

## Research proposal HECATE [Part B2]

### Section a. State-of-the-art and objectives

This application is for a programme of research directed at what is arguably the most fundamental problem in condensed matter physics: what is the equilibrium state of a system containing protons and electrons?

#### Background

##### Where should hydrogen be in the periodic table?

The hydrogen atom forms a single chemical bond, and so chemists routinely place it in Group VII. Molecular hydrogen, a near-spherical object with two *s*-electrons, might be regarded as being like a Group II element. The longstanding assumption among physicists has been that at high pressures atomic hydrogen would become like the free-electron Group I elements.<sup>1-4</sup> When sufficient mechanical energy is applied to overcome the binding energy of the electron in the covalent bond, hydrogen would transition from molecular-insulator to atomic metal. This picture of hydrogen as a group I element has been confounded by our discovery that when such pressures are applied to other group I metals (Li, Na, K), their electronic structure transforms from free electron metal to insulating states<sup>5-8</sup>. Moreover, just as this idea that atomic structures need not be metallic was taking hold, calculations on hydrogen started predicting that some molecular structures may be metallic,<sup>9;10</sup> as exhibited by the halogens.

##### The curious case of close packing

Phase I of hydrogen adopts the hexagonal close-packed structure, as one might expect from efficient packing of spheres. Curiously, if one treats the trimers in Phase IV as independent atoms (small spheres), and the free molecules as a larger spherical unit, the average structure seen in molecular dynamics calculation is that of MgB<sub>2</sub>. This is the densest possible packing for binary hard spheres mixtures with comparable radii: at high and low pressure hydrogen simply adopts the most efficient packing of the available building block. With LSMC calculation I have shown these to be the lowest free energy states for hard spheres<sup>11;12</sup>, i.e. the highest entropy. Thus so called “close packed” structures *also* allowing atoms maximal freedom to move about: at fixed density hcp maximises the minimum separation between molecules.

The question remains whether this is mere coincidence or a compelling starting point for a simple understanding of hydrogen, in particular why is it that above 100GPa the close packed solid becomes denser when it melts, a feature shares with Group I and II metals

##### Exotic Quantum Phases and Indistinguishable Particles

Adding to this conceptual confusion of whether “atomic equals metallic” is the fact that the hydrogen atom is light enough that the thermal de Broglie wavelength approaches the interatomic spacing. Under these conditions, the nuclei must be treated as indistinguishable quantum particles, which has led to the prediction of various exotic phases of matter such as superfluids, or superconductors based on either proton or electron Cooper pairs<sup>13-17</sup>

Superfluidity does not imply any abnormal electronic behaviour, but it cannot be tackled with any conventional electronic structure code because of the uncertainty in the proton positions. The theory for path integrals applied to indistinguishable particles was worked out some time ago in the context of Brownian motion<sup>18</sup>, but has so far only been applied to simple effective field theories. For hydrogen, the configuration-space sampling can be done efficiently using standard molecular dynamics codes, and compared to this, the computational cost of building a many-body representation for a few hundred atoms in the path integral formalism is modest. The same approach will allow us to tackle Phase I with the path integral written in terms of molecules, i.e. with the atoms indistinguishable pairs.

Another completely open question is how to deal with hydrogen-deuterium mixtures? The mixture of bosonic and fermionic behaviour opens the question of how mixtures would behave<sup>19</sup>. With intermolecular coupling suppressed, the free rotor behaviour should survive to higher pressures, perhaps exhibiting localization previously seen only in vibrons<sup>20</sup>. Would such localization should suppress the transition to a broken symmetry phase II, or drive phase separation by isotopes as in He?

### A realistic appraisal of DFT

Nobody who has worked through the approximations involved in density functional theory could believe the remarkable accuracy of its predictions. A mere handful of fitting parameters are sufficient to capture exchange correlation and the potential due to core electrons. Stable community codes like CASTEP and VASP have developed over 25 year to run efficiently, to the extent that DFT calculations dominate usage of academic supercomputers. Dozens of authors worldwide have run the standard codes in the standard way for hydrogen. A study of phase stability with pressure makes a nice, self-contained piece of work at the level of an MSc dissertation. Necessary though it is, HECATE is not about routine data generation at this level.

Very recently, more attention is being paid to the accuracy of the assumptions. All the popular exchange-correlation potentials give similar predictions in comparing molecular phases, but problems arise with transferrability at the metallization transition. Comparison of the popular “PBE” functional, fitted to a dataset of molecules, to “PBE-sol” the same functional fitted to solid phases and gives transition pressures different by almost 100GPa, as does incorporation of van der Waals adjustments<sup>21;22</sup>. There is no *a priori* reason to prefer one DFT functional over another, and where experimental data exists agreement between experiment and published simulation is closer than this uncertainty due to the functional. This mysterious situation may be attributable to publication bias, but my view is that DFT is more useful for showing processes and candidate structures for comparison with experiment than for definitive prediction of transition pressures.

### Quantum Entanglement Transition within Phase I

At room temperature, the hexagonal close-packed Phase I is invariably reported as stretching from ambient pressure to about 240GPa, where we have shown that it transforms to Phase III and almost immediately to Phase IV. The identification of Phase I as a single phase is based on the continuity of the vibron frequency, albeit with a turnover after a maximum value around 30GPa<sup>23;24</sup>. However, comparison of hydrogen and deuterium reveals that the low-frequency modes exhibit a quantitative change: at low pressure spectroscopy our previous work reveals the characteristic behaviour of a free rotor:  $J(J+1)$  level spacing with  $\Delta J = 2$ , and an isotopic frequency ratio  $\nu_H/\nu_D = 2$ . Our study of HD mixtures again shows distinct roton spectra from H<sub>2</sub>, D<sub>2</sub> and HD.

Just before the transition the spectrum is equally clean, but now all the modes look like harmonic oscillators with  $\nu_H/\nu_D = \sqrt{2}$ , presumably librions. This complete change in vibrational behaviour within a single phase is unprecedented in molecular systems. Data collected to date in the intermediate region is inconclusive, with Raman and IR absorption across a range of frequencies. Free energy calculation is also challenging: the harmonic approximation is invalid even at zero temperature because some of the modes are not harmonic oscillators.

The proton is a fermion, while the deuteron is a boson. This has a dramatic effect on the molecular behaviour, since the  $J=0$  energy ground state is a singlet in H<sub>2</sub> (Nuclear spin 0, para-hydrogen), but a hexuplet in D<sub>2</sub> (Nuclear spin 0 or 2: ortho-deuterium). This manifests itself in the high temperature ratios for observed rotor states with  $J$ -odd: $J$ -even being 3:1 in hydrogen, and 1:2 in deuterium. This can be detected in the intensities of Raman transition since the selection rule is  $\Delta J=2$  which does not alter the nuclear spin state. With increasing pressure  $J$  ceases to be a good quantum number, and the ortho-para distinction becomes unimportant which provides another signature of entanglement of molecular wavefunctions. Transitions between ortho and para are symmetry-forbidden and therefore slow, especially at low temperature.

We hypothesise that there is a continuous (second order) phase transition across Phase I, associated with

entanglement of the free-rotor states. As the molecular angular momentum  $J$  ceases to be good quantum number, the transition must take the mass dependence of the vibrational frequency from  $1/m$  to  $1/\sqrt{m}$  in a continuous way. The theory of such a transition, and its consequence for the experimental signal, has yet to be worked out. We will derive a theory and write code to evaluate the quantum statistical mechanics of such a system, first in the limit of distinct rotors and vibrons, which can be done by projecting out normal modes onto the molecular coordinates and quantising them appropriately. Then we will extend the theory to quantise the entangled states: as determined from coupled and inhibited rotors calculated using DFT.

Collecting better data and developing a theory of the entanglement transition will form a major part of the project.

## Crystallography of Phase II

There are several theoretical proposals for the so-called “broken-symmetry” structure of Phase II, but the data is inconclusive. The convincing evidence for the existence of the phase comes from small but sharp discontinuities in the vibron frequencies, which contain no information about molecular orientation or crystal structure. X-ray scattering has proved inconclusive because the scattering comes from the electrons, which are primarily located in the bond in centre of the molecule, such that the molecules appear almost spherical: obviously this is non-optimal for determining broken symmetry.

Neutron scattering is the optimal probe in this regime because the scattering comes from the nuclei, revealing the orientation of the molecular dumbbell. DAC technology is only now becoming able to reach the required pressures.

A curiosity in the transition from Phase I to II is the very strong isotope dependence. While the deuterium transition is at 25GPa, for hydrogen it is much higher. This implies that the role of nuclear quantum effects is critical, as one might expect if the broken symmetry is accompanied by the conversion of roton modes into librons. Hydrogen has higher ZPE than deuterium, and so will be unfavoured in the phase II where all modes are librons and have non-zero ZPE (rotors have no ZPE). The free energy of low temperature Phase II should be calculable via quantum harmonic approximation, but comparison with Phase I awaits development of the combined rotor/oscillator theory and codes.

The isotope dependence highlights another mystery with Phase II. In a classical picture it is easy to rationalise the phase by imagining Phase I as a plastic crystal of rotating diatomic dumbbells and the dumbbell rotation stopping at low temperatures, allowing for some more efficient packing. But in the quantum picture, going from spherically symmetric molecules to dumbbells means changing the quantum number from  $J = 0$  to  $J > 0$ , i.e. exciting higher energy states. So the quantum equivalent of the plastic crystal argument implies a population inversion. In interpreting experiments, one must be also aware of metastability arising through para-ortho effects.

In parallel, I will use molecular dynamics to study the Phase I - Phase II transition with classical nuclei and quantum electrons, and contrast this with path integrals (PIMD) for hydrogen, deuterium and tritium. Because heavy isotopes behave “more classically” than hydrogen, and the isotope effect is larger here than anywhere else. I will implement the recipe for calculating the isotope effect that has been proposed recently<sup>25;26</sup>. PIMD codes can be run with any mass assigned to the nucleus, and since the classical free energy is independent of the mass, it can be used as a variable to integrate continuously between classical and quantum descriptions.

Here again we go from a close packed phase involving dynamical free rotors, with some short-range order, to a long range ordered symmetry-broken structure. It should be possible to model this transition directly with molecular dynamics in the NPT ensemble, using the code we have developed for constrained molecules<sup>27</sup>. Constraining the molecular bondlength is a physically better representation, since the vibron is in its ground state, and also has practical advantages in allowing longer MD timesteps and therefore longer/larger simulation cells.

## Where are the atoms?

In a famous Nature editorial in 1988 John Maddox stated that it was a scandal that no method for determining the stable arrangement of atoms exists. At that time, Density Functional Theory (DFT) methods had the proven ability to determine the energy of the electrons given the positions of set of ions. I had some success predicting covalent or close-packed structures using analogies with other materials and phonon calculations to find symmetry-breaking distortions, or using molecular dynamics (MD) with empirical or *ab initio* forces to spontaneously find lower free energy phases. However, what was missing was any systematic theory about where to put the ions.

In the past ten years, several groups have independently discovered that for a given element, the number of enthalpy-minimising crystal structures is small<sup>28–30</sup>, enough that, for a given number of atoms in the unit cell, a search algorithm is able to find them all. The search is almost complete for elements, including hydrogen, at zero temperature with small numbers of atoms per unit cell. Structure search is an ideal Masters project, and I expect this routine work to continue apace worldwide with no help from HECATE.

To enhance structure search, I introduced the idea of searching conditioned by experimental data, e.g. in the solution of the *oC88* crystal structure in lithium<sup>8</sup>. Extensive structure searching had already been done assuming a small cell, but limited crystallographic data suggested such a complex unit cell with 42–46 atoms. Searches in this range found many candidate structures, only one of which was not ruled out by the experimental data. This *oC88* structure does not have the lowest enthalpy: it is stabilised by ZPE and vibrational free energy. There is no chance that even the most comprehensive structure search with normal methods could have revealed the correct structure.

Extensive *ab initio* structure searches in hydrogen have found the lowest energy small-cell structures within DFT up to Terapascal pressures<sup>9;10;31–34</sup>. Although this work is comprehensive within its sphere of reference, some difficulties remain. Most notably, the calculations ignore ZPE, vibrational and other entropic effects. In fact, most candidate structures based on small unit cells turn out to have zone boundary phonon instabilities, which imply a doubling of the unit cell. Moreover, structure search cannot succeed when there are exotic nuclear quantum effects, such as Phase I or the superfluid.

Structure search has been hugely successful, but it fails whenever particular interesting behaviour occurs. A better approach is needed to account for quantum and entropic effects.

## Free Energy Calculations

The temperature driven phase behaviour of hydrogen is particularly mysterious. As seen in B1, the temperature dependence of the vibrational free energy is an order of magnitude less in the quantum treatment than in the classical simulation. Moreover, most structures found in structure search turn out to have imaginary phonons. In the harmonic approximation, these lead to divergences in the free energy which e.g. in CASTEP, are dealt with by printing a warning and simply ignoring them. Several papers presenting free energies of structures with imaginary modes have been published, with no explanation of how they were treated.

*Ab initio* lattice dynamics<sup>35</sup> is the classic approach to the problem, and is now implemented in all major community codes. This involves calculating the dynamical matrix, diagonalising to find harmonic modes, and populating them according to Bose statistics. It works extremely well for harmonic crystals, but is less useful

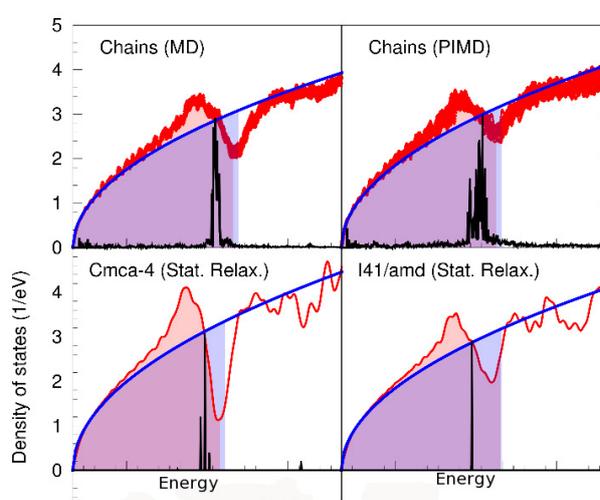


Figure 1: I have found that density of states for candidate metallic structures are free-electron-like (blue curve) except for a pseudogap at the Fermi Energy (red). The gap is associated with lattice periodicities which give strong diffraction (black peaks) at  $2k_F$ .<sup>45</sup>

in hydrogen because of the huge non-perturbative anharmonicities.

An important reason for determining vibrational frequencies is that they are precisely what are measured in spectroscopy. There are methods presented by my group and by others to deal with the failings of the theory analytically by going to anharmonic or self-consistent phonons<sup>36–38</sup>. However, calculation of self-consistent phonons in Phase IV<sup>39</sup>, shows a phonon spectrum wildly at variance with experiment. This suggests that an approach based on normal-modes is inappropriate, which is unsurprising given that molecular dynamics in Phase IV exhibit arrested rotations and fast diffusion.

The phonon spectrum can be extracted from MD. One approach is to take snapshots of the MD configurations, ignore the forces, and build a dynamical matrix from second derivatives. The other, which appears to give better results, is to take the Fourier transform of the velocity autocorrelation function to get the phonon density of states, from which the partition function can be built. If the autocorrelation function is projected onto Raman or IR active modes, then the experimental signal can be simulated.

A more direct method of testing phase stability is to use a molecular dynamics run featuring two phases. I have used three methods here: in *phase coexistence* a large supercell contains two phases and an interface: such a system equilibrates to a point on the phase boundary<sup>40;41</sup>, or eliminates the phase with higher free energy. *Constant stress MD* allows phase transformations to occur spontaneously, which enables metastability to be determined<sup>42</sup>. A related technique, the Z-method, involves MD in the NVE-ensemble<sup>41;43;44</sup>.

The Z-method is very efficient and parallelisable, and it relies on the postulate that the limit of superheating comes when a crystal has energy equal to that of the liquid. Nothing in thermodynamics implies this idea, but simulation results suggest it is true. For wider use of this efficient method, it is important to see whether a similar effect holds for entropically-driven solid-solid transitions such as II-I or formation of chains<sup>45</sup>.

A serious problem with integration methods is that the specific heat calculated in MD is seriously awry, due to the high frequency modes remaining in their ground state. Rather than using the MD energy (kT per mode), a correction to obtain the quantum specific heat can be calculated if the phonon DOS is calculated from the autocorrelation. This has not been done previously.

Rotational entropy is well sampled in classical molecular dynamics, but calculation of absolute free energies is challenging. What is required is a direct calculation of free energy differences. The ideal method for this for systems of a few hundred atoms my Lattice Switch Monte Carlo method<sup>11;46</sup>. As part of this project we will develop code to implement LSMC with CASTEP.

Structure search methods do not normally include entropic effects, although these can be added afterwards from lattice dynamics. However, there is considerable information about configurational entropy contained in the frequency by which each structure is found. I have done some preliminary work using AIRSS on  $\beta - Sn$  which shows that the high temperature, high entropy state is found proportionately more often. Care must be taken in deciding which low-T microstates belong to the high-T phase. All structure search methods can be regarded as a biased sampling of the phase space: the challenge for using them for entropy calculation is to unravel that bias. Hydrogen MD has shown that microstates associated with structures with different symmetry at low temperature actually belong to the same phase at high temperature. In addition to designing a structure search with a removable bias, it will be necessary to define which structures should be combined to form a high temperature phase.

### Phase III and the loss of covalency

Phase III is characterised by a single broad vibron whose frequency drops with pressure. The interpretation is that electrons are partially “squeezed out” of the covalent bond, making it weaker. DFT suggests that Phase III has  $C2c$  symmetry, although there are major discrepancies in its low frequency Raman signal<sup>9;47–49</sup>. It will be interesting to see whether a treating the protons as fermions will give a benzene-like symmetric state.

We have also demonstrated the stability of Phase IV over Phase III by direct observation of the transition in classical molecular dynamics. It has been theorised that the transition is associated with the tiny thermal contribution from the quantised vibrational modes (see figure in B1), but for this to be significant would require a remarkable fine balance of the other parts of the free energy. The rotating molecules in Phase IV suggest that

expansion in normal modes misses a major rotational contribution to the entropy.

### Rotational Entropy and Phase IV

In 2011 a new phase of hydrogen was identified<sup>50</sup>. Despite initial claims of conductivity, Phase IV is now accepted as a non-metallic, molecular phase, with a bandgap in the visible region<sup>47;51</sup>.

Spectroscopically, phase IV is characterised by multiple vibrons: one whose frequency approximately pressure-invariant, and others whose frequency drops with pressure, similar to Phase III. Clearly this means different types of molecule, and a combination of structure search and lattice dynamics reveal low energy metastable “mixed” structures<sup>9;10</sup> with low symmetry. The frequencies calculated by lattice dynamics are in poor agreement with experiment, but I have resolved this by molecular dynamics<sup>52</sup>. Open questions remain which we will resolve: are two<sup>47;50;53</sup> or three<sup>49;52</sup> distinct layer types and vibrons. Is the layer ordering regular and independent of pressure? Does the sudden onset of spectroscopic broadening imply the existence of a pressure-disordered phase IV’?<sup>54</sup>.

Second-order structural phase transitions are unknown in any element, but there is a possibility that the III-IV-IV’ transition may be one. Phases III and IV are both layered structures, and it is possible to regard the “mixed-layered” phase IV as alternating layers of the types seen in phase I and phase III. In a second-order transition, the relative proportion of these layer types would change continuously with increasing temperature. In molecular dynamics we have seen a dynamic transition from phase III to IV, indicating that IV has lower free energy, however, simulations have used a small number of layers, so cannot determine whether there is a gradual increase in the number of molecular layers, or a discontinuous leap to alternating layers. Experimental support for the existence of a second-order transition comes from the gradual increase in intensity of the high-frequency vibron, and continuity in the frequency of the lower vibron across the transition. The detection of a discontinuity in an experimental quantity is required to prove first order behaviour, and to this end we will carry out a more detailed study of the libron modes across the transition, which are radically different in the two layers.

### Beyond Phase IV: One dimensional liquids, superfluids, electrides and molecular metals

At the limit of current experimental pressures, DFT suggests a number of different bonding types. In addition to molecular metals, there are a group of electrides, ionic structures where the electron is localised as a pseudoanion in interstitial regions.

The most interesting structural types are determined by the Fermi-Surface nesting effect, for example Li-oC88, Na, the incommensurate phases of Ba, K, Rb and quasicrystals<sup>5;8;55;56</sup>. These complex structures typically have very large unit cells, which can sometimes only be represented as a projection from a higher dimensional space, and pseudobandgaps and strong electron-phonon coupling.

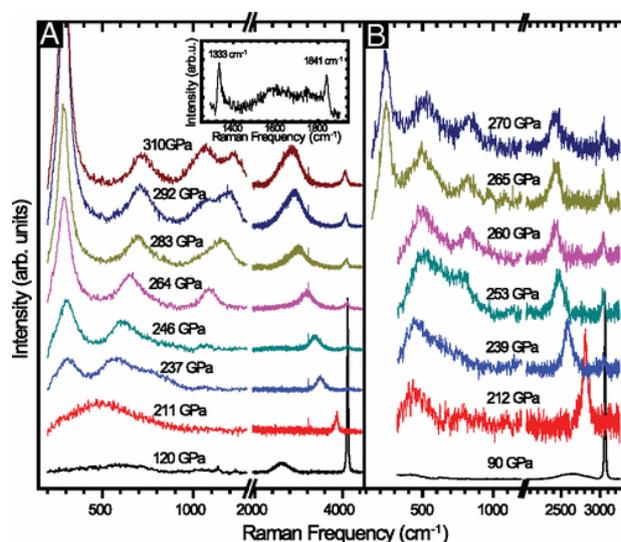


Figure 2: Raman data from our study of H<sub>2</sub> (left) and D<sub>2</sub> (right)<sup>20</sup>. These few peaks are sufficient to discriminate between dozens of DFT candidate structures.

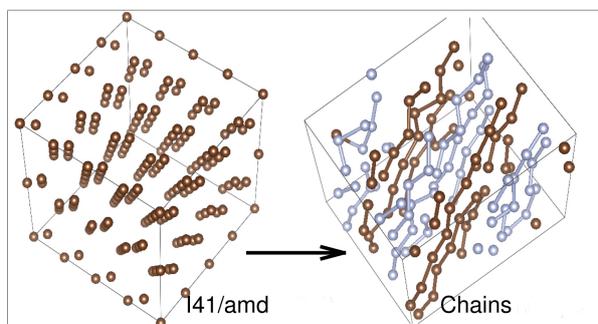


Figure 3: In MD simulations, I observed that the atomic phase *I4amd* transforms spontaneously to a 1D melt.

Such large unit cell structures cannot be found with standard structure searching, but I have just discovered such a phase in hydrogen using MD<sup>45</sup>.

Structures stabilised by Fermi surface effects often have a chainlike nature, where the interchain spacing is set by the Fermi wavevector. Weak ordering in the third dimension can lead to incommensurate host-guest structures, or even 1D melting as in Rb, K and now, theoretically at least, in hydrogen. I have derived the essential theory in terms of screening<sup>45;57</sup>.

The structure forms spontaneously on heating at 400GPa in MD and PIMD from the most stable atomic arrangement at zero temperature (*I4amd*) and persists to full 3-D melting. Extraordinarily, the hydrogen is twofold coordinated, and unlike the “chain melts” in Rb and K, all atoms participate in the melt. The pressures where this novel state of matter appears in simulation will become accessible to static DAC, within the duration of the project. An easily detected feature of the phase is the shift of the molecular vibron to a much lower frequency mode extending along the chain. The dispersion of the mode will also increase dramatically. The simulation shows proton exchange through a metastable paired state: a fully quantum treatment with indistinguishable protons is needed, but it is a tantalising hint towards superfluid behaviour<sup>58</sup>. Similarly, the 3D superfluid state should be competitive in this region<sup>14</sup>.

I have been unable to demonstrate a transition between 1D-melt and molecular metal in either direction. A free energy calculation is required, hence this issue is an early target for free energy difference calculations using my Lattice Switch MC method.

### Liquids and shock waves

Three types of liquid are expected in hydrogen, molecular insulator, metallic, and an atomic “plasma” phase.<sup>16</sup> Shock wave experiments generate both high pressure and temperature, and present clear evidence of metallization, presumably in the liquid phase.<sup>59–62</sup> Sandia’s Z-machine<sup>62</sup> has found the onset of metallic liquid hydrogen at 300GPa and low temperatures (for shock waves) of 1500–3000K, with only a weak temperature dependence. MD simulations suggest that it coincides with the onset of molecular dissociation, however the calculated transition pressure varies between 200 and 400GPa, and depends sensitively on the approximations made in the calculation. It is unclear why there is so much variation in the calculated values and whether the transition is first order<sup>63–68</sup>

Laser heating in a DAC is also able to reach the melt curve, however the signature of a liquid remains contentious, such that a recent study evaded the claim<sup>54</sup>. I will establish precisely how to distinguish the spectroscopic signals from a 3D liquid, a quantum rotor phase and a 1D melt.

## Section b. Methodology

The main scientific goals of the project are:

1. Determine structure of broken-symmetry Phase II.
2. Understand isotope effects, especially at I-II transition.
3. Determine why the liquid is denser than the solid
4. What is the slope of the melt curve above 300GPa.
5. Metallization and nature of metallic phase
6. Find exotic phases beyond 400GPa: 1D-melt, superfluid, superconductor.

The techniques I will employ to attain them are:

1. New many body theory for roton entanglement (PDRA WP1a)
2. Entropy calculation with Lattice Switch Monte Carlo for *ab initio* Hamiltonians (PDRA WP1b)
3. New methods for relating molecular dynamics to experimental signals (PDRA WP2)
4. DAC Spectroscopy above 300GPa (PDRA WP3a)
5. Neutron Scattering up to 100GPa (PDRA WP3b)

## WP 1a Theory of Quantum Phases

How does the entanglement and broken symmetry behaviour work below 120GPa in Phase I and II? What causes the isotope effect, and how would mixtures of fermions, bosons, and distinguishable particles (i.e. H<sub>2</sub> HD and D<sub>2</sub>) behave? To answer these questions I will develop new bespoke theory, a number of approaches can be envisaged, and all will be developed in this proposal.

In the simplest roton-libron transition, the fundamental object is a single molecule and the rotational arrest is treated as due to the crystal field. A single particle wavefunction is considered, and the field strength is increased, the depth of the potential well deepens until eventually it can trap a quantum state. This problem can be solved semi-analytically in the basis of free rotors: The high energy states will remain free-rotor like, so the arrested ground state must be expandable in a small number of low-J states. Calculating the crystal field is far more complicated, and I will approach this by evaluating the potential of mean torque: an obvious generalisation of the standard potential on mean force. This calculation will describe the breakdown of J as a good quantum number, and the transition from  $1/m$  to  $1/\sqrt{m}$  dependence of the frequencies.

The crystal field approach yields single-molecule wavefunctions, and so fails to incorporate dispersion. Dispersion can be measured from the difference between IR and Raman frequencies, so the validity of the crystal field approximation can be directly tested.

To include dispersion effects, I will use a tight-binding approach with the rotons as the basis set. The required input into this model is the interaction between one molecule and its neighbour. This is angle dependent, and will be calculated from the angular correlation functions derived from MD simulations. The tight-binding model gives eigenmodes stretching across the system, with distinct symmetries which will allow Raman and IR modes to be identified.

Both approaches will give a set of non-harmonic quantised eigenstates for the roton-libron modes, parameterised directly from ab initio MD. Given these, it is straightforward to evaluate the partition function and hence the free energy. This groundbreaking methodology is essential in hydrogen phase I, but will also be applicable to other systems where molecular modes are associated with good quantum numbers.

Despite missing many quantum effects, classical molecular dynamics shows a melting transition in good agreement with experiment. This may be mere coincidence, but it touches on something that has always intrigued me: to what extent are quantum and classical uncertainty related, and is there a limit in which they become the same? HECATE gives me a opportunity to probe this question in a very specific model, with outcomes testable against experimental data. PIMD simulations and evaluation of the classical partition function are both driven by calculation of microstates from DFT. In one case they are combined as beads, then integrated, in the other the visited states are combined directly. The spring-forces used in PIMD beads can be reinterpreted as a biased sampling in classical statistics.

The theory in WP 1a is directly probed by the experiments of WP3b.

## WP 1b Innovative Free Energy calculation

There has been relatively little methodological progress in free energy calculation from ab initio simulation since I reviewed the subject in 2002<sup>69</sup>. Lattice dynamics and thermodynamic integration allow total free energy to be calculated. Switching Monte Carlo methods focus on free energy differences. Phase coexistence locates conditions where free energies are equal. MD finds lower free energy phases directly, but suffers from hysteresis. One highly efficient new technique is the Z-method for determining the melt curve<sup>43;44</sup>.

I have just won a grant to hire a 1-year PDRA to develop Lattice Switch Monte Carlo and essentially identical “Phase Switch” and “Hamiltonian Switch” methods on Archer, based around the DLPOLY and DLMONTE classical MD codes. These methods involve a Monte Carlo move which switches from one macrostate to another, where the macrostates can be either different phases (including liquids) described by the same Hamiltonian, or the same phase described by different Hamiltonians. In either case, the free energy difference depends only on the *ratio* of the phase space volumes, which is accurately sampled by the single switching simulations. The LSMC codes utilises biased sampling techniques for maximal efficiency. This project will be completed before HECATE starts, but will provide a framework for extending LSMC to quantum systems.

LSMC is highly complementary to lattice dynamics. The free energy in the harmonic approximation can be used as the zero of energy in LSMC, set independently for each lattice. LSMC then probes directly only the anharmonic contribution to the free energy difference. This gives it an advantage over conventional methods of thermodynamic integration, which ultimately rely on calculating two large numbers and comparing their difference. An LSMC interface with CASTEP will be developed, enabling direct calculation of free energy differences. One of the advantages of LSMC is that the frozen degrees of freedom can easily be eliminated from the system, and the zero-point energy can be included. The procedure we will develop for this to calculate the free energy difference between two phases, as is standard in LSMC, then in a separate calculation the free energy difference between the classical-proton system and the path integral description will be evaluated. In this way, a measure of the free energy difference between the two quantum-proton systems can be found.

As we saw in B1, Fig 2, the thermal energy calculated in MD simulation massively overestimates the quantum thermal energy. Consequently, the specific heat and entropy are also overestimated. PIMD gives a recipe for solving this in direct space, but I will examine equivalent formulation in reciprocal space. As with PIMD, the MD is used to sample the configuration space and from this the phonon free energy can be calculated. Normally this is done from the velocity autocorrelation function, but an equivalent approach is to use the force autocorrelation. At a given temperature, this gives an analytic relationship via the partition function between the calculated forces and the derivatives of the *quantum* phonon energy. If the atoms are moved in MD according to the latter, the MD simulation properly includes ZPE and other quantum-nuclear effects. This has not been done previously, because the cost of solving the dynamical matrix far exceeds the cost of calculating forces from a classical potential, but in *ab initio* MD it will be only a small fraction of the electronic structure calculation.

## WP2 Electronic structure calculation and *ab initio* MD

The main tool for *ab initio* is the CASTEP electronic structure code, supported by the UKCP collaboration. Set up by myself and four others in 1991, based on codes originally written by Mike Payne in Cambridge, the UKCP collaboration has been continuously funded for code development and computer resource since, growing to a membership of over 20 groups.

CASTEP implements density functional theory using the plane wave pseudopotential method. It has a wide range of analysis features that enable direct comparison to experimental data, such as crystallography, infra-red and Raman spectroscopies, NMR, and core level spectra. It also has associated tools for theoretical analysis such as density of states, electron localization function, local charge projections and interfaces to major graphics package. It has highly efficient and optimised parallelism and is fully supported on Archer in EPCC. After a several years of being primarily a user, I am once again fully familiar with the source code as I was in the 1990s when I worked with EPCC to develop a parallel version. Part of my contribution within the NuFuSE project was to develop a GPU version. The world's leading supercomputers are now GPU based, so it is certain that this version of the code will become increasingly important during the project.

In addition to the electronic structure routines, CASTEP has a full suite of MD, PIMD, lattice dynamics, harmonic free energy calculations. Structure search is implemented via the AIRSS wrapper developed by Pickard. I have developed a suite of additional hydrogen-specific codes, which identify molecules and calculate vibron frequencies at high temperature. These enabled me to make direct comparison between calculations and Raman data for vibrons, but needs to be extended to cover low frequency modes.

I have developed modules for constrained MD using the SHAKE algorithm. For hydrogen, rigid molecule MD, has several advantages. Firstly, freezing out the vibron permits a longer integration timestep. Secondly,

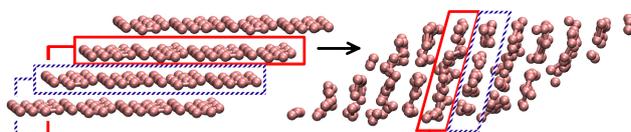


Figure 4: Transformation from Phase III to IV simulated with CASTEP at 250 GPa. Although both phases are layered structures, the transformation path reorients the layer direction. MD can be used as a tool to find more stable crystal structures.

below the melt curve, the vibron is in its ground state, so the vibrations are arguably unphysical: the reduction of heat capacity and entropy due to having fewer degrees of freedom is certainly correct.

Even ignoring nuclei motion, the simple description of electronic exchange and correlation can be problematic. The gold standard here is Quantum Monte Carlo (QMC)<sup>70</sup>, which is now available in community codes such as CASINO and has been used to drive molecular dynamics<sup>67;68;71</sup>. Although absolute energies and pressures are more accurate with QMC, no new candidate structures have yet been found with it. The one clear result of this comparison is that the popular PBE functional overstabilises molecular structures, an effect equivalent to tens of GPa<sup>21</sup>. I will use QMC results to benchmark exchange-correlation accuracy, but the final arbiter between candidate structures remains experimental evidence.

I introduced the mode projection technique to study soft and highly anharmonic phonons<sup>72</sup>. This is now proving a highly practical approach to extract the spectroscopic signal from molecular dynamics<sup>73</sup>. The Raman active vibron mode corresponds to in-phase stretches of all molecules. By projecting the MD trajectory onto this mode, and Fourier transforming the velocity autocorrelation function, we obtain the high temperature signal. I will further develop the mode projection method to deal with librons and rotons. This involves identifying molecules in the MD simulation, transforming the motion onto an appropriate molecular coordinate system, and quantising the motions in this framework, rather than wrongly assuming that all modes are harmonic. This allows different modes to be treated differently according to their possibility of quantum excitation. The MD forces can be adjusted in the spirit of SHAKE or colored noise thermostats<sup>74</sup> to match the quantum heat capacity for each mode.

Preliminary classical MD simulations in Phase I show that with increased pressure and reduced temperature, the angular momentum autocorrelation is increasingly short-lived. At the same time, orientational correlation with adjacent molecules increase. The frequency spectrum of these correlations can be related to the eigenmodes of the system via a parameterised tight binding. More data across a range of temperatures is required to accurately determine the parameters, but once this is available a fully quantum-statistical model for Phase I will be built. This will enable me to simulate the phonon density of states in the awkward region intermediate between roton and libron limits. Again, a critical question is whether the mode is associated with a single molecule, such that  $J$  is a good quantum number, or spread across the lattice. This has measurable consequences: the first case has no dispersion while the second does. The dispersion can be determined directly from neutron scattering, or inferred from the difference between the Raman and IR signals.

I will make all the trajectory and run data generated in HECATE available online and set up a resource to link to other such datasets.

### WP3a Metallization and Discovery

The strongest experimental signal available comes from Raman spectroscopy. Discontinuous changes in the Raman signal are sufficient to distinguish phase boundaries, without being able to identify the phases. The figure shows the current state of the art, and our capability to traverse the PT phase diagram. It also illustrates the fundamental questions which are to be addressed: Are there additional phases I' and IV': what lies beyond 300GPa? Does the melt line continue to ever lower temperatures, perhaps even a ground state superfluid?

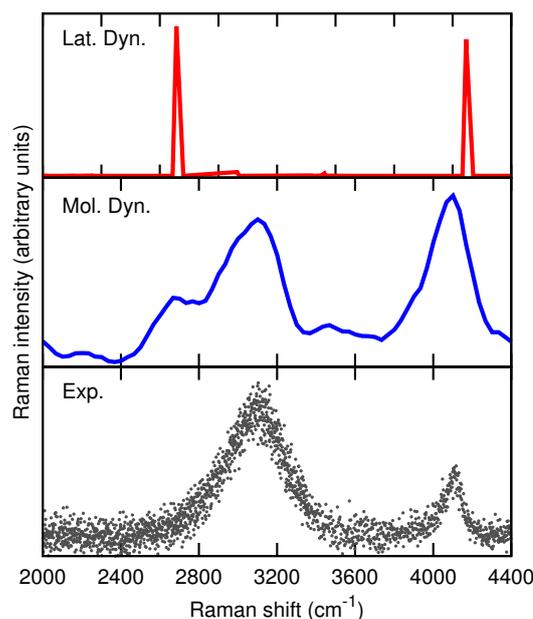


Figure 5: Vibron signal in Phase IV from lattice dynamics, from molecular dynamics using the projection method, and from spectroscopic measurement in diamond anvils, showing how temperature effects are captured by MD.

The operational principle of the DAC has not changed significantly in 50 years, but through improvements in accurate machining combined with better materials, polishing, mountings and coatings the Gregoryanz group has now reached nearly 400GPa in hydrogen. They also developed capabilities in both heating and cooling. My postdoc will have access to this technology to address the following questions:

How far does the negative slope of the melting curve persist: does it go to 0K in a super-fluid ground state? Does it turn when metallic liquid co-exists with non-metallic liquid? when both solid and liquid are metals? or when both are atomic? Will the predicted 1D melting phase be found? Does Phase IV melt directly, transform to another phase, or is there a second order transition with ever-more molecular layers to Phase I? We will probe this with spectroscopy, and closely tie to theory to determine whether observed changes in frequencies and peak widths actually correspond to melting.

Is there a metallic solid phase V above 300 GPa? Is it molecular, chainlike or atomic? Will the band gap close in the hexagonal layer of Phase III and IV, and will the electrical properties be characteristic of the low symmetry local structure or the high symmetry ensemble averaged structure - which are predicted to involve graphene-like Dirac cones.<sup>75;76</sup>

### WP 3b Neutron Diffraction of Phase I, I' and II

Neutron diffraction is the technique of choice for studies of orientational disorder, because neutrons scatter from the nuclei rather than the electrons in the bond. X-ray studies have observed only one order of diffraction in Phase II, so full structural determination is impossible. The pressure limit for neutron diffraction is imposed by the need for relatively large sample volumes, but in 2013, a leap from 30 to 100 GPa was made possible by the combination of new cells based on large synthetic gem diamonds<sup>77</sup> and high power neutron sources like the SNS at Oak Ridge. Loveday's group have shown that it is now possible to collect neutron diffraction data from samples of 0.1 mm<sup>3</sup> volume at pressures up to 100 GPa, sufficient to enable us to study Phase II.

**Phase-II** (the broken symmetry phase)<sup>78</sup> (accessible at 25 K at 40 GPa in ortho deuterium) is a major focus of our work. There are numerous predictions of its structure all of which appear to disagree with the single previous neutron diffraction study. That study claimed incommensuration on the basis of a single peak but fails to find a structural basis for an aperiodic structure. The new neutron diamond anvil cells are easily able to access these conditions their small size makes them easy to cool to kelvin temperatures and their optical transparency also allows the spin state of the sample (a crucial parameter) to be monitored optically. Hydrogen adopts Phase II at higher pressure, which will become accessible later in the project. We will obtain comparative information on phase II of para-hydrogen (up to 100 GPa and 10 K) and explore the basis for the enormous and unexplained isotope effect of the transition pressure. Single crystal diffraction studies may be required for work with hydrogen to overcome the incoherent neutron background that hydrogen produces.

In **Phase I** neutrons can determine how the rotor loses its 3D character. This can be inferred from the anisotropic thermal broadening in neutrons, e.g. if the rotation becomes 2D, the nuclear wavefunction becomes a highly prolate spheroid, while an inhibited rotor will be clear from the internuclear distances. Neutrons are the best probe for this because the electronic wavefunction is only slightly nonspherical. X-ray and spectroscopy offer hints of the onset of entanglement via secondary quantities: the  $c/a$  ratio is slightly below ideal<sup>79;80</sup> and the vibron frequency has a turnover<sup>24</sup>.

Initially we plan to use SNS for these experiments. Only the SNAP beamline at SNS has the microposition-

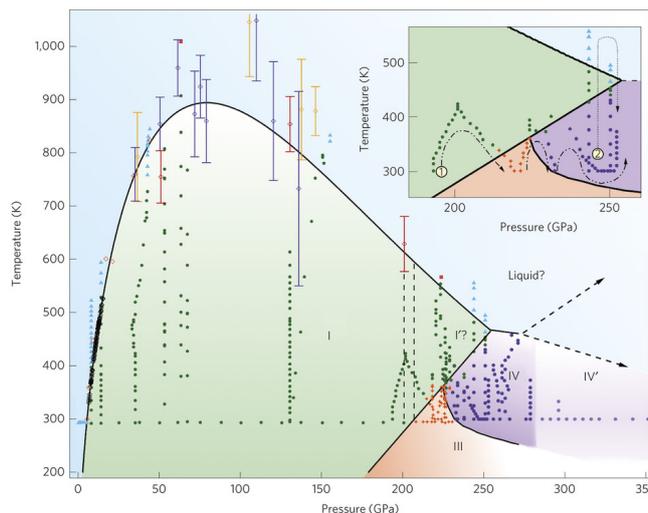


Figure 6: Results of DAC data scanning the phase diagram, from Howie et al, 2015. Dashed lines indicate possible continuations of the melt line.

ing capability needed to work with diamond anvil cells and Drs Guthrie and Loveday will share with me their programme access providing 10 days per year for the next two years. Single crystal studies will be carried out at the ILL Grenoble where we have developed the use of the unique D9 diffractometer for high pressure.

### **Associated projects**

The theoretical methods developed in HECATE will be applicable to other materials, and I will be involved in projects to ensure this happens, generally as second supervisor to students. This will involve three early career researchers “Chancellor’s Fellows”, the simulators Hermann and Martinez-Canales and shock wave scientist McWilliams. Although not funded by the HECATE, I believe it important for senior scientists such as myself to support their development.

I have vast experience with DFT simulation work, and also supervised one PhD student working on shock physics (Damian Swift, now LLNL), performing hydrocode analysis with PT equation of state, calculated using DFT<sup>81</sup>. I will work with another PhD student jointly supervised with McWilliams via his project *Hydrogen Equation of State and Plasma Phase Transition*. at the US National Ignition Facility.

## **Section c. Resources (including project costs)**

### **C1 Human resources**

The project requires 70% of the PIs time, and the ERC grant will fund 50% of this. I will be strongly involved in all parts of the research, including the PhD students, with detailed day-to-day input on all aspects of theory and simulation. I will require full-time three PDRAs with expertise in statistical mechanics of quantum system, electronic structure simulation, and extreme pressure spectroscopy. All of these will be hired externally, so only estimated salary figures are available. I request a small contribution for the time of Loveday and Gregoryanz, whose labs I will use (staff category “Senior staff”).

The University of Edinburgh will contribute additional funding for up to five PhD students, along with up to six more on spin-off projects for whom I will be second supervisor. I envisaged that some more routine studies and calculations will be carried out as half-year MSc projects: typically I supervise 1-2 of these per year. No reimbursement from the ERC grant is envisaged for collaborating institutes for the collaborating activities.

### **C2 Equipment**

The research programme relies heavily on continuous access to high-performance super-computing. Resource for the largest simulations and DFT software will be provided from the UKCP collaboration on the 118,080 core Cray XC30 Archer system at EPCC *no cost to HECATE*. Archer is the UK national supercomputer and it is hosted by the School of Physics which will provide additional time. Intermediate sized calculations with very long run times are best run on machines with large RAM and fewer cores. I already have a 64 core PowerEdge machine of the required type, and request 23kEu for an additional 64 cores. A further 9843 Eu is requested to cover an extra 10TB storage for open data and curation.

The depreciation policy of the University of Edinburgh is that only items over a value of 50kGBP are depreciated over 4 years at 25% per year, and that no such items are included for purchase in the project.

### **C3 Consumables and Samples**

WP3a exploits facilities built up at CSEC, for which I require of 5kEu per year to cover rhenium gasket foils, laser filters, diamond backing plates etc.

A major cost to the grant is the diamond anvils used to generate high pressure. Hydrogen embrittlement of diamonds causes frequent breakages, and I will require 1 pair a month across WP3, a total cost of 117kEu, plus 5kEu for hydrogen and deuterium. This appears as consumables because once the diamond has broken, it is useless, and this is not a predictable process.

### **C4 Travel**

The hydrogen problem attracts interest from across the world, and so it is essential that my PDRAs and I attend the key meetings such as AIRAPT, EHPRG and the high-pressure Gordon Conference. Although I am usually an invited speaker, all costs are seldom covered. I also request a budget to invite leading scientists and their

PDRAs to CSEC. PDRAs in WP3 and I will also carry out experiments in central facilities. Estimating an average of two trips per year between PI and PDRAs, at 2000Eu per trip (including registration fees).

I also request a budget to invite leading scientists and their PDRAs to CSEC. These external experts are expected to visit the HI and contribute to the implementation of the actions described in Annex 1 on an ad-hoc basis. Part of the travel budget is requested to cover their travel and accommodation/subsistence costs in line with the usual practice of the HI.

### **C5 Meetings**

A focused workshop on entropy, entanglement, correlation and path integrals will be held in 2017. In 2019 I will host a second workshop on extracting experimental signatures from simulations, and finally a major meeting or symposium will be held at conclusion of the project in 2021. The meetings would take advantage of Edinburgh's Higgs Centre which is an established forum for such high-profile meetings and for hosting visitors (<http://higgs.ph.ac.uk>). I have budgeted 10kEu for the small workshops, plus 20kEu for one major meeting.

### **C6 Other**

I expect to publish 2-3 high profile (PRL or better) papers per year, and another 5-6 international journals (PRB or similar), and request 15kEu towards project webhosting, open access publication and data storage costs.

## C7 Timeline

The work programme divided into three distinct Workpackages, which involve the three PDRAs. WP1 and WP3 have two strands, which could be done by different people.

Workpackages and project timeline						
Position	Role	Year 1	Year 2	Year 3	Year 4	Year 5
PI (G.J. Ackland)	Direction and involvement in all WPs (70% time/50% funded)					
	<b>Entanglement and Entropy</b>					
WP1a Postdoc	Roton-libron transitions					
WP1b Postdoc	Novel free energy methodology, latent heat					
WP1b PhD Student 1	Apply free energy methods					
	<b>Relating molecular dynamics to experiment</b>					
WP2 Postdoc	Projection method, Raman/IR calculation					
WP2 PhD Student 2	MD and PIMD calculations					
WP2 PhD Student 3	Quantum MD calculations					
WP2 Postdoc 2	Free energy and Quantum-corrected MD					
	<b>DAC Metallization and Discovery</b>					
WP3a Postdoc	DAC, IR development and data collection					
WP3a PhD student 4	DAC, phase I-IV					
WP3b PhD student 5	Neutrons, structure of phase II					
	<b>Associated CSEC work using similar techniques.</b>					
Associate student 6	Shock waves and equation of state (McWilliams)					
Associate student 7	Neutron Scattering (Loveday)					
Associate student 8	X-ray Scattering (Gregoryanz)					
Associate student 9	Structure Search (Martinez-Canales)					
Associate student 10	Hydrogen in chemical pressure (Hermann)					
Associate student 11	Hydrogen storage (Hermann)					

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