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I, Matt Ellis, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the work.

# Abstract

My research is about stuff.

It begins with a study of some stuff, and then some other stuff and things.

There is a 300-word limit on your abstract.

# Acknowledgements

Acknowledge all the things!

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# Chapter 1

## Introduction

### 1.1 Charge Transport in Organic Semiconductors

#### 1.1.1 Organic Semiconductors

Conductive polymers were first discovered in 1977 by Shirakawa et al<sup>3,4</sup> for which they were awarded the Nobel prize in Chemistry. Recently these materials have become ubiquitous in many technologies, such as in organic photovoltaic cells<sup>5</sup>, organic field-effect transistors (OFET)<sup>6</sup> and organic light-emitting diodes (OLED)<sup>7</sup>. While the other two technologies lag behind their inorganic counterparts, uptake of OLED screens is becoming ubiquitous -especially in the smartphone and television market due to their flexibility, better colour representation and lower energy consumption than standard backlit LCD displays. OLEDs have also found uses in lighting with their efficiency rivalling that of fluorescent tubes<sup>8,9</sup>. Although, industry has made large strides in fabricating and using these materials the exact nature of the charge transport is still poorly understood. Traditional theories (such as hopping and band transport) aren't applicable to many relevant materials<sup>10–14</sup> as charge transfer dynamics lies in an intermediate region where the polaron is neither fully localised or delocalised. This is due to crystals typically being formed of organic molecules weakly held together by Van der Waals (VDW) forces rather than strong covalent bonds. This allows molecules to fluctuate about their lattice sites and introduces a disorder that doesn't appear in inorganic crystals.

In order to properly quantify the performance of organic semiconductors a key prop-

erty is the charge carrier mobility. Typically, charge carrier mobilities in ‘good’ organic semiconductors (OSCs) fall between  $1\text{-}10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ <sup>15</sup>. Though higher mobilities, in pure crystals such as Rubrene, have been recorded in the range  $15\text{-}20+ \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ <sup>16,17</sup>. This is beyond the range of hopping model validity ( $\sim 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) and below that of band theory ( $> 50 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ )<sup>14</sup>. In this intermediate regime the charge carriers are typically not completely delocalised at the valence band edges (band regime) or localised to a single site/molecule (hopping regime) but delocalised over a few/tens of molecules<sup>18</sup>. Without any analytic approaches currently being valid in this regime many atomistic computational approaches have been developed to investigate the underlying charge transport mechanisms<sup>19</sup>.

## 1.2 Atomistic Simulations of Nonadiabatic Processes

In simulating processes involving electronic transfers a key approximation used in conventional molecular dynamics (MD) breaks down. That is the Born-Oppenheimer or adiabatic approximation<sup>20</sup>. This approximation, relied upon for almost a century<sup>21</sup>, hinges on the fact that nuclei are much more massive than electrons and are approximately stationary with respect to electron movement<sup>22</sup>. This results in nuclear evolution that is governed by a single, adiabatic, potential energy surface. However, in many interesting processes, such as the proton coupled electron transfer in photosynthesis and respiration<sup>23–25</sup>, non-radiative decay and photochemical processes, electronic transitions between adiabatic potential energy surfaces occur<sup>26</sup>. Simulating these processes requires non-adiabatic molecular dynamics (NAMD) techniques to be developed, to correctly capture dynamical properties.

There have been many techniques proposed for use in NAMD such as the quantum classical Louiville equation<sup>27</sup>, multiple spawning<sup>28</sup> or nonadiabatic Bohmian dynamics<sup>29</sup>. However, two of the most popular are trajectory surface hopping<sup>30</sup> and mean-field approaches<sup>31</sup>. This is probably due to their relative simplicity to implement, efficiency for

large systems and proven efficacy in a wide variety of situations<sup>32</sup>. In these approaches the general aim is to treat as much of the system as possible with (computationally cheaper) classical mechanics. While handling all necessary parts with quantum mechanics<sup>33</sup>. In Surface Hopping, Ehrenfest and Coupled-Trajectory Mixed Quantum-Classical molecular dynamics (CTMQC) one treats the nuclear subsystem classically and the electronic one quantum mechanically. The nuclei are normally propagated using a velocity verlet algorithm according to Newton's laws and electrons using a fourth order Runge Kutta algorithm according to the time-dependent Schrödinger equation. The wavefunction is normally expanded as a linear combination of adiabatic or diabatic states. The nuclei and electrons can also interact. Taking account of this interaction is where these techniques differ. No one technique is perfect, the issues for surface hopping and Ehrenfest are well documented and have been discussed in detail<sup>34–38</sup>. CTMQC is a fairly new technique and its issues are still mostly unknown. In this document I will discuss CTMQC in depth and present results from my own implementation of it as well as presenting its drawbacks. I will also compare these results to Ehrenfest and Trajectory Surface Hopping (TSH).

### 1.2.1 Surface Hopping and Ehrenfest Dynamics

An important technique in the field of mixed quantum classical nonadiabatic molecular dynamics is Ehrenfest dynamics. Assuming we treat the nuclei classically the Ehrenfest equations can be rigorously derived from the electronic Schrödinger equation. This is done by assuming that the nuclei's motion is provided by a single population weighted average potential energy surface. This average is taken from the adiabatic potential energy surfaces (eigenvalues of the Hamiltonian) where weights are provided by the populations of each adiabatic state. This effective potential energy surface is shown in fig 1.1. In this way the electronic

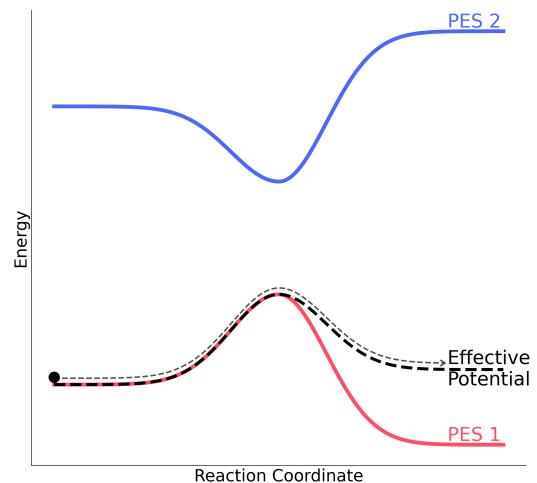


Figure 1.1: An example of a typical Ehrenfest simulation near an avoided crossing. The black lines represent the adiabatic potential energy surface due to the ground (PES 1) and excited (PES 2) state. The red line represents the population weighted average potential the nuclei travel on.

subsystem influences the propagation of the nuclei. The propagation of the forces and the electrons are controlled by equations (1.1) and (1.2).

$$F_v^{Ehren} = \sum_i^{N_{st}} |C_i|^2 \nabla_v E_i + \sum_{i,j}^{N_{st}} C_i^* C_j (E_j - E_i) d_{ij,v} \quad (1.1)$$

$$\hbar \vec{C}_m = C_m E_m - i \hbar \sum_n^{N_{st}} C_n d_{mn}^{ad} \quad (1.2)$$

In the above equations  $C_i$  is the adiabatic expansion coefficient for state  $i$ ,  $E_m$  is the energy of adiabatic state  $m$ ,  $d_{mn,v}^{ad}$  is the nonadiabatic coupling (in the adiabatic basis) between states  $m$  and  $n$  for atom  $v$ . The  $d_{mn}^{ad}$  are the nonadiabatic coupling elements expressed in the adiabatic basis. Although the Ehrenfest method has been applied with success in many systems<sup>39–41</sup> it has a number of key shortcomings. Namely, its inability to capture the branching of the nuclear wavefunction as propagation occurs on only a single potential energy surface and its poor account of the decoherence of the electronic and nuclear subsystem after an avoided crossing. Ehrenfest also violates detailed balance by populating all adiabatic states evenly<sup>20,42</sup>. In the limit of infinite states this results in infinite electronic temperature<sup>43</sup>. Possibly the most popular technique in NAMD is trajectory surface hopping. In trajectory surface hopping the shape of the potential energy surface is determined by a series of discrete stochastic hops between adiabatic potential energy surfaces<sup>42</sup>. See fig 1.2. The probability of these hops is determined by the non-adiabatic coupling between states. A swarm of trajectories are used and the probability a hop (non-adiabatic coupling) determines how many of these change state. The nuclear dynamics are dictated by the shape of the energy surface they are travelling on. This method can capture the branching of nuclear wavepacket unlike Ehrenfest. However, it still suffers from a number of issues. The original ‘fewest switches surface hopping’ proposed by John Tully suffered from bad overcoherence of the nuclear and electronic subsystems. That is the electronic and nuclear motion was coupled long after the region of high non-adiabatic coupling (crossing region). The fact that the hops are instant leads to discontinuities and methods need to

be implemented to fix these such as velocity re-scaling. Finally, perhaps the most important shortcoming is that this technique has not been derived from first principles and cannot be guaranteed to work generally. These problems have lead to a number of other techniques being developed. One of these, CTMQC, is the subject of this report.

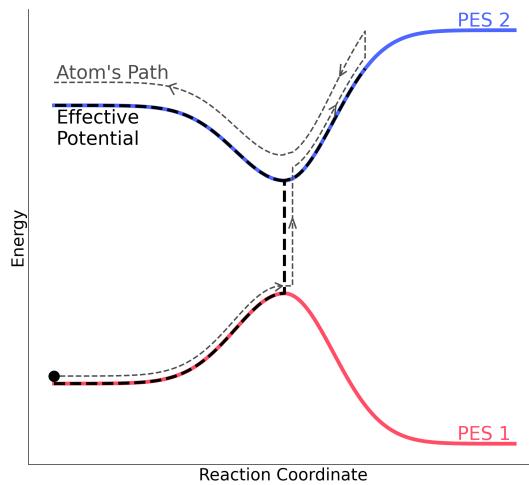


Figure 1.2: An example of a typical Surface Hopping simulation near an avoided crossing. The black lines represent the adiabatic potential energy surface due to the ground (PES 1) and excited (PES 2) state. The red line represents the discontinuous effective potential the nuclei travel on.

## Chapter 2

# CTMQC applied to the Tully Models

The Tully models, first proposed by John Tully in 1990<sup>44</sup>, are a collection of simple 1 dimensional model systems. They were designed to be simple enough to obtain accurate quantum results to benchmark new nonadiabatic molecular dynamics (NAMD) methods against. Originally there were 3, 1 dimensional, 1 atom models. However, in this work an extra model has been introduced with parameters taken from Gossel, 18<sup>45</sup>. This is to allow a full comparison of my implementation of CTMQC with the literature. In this chapter my implementation of CTMQC will be tested using these model systems and by comparing my results with those in the literature.

In each of the Tully models the (diabatic) Hamiltonian is a function of nuclear positions and is a  $2 \times 2$  matrix that takes the form:

$$\hat{H} = \frac{\hat{P}^2}{2M} + \begin{pmatrix} H_{11}(\mathbf{R}) & H_{12}(\mathbf{R}) \\ H_{21}(\mathbf{R}) & H_{22}(\mathbf{R}) \end{pmatrix} \quad (2.1)$$

The nuclear mass has been set to 2000 a.u.. This was set to be very close to the proton's mass of 1836 a.u. so we can expect significant quantum effects that classical theory couldn't replicate. The values of the Hamiltonian matrix elements are set to produce systems that resemble common features in a typical nonadiabatic simulation such as avoided crossings and regions of extended coupling. The parameters used in each systems' Hamiltonian where taken from Gossel, 18<sup>45</sup> in order to compare the 2 implementations. These can be found in appendix A.

In order to propagate dynamics in the adiabatic basis we need to calculate various quantities from the hamiltonian at each timestep. These are, for Ehrenfest, the (adiabatic) nonadiabatic coupling vector ( $\mathbf{d}_{lk}^{(I)}$ ) and the adiabatic energies ( $E_l^{(I)}$ ). In the full CTMQC simulations we must also calculate the adiabatic momentum term  $\mathbf{f}_l^{(I)}$  from the Hamiltonian. The adiabatic energies are the eigenvalues of the Hamiltonian. The adiabatic NACV can be calculated via an (explicit Euler) finite difference method and equation (2.2) below.

$$\mathbf{d}_{lk}^{(I)} = \langle \psi_l^{(I)} | \nabla \psi_k^{(I)} \rangle \quad (2.2)$$

Where  $\psi_l^{(I)}$  is the adiabatic electronic basis function for adiabatic state l. This is given by the eigenvector of the Hamiltonian, on replica I, corresponding to state l. Illustrations of these 2 properties can be found below in fig 2.1 for each of the 4 models systems.

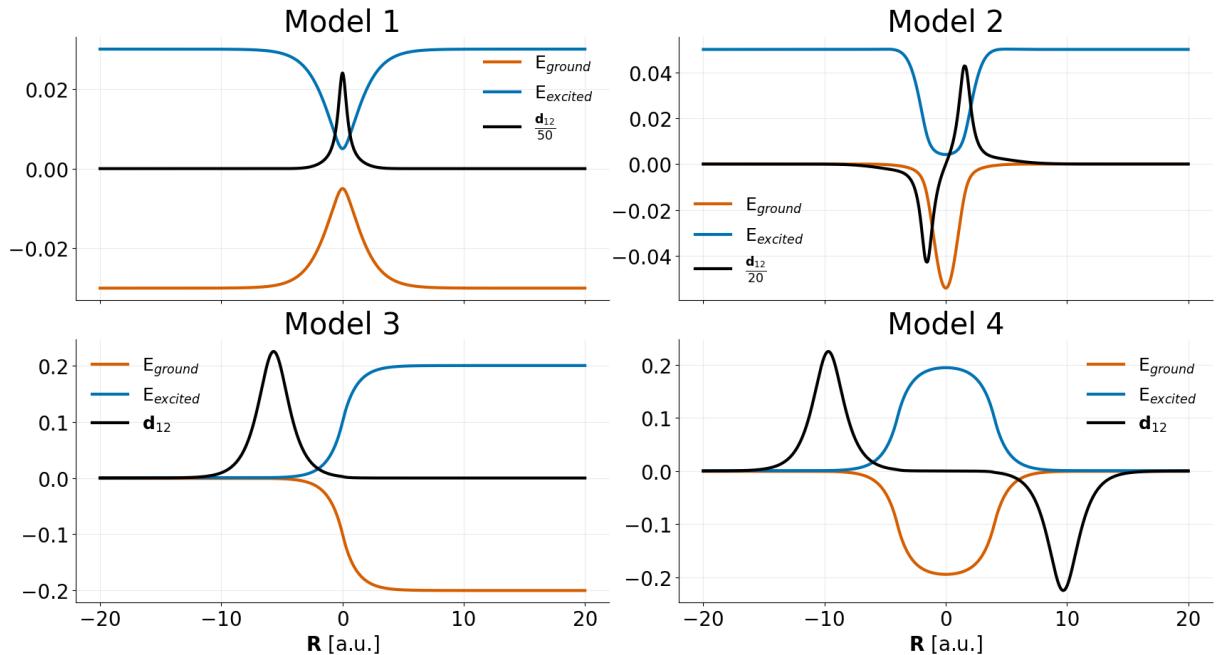


Figure 2.1: Adiabatic potential energy surfaces (orange and blue) and element 1, 2 of the nonadiabatic coupling vector (black) for the 4 model systems. For parameters see appendix A.

In order to initialise the simulations coordinates and velocities were sampled from the Wigner phase-space distribution of a gaussian nuclear wavepackets given by equation (2.3). A derivation of this can be found in appendix B. The nuclear positions/velocities were then propagated using a velocity verlet algorithm and the adiabatic expansion coefficients were propagated using a 4<sup>th</sup> order Runge-Kutta method.

$$\chi(R, 0) = \frac{1}{(\pi\mu^2)^{\frac{1}{4}}} e^{-\frac{(R-R_0)^2}{2\mu^2} + ik_0(R-R_0)} \quad (2.3)$$

The adiabatic coefficients were initialised purely on the ground state and the initial width of the nuclear wavepacket was set to  $\mu = \sqrt{2}$  bohr. 2 values of initial momenta  $k_0$  were chosen for each model, 1 low value and another higher one. Full details of all input parameters can be found in appendix A. I have implemented a serial version of CTMQC acting on Tully's toy model systems and real molecular systems using couplings derived from the analytic overlap method<sup>46</sup> within the software package CP2K<sup>47</sup> and for Tully's model systems as standalone python code. These are accessible publicly via github repositories at: [github.com/95ellismle](https://github.com/95ellismle).

## 2.1 Testing My Implementation

The motivation behind implementing CTMQC for the Tully models was to serve as a verifiable base for later extensions, such as integrating CTMQC within the fragment-orbital based (FOB)<sup>48</sup> framework which will be discussed in a later chapter? . Using such simple systems will also help to clarify how each new parameter works and make testing and debugging easier. As well as many numerical tests on individual terms in the equations, I have implemented some physical tests on the overall system dynamics. In this section, I will outline the key tests I have performed on both the Ehrenfest and full CTMQC parts of the equations. These are: verifying we obtain Rabi oscillation in the limit of fixed nuclear geometries, checking energy and the norm of the wavefunction is conserved and verifying the time-derivative of the sum over trajectories of adiabatic populations is 0.

### 2.1.1 Rabi Oscillation

...

### 2.1.2 Energy Conservation

...

### 2.1.3 Norm Conservation

In appendix ?? it is shown that the norm of the adiabatic coefficients

### 2.1.4 Time Derivative of Trajectory-Sum of Adiabatic Populations

...

## Chapter 3

# CTMQC applied to molecular systems

## Chapter 4

# Extending surface hopping for larger systems

Fragment-orbital based surface hopping (FOB-SH) is a technique developed within the Blumberger group<sup>48</sup> designed to simulate large molecular systems. It has had much success in the study of organic crystalline materials<sup>18,49</sup>. Most notably the electron/hole mobilities of a variety of common organic semi-conducting materials were measured within a factor of 2 of experimental measurements. However, in order to study very large amorphous and semi-crystalline systems some more memory/computation optimisations were required and electrostatic interactions (which weren't important in previous systems) needed to be accounted for. In this chapter I outline some minor improvements I implemented within the surface hopping code as well as the method used to implement the electrostatic interactions.

### 4.1 Code Optimisations

## Chapter 5

# Charge transfer in amorphous systems

Although it is important to know the maximum bound on the mobility of the charge carrier in a perfect crystal of an organic semiconductor, in reality it is very difficult to control defect formation in OSs<sup>50?</sup>. This is due to van der Waals forces only weakly holding molecules at lattice sites, allowing molecules greater freedom than in traditional inorganic crystal, and increasing the chance of defect formation which can trap/scatter charge carriers reducing overall mobility. This means it is important to investigate and characterise charge transport properties for not just perfectly crystalline OSs but also those that show a range of amorphicity.

The molecule chosen to investigate amorphous films was pentacene. This molecule is a popular organic semiconductor and the subject of much research due to its high field effect mobility<sup>51</sup>, use in device applications<sup>52</sup> and, more recently, the use of functionalization to alter device properties<sup>53,54</sup>. The pentacene molecule consists of 5 joined benzene rings (36 atoms) and crystals typically pack with a herringbone motif as shown in figure 5.1.

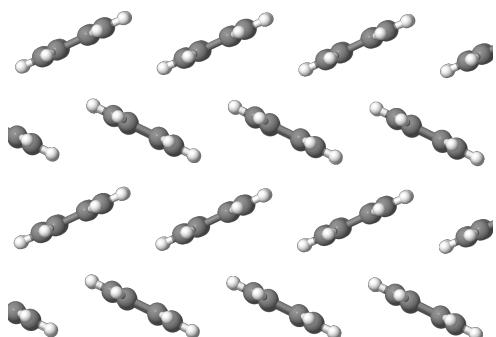


Figure 5.1: An example of the herringbone packing typically found in Pentacene crystals

## 5.1 Creating Amorphous Pentacene

In order to create the amorphous pentacene systems a melt-quench technique was used. This is a standard technique, often used to create amorphous systems in both computational and experimental fields<sup>55–59</sup>. The procedure followed is shown in figure 5.2.

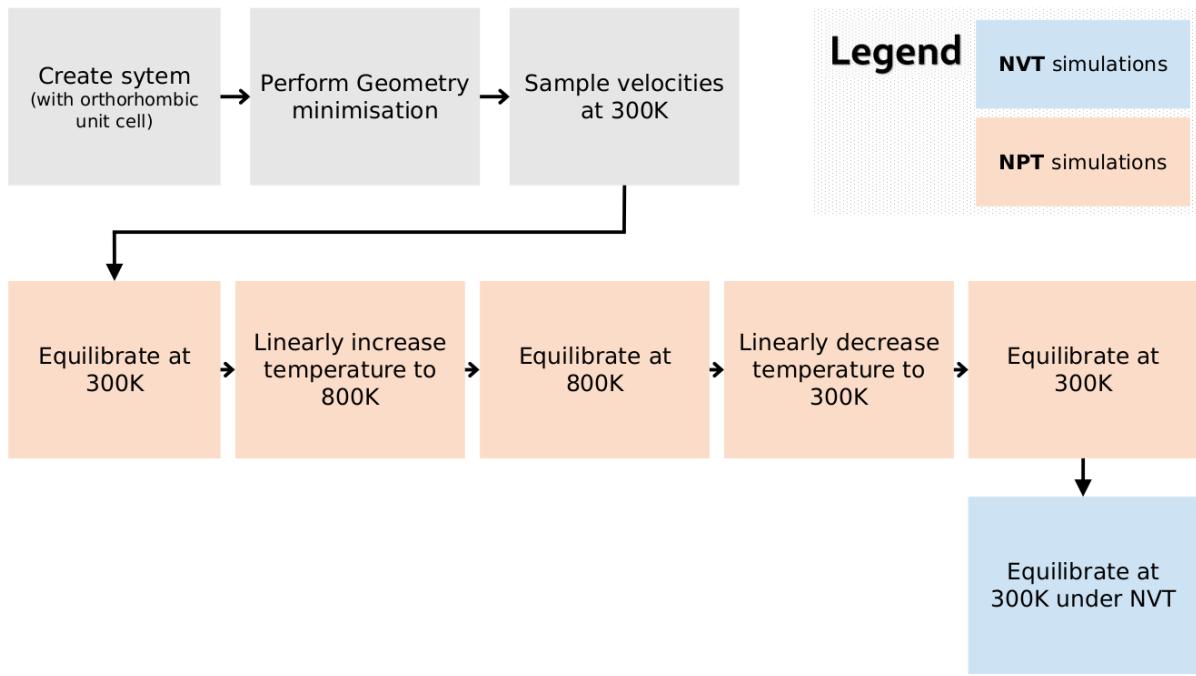


Figure 5.2: The melt-quench scheme used to create amorphous pentacene systems. Blue boxes indicate steps using an NPT ensemble, orange boxes indicate use of a NVT ensemble.

In this procedure, the system was initialised with an individual pentacene molecule on a regular 3D grid using an orthorhombic unit cell. This was chosen to make analysis of the resulting structures easier than with the triclinic unit cell typically used to simulate pentacene crystals. The velocities were initially randomly sampled from a gaussian distribution and a Nose-Hoover thermostat and barostat was used to control the temperature and pressure. The Lammps molecular dynamics package was used<sup>60,61</sup> and electrostatic interactions were handled with Lammps' particle-particle-particle-mesh ewald method<sup>62</sup>. RESP<sup>63</sup> (restrained electrostatic potential) partial charges were parameterised using Gaussian 16<sup>64</sup> with the B3-LYP level of theory and a G-311g(d) basis set. The use of partial charges was essential in the creation of the amorphous systems and will be discussed further in section 5.3.2. Finally, for inter and intra molecular interactions the general AMBER force-field<sup>65</sup> (GAFF) was applied. There doesn't seem to be one

predominant forcefield to use in simulations of pentacene though parameters from GAFF have been used in a number of studies<sup>66–72</sup>.

Four different quenching times were used spanning 4 orders of magnitude: 0ns, 1ns, 10ns and 100ns. For the 0ns, 1ns and 10ns quenching simulations 3,000 molecules were simulated. In the 100ns quenched structure 3060 molecules were simulated. The initial structure for the 1ns and 10ns quenched structures were taken from a restart of the 0ns quenched simulation after the 800K equilibration step. The 0ns and 1ns quenched structure were carried out under 1 atmosphere of pressure in x, y and z. However, the 10ns quenching required a small increase to 5 atmospheres as the structure had a tendency to deform such that one of the cell vectors became either very large or very small. In the 100ns quenched structure I updated the barostat target pressure (before the phase transition) to account for similar deviations in simulation box dimensions.

## 5.2 Structure of the quenched simulations

A movie showing the full 100ns melt-quench simulation can be found here: <https://youtu.be/6IQcYErQHVs>. Still images of the final snapshot of each different quenching time are shown in figure 5.3 below.

### 5.2.1 Final Structure Snapshots

We can see qualitatively that as we increase the quenching time from a) → d) the structure starts to look more ordered and crystal layers are starting to be formed. Looking longer at the structure we see that lower quench times tend to form small crystal clusters. In the 0ns quenched structure these clusters tend to be just ~7-10 molecules in size. As we increase the quenching time to 1ns we see 1D channels of crystalline pentacene start to form throughout the structure, though the structure is still relatively disordered due to these channels being randomly oriented with respect to one another. As we increase the quenching time these crystal fragments become larger until in the 100ns quenched structure the whole system is comprised of just 2 crystals. The reason for this is, as we decrease the rate of cooling (increase quench time) we also decrease the rate of crystals being seeded. This allows any crystals that have formed to grow larger without being

impeded by the growth of any other crystals. This can most clearly be seen in the animation of the [100ns melt quench simulation](#) linked above.

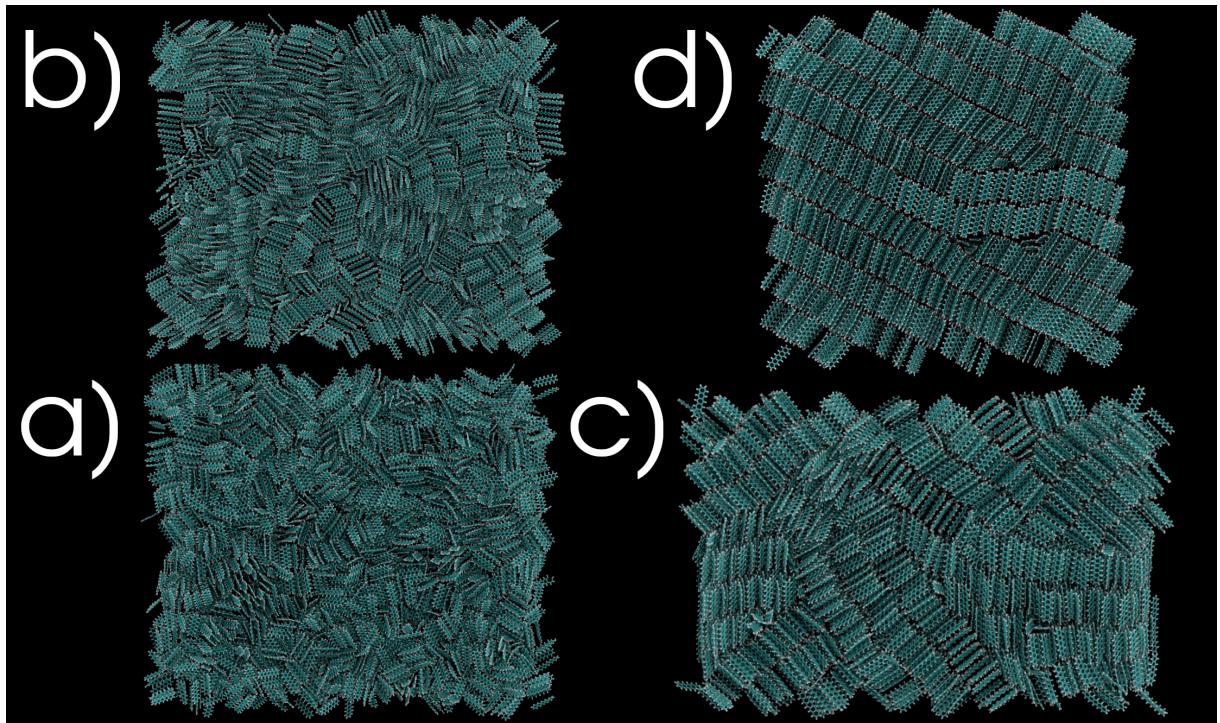


Figure 5.3: The final snapshot of each quenching simulation visualised in VMD<sup>1</sup> and rendered with Tachyon<sup>2</sup>. Snapshots are ordered by quenching time i.e. a) is the 0ns quench, b) is the 1ns quench and so on.

### 5.2.2 Molecular Packing

We can isolate clusters in each of the different structures shown in figure 5.3 to reveal the molecular packing within. In figure 5.4 a DBSCAN-like algorithm has been applied to the final structure from the 100ns quench to cluster molecules based on the molecular density in a given region of space. These clusters have then been highlighted by different colours. The top-most green cluster has been rotated such that, on the left, we are viewing it at an angle perpendicular to the plane of molecules, as shown by the cartoon eye. Comparing this plane to the crystal plane to the right of it we can see a remarkable similarity in the packing motif. The herringbone packing has formed and (as can be seen in figure 5.7 in section 5.2.4) the herringbone intersection angle is remarkably similar to the crystal plane. This serves as a confirmation of the choice of force-field and the parameterisation of the partial charges.

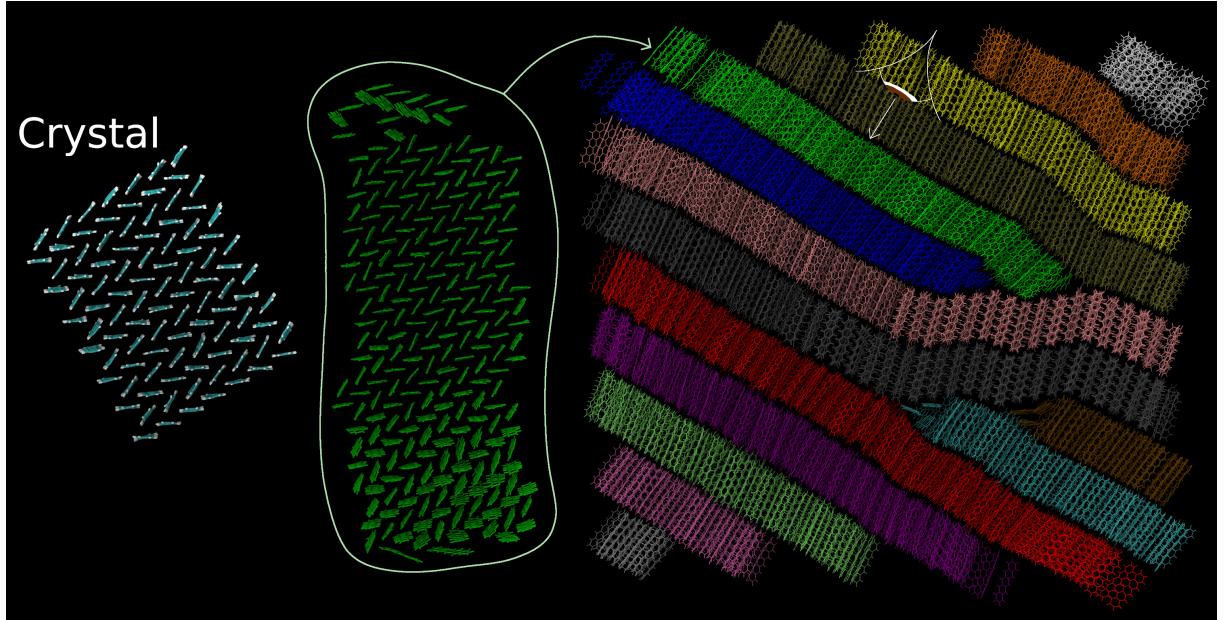


Figure 5.4: The 100ns quenched structure with different clusters shown with different colours. A bird's eye view of the green cluster has been shown on the left to demonstrate the herringbone packing within each cluster/layer. The far-right image labelled 'Crystal' is a snapshot of a crystal plane after a short MD equilibration.

Although this herringbone packing pattern is most obvious in the 100ns quenched structure, it can also be seen in the other structures. At the other extreme in the 0ns quenched structure we see small clusters ( $< 15$  mols) of pentacene crystals forming. This is shown in figure 5.5. As the quench time increases these crystal fragments have more time to grow unimpeded by other crystals seeded nearby.

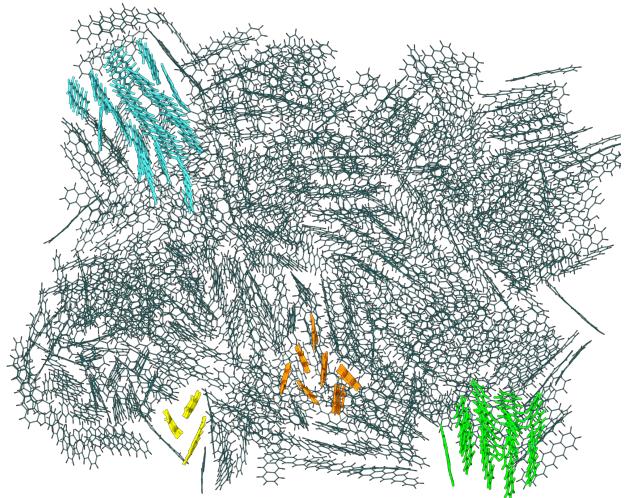


Figure 5.5: A slice from the 0ns quenched structure with selected clusters of herringbone-like packing highlighted.

To quantify the change in the structure for the differently quenched structures 4 macroscopic properties can be plotted: the mass density, the angular distribution, the radial distribution function and the orientational order parameter. These are discussed in the following sections.

### 5.2.3 Mass Density

The mass density of the 4 different quenching simulations can be seen below in figure 5.6. This was calculated by dividing the total mass of the atoms in the system by the volume (product of cell vectors) of the simulation box. The first thing to notice in this graph is as we increase the quenching time we increase the density of the final sample. This is due to the molecules packing more efficiently in the crystal than in an amorphous structure. We also see very clearly in the plots the sudden increase in density associated with the phase transition from liquid to solid Pentacene. In the 1ns quench structure (quenched with the barostat set to 1 atmosphere) this occurs around Pentacene's experimental melting of 530.15K<sup>73</sup> providing confirmation of the choice of force-field. The 0ns, 1ns and 10ns runs were performed in a single 24 hour run. The 100ns quench was performed using many restarts, the discontinuities in the density for the 100ns structure come from these restarts. I don't believe they affect the final structure as these only occur while the system is in the liquid state.

### 5.2.4 Angular Distribution

The angular distribution shows the distribution angles each molecule makes with the other molecules in the system. In figure 5.7 it was calculated by calculating the angle of an axis of each molecule with its nearest neighbours (a 20Å center of mass cutoff was used). This data was then grouped into a histogram which is plotted below. In figure 5.7 we can see as the quenching time increases we start to notice an ever more prominent peak appear at either extreme of the x axis. This is because the molecules are aligning parallel with one another. The symmetry of the plot is an artefact of the melt stage of the simulation where each molecule was free to rotate randomly.

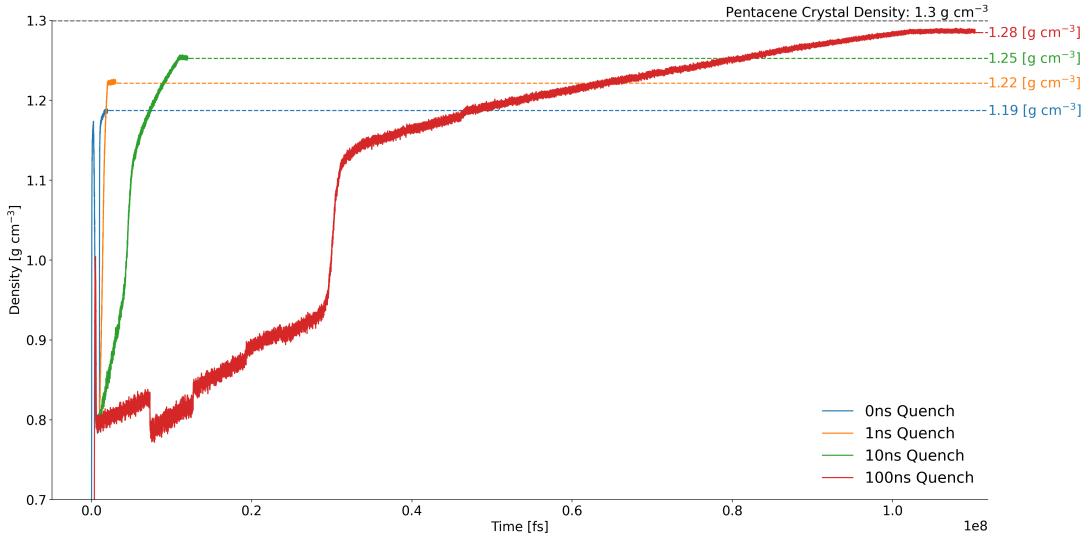


Figure 5.6: A time series of the density of the quenched structures. The black line shows the experimental mass density of crystal pentacene.

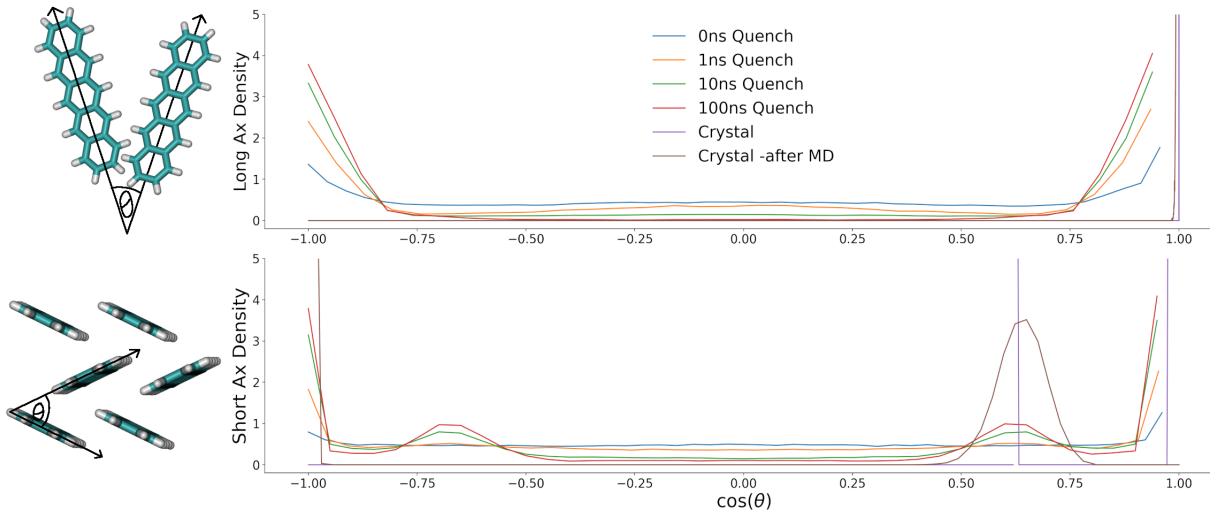


Figure 5.7: The angular distribution for the 4 different quench times is shown above. The brown and purple lines are from a perfect crystal before and after a short MD run. The others are after the various melt-quench simulations. On the right is a schematic showing which angles are referenced in each plot.

If we now look at the short axis plot we can see that, again, as the quench time increases we start to see a more ordered structure start to form. This time the herringbone intersection angle between molecules ( $54.3^\circ$ <sup>74</sup>) within the herringbone structure is retrieved. This is a result of using partial charges in the simulation -running the same simulations without partial charges results in an unrealistic face-to-face stacking. The brown and purple line show the same calculation run on a crystal of pentacene before and

after MD. The purple line comes from an analysis of a repeated unit cell, hence we get 2 delta functions: one at  $54.3^\circ$  and one at  $0^\circ$ . This structure was then equilibrated with electrostatics for 50ps and we start to see a broadening of the herringbone intersection angle and to a lesser extent (on the left side) a broadening of the angle between parallel pairs.

### 5.2.5 Radial Distribution Function

The radial distribution function (RDF) describes the change of density from each particle in the system and is normalised to the bulk density (i.e.  $\frac{N}{V}$ ). This was calculated by counting the number of atoms within a spherical shell from each atom and then dividing by the volume between these spheres. This local density was then normalised to the bulk crystal density. In systems with atoms regularly placed throughout the system we would expect to see sharp peaks in the RDF as there would be many gaps with no atoms. Conversely, with a totally amorphous system we would expect to see (once we reach twice the Van der Waals radius from each atom) a flat line at 1 as local density should be very similar to the global density. This pattern is what we observe in figure 5.8 below. The sharp peaks of the purple line show the RDF of a perfect crystal (repeated unit cell) confirming we have a highly ordered system. On the other extreme the blue line shows very weak ordering of the atoms' positions with any ordering vanishing after  $\sim 12.5\text{\AA}$  from each atom. This is due to the 0ns structure comprising primarily of small crystal fragments giving rise to a small amount of very local order but over longer distances this order vanishes. Again, as the quench time increases, the ordering increases resulting in larger peaks that more closely match the RDF of the crystal after a short MD equilibration.

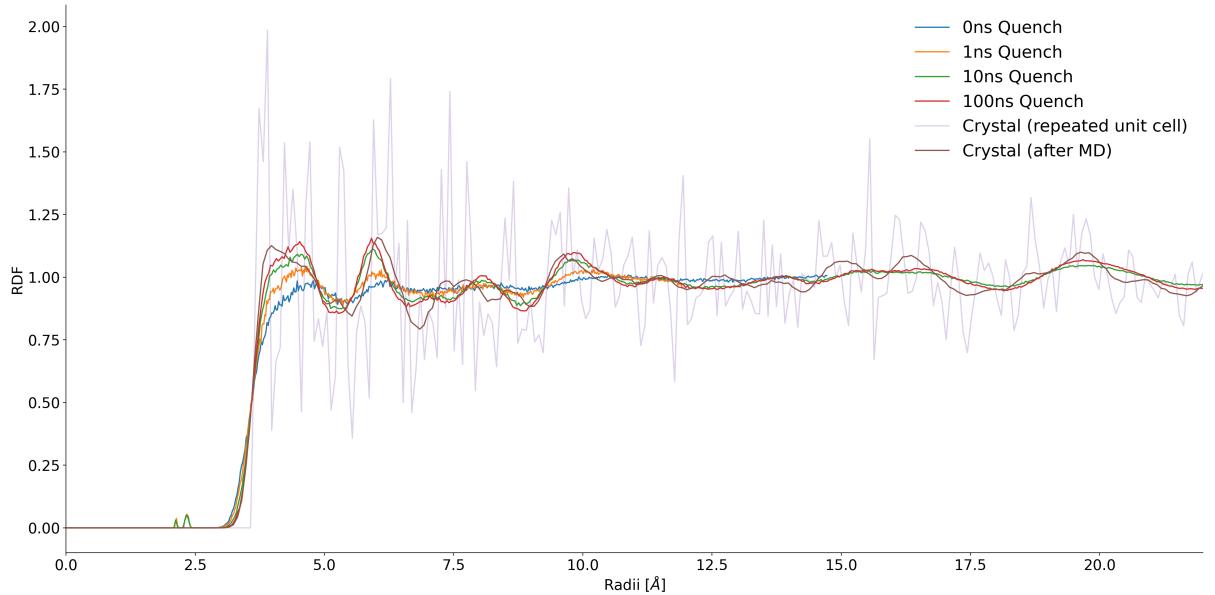


Figure 5.8: The carbon-carbon radial distribution function for 4 different quenching times and a crystal before and after 50ps of MD. The quenches (0, 1, 10 and 100ns) are shown in blue, orange, green and red respectively. The crystal data are shown in purple and brown.

### 5.2.6 Orientational Order Parameter

The orientational order parameter gives a single number describing how aligned the molecules within a system are. Values lie on a scale from -0.5 to 1, where 1 denotes all molecules are aligned, 0 denotes a random alignment of molecules and -0.5 denotes an anti-alignment with respect to the reference vector. The formula for the orientational order parameter is given below in equation (5.1).

$$S = \frac{3}{2} \frac{1}{N_{mol}} \sum_i^{N_{mol}} \left[ \frac{\mathbf{v}_i \cdot \mathbf{v}_{ref}}{|\mathbf{v}_i| |\mathbf{v}_{ref}|} \right]^2 - \frac{1}{2} \quad (5.1)$$

Where  $\mathbf{v}_i$  is the vector describing the long or short axis of molecule i. The reference vector  $\mathbf{v}_{ref}$  was defined as the average over  $\mathbf{v}_i$  i.e:  $\mathbf{v}_{ref} = \langle \mathbf{v}_i \rangle_i$ .  $N_{mol}$  is the number of molecules and i indicates a molecule index.

In figure 5.9 we can see the change in the orientational order parameter with quenching time and, as seen in the previous sections, as we increase the quenching time we increase (orientational) order in the system.

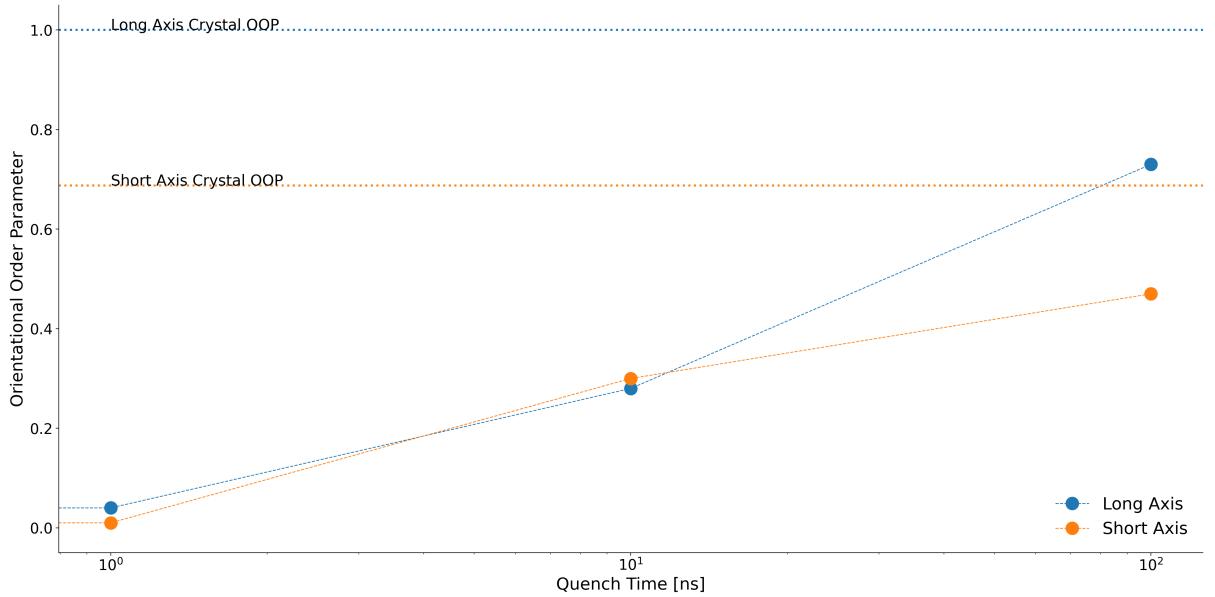


Figure 5.9: The change in the orientational order parameter (OOP) with respect to the quenching time. The blue data represents the values for the long axis and the orange data represents the short axis values. The horizontal lines show the theoretical value for a perfect crystal.

## 5.3 Charge Transfer Properties

We have seen that the final structure of the pentacene systems becomes more ordered and crystal-like as the quenching time is increased. It would be good now to see how this affects the charge transfer properties. A key quantity governing charge transfer rates is the ratio between electronic coupling and reorganisation energy,  $\frac{H_{ab}}{\lambda}$ . Seeing as we have a single molecule system, by plotting the electronic coupling we can get a qualitative view of the charge transfer dynamics and see which paths are the most likely within the structure.

### 5.3.1 Coupling Graphs

In figure 5.10 the graph of electronic couplings between molecules has been plotted for each of the quenched systems and a crystal system after a short equilibration run with MD. In this figure the centers of mass each molecule is represented by a small black dot and the calculated coupling value with a coloured line (red, green blue). That is, if 2 molecules have a non-negligible coupling between them they would be represented by 2 black dots with either a red, green or blue line connecting them. The couplings were

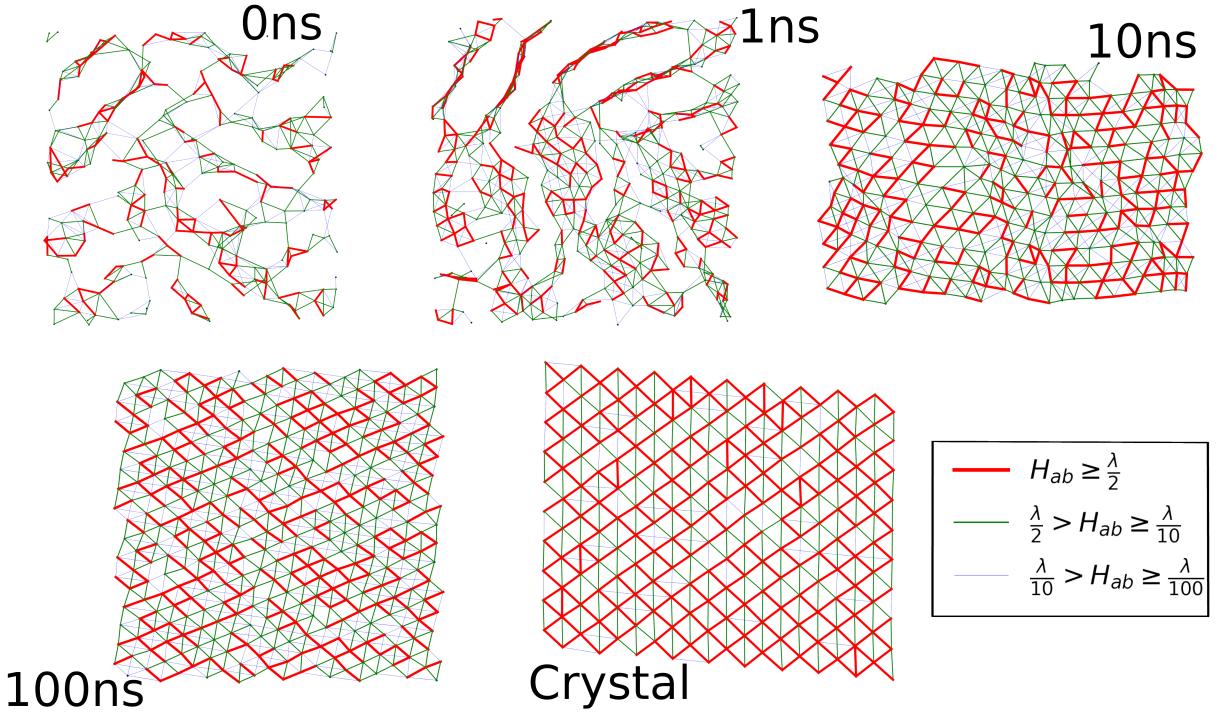


Figure 5.10: A representative network of electronic coupling that each quenched structure has formed. Each structure is labelled by the quench time (e.g. 0ns, 1ns, 10ns) or Crystal for a crystal after a short MD equilibration. Coupling strengths are categorised as high (red), medium (green) and low (blue). The definitions of the categories are given in the legend in the bottom right corner.

calculated via the analytic overlap method<sup>46</sup> and a pertinent cluster of molecules was selected for each quench time. For the 0ns and 1ns quench times this was simply a slice 1 molecule thick in the z dimension, containing a few hundred molecules. For the 10ns and 100ns quenched structures a reasonable cluster of molecules was chosen after applying a density based clustering algorithm on the superstructure. For the crystal a plane from the crystal was chosen. All panes in figure 5.10 show the coupling of the selected system from an angle perpendicular to the plane of molecules.

We can see in the graph of the 0ns quenched structure there is very little order to the coupling network. Only very small fragments of high (red) coupling are formed and each one is connected via weak or medium coupling. We can define a 'high coupling fragment' as any set of molecules which can all be reached from any member of the set via an unbroken path of high coupling. The mean size of these high coupling fragments in

the 0ns structure is 4.1 molecules and there are 503 of them. In this structure we would expect to see a localised polaron (over a  $\sim 3$  molecules) and low mobilities due to the lack of conductive channels in the structure. The mean size of fragments increases and the number of fragments decreases as we increase the quenching time as shown in table 5.1.

Quench Time [ns]	Mean Fragment Size	Fragment Size Std Dev	Num Fragments
0	4.2	3.8	503
1	4.5	5.0	493
10	6.5	9.3	373
100	8.7	16.2	292

Table 5.1: The change in the number of high coupling fragments, and the mean and standard deviation of their size, found in each structure as the quenching time was varied.

We can see in table 5.1 that as the quenching time increases, the size of the highly coupled fragments (how many molecules are connected) increases and fewer of them are formed. The standard deviation also increases showing in the 0ns quenched structure most fragments are very small but as we increase the quench time we still get smaller fragments but much larger ones can now form too. These larger fragments can act as regions of high conductivity allowing much larger mobilities to be achieved than in the quicker quenching times.

### 5.3.2 Molecular Dynamics without Partial Charges

## Chapter 6

# Extending surface hopping with electrostatics

### 6.1 Electrostatics interaction within FOB-SH

FOB-SH is a variant of Tully's original fewest switches surface hopping (ref John Tully 1990 original surface hopping paper). The electron and nuclear dynamics are dictated by the Hamiltonian, where the spatial derivative of the diagonal elements (site-energies) give the nuclear forces which come from a classical forcefield and the off-diagonal elements (electron couplings) are proportional to the overlap of the diabatic wavefunctions. Each site-energy,  $H_{\gamma\gamma}$ , is defined as the potential energy of the system where the excess charge is localised on a single molecule,  $\gamma$ . The input parameters such as the charge distribution or the strength of the bonds are different for molecule  $\gamma$  than the other molecules, resulting in different forces/potentials. The different potentials from each permutation of the charge state are saved as the site-energies, the forces are saved in a different array of size ( $N_{states}, N_{atoms}, 3$ ). To implement electrostatic interactions the potential and the forces within the surface hopping framework will have to be altered.

To calculate the electrostatic contribution from each atom to the forces and potential the standard Ewald method was chosen, with some additional tricks to reduce the computational cost. The Ewald method, first published by Paul Ewald in 1921 (NEED REF), is a near ubiquitous method used to evaluate the potential and forces from a set of point charges. This is equivalent to carrying out the much slower to converge (NEED REF) and conditionally convergent traditional coulomb sum. The Ewald method relies

on separating the traditional coulomb summation into 2 quickly converging parts; a long range term and short range term. The short range term is carried out in real space and the long range term is carried out in reciprocal space

## Chapter 7

# General conclusions

## Appendix A

### Tully Model Paramters

#### A.1 Model 1 -Single Avoided Crossing

	Quantity	Value	Unit
Hamiltonian Paramters:			
$H_{11}(\mathbf{R}) = A \tanh(B\mathbf{R})$	Initial Position	-20	a.u.
$H_{12}(\mathbf{R}) = Ce^{-D\mathbf{R}^2}$	Initial Velocities	15.0, 25.0	a.u.
$H_{21}(\mathbf{R}) = H_{12}(\mathbf{R})$	Initial Adiab Pop	ground state	-
$H_{22}(\mathbf{R}) = -H_{11}(\mathbf{R})$	Simulation Time	6000, 4000	a.u.
Where $A = 0.03$ , $B = 0.4$ , $C = 0.005$ and $D = 0.3$	$\sigma_v^{(I)}$	0.5	a.u.
	M ( $\sigma$ constant)	40	-
	$\Delta t_{\text{nuclear}}$	0.1	fs
	$\Delta t_{\text{electronic}}$	0.01	fs
	$\frac{\delta \mathbf{R}_{lk,v}^{(I)}}{\delta t}$ threshold	0.15	a.u.
	$N_{rep}$	200	-

## A.2 Model 2 -Dual Avoided Crossing

	Quantity	Value	Unit
Hamiltonian Paramters:			
$H_{11}(\mathbf{R}) = 0$	Initial Position	-8	a.u.
$H_{12}(\mathbf{R}) = Ce^{-D\mathbf{R}^2}$	Initial Velocities	16.0, 30.0	a.u.
$H_{21}(\mathbf{R}) = H_{12}(\mathbf{R})$	Initial Adiab Pop	ground state	-
$H_{22}(\mathbf{R}) = -Ae^{-B\mathbf{R}^2} + E$	Simulation Time	2500, 1500	a.u.
Where A = 0.1, B = 0.28, C = 0.015, D = 0.06 and E = 0.05	$\sigma_v^{(I)}$	0.5	a.u.
	M ( $\sigma$ constant)	40	-
	$\Delta t_{\text{nuclear}}$	0.1	fs
	$\Delta t_{\text{electronic}}$	0.01	fs
	$\frac{\delta \mathbf{R}_{ik,v}^{(I)}}{\delta t}$ threshold	0.15	a.u.
	$N_{rep}$	200	-

## A.3 Model 3 -Extended Coupling

	Quantity	Value	Unit
Hamiltonian Paramters:			
$H_{11}(\mathbf{R}) = A$	Initial Position	-15	a.u.
$H_{12}(\mathbf{R}) = \begin{cases} Be^{C\mathbf{R}}, & R \leq 0 \\ B(2 - e^{-C\mathbf{R}}), & R > 0 \end{cases}$	Initial Velocities	10, 30	a.u.
$H_{21}(\mathbf{R}) = H_{12}(\mathbf{R})$	Initial Adiab Pop	ground state	-
$H_{22}(\mathbf{R}) = -H_{11}(\mathbf{R})$	Simulation Time	5000, 1500	a.u.
Where A = $6 \times 10^{-4}$ , B = 0.1 and C = 0.9	$\sigma_v^{(I)}$	0.5	a.u.
	M ( $\sigma$ constant)	40	-
	$\Delta t_{\text{nuclear}}$	0.1	fs
	$\Delta t_{\text{electronic}}$	0.01	fs
	$\frac{\delta \mathbf{R}_{ik,v}^{(I)}}{\delta t}$ threshold	0.15	a.u.
	$N_{rep}$	200	-

## A.4 Model 4 -Dual Arch

Hamiltonian Paramters:

$$H_{11}(\mathbf{R}) = A$$

$$H_{12}(\mathbf{R}) = \begin{cases} B \left[ -e^{C(\mathbf{R}-D)} + e^{C(\mathbf{R}+D)} \right] & R \leq -D \\ B \left[ e^{-C(\mathbf{R}-D)} - e^{-C(\mathbf{R}+D)} \right] & R \geq D \\ B \left[ 2 - e^{C(\mathbf{R}-D)} - e^{-C(\mathbf{R}+D)} \right] & -D < R < D \end{cases}$$

$$H_{21}(\mathbf{R}) = H_{12}(\mathbf{R})$$

$$H_{22}(\mathbf{R}) = -H_{11}(\mathbf{R})$$

Where  $A = 6 \times 10^{-4}$ ,  $B = 0.1$  and  $C = 0.9$

Quantity	Value	Unit
Initial Position	-20	a.u.
Initial Velocities	10, 40	a.u.
Initial Adiab Pop	ground state	-
Simulation Time	6000, 2000	a.u.
$\sigma_v^{(I)}$	0.5	a.u.
M ( $\sigma$ constant)	40	-
$\Delta t_{\text{nuclear}}$	0.1	fs
$\Delta t_{\text{electonic}}$	0.01	fs
$\frac{\delta \mathbf{R}_{lk,v}^{(I)}}{\delta t}$ threshold	0.15	a.u.
$N_{rep}$	200	-

## Appendix B

# Wigner Distribution Derivation

The nuclear wavepacket (at time 0) is given by:

$$\chi(R) = \frac{1}{(\pi\mu^2)^{\frac{1}{4}}} e^{-\frac{(R-R_0)^2}{2\mu^2} + ik_0(R-R_0)} \quad (\text{B.1})$$

The Wigner quasiprobability function for momentum and position ( $p, R$ ) is given by:

$$W(p, R) = \frac{1}{\pi\hbar} \int_{-\infty}^{\infty} \chi^*(R+y)\chi(R-y)e^{\frac{2ipy}{\hbar}} dy \quad (\text{B.2})$$

However, both Ehrenfest and CTMQC require atomic positions as input so we must extract the position and velocity probability densities from this. We get these from the marginal integrals of the Wigner distribution i.e.

$$|f(R)|^2 = \int_{-\infty}^{\infty} W(R, p) dp \quad (\text{B.3})$$

$$|f(p)|^2 = \int_{-\infty}^{\infty} W(R, p) dR \quad (\text{B.4})$$

In order to calculate these marginal integrals we must first crunch through the maths of equation (B.2). Substituting eq (B.1) into (B.2):

$$W(p, R) = \frac{1}{\pi\hbar} \int_{-\infty}^{\infty} \frac{1}{\mu\sqrt{\pi}} e^{-\frac{(R+y-R_0)^2}{2\mu^2} - 2ik_0y - \frac{(R-y-R_0)^2}{2\mu^2}} e^{\frac{2ipy}{\hbar}} dy \quad (\text{B.5})$$

Simplifying the 2 quadratic equations (equation (B.5)) we get:

$$W(p, R) = \frac{1}{\pi \hbar} \int_{-\infty}^{\infty} \frac{1}{\mu \sqrt{\pi}} e^{-\mu^{-2}(y^2 - 2ik_0 y \mu^2 + (R-R_0)^2)} e^{\frac{2ipy}{\hbar}} dy \quad (\text{B.6})$$

We can now take the expressions not dependant on  $y$  outside of the integral and combine the exponents.

$$W(p, R) = \frac{1}{\pi \sqrt{\pi} \mu \hbar} e^{-\frac{(R-R_0)^2}{\mu^2}} \int_{-\infty}^{\infty} e^{-\frac{y^2 + 2iy\mu^2(\frac{p}{\hbar} - k_0)}{\mu^2}} dy \quad (\text{B.7})$$

Integrating we get:

$$\int e^{-\frac{y^2 + 2iy\mu^2(\frac{p}{\hbar} - k_0)}{\mu^2}} dy = \frac{\sqrt{\pi} \mu}{2} e^{-\frac{\mu^2}{\hbar^2}(p - \hbar k_0)^2} \operatorname{erf} \left[ \frac{y}{\mu} + i \left( \frac{p\mu}{\hbar} - \mu k_0 \right) \right] \quad (\text{B.8})$$

Applying limits we get:

$$\int_{-\infty}^{\infty} e^{-\frac{y^2 + 2iy\mu^2(\frac{p}{\hbar} - k_0)}{\mu^2}} dy = \sqrt{\pi} \mu e^{-\frac{\mu^2}{\hbar^2}(p - \hbar k_0)^2} \quad (\text{B.9})$$

Substituting this back into the Wigner distribution (equation (B.2)) we finally get:

$$W(p, R) = \frac{1}{\pi \hbar} e^{-\frac{(R-R_0)^2}{\mu^2}} e^{-\frac{(p - \hbar k_0)^2}{\hbar^2/\mu^2}} \quad (\text{B.10})$$

Taking the marginal integrals we get the position and velocity probability distributions:

$$|f(R)|^2 = \frac{2}{\mu \sqrt{\pi}} e^{-\frac{(R-R_0)^2}{\mu^2}} \quad (\text{B.11})$$

$$|f(p)|^2 = \frac{2}{\frac{\hbar}{\mu} \sqrt{\pi}} e^{-\frac{\mu^2}{\hbar^2}(p - \hbar k_0)^2} \quad (\text{B.12})$$

The above distributions are randomly sampled to get initial atomic velocities and positions for each simulation.

## Appendix C

# Norm Conservation in CTMQC and Ehrenfest

A statement of the conservation of the norm is given below in equation (C.1)

$$\frac{d}{dt} \sum_l |C_l(t)|^2 = \sum_l C_l^*(t) \frac{dC_l(t)}{dt} + \frac{dC_l^*(t)}{dt} C_l(t) = 0 \quad (\text{C.1})$$

Because the adiabatic populations are real we can remove any imaginary parts.

$$\frac{d}{dt} \sum_l |C_l(t)|^2 = 2\mathbb{R} \left[ C_l^*(t) \frac{dC_l(t)}{dt} \right] \quad (\text{C.2})$$

Substituting the equation for the evolution of the adiabatic coefficients (and removing the purely imaginary term into (C.2) we get equation (C.4)

$$\begin{aligned} \frac{d}{dt} \sum_l |C_l(t)|^2 &= 2 \sum_l \mathbb{R} \left[ \frac{-i}{\hbar} \cancel{\epsilon_{BO}^l} C_l(t)^* \cancel{C_l(t)} - \sum_k C_l(t)^* C_k(t) d_{lk}^{ad} - (K^{sum} - K_l^{ad}) C_l(t)^* C_l(t) \right] \\ &\quad (\text{C.3}) \end{aligned}$$

$$= -2 \sum_l \mathbb{R} \left[ \sum_k C_l(t)^* C_k(t) d_{lk}^{ad} - (K^{sum} - K_l^{ad}) C_l(t)^* C_l(t) \right] \quad (\text{C.4})$$

Where:

$$K^{sum} = \sum_{v=1}^{N_n} \sum_k \frac{\mathcal{Q}_{lk,v}(t)}{\hbar M_v} \cdot |C_k(t)|^2 \mathbf{f}_{k,v}(t) \quad (\text{C.5})$$

$$K_l^{ad} = \sum_{v=1}^{N_n} \sum_k \frac{\mathcal{Q}_{lk,v}(t)}{\hbar M_v} \cdot \mathbf{f}_{l,v}(t) \quad (\text{C.6})$$

The NACE term evaluates to 0 due to the anti-symmetry of the NACE giving us equation (C.8).

So far, we have proved that the norm should be conserved here for all terms apart from the quantum momentum terms i.e. Ehrenfest.

$$\frac{d}{dt} \sum_l |C_l(t)|^2 = 2 \sum_l \mathbb{R} \left[ (K^{sum} - K_l^{ad}) C_l(t)^* C_l(t) \right] \quad (\text{C.7})$$

$$= 2 \left[ K^{sum} - \sum_l K_l^{ad} |C_l(t)|^2 \right] \quad (\text{C.8})$$

However,  $K^{sum} \equiv \sum_l K_l^{ad} |C_l|^2$ , therefore the norm should be conserved when summed over trajectories. This statement doesn't apply to individual trajectories though, and the norm may or may not be conserved for each of them. This is because they are coupled via the quantum momentum and population may transfer between trajectories.

## Appendix D

# Colophon

This is a description of the tools you used to make your thesis. It helps people make future documents, reminds you, and looks good.

(example) This document was set in the Times Roman typeface using L<sup>A</sup>T<sub>E</sub>X and Bib<sup>L</sup>T<sub>E</sub>X, composed with the Atom text editor.

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