the peak is lower and the width is wider when NQE is considered. This is consistent with the fact that ZPE contributes to the delocalization of particles. The O-O, O-H, and H-H pair-correlation functions converge with PI+GLE 2 replicas. Thus 2 beads are enough to ensure convergence. In all of our simulations, we use PI+GLE with $P = 2$. Note that we did not test PI+GLE with 1 replica. In principle PI+GLE with 1 replica should recover quantum mechanical results up to the harmonic limits, which may already be
close to the full quantum mechanical results. However, with 1 replica the noise that must be used is too large and it masks the real potential. The sampling is be very inefficient with 1 replica.
Figure 4.2: Convergence of the path-integral with generalized Langevin dynamics. The pair correlation functions of OO, OH and HH of P21/c superionic phase at 1.6TPa and 1000K. The black line shows the pair correlation function generated from classical simulation, while blue, green and red lines show the pair correlation functions generated by PI+GLE with 2, 4 and 8 replicas. It shows that quantum mechanically, the pair correlation functions are less structured than their classical counterparts. As a consequence we should expect quantitative effects of NQE on superionic phases. The shortest separation distance among the particles decreases in the quantum simulation, which is consistent with the zero point motion. However, the difference between PI+GLE with more than 2 replicas are negligible. Therefore, we conclude the NQE is significant in superionic phases, and PI+GLE with two replicas is enough to reach convergence.
4.2.3 Simulation details

To investigate the NQE on SI phases, we use constant pressure first principle Path-Integral Molecular Dynamics (NPT-PIMD) to study the phase boundaries between solid ice and SI ice, as well as the boundary between different SI phases. As shown in ref [55], even at the highest temperature covered in this study, superionic ice is electronically insulating. Therefore the electron part can be modelled within the Born-Oppenheimer (BO) approximation. We apply Density Functional Theory (DFT) to compute the ground state of electrons. The nuclei were treated quantum mechanically via PIMD.

To perform NPT-PIMD, we use the same simulation cell for all replicas. We assign a fictitious mass to the cell. The shape and volume of the cell is driven by the difference between internal stress and external pressure, as well as the thermostat. The cell dynamics is simulated classically. Only the centroid of each atom’s replicas is scaled with respect to the shape and volume [56]. One can show that the following probability distribution is stationary with respect to the Liouville operator corresponding to the cell dynamics:

\[
\rho(p, q, \alpha, V) = \frac{1}{Z} \exp\left\{-\frac{\beta}{n}\left[H_n(p, q) + nP_{ext}V + \frac{\alpha^2}{2\mu}\right]\right\}
\]

(4.10)

where \(H_n\) is the Hamiltonian of the fictitious classical system, \(p\) and \(q\) are the momentum and position of fictitious particles in normal mode, respectively. \(n\) is the total number of replicas, \(\alpha\) is the ”momentum” of cell, and \(\mu\) is the ”mass” of cell.

To understand the phase boundary between CP-SI and P21/c-SI, we study the reversible transition between these two phases. As explained in [55], hydrogen ions are highly diffusive in SI ice phases, which reduce the hysteresis effect significantly. Therefore, NPT simulation can yield an accurate estimation of the phase boundary. In both of the classical and quantum mechanical simulations, we found the uncer-
tainty of transition pressure from reversible simulation is about 100-200GPa, which is comparable to other more sophisticated methods.

We use the i-pi package with Quantum Espresso to perform the PI+GLE calculation. Quantum Espresso is a powerful software package that provides distributed plane-wave based DFT calculations with various pseudo-potentials. And i-pi package is a python package to sample the ionic positions based on the inter-atomic forces calculated from DFT. At each step, the BO potential and forces on each atom are calculated via Quantum Espresso. Then, atomic positions and forces of each replica are passed to the i-pi server. The i-pi server will perform one step of colored noise Langevin dynamics for the classical isomorphism and pass new atomic positions back to each replica. And this process will continue until enough statistics are accumulated. In the BO calculation, we use similar parameters as in the previous chapter. We used gamma point sampling, with the PBE density functional and norm conserving pseudopotentials. Since the NQE depends on the mass of hydrogen, we do not replace hydrogen with deuterium. We use hydrogen in all of our simulations performed in this chapter. We use a plane wave energy cutoff of 1500 eV, with the effective constant energy cut-off technique. This parameter set has been shown to be well suited for high pressure superionic ice phases.

To start our simulation, the two replicas of our system were initialized to the same configuration generated by classical simulations at 1.3 TPa and 1600 K. Under this thermodynamic condition, the system is in the CP-SI phase. The diffusive hydrogen helps the system reach equilibrium rapidly. We find that the potential energy converges in less than 0.2 ps, and we wait for 1ps to ensure equilibrium at each step. We ramp up pressure every 1ps from 1.3 TPa to 1.75 TPa and then ramp down to 1.6 TPa. When NQE is included, we found the transition pressure between the CP-SI and P21c-SI is [1.6 TPa, 1.75 TPa], which is significantly higher than the transition pressure in the classical limit. The change of transition pressure indicates that the presence of NQE make CP-SI phase more stable than the P21c-SI phase.
In addition, we examined the NQE on the melting temperature of solid ice phases. We start from SI phases at 1.3TPa, 1600K for CP-SI and at 1.9TPa, 1600K for P21/c-SI, and then gradually decrease the temperature until the system freezes. Once the system is in solid phase, we raise the temperature until it melts. We take the median of this reversible transition temperature range as the melting temperature. We find NQE has minor effects on the melting temperature of P21/c solid ice, the difference is less than our simulation uncertainty. However, the melting temperature of P3121, which is the solid ice phase at 1.3TPa, is decreased from 1600K to 1400K when NQE is considered.

4.3 Superionic Phase Diagram with Nuclear Quantum Effects

The simulation results reveal that NQE changes the SI phase boundary quantitatively. It pushes the phase boundary from [1.4 TPa, 1.6 TPa] to [1.6 TPa, 1.75 TPa]. Pickard et al. estimated the phase boundary via QHA and they found the phase boundary between CP like phases and P21/c phase is around 1.8TPa [6]. Their result is higher than the classical simulation results reported in [55], but is closer to our simulation results when NQE is taken in to account. Both of these two results show that NQE makes CP-SI phase more stable than P21/c-SI. The difference between QHA and our prediction for the phase boundary in Fig 4.3 likely reflects the more accurate treatment of anharmonicity, which has been shown to be very strong in P21/c-SI phase [55], in our simulation.

In order to understand why NQE enhances the stability of CP-SI vs P21c-SI, we can use a simple perturbative argument. On the phase boundary between CP-SI and P21/c-SI the two phases have same free energy. NQE will correct the free energy on
Figure 4.3: The phase diagram of superionic phase for water ice, with NQE included. The red, green and grey area are P21/c-SI, CP-SI and solid phase, respectively. Black dash line indicates the phase boundary without NQE. Blue dash line indicates the phase boundaries calculated with semi-harmonic approximation. The difference of the phase boundary with and without NQE is significant. Both path-integral and QHA computation results show that the NQE makes CP-SI more stable than P21/c-SI.

both phases. In order to better quantify the effects of NQE on the phase boundaries, we look at the perturbation of free energy. Following ref [57], the free energy can be expanded to the lowest order in $\hbar$ according to:

$$F = F_{cl} + \frac{\hbar^2}{24T^2} \sum_i \frac{1}{m_i} \left( \frac{\partial U}{\partial q_i} \right)^2 + O(\hbar^3)$$

where $F_{cl}$ is the free energy in the classical limit, $m_i$ is the mass of the $i$th particle, and $\left( \frac{\partial U}{\partial q_i} \right)^2$ is the mean squared force acting on particle $i$. As shown in this formula, the lowest order is $\hbar^2$.

Neglecting higher order terms in $\hbar$, NQE effects are dominated by the $\hbar^2$ term, i.e.,

$$\frac{\hbar^2}{24T^2} \sum_i \frac{1}{m_i} \left( \frac{\partial U}{\partial q_i} \right)^2$$

which indicates that a more constrained system will have a larger free energy correction from NQE, and thus should be less stable when the quantum
effects is included. We know that the P21/c-SI phase is denser than CP-SI, therefore, when NQE is included, one would expect the P21c-SI have higher free energy than the CP-SI phase. To verify it, we calculate the lowest order corrections on both CP-SI and P21/c-SI, from 1100K to 2000K, as shown in Fig4.3. One can see that in the temperature range we studied, the corrections from NQE is consistently higher in the P21/c-SI phase than the CP-SI phase. This is consistent with the simulation results that NQE stabilizes the CP-SI phase over the P21c-SI phase.

A similar argument explains the reduced melting temperature for P3121. When P3121 melts into the CP-SI phase, the oxygen sublattice readjust and form a close-packing structure with a higher symmetry. This more symmetric sublattice provide more space for hydrogen and thus hydrogen’s movements are less constrained in the CP-SI, which make it more stable when NQE is considered. However, in the crystalline P21/c to P21/c-SI transition, the oxygen sublattice is essentially the same in the competing phases. In this case NQE will have similar corrections on both of the solid and SI phases. Therefore it only has minor effects on the melting temperature of solid P21/c.

4.4 Conclusion

To summarize, we find the NQE modifies quantitatively the SI ice phase boundaries. Compared to the classical results, NQE make CP-SI phase more stable and increases the transition pressure from 1.4-1.6TPa to 1.6-1.75TPa. Meanwhile, NQE reduces the melting temperature of hydrogen sublattice by about 200 K in CP like solid phases, but has little impact on the melting temperature of P21/c. In addition, we show the free energy correction from NQE is larger on the high pressure phases, but it does not necessarily have a larger impact on the phase boundary. The free energy corrections
Figure 4.4: **First order approximation to the free energy corrections from NQE.** The red and blue lines are the corrections at 1.9TPa and 1.3TPa, respectively. At 1.9TPa the system is in P21/c-SI or solid P21/c phase, and at 1.3TPa the system is in CP-SI or P3121 phase. The NQE correction is significantly higher in P21/c-SI phase than in CP-SI phase, which makes CP-SI more stable with NQE.

on competing phases may cancel. Lastly, the transition pressure difference between PIMD and QHA estimations indicates the anharmonicity is strong in SI phases and impacts the phase boundary.
Chapter 5

Chemical Bonding and Electronic Structure of High Pressure Ice

5.1 Introduction

In this chapter we investigate the chemical bonding and the electronic structure of the SI phases. At standard temperature and pressure conditions, water and ice are formed with covalently bounded molecular units. The interactions among different units is due to the hydrogen bonds. In this structure, hydrogen is closer to the covalently bonded oxygen, and the arrangement of hydrogen follows the famous "ice rule", which states each oxygen is covalently bonded to two hydrogen atoms, and that the oxygen atom in each water molecule forms four hydrogen bonds with other oxygens. However, in high pressure structures such as ice-X in which the hydrogen is equispaced between nearest oxygens and the molecular units no longer exist. It indicates water and ice undergo a transition from a molecular system to an ionic system.

Materials under high pressure also have very interesting and sometime astonishing properties. Theoretical and experimental results showed that in many condensed systems the energy gap will reduce at higher pressure. For example GaAs undergoes
a semiconductor-metal transition at about 25 GPa [58]. However, the counter example also exists. For example, first principle studies showed evidence that Lithium does not follow the intuitive expectations of quantum mechanics by becoming even more free-electron-like at higher densities. Instead, at high pressure its electronic structure departs radically from nearly free-electron behaviour, and its common symmetric structure becomes unstable to a pairing of the ions [59]. As a result, Lithium may become an insulator at higher pressure. Water and ice phases are known to be good insulators, and previous researches showed that zero temperature water ice has decreasing band gap as pressure increases. The studies of zero temperature ice phases also showed the metalization of water and ice is difficult. Zero temperature studies based on DFT suggest that water ice should remain electronically insulating up to the extremely high pressure of about 5 TPa. Can things be different in the finite temperature superionic phases?

Recently, an even more interesting discovery was made: crystalline hydrogen sulfide, a material made by H$_2$S, a sister molecule of water, becomes superconducting at pressure higher than 140 GPa [15] with the highest known critical temperature. H$_2$S is very similar to water molecule, with oxygen replaced by sulfur. Though metallization is not yet achieved for water ice, it has been proven that at pressure higher than 96 GPa, H$_2$S will become a metal and superconducting. H$_2$S also has a complex phase diagram and theoretical studies showed that at high pressure H$_2$S may decompose to elemental hydrogen and H$_3$S [60] that has important implications on the formation of high $T_c$ superconductor. In our study we did not search for different stoichiometries. Though our simulation indicates superionic water is still electronically insulating, it did not exclude the possibility of metallization or even superconductivity with different stoichiometries. We leave this question to further researches.

In this chapter, we investigate the chemical bonding and electronic structure from
ice Ih to the high pressure superionic phases. We identified several patterns of the electronic structure as a function of pressure. Firstly, we studied the distribution of maximally localized Wannier function centers (MLWCs). MLWCs provide a classical correspondence for the location of an electron in a quantum-mechanical electronically insulated system [61, 62, 63], allowing for the definition of insightful pair-distribution functions between electrons and ions. We found the MLWCs are tetrahedrally distributed around oxygen ions and the radial distribution along nearest oxygen ions is unimodal, very different from the bimodal distribution that reflects the donor and acceptor character of the H bonds in normal water and ice. It shows evidence that at high pressure ionic bonds replace the covalent and hydrogen bonds between molecular units that characterize the low pressure phases of water. We evaluated the dynamic Born charge, which is defined as the change of polarization induced by a displacement of an ion in condensed phase, for hydrogen and oxygen ions in all of the superionic phases. The dynamic Born charge are similar for all superionic phases, indicating the electronic structure does not change appreciably across different superionic phases.

Secondly, we investigate the electronic density of states for each phase. As the pressure increases, the band width increases as a consequence of the increased density. In high pressure superionic phases such as CP-SI and P21/c-SI, the gap between s and p states closes and the electronic state no longer has clear s or p character. The band gap reduces as the pressure increases up to the CP-SI phase. However, the presence of the P21c-SI phase makes the band gap no longer a monotonic decreasing function of pressure. We find the band gap increases when the system transits from the CP-SI phase to the P21/c-SI phase.

We will briefly introduce the methods such as the maximally localized Wannier functions and projected density of states (pDOS) and electron density projection we used to analyze the electronic structure. Then the computation results are presented. In the last part we will discuss the chemical bonding and electronic structure in more details.
## 5.2 Methodology

To have a complete picture of the chemical bonding and electronic structure of water ice, we investigate four different ice phases over a vast range of thermodynamic conditions, which includes zero temperature hexagonal ice (Ih) and three superionic phases, BCC-SI, CP-SI, and P21c-SI. Ih ice is a low pressure structure that reflects the electronic structure of ice under normal thermodynamic condition. We use its zero temperature electronic structure as a reference to compare with other more complex structures in superionic phases. At temperatures above 1400 K, the hydrogen ions are diffusive in superionic phases. And they may change the electronic structure qualitatively. Therefore, we apply molecular dynamics to simulate the superionic phases and use the ensemble average to estimate the electronic structure of superionic phases.

The zero temperature Ih ice crystal structure is optimized via Born-Oppenheimer molecular dynamics. Ice Ih is a molecular crystal and it has been shown that the vdW interaction is important to correctly describe the volume change between ice Ih and liquid water. Therefore we use the recently developed PBE0+TS vdW functional [64] that includes vdW interactions and correctly describes the volume discontinuity at melting. In the superionic phases the equilibrium density is largely dictated by the PV term in the enthalpy and we expect that vdW interactions should be much less important. In the superionic phases the hydrogen ions behave like bare protons and thus the vdW interaction does not affect the stability and structure of superionic phases significantly. For superionic phases, we apply first principle Car-Parrinello Molecular Dynamics (CPMD) with PBE to simulate the trajectory of molecular movements. The pressure and temperature of BCC-SI, CP-SI, and P21c-SI are fixed at 200GPa and 2200K, 1.3TPa and 1600K, and 1.9TPa and 1600K, respectively. The simulation configuration setup is the same as discussed in the previous chapters. For each simulation, once the system reach equilibrium, we take 100 snapshots over the trajectories to represent the ensemble of the superionic phases. In all of the simulations nuclear
quantum effects are ignored. We have shown that NQE changes the high pressure ice phase boundaries. However, NQE does not change the structure of each stable phase significantly. We found in the full quantum simulations the structure formed by the centroid of each polymer is almost indistinguishable with the classical simulations.

5.2.1 Chemical bonding and maximally localized Wannier function center

It is well known that at room temperature and pressure, hydrogens and oxygens form covalent bonds and nearby water molecules have strong hydrogen bonding interaction. But in high pressure phases the water molecules cease to exist as distinct entities while oxygens and hydrogens behave like ions in ionic compounds. How does this structural change affect the electronic structure? To answer this question, we studied the Maximally Localized Wannier functions of the $P2_1/c - SI$ phase. Wannier function is an alternative representation of the single particle wavefunction for crystalline system. Crystalline periodicity implies that the eigenstates of the Kohn-Sham Hamiltonian are Bloch states and they satisfy Bloch theorem. In the case of insulators, when the occupied bands are separated by an energy gap from the unoccupied states, it is possible to perform a unitary transformation of the occupied subspace such that each state is now maximally localized in space. The condition of maximal localization corresponds to minimize the spread of the new wavefunctions. The new wavefunctions are no longer eigenstates but are linear superpositions of eigenstates.

Marzari and Vanderbilt developed a maximal localization criterion that minimize a localization functional corresponding to the sum of the second-moment spread of each Wannier charge density about its own center of charge. Mathematically the maximally localized Wannier functions minimize the objective functional

$$\Omega = \sum_n <r^2>_n - <\vec{r}>_n^2$$
where $< r^2 >_n = < n|r^2|n >$, $< \vec{r} >_n = < n|\vec{r}|n >$, and $|n >$ is the nth Wannier function. The Maximally Localized Wannier function is computationally tractable and has important implications on the nature of bonding. In particular, the charge center of a Maximally Localized Wannier function provides a kind of classical correspondence for the location of an electron in a quantum-mechanical insulator [61, 62, 63], allowing for the definition of insightful pair-distribution functions between electrons and ions. This is important for us to understand the chemical bonding of high pressure ice.

As we mentioned in Chapter 3, the highly compressed ice behaves like a network of highly compressed oxide ions [23]. We find a similar behavior in the $P2_1/c$-SI phase. The superionic phase is ionically conducting but electronically insulating. Thus we can characterize its valence electronic structure in terms of Maximally Localized Wannier functions [65]. In particular it is interesting to plot the distribution of distances between each MLWC and the nearest O atom, as shown in Fig. 5.1. This shows a unimodal distribution, very different from the bimodal distribution observed in liquid water or ice at standard pressure conditions [9], which shows donor and acceptor hydrogen-bonds (H-bonds). Figure 5.1 also reports the distribution of the MLWC in real space. The MLWC distribute tetrahedrally around O, which is in agreement with a nominal $O^{2-}$ charge state [66]. The dramatic change in the MLWC distribution of superionic ice relative to standard water signals a dramatic change in the nature of the chemical bond: at high pressure ionic bonds replace the H-bonds between molecular units that characterize the low pressure phases of water.
Figure 5.1: The radial distribution function of the MLWC. The cartoon shows the distribution of the MLWC in real space. The red and silver balls are the oxygen and hydrogen atoms, respectively. The blue region indicates the MLWC. The MLWC distribution from a liquid water simulation at standard temperature and density [9] is also shown for comparison. The dramatic change in the MLWC distribution signals a dramatic change in the chemical bond from low to high pressure phases of water (see text).

The distribution of MLWC indicates that ions in the superionic ice phases can be roughly viewed as $O^{2-}$ and $H^+$. However, in the condensed phase, the nominal ionic charges are ill-defined. On the other hand, dynamical Born charges, which represents the response of the system to a perturbation, are well-defined for an electronically insulating system like superionic ice. The electronic contribution to the Born effective charge tensor associated to atom $i$ is given by:

$$Z_{i, \alpha \beta} = \Omega \frac{\partial P^{\alpha}}{\partial r_{\beta}}$$
where $\Omega$ is the unit cell volume, $P^\alpha$ is the total polarization along direction $\alpha$, and $r^i_\beta$ is the coordinate of ion $i$ in direction $\beta$. We measure Born effective charge tensor in the unit of electron charge $e$. We calculated the dynamical Born charges for a large number ($\sim 100$) of snapshots along the dynamical trajectories. Since the original definition of Born charge is inconvenient to calculate, we used the electric enthalpy method [67], which gives $Z^*_{i,\alpha\beta} = \frac{\partial F_{i,\alpha}}{\partial E_\beta}$, where $\partial F_{i,\alpha}$ is the change of atomic force in direction $\alpha$ on ion $i$ due to an homogeneous electric field $\partial E_\beta$ applied in direction $\beta$. Following [68], we analyse the charge tensor in terms of isotropic and anisotropic components.

We decompose the charge tensor into three parts, according to the representations of the spatial rotations [68]. Among them, $L=0$ is the isotropic part, which is given by the trace of the charge tensor. $L=1$ and $L=2$ are the anisotropic parts, which correspond to the antisymmetric and to the traceless symmetric decomposition of charge tensor, respectively. The magnitude of each component can be quantified with the 2-norm of matrices. Table 5.2.1 summarizes the results. $L=0$ is the dominant component in all of the cases. There is also a large contribution from the $L=2$ part, especially for H, in these two phases.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Atom</th>
<th>$&lt;Z_0&gt;$</th>
<th>$L=0$</th>
<th>$L=1$</th>
<th>$L=2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2$_1$/c-SI</td>
<td>O</td>
<td>$-2.4 \pm 0.2$</td>
<td>85%</td>
<td>4%</td>
<td>11%</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>$1.2 \pm 0.1$</td>
<td>71%</td>
<td>3%</td>
<td>26%</td>
</tr>
<tr>
<td>CP-SI</td>
<td>O</td>
<td>$-2.4 \pm 0.2$</td>
<td>80%</td>
<td>5%</td>
<td>15%</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>$1.2 \pm 0.1$</td>
<td>60%</td>
<td>3%</td>
<td>37%</td>
</tr>
</tbody>
</table>

Table 5.1: The decomposition of the effective charge tensor

In the CP-SI and P2$_1$/c-SI phases we find the average isotropic component are $+(1.2 \pm 0.1)$ and $-(2.4 \pm 0.2)$ for hydrogen and oxygen ions respectively. The corresponding values in the BCC-SI phase are $+(1.0 \pm 0.1)$ and $-(2.0 \pm 0.2)$. The small difference from the nominal values indicates a contribution due to the electronic response. The average isotropic components of the effective charges are the same at
different snapshots and do not change appreciably in the zero-temperature counterparts, which indicates that the electronic structure does not change appreciably across the solid to superionic transition.

### 5.2.2 Electron density of states

To understand the effects of pressure on electronic structure, we investigate the electron density of states (DOS) in these phases. For a given snapshot, we evaluate the eigenvalues of the Hamiltonian within DFT. For superionic phases, we take the average of the DOS over 100 snapshots, whereas at zero K Ih only has a single snapshot. The DOS is shown in Fig 5.2. The width of the valence band greatly increases from about 20 eV in ice Ih to more than 40 eV in the P21/c-SI phase. We compute the electronic gap as difference between the single particle energies of the conduction band minimum and the valence band maximum. Note that the eigen values of electron states also give unoccupied states. However, they are the unoccupied states of the Kohn-Sham Hamiltonian and do not correspond to excited quasi-particle states in the system. We found except for the newly discovered $P21/c$-SI phase, the band gap decrease when pressure is increased. The electronic band gap is reduced from about 6 eV in Ih ice to about 2.6 eV in CP-SI phase. However, we notice when it transforms to P21c-SI phase, the band gap increases from about 2.6 eV to about 3.2 eV.

We also looked at the partial DOS (pDOS) on the oxygen ions which is defined as the decomposition of DOS on angular momentum components about the oxygen atom. This is defined as follows. Let the wavefunction of the n-th occupied state be $\Psi^n(r)$, then the projection of the wavefunction on angular momentum state $l,m$ can be written as

$$\Psi_{l,m}^n(r) = \int_{4\pi} d\hat{r} Y_{lm}^*(\hat{r}) \Psi^n(r,\hat{r})$$

where the origin is on oxygen ions and $Y_{lm}$ are spherical harmonics. Substitute
\( \Psi_n(r, \mathbf{\hat{r}}) \) with the plane wave expansion \( \Psi_n(r, \mathbf{\hat{r}}) = \frac{1}{\sqrt{\Omega}} \sum_G c^n_G e^{iG \cdot r} \), one has

\[
\Psi_{l,m}^n(r) = \frac{4\pi i^l}{\sqrt{\Omega}} \sum_G c^n_G j_l(G r) Y_{l m}^{*} (\mathbf{\hat{G}})
\]

where \( \Omega \) is the volume of the system, and \( c^n_G \) is the coefficient of plane wave \( G \). The projection of n-th occupied DOS on state \( l, m \) is simply defined as

\[
W^n_l = \sum_m \int_R d r r^2 |\Psi_{l m}^n(r)|^2
\]

where \( R \) is a cutoff radius that we fixed to be 1 a.u. in all phases. We checked that a different \( R \) would change pDOS quantitatively, but not qualitatively. For each superionic phase, we compute the averaged pDOS over 100 snapshots. Fig5.3 shows the pDOS for \( l = 0(s), 1(p), 2(d) \). The character in the parenthesis indicates the corresponding atomic orbital. The projection on higher angular momentum is negligible. Note that in the low pressure ice-Ih phase the \( s \) and \( p \) states are well separated. But at high pressure phases there is no longer a clear separation, which indicates a hybridization of \( s \) and \( p \) orbitals.
Figure 5.2: **The total density of states and inverse participation ratio of P21c-SI and CP-SI phases.** The figure shows the total density of states of electrons and the inverse participation ratio (IPR) in the CP-SI and P21c-SI phases. The red squares are the IPR of the electron states. And the blue line indicate the total density of states. The dash line indicate the position of Fermi level.
Figure 5.3: **Projected electron density of states** The figure shows the projected density of states of electrons in four phases including zero temperature ice Ih (upper left), BCC-SI (upper right), CP-SI (lower left) and P21c-SI (lower right). The blue, green and red lines are the pDOS on s orbital (l0), p orbital (l1) and d orbital (l2), respectively. For the valence band, the projection on d orbital is always close to zero, even at the highest pressure. As the pressure increases, the valence band range expands from about 20 eV in ice Ih to about 50 eV in P21-SI. And the band gap gradually reduces from ice Ih to CP-SI. However, we found P21c-SI has a larger band gap compared to CP-SI. Also, at higher pressure, the p states extend to the lower energy region and mix with the s states.

In addition, we evaluate the inverse partition ratio (IPR) for the P21c-SI and CP-SI states. The IPR is defined as $IPR = \frac{\int_{\Omega} |\Psi_n(r)|^4 dr}{(\int_{\Omega} |\Psi_n(r)|^2 dr)^2}$, where $\Psi_n(r)$ is the wavefunction of the n-th state. IPR measures the localization of a given state. If a state is fully delocalized, then as the volume $\Omega \to \infty$, $IPR \to 0$. On the other hand if a state is localized, then it will have a finite IPR. Fig 5.2 summarizes the DOS and IPR of each phase. As shown in this figure the inner states are localized and tightly
bound to the core oxygen ions. The states close to the Fermi surface are less localized.

Lastly, we looked at the two dimensional plots of the electron density on a plane in the three superionic phases. The structure of BCC-SI and FCC-SI phases have well defined first shell of nearest neighbours. To include the nearest neighbours, we project the density of electrons on the [110] and [100] planes of these two phases, respectively. In the P21c-SI, due to the lower symmetry there is not a well defined first shell of neighbours. Instead, each oxygen has 13 oxygen neighbours within close distance. However, if we connect each oxygen with the first three nearest neighbours, it forms a layered structure where each layer is similar to a highly distorted honeycomb lattice, as shown in Fig 5.4. This plane is also parallel to the highly diffusive quasi two dimensional plane in the P21c-SI phase [55]. The details of this quasi two dimensional diffusion plane can be found in chapter 3. Thus for P21c-SI, we look at the projection on this plane. The figures show the contour of the total electron density on these planes.
Figure 5.4: **The layered structure of P21c-SI oxygen sublattice** The figure shows the structure of the layered oxygen sublattice in P21c-SI phase. The red dots indicate the centroid of oxygen ions, and red stick indicate the link between nearest oxygen neighbours. It shows a two-dimensional layered structure. This is consistent with the two-dimensional diffusion plane found in P21c-SI. The diffusive plane is between two adjacent layers. The oxygen sublattice in P21c-SI can be viewed as a highly distorted honey-comb structure. However, oxygen ions in the same layer are not on the same plane.

Fig 5.5 shows the projection of electron density on the three planes of BCC-SI, CP-SI, and P21/c-SI phases. These figures confirm the ionic picture of high pressure ice phases and the electron densities are localized on the oxygen. In addition, it shows that electrons density has a roughly spherical symmetric distribution around oxygen ions, which is in consistent with the fact that high pressure ice phases have a nominal $O^{2-}$ charge state. However, the electron density distribution of the $P21/c - SI$ deviates slightly from the spherical symmetric distribution, which reflects the lower symmetry of the oxygen background in P21/c-SI phase. This asymmetric structure also splits the degenerated $p$ states. As shown in Fig 5.3, the top two valence band
states have higher energy and are separated from other lower states. We investigated the projection of the top two electron states in P21/c-SI phase. As shown in Fig 5.6, the top two electron states have strong $p$ orbital characters. One of the state is perpendicular to the diffusion plane and the other one is in parallel to the diffusion plane. It shows the degenerated $p$ states in BCC-SI and CP-SI phase are splitted in the P21/c-SI phase due to the lower symmetry.

Figure 5.5: **The projection of electron density of BCC-SI, CP-SI, and P21/c-SI phases.** The projected planes are [110] for BCC-SI, [100] for CP-SI, and the quasi two dimensional diffusion plane for P21/c-SI, respectively. See text for the details. The contour shows the density distribution of electrons. The black dots indicate the average location of oxygen ions. For P21/c-SI phase we also added the projected distribution of hydrogen ions. The distribution of electron density are spherical symmetric in the BCC-SI and CP-SI phases, but distorted in the P21/c-SI phase.
Figure 5.6: The projection of electron density of the top two valence band stats of P21/c-SI phases. The projected planes is the quasi two dimensional diffusion plane for P21/c-SI. The contour shows the density distribution of electrons. The black dots indicate the average location of oxygen ions. The top two valence band stats show strong $p$ orbital characters. The first state has an orientation that is perpendicular to the diffusion plane and the second state has an orientation that is in parallel with the diffusion plane.

5.3 Discussion

Our results show a clear pattern of the electronic structure as a function of pressure. As the pressure increases, the distance between hydrogen and oxygen reduces and at sufficiently high temperature the hydrogens become fully diffusive. As a result, the covalent bond between oxygen and hydrogen breaks, leaving electrons tetrahedrally distributed around oxygens. The bonding between hydrogen and oxygen also become more ionic under high pressure. In fact, as shown in ref [23], in high pressure ice phases the coexistence of oxygen and hydrogen in the lattice allows the electron transfer that electronegativity mandates, towards a formal $(H^+)_2(O^{2-})$ extreme. As shown in ref [23], if we remove all hydrogen ions and replace them with uniform posi-
tive background charge, the resulting electronic DOS is very similar to the true DOS, indicating the hydrogen ions acting like a uniform background. This is in consistent with our calculation of MLWC.

The partial DOS from our calculation showed evidence on the change of electron band structure. First, we notice the band width increased significantly at higher pressure. In Ice Ih, the $s$ and $p$ states are well separated, with a gap of more than 10 eV. As the pressure increased, the band width increases, causing the gap between $2s$ and $2p$ close at higher pressure. The gap between $2s$ and $2p$ is only about 3 eV in the BCC-SI and totally disappears in CP-SI and P21c-SI. In addition, the pDOS shows that in lower pressure phases such as ice Ih and BCC-SI, each occupied state are dominated by either $s$ or $p$ component. However in high pressure superionic phases, the state is formed by a mixture of $s$ and $p$ components. This result indicates that as the pressure increase, the gap between $2s$ and $2p$ orbital reduces, resulting a hybridisation between $2s$ and $2p$ states. We noticed in the low symmetry P21/c phase the distribution of electron density diviates from spherical symmetric distrition, and the degenerated $p$ states split in the P21/c phase.

Previous static calculations have suggested the band gap of ice monotonically decreases under pressure. If this trend continues, ultimately high pressure ice will become a conductor. In our simulation, we find a similar trend from Ih ice to CP-SI phase. The electronic band gap reduced from $\approx 6$ eV in Ih ice to 2.6 eV in CP-SI phase. However, we notice when it transform to P21c-SI phase, the band gap increases from 2.6 eV to 3.2 eV. It is known that PBE tends to underestimate the band gap of water [69, 70], but the variation of the band gap under pressure should be reasonable. Thus it still provides a reasonable estimation of the band gap reduction as a function of pressure. The band gap depends on two main factors: the band width and the relative location of the valence band and conduction band. With fixed band width, the band gap increases as the separation between the valence band and the
conduction band increases. With similar arguments, if the band locations are fixed, the band gap will decrease if the band width increases. In a simple tight binding model one would expect that the band width is larger if the hopping parameter is larger. As the pressure increases, the distance between atoms decreases, the hopping parameter increases and so does the band width. Therefore, at higher pressure the band width is greatly increased, as shown in Fig 5.3. This explains why we see a decreasing band gap in most of the high pressure ice phases.

On the other hand, extremely high pressure may also affect the relative location of valence band and conduction band and thus changes the band gap. For a state localized on a single atom, the electronic wavefunction is dominated by the potential associated to the atom about which the electron is localized. Thus the effective single electron potential can be approximated as the Coulomb interaction with the center atoms. The surrounding atoms only affect the boundary condition. Due to the Pauli exclusion principle, the electrons on nearby atoms provide a repulsive effective potential. Therefore, qualitatively, the single electron potential can be approximated as a truncated coulomb potential: the potential is coulomb-like up to radius $R$ and it goes to infinity beyond $R$, where $R$ measures the distance from nearby atoms. At low pressure, the average distance between different atoms is large and it only has minor effects on the atomic orbital. However, as the pressure increased, the system are compressed and the distance between different atoms is greatly reduced. When the average distance between nearest atoms is close to the size of the electron’s orbital, there will be a significant overlap between different atoms’ electrons and the electron wave function will be strongly constrained due to the interaction from the electrons on neighbouring atoms. This radial constraint will penalize electron states that have multiple radial nodes and raise the energy of those states, such as the $2s$ and $3s$ states. If the effect of the repulsive potential at $R$ becomes dominant the sequence of levels may change from the hydrogenic sequence to that of a spherical square well potential.
The above two factors have opposite effects on the band gap. For high pressure ice phases the highest valence band is dominated by the $2p$ states and the lowest conduction band is dominated by the $3s$ states. At lower pressure, the constraint from the neighboring electrons is weak so the first factor dominate the behavior of band gaps and thus we see the band gap decreases at higher pressure. However at extremely high pressure the constraint effect is strong and it raises the energy level of the $3s$ states, which may explain the increased band gap from the FCC-SI to P21c-SI phase transition.
Appendix

1. Constant Pressure Car-Parrinello Molecular Dynamics

Density Functional Theory

In this section, I will briefly review the basics of density functional theory (DFT). I will mainly focus on the important concepts. The details can be found in standard textbooks.

In the solid state physics or material science, one faces a very complex many-body system. The total number of particles, including nuclei and electrons is at the order of $10^{23}$. Since the electrons are much lighter than nuclei, usually it is reasonable to assume that at any snapshot, all nuclei are fixed. If a system is electronically insulating, then electrons are staying on the ground states and one only needs to find the ground states with fixed nuclei as external potential. This is the so called Born-Oppenheimer approximation. However, even with this approximation, there is little hope to solve the full quantum mechanical problem directly and thus approximations must be made. Several post-Hartree-Fock ab-initio quantum chemistry methods have been proposed, for example, configuration interaction and Coupled cluster[71]. However, these methods have computational cost increasing rapidly with the number of electrons, which makes them impossible to apply on large systems. Full configuration
interaction is exact but has exponential cost with the number of electrons. Coupled cluster methods are very accurate though not exact, and they scale as $N^6 - N^7$, where $N$ is the number of electrons. DFT, on the other hand, transforms this complex problem to a much simpler system of noninteraction electrons in a local effective field $V_{\text{eff}}(r)$. From DFT one can solve the exact ground state electron density. And the ground-state energy of the system is a functional of the electron density.

Compared to the full quantum mechanical solution, which tries to solve the time dependent many-body Schrödinger equation

$$\hat{H}(t)\Psi(r_1, s_1, r_2, s_2, ..., r_N, s_N, t) = E(t)\Psi(r_1, s_1, r_2, s_2, ..., r_N, s_N, t)$$

where $s_i$ represents the spin components, DFT offers an appealing alternative that can map the original many-body system to a single-body system. Instead of the wavefunction $\Psi(r_1, s_1, r_2, s_2, ..., r_N, s_N, t)$, DFT depends solely on the electron density $n(r, t)$. One can show that there is a one-to-one mapping between $n(r, t)$ and $\Psi(r_1, s_1, r_2, s_2, ..., r_N, s_N, t)$, thus $n(r, t)$ uniquely determines the wavefunction.

Further more, the Kohn-Sham theory shows that the fully interacting system with the real potential can be mapped exactly into a fictitious non-interacting system where the electrons move within an effective Kohn-Sham single-particle potential:

$$\left(-\frac{1}{2}\nabla + V_{\text{ext}}(r) + V_{\text{H}}(r) + V_{\text{xc}}(r)\right)\psi_i(r) = \epsilon_i\psi_i(r)$$

where $V_{\text{ext}}$, $V_{\text{H}}$ and $V_{\text{xc}}$ are the external potential, Hartree potential, and exchange-correlation potential, respectively, and $\psi_i(r)$ is the wavefunction corresponding to the electron density. In the Kohn-Sham theory, the electron density is given by $n(r) = 2 \sum_i |\psi_i(r)|^2$, where 2 stands for double occupation and $i = 1, 2, ..., N/2$, $N$ being the number of electrons. The sum of these three terms is the effective single-particle potential. Note that the Hartree potential and exchange-correlation potential are functional of electron density. Varying the wavefunction will change the effective single-particle potential. Thus this equation must be solved iteratively to make it
self-consistent.

DFT provides a very elegant framework to solve the ground state of a many-body electron system. However, practically, the exact form of the exchange-correlation potential is not known. Therefore, approximations must be made. Popular choices include Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA). LDA assumes the exchange-correlation potential is strictly local, thus the exchange-correlation energy functional can be written as

$$E_{xc}^{LDA} = \int \rho(r) \epsilon_{xc}(\rho) \, dr$$

GGA improves it by allowing non-local functional forms. Essentially, on a given point, GGA depends on not only the density $n(r)$, but also the gradient of $n(r)$. This is like the Taylor expansion for a function. One particular form of GGA is the famous Perdew-Burke-Ernzerhof functional (PBE)\cite{72}. It is a parameter free GGA and has been proven to be able to give accurate results for various systems. We use PBE functional extensively in our research.

DFT is one of the fundamental building blocks for more complex simulations or analysis. Once we found the ground state by minimizing the density functional, we can compute various physical quantities such as the atomic force, electronic band structure, density of states and so on. We can also use DFT to find the crystal structure at zero temperature by minimizing the system’s energy.

**Constant-pressure Car-Parrinello molecular dynamics**

Although DFT is a powerful tool model materials at atomic level, it is computationally expensive, which prevents it to apply on big systems. At finite temperature, in order to have an accurate statistics, one usually needs to accumulate data with a long molecular dynamics simulation, which may have tens of thousands of different con-
figurations. For each configuration, it takes several minimization iterations to solve the Kohn-Sham equation in DFT framework. Thus, the total required computational resource to perform a naive DFT molecular dynamics is unaffordable. Car and Parrinello proposed an innovative way to alleviate this problem[73]. They showed that if one introduces a proper fictitious dynamics for electrons, then it can keep electrons close to the ground state. Thus it does not require the expensive self-consistent minimization at each step and the system’s energy can be computed on-the-fly. They purposed an extended Lagrangian which includes the dynamics of both nuclei and electrons. The Car-Parrinello Lagrangian is defined as

\[
L_{CP} = \frac{1}{2} \left( \sum_I M_I \dot{R}_I^2 + \mu \sum_i \int \, d\mathbf{r} |\dot{\psi}_i(\mathbf{r}, t)|^2 \right) - E[\psi_i, R_I]
\]

where the index \(I\) and \(i\) iterate over nuclei and electronic states, respectively, \(\mu\) is the fictitious mass of electron that controls the dynamical response of the electronic orbitals, \(E[\psi_i, R_I]\) is the Kohn-Sham energy density functional, and \(\psi_i(\mathbf{r}, t)\) is the time dependent Kohn-Sham orbital. The orbitals \(\psi_i\) are orthonormal and subjected to the following condition

\[
\int \, d\mathbf{r} \psi_i^*(\mathbf{r}, t) \psi_j(\mathbf{r}, t) = \delta_{ij}
\]

This Lagrangian generates a dynamics of nuclei and orbitals through the equations of motion:

\[
\mu \ddot{\psi}_i(\mathbf{r}, t) = -\frac{\delta E}{\delta \dot{\psi}_i^*(\mathbf{r}, t)} + \sum_k \Lambda_{ik} \psi_k(\mathbf{r}, t)
\]

\[
M_I \ddot{R}_I = -\nabla_{\mathbf{R}_I} E
\]

where \(\Lambda_{ik}\) are the Lagrange multiplier. The Lagrange multiplier is given by \(\Lambda_{i,k} = <\psi_i|\hat{H}|\psi_k> - \mu <\dot{\psi}_i|\dot{\psi}_j>\). In this dynamics electronics and ionic structure evolve simultaneously. Note that the dynamics for orbitals is fictitious.

CP dynamics conserves the total energy \(H_{CP} = K + K_e + E[\psi_i, R_I]\), where \(K\) is the kinetic energy of nuclei \(K = \sum_I \frac{1}{2} M_I \ldots R_I^2\), and \(K_e\) is the fictitious kinetic energy of
electrons $K_e = \sum_i \frac{1}{2} \mu \int dr |\psi_i|^2$. At zero temperature, when the energy is minimized, $\ddot{\psi}_i = 0$, the above equations of motion is equivalent to the Kohn-Sham equation and the eigenvalues of the Lagrange multiplier matrix are equal to the occupied Kohn-Sham eigenenergies. The electronic system lies on the BO surface. At finite temperature, if we assume all ions are fixed, we can minimize the energy with respect to the electronic degree of freedom and achieve the exact BO approximation. This is equivalent to assume all electrons have zero fictitious mass. With zero fictitious mass, electron will always stay on the ground state and the system is guaranteed to stay on the BO surface.

In practice, to make the simulation tractable, we must assign a finite fictitious mass for electron. With finite fictitious mass, CPMD is no longer on the BO surface. However, the nuclear dynamics generated by CPMD is an excellent approximation of the Born-Oppenheimer time evolution when orbital dynamics is fast and follows adiabatically nuclear motion. The adiabacity condition require the $\omega_{cv}^{min} >> \omega_R^{max}$, where $\omega_{cv}^{min}$ is the lowest frequency of the electronic orbitals oscillate around the instantaneous ground state, and $\omega_R^{max}$ is the highest frequency of ionic system. For small deviations of the electronic orbitals $\omega_{cv} = \sqrt{\frac{\epsilon_c - \epsilon_v}{\mu}}$, where $\epsilon_c$ and $\epsilon_v$ are the ground state Kohn-Sham eigenvalues for the valence and conduction states, respectively, and $\mu$ is the fictitious mass of electron. The ionic frequency $\omega_I^{max}$ can be estimated via velocity-velocity power spectrum. When $\omega_{cv}^{min} >> \omega_R^{max}$, the fast oscillatory motions of the electrons average out on the time scale of nuclear dynamics and thus the forces acting on the nuclei are close to the BO forces.

CPMD is usually implemented via velocity Verlet algorithm. Consider a harmonic system with the highest characteristic frequency of $\omega^{max}$. In order to have enough samples of the dynamics, the minimum time step need to be one order of magnitude less than $\frac{2\pi}{\omega^{max}}$, or $\Delta t = \frac{\pi}{\omega}$. The highest frequency of our system is associate with dynamics of electrons, which is $\omega_e^{max} = \sqrt{\frac{E_{cut}}{\mu}}$, where $E_{cut}$ is the plane wave energy
cut-off. Thus the minimum time step is \( c \ast \sqrt{\frac{\mu}{E_{\text{cut}}}} \). As we can see, though a smaller fictitious electron mass improves the adiabaticity and reduces the discrepancy between CPMD and the BO surface, it limits the minimum time step we can use. In practice, one needs to experiment with different time steps and pick the largest one that will not cause significant drift in ionic system’s energy.

It has been shown that constant-volume molecular dynamics simulation may introduce significant hysteresis effects which prevents phase transition[28]. In order to estimate reliable phase boundaries, we need a constant pressure simulation (NPT ensemble) which allows both the shape and the volume of the cell to fluctuate. Great progress was achieved to adapt ab-initio molecular dynamics with variable cell constant pressure simulations (NPT-AIMD). In the work of Parrinello and Rahman[28, 74], they argued that in an MD simulation of a crystal phase transition, it is necessary to treat the simulation supercell edges \( \vec{a}, \vec{b}, \vec{c} \) as dynamical variables. The Lagrangian is extended to include the dynamics of edges as

\[
L(s, h, \dot{s}, \dot{h}) = \frac{1}{2} \sum_I m_I s_I^T G s_I - V(s, h) + \frac{1}{2} W Tr(\dot{h}^T \dot{h}) - p_{\text{ext}} V
\]

where \( s_I \) is a position vector in fractional coordinates for atom \( I \), \( h \) is the symmetric matrix of the supercell, tensor \( G = h^T h \), \( p_{\text{ext}} \) is the external pressure, \( V \) is the volume of the supercell, and \( W \) is a fictitious mass associated with the cell. Integrating the above dynamics generates \( NPH \) ensemble and the enthalpy \( H = E + p_{\text{ext}} V \) is conserved. If we combine the Parrinello-Rahman dynamics with external thermostats such as Nose-Hoover or Langevin dynamics, then we have the required \( NPT \) ensemble.

In our research, we use the QUANTUM ESPRESSO [75] software package to perform the NPT-AIMD simulations. QUANTUM ESPRESSO uses planes waves as the wave function basis. The wave function is expanded in to a subset of plane waves \( \phi_{k_i}, E(k_i) < E_{\text{cutoff}} \), where \( k_i \) is the wave vector, and \( E_{\text{cutoff}} \) is the energy cut-off for
this subset. $E_{cutoff}$ should be large enough such that the expansion converges to the real wave function. However, the plane wave basis set is usually poorly suited to suit the expansion of electronic wavefunctions because a very energy cut-off is required to converge to the rapidly oscillating wavefunctions in the core region. Fortunately, most physical and chemical properties are dominated by the valence electrons and the core electrons are tightly bounded. At the region that is away from the core electrons, the wavefunctions for valence electrons are much smoother and can be accurately described by plane waves. If we replace the highly oscillating real wavefunctions with a smoothed effective wavefunction, then, as long as the smoothed wavefunctions of valence electrons agrees with the real wavefunction in the region that is relevant for bonding, the physics and chemical properties can be accurately evaluated. This is the spirit of pseudopotential (PP). Essentially, the PP is an effective potential to replace the full electron potential, so that the core electrons are eliminated and the valence electrons have wavefunctions with less nodes, as show in Fig 5.7. With the PP, not only we have plane wave convergence with smaller energy cut-off, we also reduce the total number of electrons we need to model (valence electrons only).
Figure 5.7: **Pseudopotential and wavefunction.** This figure is taken from ref [10]. The dash blue lines show the Coulomb like potential and highly oscillating wavefunctions near the core of the atom. The solid red lines show the fitted pseudopotential and the equivalent pseudo wavefunction. The pseudopotential and pseudo wavefunction matches the real potential and wave function beyond the cutoff radius $r_c$. Thus they preserve the physical and chemical properties. In the core region, pseudo wavefunction is much smoother than the real wavefunction, which makes the plane wave expansion more accurate.
2. Empirical Force Potential for Water and Ice

DFT provides an accurate computational tool to model high pressure water and ice. However, it requires heavy computations and scales as $N^3$, where $N$ is the number of particles. Therefore, it makes large scale simulations unaffordable. In cases that requires a large scale simulation, for example, the hyperuniformity computation, one needs to find an alternative way to model the system. In our simulation, we used an empirical water force field to alleviate this problem. A force field parameterize the interactions between atoms and using either experimental or high accuracy simulation results to fit parameters of the force field. When correctly formulated, a force field is able to capture most of the important physical interactions between atoms, and the simulation results generated from force field can be very close to the experimental or high accuracy simulation results.

In our hyperuniformity simulation, we employ an all-atom polarizable and dissociable force field, which was proposed by Pinilla et al [36]. The form of the potential is based on the form originally proposed by Tangney and Scandolo for the description of amorphous SiO2 [76]. The potential has a Morse-like interaction term and a long-range electrostatic contributions. The Morse-like potential is defined as:

$$U_{Morse}(r) = D_1[e^{\gamma_1[1-(r/r_1^0)]} - 2e^{\gamma_1^2/2}[1-(r/r_1^0)]^2]$$

$$+ D_2[e^{\gamma_2[1-(r/r_2^0)]} - 2e^{\gamma_2^2/2}[1-(r/r_2^0)]^2]$$

where $r$ is the distance between two atoms, and $D_i$, $r_i$ and $gamma_i$ are fitting parameters. And the electrostatic part contains charge-charge, charge-dipole and dipole-dipole interactions, which reads as:

$$U_e = \frac{1}{2} \sum_i \sum_{j \neq i} \left[ \frac{q_i q_j}{r_{ij}} - 2q_j \frac{r_{ij} \cdot p_i}{r_{ij}^3} + p_i \cdot T_{ij} \cdot p_j \right] + \sum_i \frac{p_i^2}{2\alpha}$$

where $q_i$ and $\alpha_i$ are the charge and polarization of atom $i$. Note that the charge $q_i$ is not necessarily the effective charge of each atom. Instead they are treated as
fitting parameters. For water system, only oxygen atoms have polarization. We treat hydrogen atoms as a point charge. The tenor $T$ is the dipole propagator, where $T_{ij} = [I - 3r_{ij}r_{ij}^T]r_{ij}$. Finally, the effect of neighboring atoms on the dipole of a particular atom is included by using the short-range corrections as described by Wilson et al [77].

$$p_i^{\text{short}} = \alpha_i \sum_{j \neq i} \frac{q_j r_i}{r_{ij}^3} f_{ij}(r_{ij})$$

where

$$f_{ij} = c_{ij} e^{-b_{ij} r_{ij}} \sum_{k=0}^{4} \frac{(b_{ij} r_{ij})^k}{k!}$$

The dipoles on each ion are found self-consistently at each time step by iterating to self-consistency the equation

$$p_i^n = \alpha E(\text{other ions}) + p + p_i^{\text{short}}$$

The fitting parameters are fitted to minimize the distance between force filed and ab-initio forces under certain measure. The details of the minimization process can be found in [36]. We tested this force field with ab-initio forces at 50GPa and we found that it generally matches the result from ab-initio simulations. The most stable structure it finds is ice-X, which is in consistent with experimental and ab-initio results. At finite temperature, it replicates the BCC superionic phase, though it tends to underestimate the melting temperature of hydrogen sublattice and overestimate the diffusivity of hydrogens. At pressure higher than 200 GPa, we found it no longer a good approximation of the real force. The stable structure is no longer consistent with ab-initio results. We want to point out that usually a force field only works well in a narrow range of thermodynamic condition. Under a different condition, the parameters may need to be refit, or even worse, the entire parameterization may not be able to capture the most important physical interactions anymore. This is why we see a large deviation of the force field and DFT simulations at higher pressure.
3. Path integral with generalized Langevin dynamics

As we mentioned before, in order to simulate a quantum mechanical system with path integral molecular dynamics technique, one needs to introduce many replicas of the system to reach convergence. Thus it requires a lot of computational resource and make large scale computation impracticable. Fortunately a recently developed technique called generalized Langevin dynamics (GLE) helped to alleviate this problem. Here I will briefly discuss the mathematics behind this method.

**Generalized Langevin dynamics**

The basic idea of GLE is to construct a Langevin dynamics in an extended space. The extended space does not have any physical meaning, it simply acts as a mathematical tool to control the colored noise of the Langevin dynamics in the original space. Once integrate out unobservable variables, the equations of motion read as

\[ \dot{q} = p \]

\[ \dot{p} = -V'(q) - \int_{-\infty}^{t} K(t-s)p(s)ds + \zeta(t) \]

where \( K(t) \) is the friction kernel and \( \zeta(t) \) is correlated (colored) noise. In the extended space, the only nonlinear term is \( V'(q) \). If the potential is harmonic, the equations of motion can be integrated analytically. Then one can tune parameters that controls kernel \( K \) and colored noise \( \zeta(t) \) until a desired response of the thermostat is obtained. Specifically, to design a GLE dynamics that behaves like a quantum thermostat, one needs to tune the thermostat that enforces the distribution of positions and momenta are consistent with a quantum harmonic oscillator and does so over a wide range of frequencies.

\[ c_{qq}(\omega) = \frac{1}{\omega^2} c_{pp}(\omega) = \frac{\hbar}{2\omega \coth} \frac{\hbar \omega}{2k_B T} \]

Effectively, the thermostat enforces different temperatures to different vibration modes.
GLE has a problem known as zero-point energy leakage. This is due to the anharmonic coupling that causes a flow of heat from high frequency mode to low frequency mode. This problem can be somewhat mitigated by tuning GLE such that the effective temperature are still correct for each mode even if there is a heat flow. However, to increase the accuracy systematically and be able to include more subtle quantum effects such as tunneling, one needs to combine GLE with PIMD.

**PI+GLE**

For a PIMD system, there are two sets of vibrations: one is from the real physical vibration, and the other one from the ring polymer. In order to create a non equilibrium Langevin dynamics that enforces the quantum mechanical equilibrium distribution, one must replace $q^2$ with the average of $q^2$ obtained from the ring polymer as

$$<q^2>_P = \frac{1}{P} P \sum_{k=0}^{P-1} <q_k^2> = \frac{1}{P} P \sum_{k=0}^{P-1} c_{qq}(\omega_k)$$

where $\omega_k$ are normal mode of the ring polymer. The last equality holds with a GLE whose frequency-dependent position fluctuation $c_{qq}(\omega)$ has been applied separately to each bead of the ring polymer. From this equation one can see that we cannot tune the parameters in the GLE action on each bead, instead we need to solve the following equation:

$$\frac{1}{P} P \sum_{k=0}^{P-1} c_{qq}(\omega_k) = \frac{\hbar}{2\omega} \coth \frac{\hbar \omega}{2k_B T}$$

This equation does not have an unique solution, instead, one needs to pick a particular solution by means of an appropriate boundary condition. In particular, one would hope in the limit that has 1 replica and infinite replicas, the effective temperature should be a constant across all frequencies. This is in consistent with the fact that with infinitely many replicas, PIMD along is guaranteed to converge to the true quantum distribution. With this boundary condition, the above equation can be solved via an iterative algorithm, and the frequency dependent position fluctuation $c_{qq}(\omega)$ can be
represented as

\[ c_{qq}(\omega) = \left( \frac{P k_B T}{\omega^2} \right) g_p \left( \frac{\hbar \omega}{2 k_B T} \right) \]

where function \( g_p(x) = \left( \frac{k_B T}{P} \right)^2 \left( \frac{2 x \hbar}{k_B T} \right)^2 c_{qq} \left( \frac{2 x k_B T}{\hbar} \right) \). We want to point out that when fitting the parameters in PI+GLE, the above equation is not the only criteria. For applications of the quantum thermostat to anharmonic problems the strength of the coupling between the thermostat and the Hamiltonian dynamics and the efficiency of the sampling can be just as important as the agreement on \( c_{qq}(\omega) \). To achieve systematic convergence, it is suggested that the sampling efficiency should not differ too much between the fit for different number of beads.
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