

# 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>6,7</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>8</sup>, organic field-effect transistors (OFET)<sup>9</sup> and organic light-emitting diodes (OLED)<sup>10</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>11,12</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>13–17</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>18</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>19,20</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>17</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>21</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>22</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>23</sup>. This approximation, relied upon for almost a century<sup>24</sup>, hinges on the fact that nuclei are much more massive than electrons and are approximately stationary with respect to electron movement<sup>25</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>26–28</sup>, non-radiative decay and photochemical processes, electronic transitions between adiabatic potential energy surfaces occur<sup>29</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>30</sup>, multiple spawning<sup>31</sup> or nonadiabatic Bohmian dynamics<sup>32</sup>. However, two of the most popular are trajectory surface hopping<sup>33</sup> and mean-field approaches<sup>34</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>35</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>36</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>37-41</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

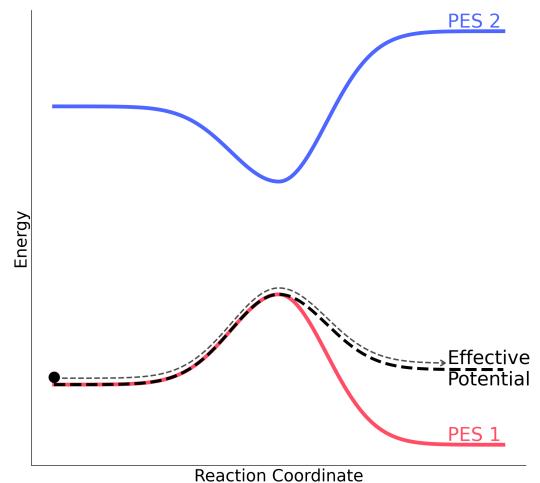


Figure 1.1: An example of a typical Ehrenfest simulation near an avoided crossing. The black lines represent the adiabatic potential energy surface due to the ground (PES 1) and excited (PES 2) state. The red line represents the population weighted average potential the nuclei travel on.

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

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

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

In the above equations  $C_i$  is the adiabatic expansion coefficient for state  $i$ ,  $E_m$  is the energy of adiabatic state  $m$ ,  $\mathbf{d}_{mn,v}^{ad}$  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>42–44</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>23,45</sup>. In the limit of infinite states this results in infinite electronic temperature<sup>46</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>45</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, will be studied in this thesis and is the semi-classical limit of the exact factorisation of the time-dependent Schrödinger equation.

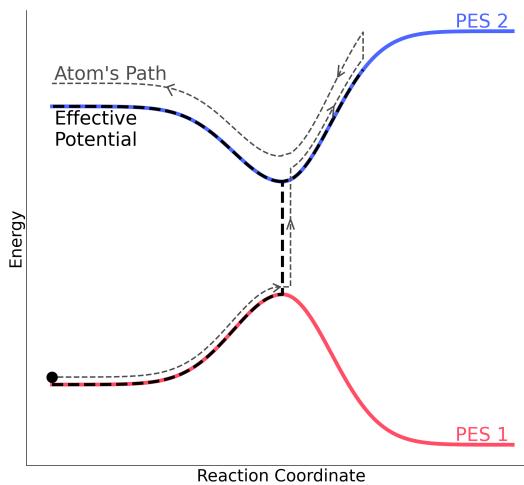


Figure 1.2: An example of a typical Surface Hopping simulation near an avoided crossing. The black lines represent the adiabatic potential energy surface due to the ground (PES 1) and excited (PES 2) state. The red line represents the discontinuous effective potential the nuclei travel on.

### 1.3 Exact Factorisation

Exact factorisation<sup>47</sup> involves separating the total molecular wavefunction into a nuclear component and electronic component. Where the electronic component is parametrically dependent on the nuclear coordinates,  $\mathbf{R}$ . This is shown below in eq (1.3) where  $\chi$  is the nuclear wavefunction and  $\Phi$  is the electronic one.

$$\Psi(\mathbf{R}, \mathbf{r}, t) = \Phi_{\mathbf{R}}(\mathbf{r}, t)\chi(\mathbf{R}, t) \quad (1.3)$$

In the above equation (and throughout this report) I will denote nuclear coordinates and electronic coordinates  $R$  and  $r$  respectively. The nuclear and electronic wavefunctions then obey separate, but coupled, time-dependent Schrödinger equations for spatial and temporal evolution. In this report, I will be focussing on the semi-classical limit of these equations, named Coupled-Trajectory Mixed Quantum-Classical Molecular Dynamics (CTMQC), and give results of a combination of this and the AOM method explained in section ??.

The equations for the evolution of the electronic and nuclear wavefunctions in the exact factorisation<sup>47</sup> are given below:

$$\hbar \frac{\delta}{\delta t} \Phi_{\mathbf{R}}(\mathbf{r}, t) = (\hat{H}_{BO} + \hat{U}_{en}[\Phi_{\mathbf{R}}, \chi] - \varepsilon(\mathbf{R}, t)) \Phi_{\mathbf{R}}(\mathbf{r}, t) \quad (1.4)$$

$$\hbar \frac{\delta}{\delta t} \chi(\mathbf{R}, t) = \left( \sum_{v=1}^{N_n} \frac{[-\hbar \nabla_v + \mathbf{A}_v(\mathbf{R}, t)]^2}{2M_v} + \varepsilon(\mathbf{R}, t) \right) \chi(\mathbf{R}, t) \quad (1.5)$$

Where  $\hat{H}_{BO}$  is the Born-Oppenheimer Hamiltonian, that is  $\hat{T}_e + \hat{W}_{ee} + \hat{W}_{nn} + \hat{V}_{en}$ . Where  $\hat{T}_e$  is the electronic kinetic energy operator,  $\hat{W}_{ee/nn}$  is the electron-electron/nuclei-nuclei interaction and  $V_{en}$  is the electronic-nuclear potential.

The  $\hat{U}_{en}$  is an electronic-nuclear coupling operator (ENCO). This is defined as

$$\hat{U}_{en}[\Phi_{\mathbf{R}}, \chi] = \sum_{v=1}^{N_{nuc}} \frac{1}{M_v} \left[ \frac{[-\hbar \nabla_v - \mathbf{A}_v(\mathbf{R}, t)]^2}{2} + \left( \frac{-\hbar \nabla_v \chi}{\chi} + \mathbf{A}_v(\mathbf{R}, t) \right) \left( -\hbar \nabla_v - \mathbf{A}_v(\mathbf{R}, t) \right) \right] \quad (1.6)$$

Where the  $\mathbf{A}_v$  is a time-dependent vector potential (TDVP), given by  $\langle \Phi_{\mathbf{R}}(t) | -\hbar \nabla_v \Phi_{\mathbf{R}} \rangle_{\mathbf{r}}$  and  $M_v$  is the mass of nuclei  $v$ . Finally  $\epsilon(\mathbf{R}, t)$  is a time-dependent scalar potential energy surface (TDPES), given by  $\langle \Phi_{\mathbf{R}}(t) | \hat{H}_{BO} + \hat{U}_{en}^{coup} - \hbar \frac{\delta}{\delta t} | \Phi_{\mathbf{R}}(t) \rangle_{\mathbf{r}}$ .

The effects of the TDPES, TDVP and the ENCO have been investigated in multiple works<sup>1,48–51</sup>. The TDPES and TDVP are both responsible for the evolution of the system<sup>48</sup>. The TDPES provides exact classical forces on the nuclei. In fact, an alternative independent-trajectory semi-classical scheme has been investigated using these exact forces<sup>1</sup>. This found the TDPES is responsible for the splitting of the nuclear wavepacket in regions of high non-adiabaticity by taking the shape of a step function between the 2 adiabatic potentials. This is demonstrated in figure 1.3, which was adapted from an image in Agostini, 15<sup>48</sup>.

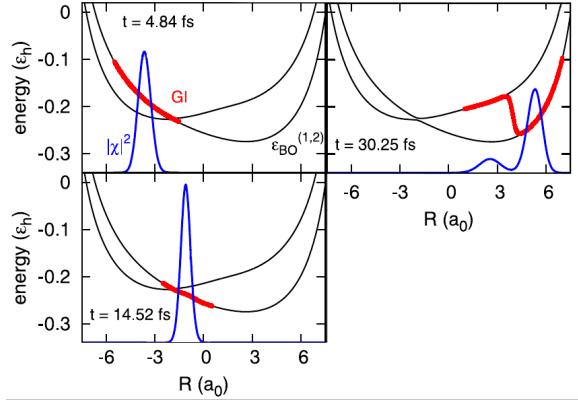


Figure 1.3: A demonstration of how the TDPES can cause the splitting of the nuclear wavepacket in non-adiabatic regions. The red line represents the TDPES and the blue is the nuclear density. Figure adapted from Agostini, 15<sup>1</sup>

Finally the electronic-nuclear coupling operator (ENCO) is responsible for other non-adiabatic effects in the system such as electronic nonadiabatic transitions and decoherence<sup>48</sup>.

## 1.4 Approximations leading to CTMQC

Starting from the exact factorisation equations, 6 approximations have been made to derive the CTMQC equations. These are discussed in detail in Ref.<sup>2</sup>. In the interest of completeness I have summarised them below.

### 1.4.1 Classical Nuclei

Techniques that include nuclear quantum effects (NQEs); such as multiple spawning<sup>31</sup>, ring-polymer surface hopping<sup>52</sup> and nonadiabatic Bohmian dynamics<sup>53,54</sup> although extremely accurate, cannot be applied to hundreds or thousands of molecules, due to their high computational cost. Further, in many systems of interest NQEs are negligible, especially at room temperature. For this reason the classical limit of the nuclear Schrödinger equation (1.5) is taken when deriving the CTMQC equations.

### 1.4.2 Neglect the ENCO in the TDPES

The electron-nuclei coupling operator is omitted in the expression for the time-dependent potential energy surface. This is justified as the first term ( $(-\hbar\nabla_{\mathbf{v}} - \mathbf{A}_{\mathbf{v}}(\mathbf{R}, t))^2$ ) contains a second order derivative which is expensive to calculate and has a negligible effect compared to the second term in the ENCO<sup>55</sup>. However, the rest of the ENCO is equal to zero when averaged over  $\Phi_{\mathbf{R}}(\mathbf{r}, t)$  so it does not contribute to the TDPES.

### 1.4.3 Derivative of the Adiabatic Coefficients

The derivative of the adiabatic coefficients appears in the electronic evolution equations. However, we can re-write the derivative of the adiabatic coefficients in terms of their modulus and phase:

$$\nabla_{\mathbf{v}} C_l^{(I)}(t) = \left[ \underbrace{\frac{\nabla_{\mathbf{v}} |C_l^{(I)}(t)|}{|C_l^{(I)}(t)|}}_{\text{(Term 1)}} + \underbrace{\frac{i}{\hbar} \nabla_{\mathbf{v}} \gamma_l^{(I)}(t)}_{\text{(Term 2)}} \right] C_l^{(I)}(t) \quad (1.7)$$

It has been found that the first term is negligible compared to the second<sup>1,49,50</sup> so it doesn't need to be calculated and we can remove it. It was also assumed that the NACVs are localised in space meaning that, after some algebra, the spatial derivative of the adiabatic coefficient can be written as:

$$\nabla_{\mathbf{v}} C_l^{(I)}(t) = \frac{i}{\hbar} \nabla_{\mathbf{v}} \gamma_l^{(I)}(t) C_l^{(I)}(t) = -\frac{i}{\hbar} \int^t dt' \nabla_{\mathbf{v}} \epsilon_l^{(I)} C_l^{(I)}(t') = -\frac{i}{\hbar} \mathbf{f}_l^{(I)} C_l^{(I)}(t) \quad (1.8)$$

Where  $\epsilon_l^{(I)}$  is the energy of the  $l^{th}$  adiabatic potential energy surface for trajectory I,  $C_l^{(I)}$  is the adiabatic expansion coefficient for state l and trajectory I. The  $\mathbf{f}_l^{(I)}$  is the time-integrated adiabatic force (adiabatic momentum).

#### 1.4.4 Gaussian Nuclear Wavepackets

In order to calculate the quantum momentum -the new term in CTMQC. Knowledge of the nuclear distribution is needed. However, as we treat the nuclei as point particles we need to re-construct the nuclear density from the atomic positions. This is done by smoothing out the atomic positions by placing a gaussian of width  $\sigma$  centered on each atomic position and combining these gaussians to produce the final nuclear density. This introduces an empirical parameter ( $\sigma$ ) which will be discussed later in this thesis. It should be noted, the nuclei are still propagated classically, the width parameter is only used in the calculation of the quantum momentum.

#### 1.4.5 Separating the Effects of Decoherence and NACVs

So as to not introduce any population transfer (due to the quantum momentum) when the NACV is zero a fifth approximation has been introduced. Namely the quantum momentum depends on pairs of states -l,k. This enables the separation of the ‘competing’ effects of the NACV and the Quantum Momentum.

### 1.5 The CTMQC equations

#### 1.5.1 Adiabatic Basis

The equations for the propagation of the classical nuclei and the expansion coefficients in the CTMQC framework in the adiabatic basis are given below:

$$\dot{\mathbf{P}}_v^{(I)} = \underbrace{-\sum_k |C_k^{(I)}|^2 \nabla_v \epsilon_k^{(I)} - \sum_{k,l} C_l^{(I)} C_k^{*(I)} (\epsilon_k^{(I)} - \epsilon_l^{(I)})}_{\text{Ehrenfest}} - \underbrace{\sum_{l,k} |C_l^{(I)}|^2 \left( \sum_{v'=1}^{N_n} \frac{2}{\hbar M_{v'}} \mathcal{Q}_{lk,v'}^{(I)} \cdot \mathbf{f}_{l,v'}^{(I)} \right) \left[ |C_k^{(I)}|^2 \mathbf{f}_{k,v}^{(I)} - \mathbf{f}_{l,v}^{(I)} \right]}_{\text{Quantum Momentum}} \quad (1.9)$$

$$\dot{C}_l^{(I)} = \underbrace{-\frac{i}{\hbar} \epsilon_l^{(I)} C_l - \sum_k C_k^{(I)} d_{lk}^{ad(I)}}_{\text{Ehrenfest}} - \underbrace{\sum_{v=1}^{N_n} \sum_k \frac{\mathcal{Q}_{lk,v}^{(I)}}{\hbar M_v} \cdot [\mathbf{f}_{k,v}^{(I)} - \mathbf{f}_{l,v}^{(I)}] |C_k^{(I)}|^2 C_l^{(I)}}_{\text{Quantum Momentum}} \quad (1.10)$$

Where the  $\epsilon_k$  term is the potential energy on the  $k^{th}$  potential energy surface.  $C_l$  is the adiabatic expansion coefficient corresponding to the  $l^{th}$  state. The sum over  $k$  and  $l$  indicates a sum over all states, the  $(I)$  superscript is a replica index and the  $v$  is an atom index.  $M_v$  is the nuclear mass and  $d_{lk}^{ad(I)}$  represents the non-adiabatic coupling element (in the adiabatic basis) between adiabatic states  $l$  and  $k$ . The 2 new terms in this scheme not seen in other NAMD methods are the  $\mathcal{Q}_{lk,v}^{(I)}$  and the  $\mathbf{f}_{k,v}^{(I)}$ . These are the quantum momentum and the adiabatic momentum. The adiabatic momentum term is defined in equation (1.8) this keeps a record of the previous forces on each adiabatic state in the system. The quantum momentum term couples the trajectories together (making this a coupled-trajectory scheme). Together the history dependent force and quantum momentum are responsible for the decoherence in the ‘Quantum Momentum’ parts of the above equations<sup>3</sup>. Notably, although these equations have been derived from the exact factorisation equations separately from Ehrenfest they do contain the Ehrenfest equations within them (marked ‘Ehrenfest’). This scheme can therefore be seen as an Ehrenfest scheme with a correction that captures branching of the nuclear wavefunction and decoherence within it.

We can also see in equation (1.10) if we are in a pure adiabatic state i.e. all population on a single adiabatic state, there is no contribution from the quantum momentum part of the equations. In this scenario the evolution equations become simply Ehrenfest equations. For example, if all the population is localised on a single adiabatic state then the term  $|C_k^{(I)}|^2 C_l$  is only non-zero when  $l = k$ . However, when  $l = k$ , the term  $[\mathbf{f}_{k,v}^{(I)} - \mathbf{f}_{l,v}^{(I)}]$  is zero as  $\mathbf{f}_{k,v}^{(I)} = \mathbf{f}_{l,v}^{(I)}$ . Therefore, the quantum momentum term can be seen to only kick in when there is a mixing of adiabatic states. In the adiabatic formulation of these equations it is the adiabatic NACV  $\mathbf{d}_{lk,v}^{ad,(I)}$  that is responsible for the initial mixing of the

populations from pure adiabatic states.

## 1.6 Calculating the Quantum Momentum

The technique for calculating the quantum momentum term is outlined in detail in the SI of min, 17<sup>56</sup>. The original equations given in Agostini, 16<sup>2</sup> present a quantum momentum term without state indices (l,k). This, due to approximations made in the derivation of CTMQC, results in population transfer even when the non-adiabatic couplings between states are zero. Therefore, Agostini et al enforced this condition with the pair-wise state dependence on the quantum momentum. The quantum momentum is defined in equation (1.11) as:

$$\mathcal{Q}_v^{(I)} = \frac{-\hbar \nabla_v |\chi^{(I)}|}{|\chi^{(I)}|} \frac{-\hbar \nabla_v |\chi^{(I)}|^2}{2|\chi^{(I)}|^2} \quad (1.11)$$

In order to reconstruct the nuclear density, Gaussian distributions are used as in equation (1.12) below:

$$|\chi^{(I)}(t)|^2 = \frac{1}{N_{tr}} \sum_{J=1}^{N_{tr}} \prod_{v=1}^{N_n} g_{\sigma_v^{(J)}(t)} \left( \mathbf{R}_v^{(I)}(t) - \mathbf{R}_v^{(J)}(t) \right) \quad (1.12)$$

Where,  $N_{tr}$  is the number of trajectories,  $N_n$  is the number of atoms,  $\sigma_v^{(J)}(t)$  is a time-dependent width parameter for each gaussian  $g$  and  $\mathbf{R}_v^{(J)}$  represents the atomic position of atom  $v$  on trajectory  $J$ .

This results in a linear expression for the quantum momentum. The full details of the derivation are given in the supplementary information of Min, 17<sup>56</sup>. The resulting linear expression for the quantum momentum is given below:

$$\mathcal{Q}_{lk,v}^{(I)} = \alpha_v^{(I)} \mathbf{R}_v^{(I)} - \mathbf{R}_{lk,v} \quad (1.13)$$

Where  $\mathbf{R}_v^{(I)}$  are the nuclear coordinates on trajectory I on atom  $v$ . The  $\alpha_v^{(I)}$  term is a weighted average over trajectories of the product of the gaussian's assigned to each atomic

coordinate, i.e:

$$\alpha_v^{(I)} = \sum_J^{N_{tr}} \frac{\hbar \prod_{v'} g_{\sigma_{v'}^{(J)}(t)} \left( \mathbf{R}_{v'}^{(I)}(t) - \mathbf{R}_{v'}^{(J)}(t) \right)}{2\sigma_v^{(J)}(t)^2 \sum_K^{N_{tr}} \prod_{v'} g_{\sigma_{v'}^{(K)}(t)} \left( \mathbf{R}_{v'}^{(I)}(t) - \mathbf{R}_{v'}^{(K)}(t) \right)} \quad (1.14)$$

Along with the  $\mathbf{R}_{lk,v}$  term the  $\alpha_v^{(I)}$  performs the job of coupling the trajectories together. The  $\mathbf{R}_{lk,v}$  term also given in the SI of Min, 17<sup>56</sup> is defined for each Cartesian dimension as:

$$R_{lk,v} = \sum_I^{N_{tr}} R_v^{(I)}(t) \alpha_v^{(I)}(t) \frac{|C_k^{(I)}(t)|^2 |C_l^{(I)}(t)|^2 (f_{k,v}^{(I)}(t) - f_{l,v}^{(I)}(t))}{\sum_J |C_k^{(J)}(t)|^2 |C_l^{(J)}(t)|^2 (f_{k,v}^{(J)}(t) - f_{l,v}^{(J)}(t))} \quad (1.15)$$

Where the bold notation for vectors has been replaced by normal font indicating that this applies to each cartesian dimension independently. Further, in this expression  $R_{lk,v}$  is symmetric,  $R_{lk} = R_{kl}$  meaning that  $Q_{lk} = Q_{kl}$ . At first sight, the  $R_{lk}$  term seems to be another weighted average. However, this isn't quite the case as the denominator can be negative. This causes equation (1.15) to be very sensitive to errors in the calculation of the denominator of this fraction. Any inaccuracies can lead to the denominator approaching zero faster than the numerator causing large spikes in the quantum momentum term. This will be discussed in greater detail in the following chapters.

## Chapter 2

# CTMQC applied to the Tully Models

The Tully models, first proposed by John Tully in 1990<sup>57</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>3</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>3</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 a 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.

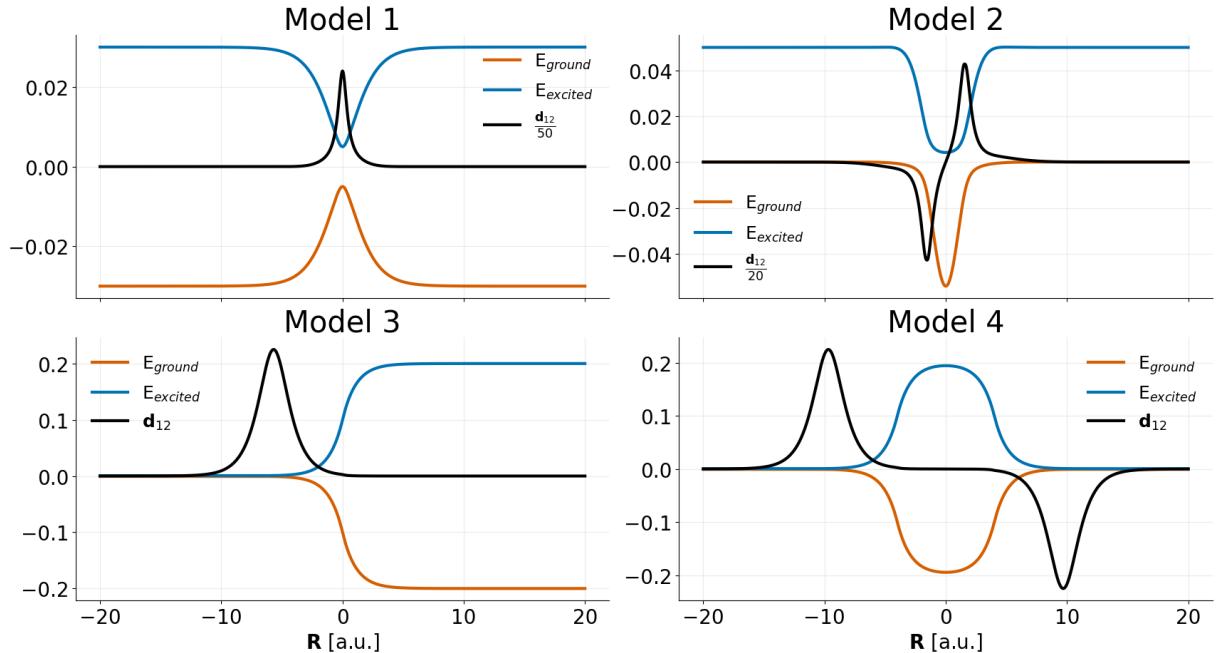


Figure 2.1: Adiabatic potential energy surfaces (orange and blue) and element 1, 2 of the nonadiabatic coupling vector (black) for the 4 model systems. For parameters see appendix A.

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>58</sup> within the software package CP2K<sup>59</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>60</sup> framework which will be discussed in a later chapter<sup>7</sup>. 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: ...

### 2.1.1 Comparisons To Literature

There have been 2 papers published applying CTMQC to the Tully models<sup>2,3</sup> and both contain results for the 4 Tully models shown in fig 2.1. The results contain data on the (ground state) adiabatic populations and a coherence indicator as shown in equation (2.4) for 16 different simulations (a low and high initial momentum simulation of Models 1, 2, 3 and 4).

$$|\rho_{12}(t)|^2 = \frac{1}{N_{tr}} \sum_{I=1}^{N_{tr}} |C_1^{(I)}(t)|^2 |C_2^{(I)}(t)|^2 \quad (2.4)$$

In order to compare to results in the literature the same setup had to be used. In this case this meant sampling individual trajectory initial conditions (positions and momenta) from a Wigner distribution with a mean position and momenta given in appendix A. The wavefunction was initialised purely on the ground state and the same integrator was used for the nuclear and electronic propagation (velocity verlet and RK4 respectively).

### 2.1.2 Ehrenfest

My results as well as the relevant data taken from Agostini, 16 and Gossel, 18<sup>2,3</sup> are shown in figure 2.2 for Ehrenfest dynamics. This is equivalent to full CTMQC dynamics where the quantum momentum term is set to 0. Hence, we can test most parts of the code (i.e. Runge-Kutta propagation, velocity verlet, inputs, force calculations etc...) while ignoring the new quantum momentum and accumulated adiabatic force terms.

The results in figure 2.2 show that both the adiabatic populations and coherence indicator give exactly the same results as in the literature, within reasonable error. Any deviations of results come from either a slightly different initial sampling of positions (sampled from a Wigner distribution) or small errors in retrieving data from the graphs in each paper. For example, in the case of the high initial momentum simulation of model 4 all 3 results show some differences though the trend is very similar. This is true also in the Model 2 results where the Agostini, 16 populations show some transient oscillations before settling onto the same equilibrium population. This may be due to a

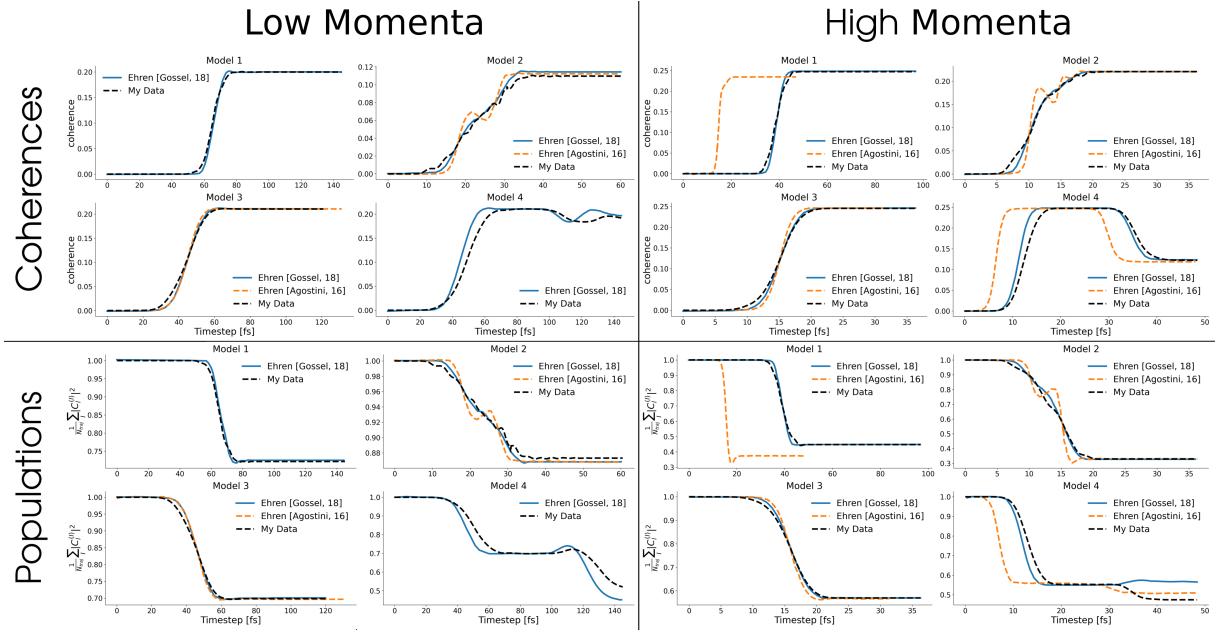


Figure 2.2: A comparison of my implementation of Ehrenfest (for 4 model Hamiltonians) and results from the literature. The black dashed lines show my data (ground state ad pops), the orange dashed lines are data from Agostini, 16<sup>2</sup> and the blue solid lines are from Gossel, 18<sup>3</sup>. The figures are labelled with their model number, whether the initial momentum was high or low and whether the populations or coherence indicator was plotted.

smaller spread of positions being used in the initial sample leading to similar oscillations that aren't smoothed out in the averaging over all trajectories. There are also a couple of models that start at a slightly different initial mean position in Frederica, 16 thus they hit the nonadiabatic crossing region sooner. These are model 1 and 4 for the high momentum case.

Although not all results are exactly the same, I believe the populations agree well enough within a reasonable error to serve as a confirmation of my implementation.

### 2.1.3 CTMQC

To test the full CTMQC equations I now turn on the quantum momentum ( $\mathcal{Q}_{l,k,v}^{(I)}$ ) and accumulated adiabatic force ( $\mathbf{f}_{l,v}^{(I)}$ ) terms. These provide the extra decoherence that is missing in the standard Ehrenfest representation and allow populations of individual trajectories to collapse onto a single adiabatic state. Without these terms (e.g. in Ehrenfest dynamics) all trajectories follow the same mean potential energy surface and detailed

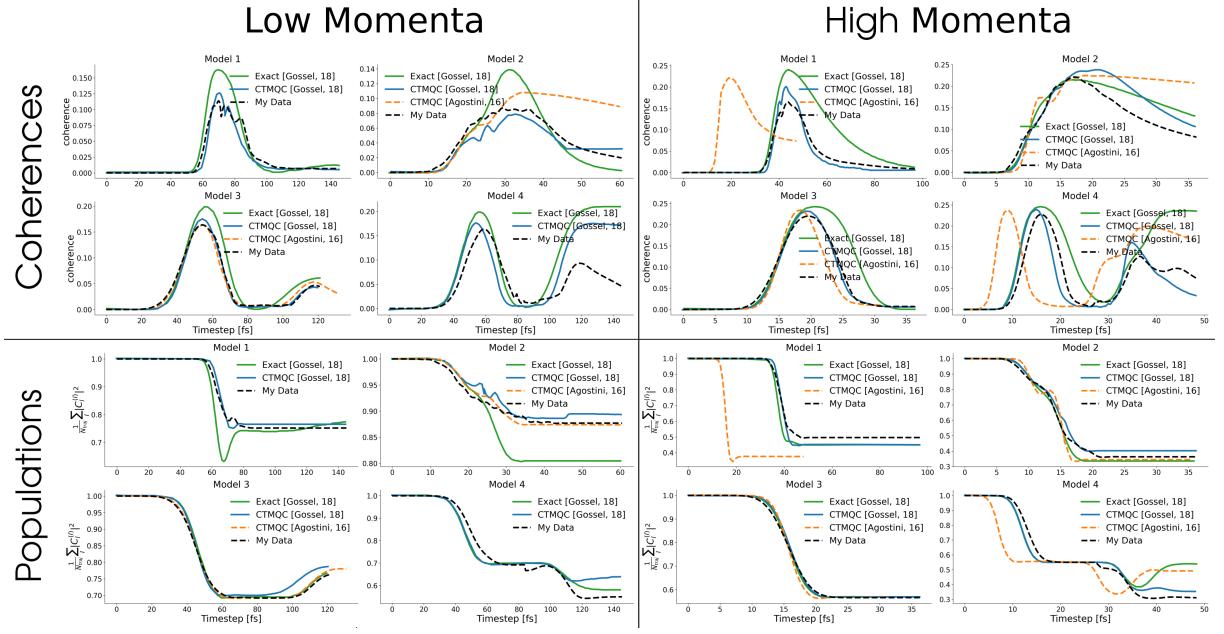


Figure 2.3: A comparison of my implementation of full CTMQC (for 4 model Hamiltonians) and results from the literature. The black dashed lines show my CTMQC data (ground state ad pops), the orange dashed lines are data from Agostini, 16<sup>2</sup> and the blue solid lines are from Gossel, 18<sup>3</sup>. The solid green line shows data from exact quantum mechanical simulations given in Gossel, 18. The figures are labelled with their model number, whether the initial momentum was high or low and whether the populations or coherence indicator was plotted.

balance is not conserved.

The results for my implementation are given in figure 2.3. This time, unlike in the Ehrenfest code, we see some major discrepancies between the 3 results. These cannot solely be explained as small errors from slightly different sampling of initial positions. We can see that the errors mainly appear in the coherence indicator, looking at the bottom row in figure 2.3 it appears that both the Agostini and Gossel results match mine (in dashed black line) very closely. The largest difference is seen in model 4, high momentum where the Gossel data and mine follow a similar trend and the Agostini data follows the exact curve more closely. However, looking at the coherence indicators in the above row we see a different story. My data tends to follow the Gossel data fairly closely, while the Agostini data follows a different pattern. This is due to differing parameters being used to calculate the quantum momentum term.

To calculate the quantum momentum one must take the spatial derivative of the nuclear density. However, the nuclei are classical and represented by a point. In order to calculate the nuclear density the procedure outlined in the supplementary information of Min, 17<sup>56</sup> was to smear out the nuclear density by describing each classical atom with a gaussian distribution of width  $\sigma$  and mean  $\mathbf{R}_v^{(I)}(t)$  (i.e. the atomic position). The method for determining the parameter  $\sigma$  has not been outlined therefore it is very hard to develop a method to exactly reproduce the results found in the 2 CTMQC papers. In figure 2.3 a constant sigma of  $\sigma = 0.35$  bohr was taken to closely match the Gossel, 18 data. The fact that the curves match in many cases almost exactly makes me think this was the method employed in Gossel, 18 too. It also serves as a confirmation of the full implementation of CTMQC.

#### 2.1.4 Norm Conservation

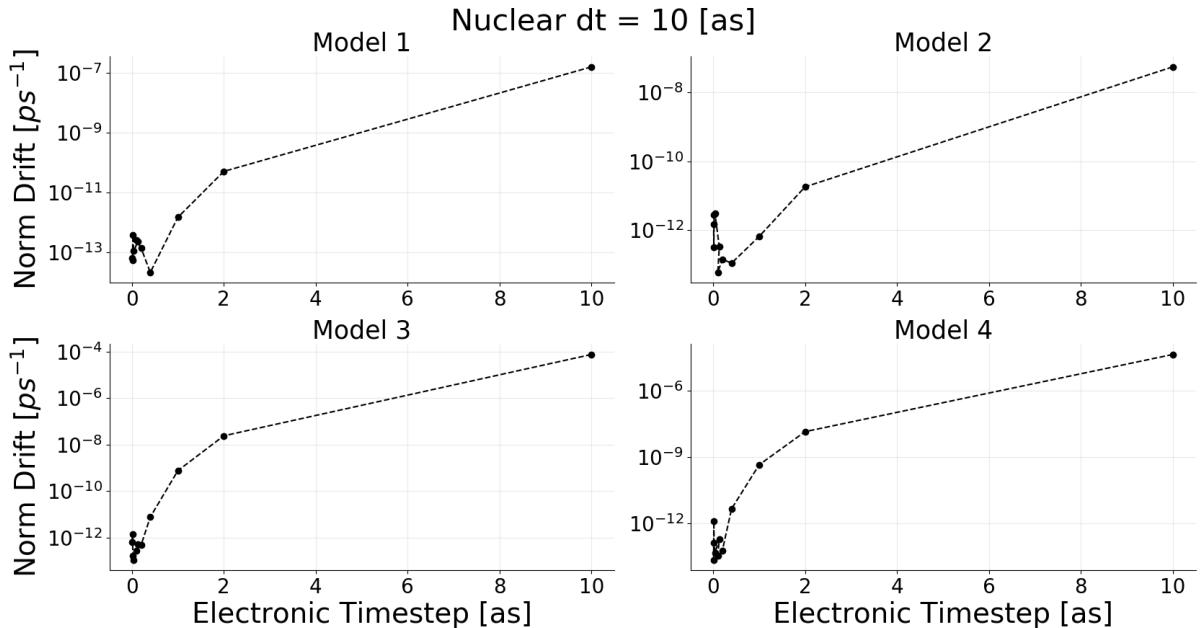


Figure 2.4: The norm conservation averaged over all replicas for Ehrenfest simulations with various electronic timesteps for each Tully model using a initial high momenta.

In appendix E, it is shown that the norm of the adiabatic expansion coefficients should be conserved throughout the simulation. In order to test this various simulations were carried out with various size electronic timesteps (i.e. the timestep used to propagate the electronic subsystem). As can be seen in figure 2.4, the norm of the wavefunction

is conserved within numerical error ( $10^{-12}$ ) when using a sufficiently small timestep in every Tully model. However, when we now use the full CTMQC equation we see a very different picture.

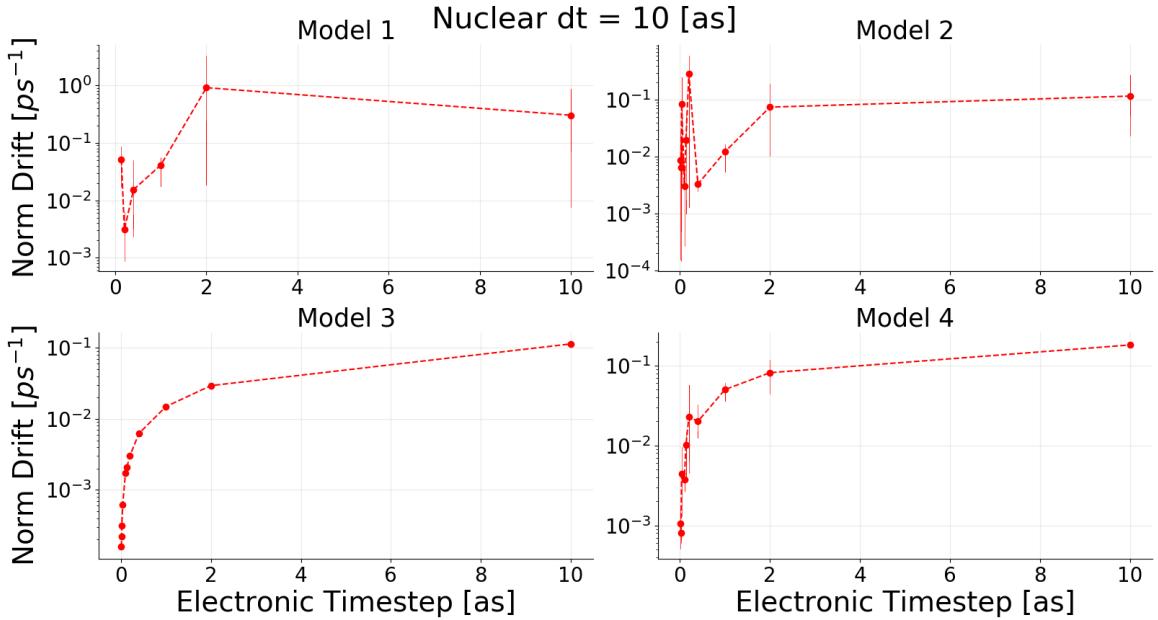


Figure 2.5: The norm conservation when using standard CTMQC as outlined in the literature for each of the Tully models. These simulations were ran with a high initial momentum. The red markers show data points and vertical bars show error bars associated with each point.

In figure 2.5, we can see that only in Model 3 we see a similar trend as in Ehrenfest for the norm conservation -i.e. a decreasing electronic timestep gives a rapidly decreasing norm drift. In models 1 and 2 we see that the norm drift doesn't get much better as we decrease the timestep and there are large error bars associated with each data point. In model 4 this is less pronounced but is still clearly effected. This is due to an instability in the way the quantum momentum term ( $\mathcal{Q}_{lk,v}^{(I)}$ ) is calculated.

The calculation of the quantum momentum is discussed in detail in Min, 17<sup>56</sup> and outlined in the introduction to the thesis in section 1.6. As mentioned in that section, the denominator in the expression for  $\mathbf{R}_{lk,v}$  may be positive or negative and when it switches between the 2 it can approach zero very closely. If this denominator approaches zero more quickly than the numerator then we can see large spikes in the  $\mathbf{R}_{lk,v}$  term which can

lead to large norm drifts.

#### 2.1.4.1 Quantum Momentum Instabilities

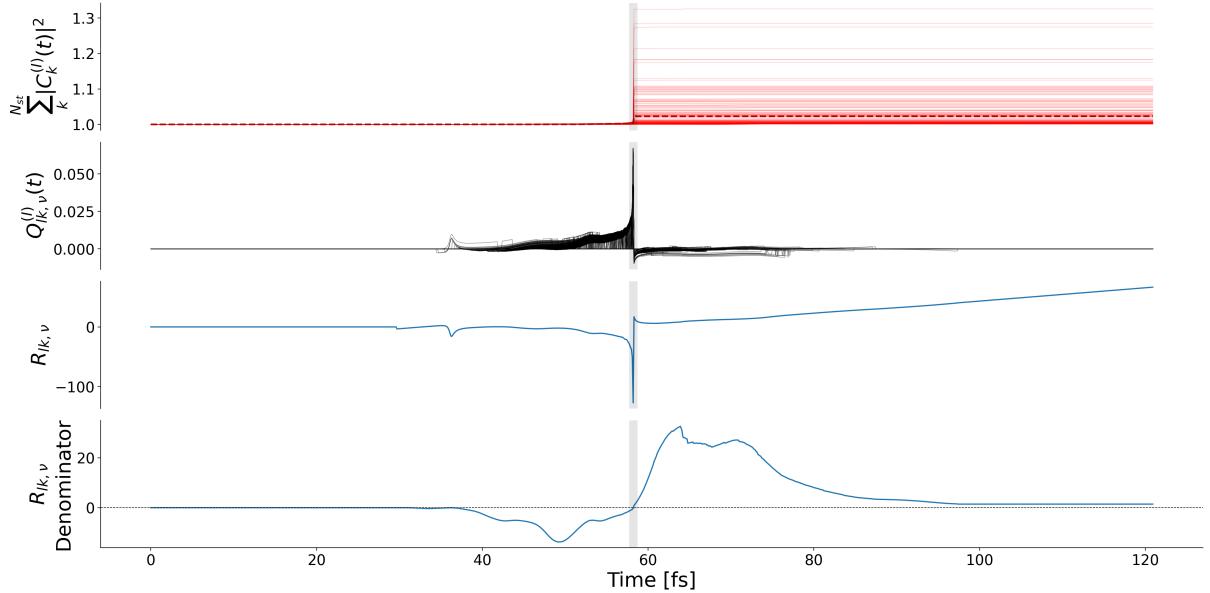


Figure 2.6: As the denominator of the  $\mathbf{R}_{lk,v}$  term approaches zero (bottom panel) the full  $\mathbf{R}_{lk,v}$  term (2<sup>nd</sup> to bottom panel) can approach infinity which propagates through the  $\mathcal{Q}_{lk,v}^{(I)}$  term (2<sup>nd</sup> to top panel) causing discontinuities and norm drift in the populations (top panel). The grey vertical bar denotes the region the denominator approaches 0.

As we can see in figure 2.6, as the denominator of the  $\mathbf{R}_{lk,v}$  term approaches 0 the full  $\mathbf{R}_{lk,v}$  term may spike causing a discontinuity in the populations. The reason this only occurs in Models 1, 2 and 4 is due to the fact that the difference in the adiabatic momenta terms ( $\mathbf{f}_{l,v}^{(I)} - \mathbf{f}_{k,v}^{(I)}$ ) doesn't cross 0 in Model 3. In order to correct for this I have investigated a number of corrections to the calculation of the quantum momentum. These depend on the detection of the spikes/divergences in the  $\mathbf{R}_{lk,v}$  term and then the appropriate treatment of them. In order to detect the divergences a simple threshold on the  $|\frac{\delta}{\delta t} \mathbf{R}_{lk,v}|$  is applied when the denominator of the  $\mathbf{R}_{lk,v}$  is sufficiently close to 0. For example, if the absolute time-derivative of the  $\mathbf{R}_{lk,v}$  term is larger than a value (say 5) and the bottom of the fraction in equation (1.15) is within 0.1 of 0 then we assume the  $\mathbf{R}_{lk,v}$  term is diverging and the simulation code then uses a different method of propagating the electronic coefficients.

The alternative propagation methods I have investigated are:

1. Use Ehrenfest Dynamics (set  $\mathcal{Q}_{lk,v}$  term to 0).
2. Extrapolate the value of  $\mathbf{R}_{lk,v}$  from values before the divergence (see appendix C.1).
3. Switch to using the alternative intercept  $\mathbf{R}_{0,v}^{(I)}$  (see appendix C.2).

of these 3 methods, method 3 was the most successful in reducing the norm drift in the Tully Models as can be seen in figure 2.7. In figure 2.7 we see the norm drift results after

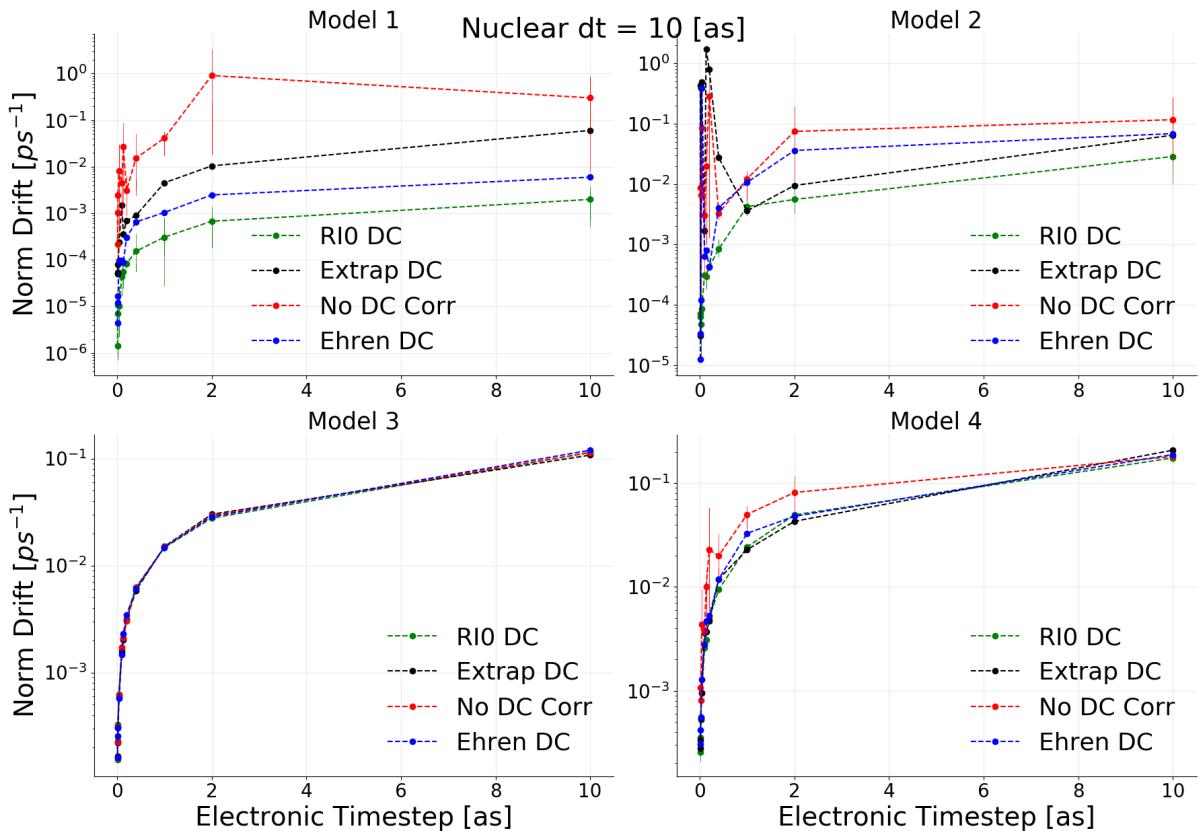


Figure 2.7: Norm conservation in CTMQC after applying a divergence correction to the  $\mathbf{R}_{lk,v}$  term. RI0 refers to method 3, Extrap DC refers to method 2 and Ehren DC refers to method 1. No DC Corr shows the population norm without any corrections applied.

the 3  $\mathbf{R}_{lk,v}$  correction methods have been applied. The red curve shows the original data (as in figure 2.5) with its large divergences in the norm drift. The green curve shows the alternative intercept method, the blue curve shows the effect of switching to Ehrenfest during the  $\mathcal{Q}_{lk,v}^{(I)}$  spikes and the black shows a method that involved extrapolating the  $\mathbf{R}_{lk,v}$  value from data before the spike began. We can see clearly all 3 methods improve

the norm drift, though using the alternative intercept seems to help the most. Model 3 is not affected as we do not see these divergences in the  $\mathbf{R}_{lk,v}$  due to the denominator in this particular model never crossing from positive to negative (through zero). It is important to note that in each of the models with the divergence correction applied all models exhibit the expected trend of decreasing the time-step improves norm conservation. However, the norm conservation in all 4 models is still significantly higher ( $\sim 7\text{-}8$  orders of magnitude) higher than that of Ehrenfest. I think this is due to the product of the adiabatic populations,  $|C_l^{(I)}|^2|C_k^{(I)}|^2$ , being used in the calculation of the quantum momentum which can be a more quickly varying quantity than just the adiabatic populations alone.

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

In the SI of Min, 17<sup>56</sup> a conservation equation (S27) is given. This is repeated below in equation (2.5)

$$\sum_I \mathcal{D}_{lk,v}^{(I)}(t) \left( f_{k,v}^{(I)} - f_{l,v}^{(I)} \right) |C_k^{(I)}(t)|^2 |C_l^{(I)}(t)|^2 = 0 \quad \forall l,k,v \quad (2.5)$$

An example time-series of this quantity is given in figure 2.8 for each Tully model. The data used to calculate come from simulations of each of the Tully models using the parameters given in appendix A. No smoothing was used for the  $\mathbf{R}_{lk,v}^{(I)}$  term. It can be seen in this figure that the conservation quantity hovers around 0 for each model with a maximum deviation of  $10^{-15}$ .

### 2.1.6 Energy Conservation

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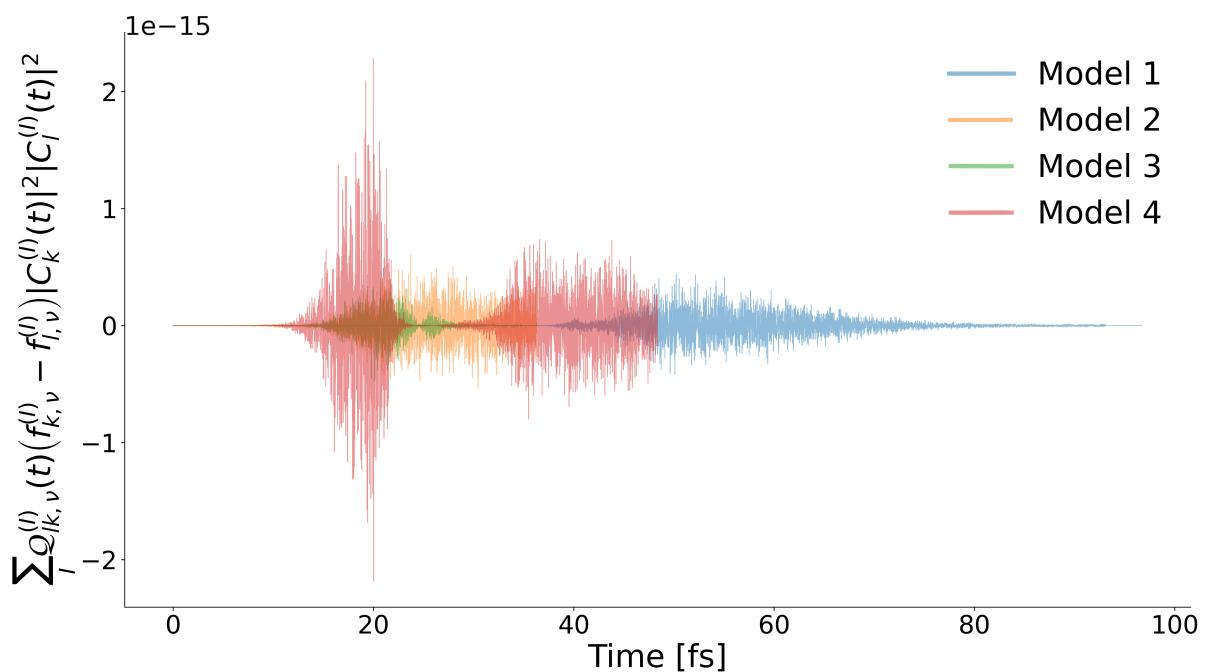


Figure 2.8: The conserved quantity given in equation (2.5). Each color represents data outputted by a simulation using a different model (specified in the legend). Each time-series is plotted with a translucent color meaning each model's data can be seen at once.

## 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

# $\mathbf{R}_{lk,v}$ Alternatives

### C.1 $\mathbf{R}_{lk,v}$ Extrapolation

### C.2 Alternative Quantum Momentum Intercept

In Agostini, 16<sup>2</sup> another quantum momentum intercept term is discussed. This term is not used because, as previously discussed in section 1.4, it leads to unphysical transfer of population between adiabatic states when the nonadiabatic coupling elements are 0. However, it can be used in these Tully Models as an effective fix to the discontinuities caused by the  $\mathbf{R}_{lk,v}$  term.

The other quantum momentum intercept,  $\mathbf{R}_{0,v}^{(I)}$ , comes directly from the construction of the nuclear density using a linear combination of a product of gaussians (see equation (1.12) in the introduction). It is defined as in equation (C.1) below:

$$\mathbf{R}_{0,v}^{(I)} = \sum_{J}^{N_{tr}} \left[ \frac{\hbar \prod_{v'} g_{\sigma_{v'}^{(J)}(t)} \left( \mathbf{R}_{v'}^{(I)}(t) - \mathbf{R}_{v'}^{(J)}(t) \right)}{2 \sigma_v^{(J)}(t)^2 \sum_{K}^{N_{tr}} \prod_{v'} g_{\sigma_{v'}^{(K)}(t)} \left( \mathbf{R}_{v'}^{(I)}(t) - \mathbf{R}_{v'}^{(K)}(t) \right)} \mathbf{R}_v^{(I)} \right] \quad (\text{C.1})$$

However, as switching to this intercept directly may cause discontinuities in itself a smoothing parameter is applied to ease the switch. This is given in equation (C.2) below:

$$[1 - A(t)] R_{good}(t) + A(t) R_{bad}(t) = R_{effective}(t) \quad (\text{C.2})$$

$R_{good}$  refers to the intercept that should be switched to (e.g. for the detection of a spike in the  $R_{lk,v}^{(I)}$  we switch to the intercept in in equation (C.1)).  $R_{lk,v}^{(I)}$  refers to the intercept that is being switched from (e.g. when it is detected that the divergence of  $R_{lk,v}^{(I)}$  has finished then we switch from the alternative intercept back to  $R_{lk,v}^{(I)}$ ).  $A(t)$  is a smoothing parameter and is given in equation (C.3) below:

$$A(t) = \frac{D_v^{(I)}}{2} \left[ \tanh\left(t - \frac{t_{final} + t_{init}}{0.6Ndt}\right) + 1 \right] \quad (\text{C.3})$$

Where  $D_v^{(I)}$  is the distance between the 2 intercepts (e.g.  $D_v^{(I)} = R_{lk,v}^{(I)} - R_{0,v}^{(I)}$ ),  $N$  is the number of steps to take before settling solely on one intercept,  $t_{init}$  is the time of detection of the divergence,  $t_{final}$  is the time at which the code settles on 1 intercept and  $dt$  is the timestep taken.

A cartoon of this process is given in figure C.1

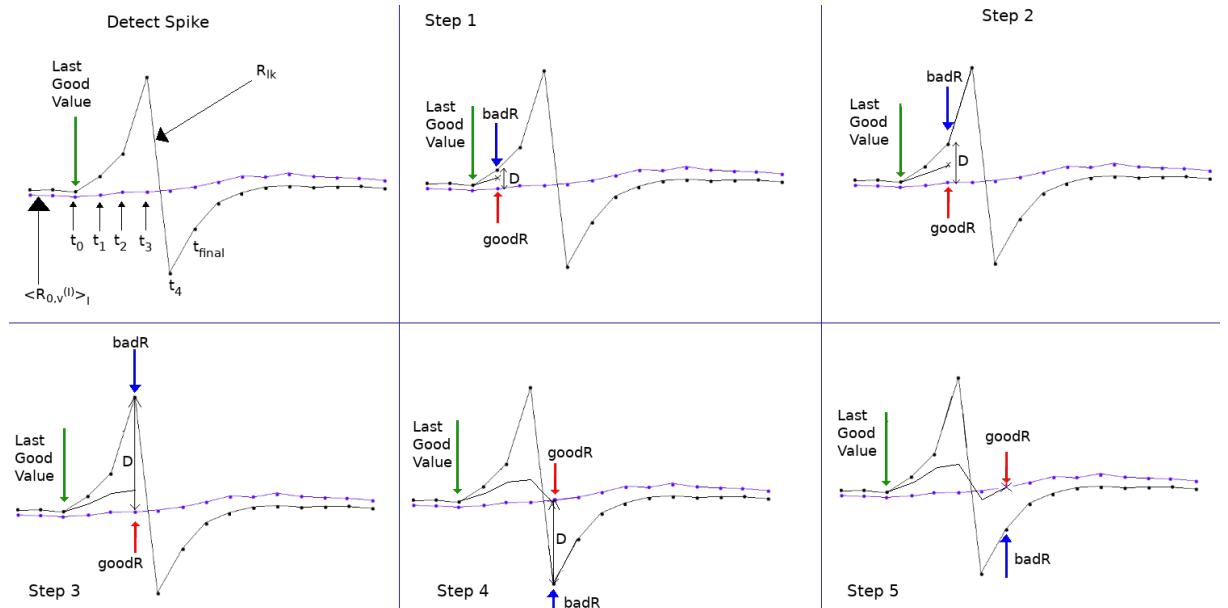


Figure C.1: A crude demonstration of the principle behind the smoothing procedure in switching between intercepts. The black line shows an intercept begin to diverge and the alternative intercept is shown in purple. As the step is incremented the amount of the alternative intercept that makes up the effective intercept is increased until only 1 intercept is used.

## Appendix D

# Rabi Oscillation

The time dependant Schrödinger equation is given below:

$$\hbar \frac{\delta}{\delta t} \Phi(\mathbf{R}(t), t) = \hat{H}(\mathbf{R}(t), t) \Phi(\mathbf{R}(t), t) \quad (\text{D.1})$$

If we hold the nuclear coordinates in place (e.g. remove time-dependence from nuclear coordinates) we get an ordinary differential equation as shown below:

$$\hbar \frac{d}{dt} \Phi(\mathbf{R}, t) = \hat{H}(\mathbf{R}, t) \Phi(\mathbf{R}, t) \quad (\text{D.2})$$

This has the following general solution.

$$\Phi(\mathbf{R}, t) = e^{\hbar \hat{H} t} \Phi(\mathbf{R}, 0)$$

## Appendix E

# Norm Conservation in CTMQC and Ehrenfest

A statement of the conservation of the norm, for a single trajectory, is given below in equation (E.1)

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

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

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

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

$$\frac{d}{dt} \sum_l |C_l(t)|^2 = 2 \sum_l \mathbb{R} \left[ \underbrace{\frac{-i}{\hbar} \varepsilon_{B\theta}^l C_l(t)^* C_l(t)}_{\text{purely imaginary}} - \sum_k \left[ C_l(t)^* C_k(t) d_{lk}^{ad} - (A_l - B_l) C_l(t)^* C_l(t) \right] \right] \quad (\text{E.3})$$

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

Where:

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

$$B_l = \sum_{v=1}^{N_n} \sum_k \frac{\mathcal{Q}_{lk,v}(t)}{\hbar M_v} \cdot \mathbf{f}_{l,v}(t) |C_k(t)|^2 \quad (\text{E.6})$$

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

$$\frac{d}{dt} \sum_l \left| C_l^{QM}(t) \right|^2 = 2 \sum_l \mathbb{R} [(A_l - B_l) C_l(t)^* C_l(t)] \quad (\text{E.7})$$

$$= 2 \left[ \sum_l A_l |C_l(t)|^2 - \sum_l B_l |C_l(t)|^2 \right] \quad (\text{E.8})$$

However,  $\sum_l A_l |C_l|^2 \equiv \sum_l B_l |C_l|^2$ , therefore there is no change in the population and the norm should be conserved.

## Appendix F

# Adiabatic State Initialisation

By diagonalising the Hamiltonian we get the adiabatic energies (eigenvalues) for each state and transformation matrix (eigenvectors) to calculate diabatic states  $\mathbb{U}$ . We can calculate diabatic coefficients corresponding to each adiabatic state via equation (F.1) below.

$$\mathbb{U}\mathbf{C}_n = \mathbf{u}_n \quad (\text{F.1})$$

Where  $\mathbb{U}$  is the transformation matrix of size  $(N_{\text{mol}}, N_{\text{mol}})$ ,  $\mathbf{C}$  is a complex vector of size  $N_{\text{mol}}$  containing coefficients for adiabatic state  $n$  and  $\mathbf{u}$  is a complex vector of size  $N_{\text{mol}}$  containing coefficients for diabatic state  $n$ .

Seeing as we would like to find the diabatic population corresponding to each adiabatic state we localise coefficients on each pure adiabatic state and carry out the transformation e.g:  $C_i = (1+0i, 0+0i, 0+0i, \dots)$  when we want to find the diabatic coefficient corresponding to state 1 and  $C_i = (0+0i, 1+0i, 0+0i, \dots)$  when we want to find the diabatic coefficient corresponding to state 2 etc.. Therefore, the column,  $n$ , of the transformation matrix,  $\mathbb{U}$ , gives the diabatic coefficients corresponding to adiabatic state,  $n$ , as shown below in equation (F.2)

$$U_{in} = u_i \quad (\text{F.2})$$

Where  $n$  is the adiabatic state index and  $i$  is the diabatic (molecular) state index.

Once we have the diabatic state corresponding to each adiabatic state, and the en-

ergy of that adiabatic state, we can find which state best fulfills the requirements of being close to the center of the system and being within  $3KT$  of the ground state. In order to do this, we can loop over each adiabatic state in increasing order of energy. The center of the system is calculated and the population weighted average center of mass,  $\mathbf{R}_n$  of the diabatic coefficients corresponding to adiabatic state  $n$  is calculated as in equation (F.3).

$$\mathbf{R}_n = \sum_i |u_i|^2 \mathbf{R}_{COM,i} \quad (\text{F.3})$$

The Euclidean distance between the center of the system and  $\mathbf{R}_{COM,i}$  is calculated and if this distance is below some threshold value then we initialise the surface hopping trajectory on that adiabatic state. If we do not find any states within  $3KT$  of the ground state and within an acceptable radius of the center we start again this time increasing the maximum allowed distance from the center. If this maximum allowed distance is increased such that we reach another threshold distance the energy threshold is increased this time until a state is found that is close enough to the center. In this way we find an adiabatic state, which when transformed, gives a diabatic population close to center of the system and near the ground state energy.

## Appendix G

# 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 (specifically LuaTeX) and BibTeX, composed with Vim Used Archer, Kathleen etc...

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