

# IMPERIAL

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## Understanding and Controlling Electron-Nuclear Coupled Dynamics in Molecules

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## **Statement of Originality**

I can confirm that the work presented in this thesis is my own, and where other work is used it is clearly indicated and referenced in the text.



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# Abstract

Recent advances in attoscience have shown that electron cloud dynamics in molecules, initiated by superpositions of electronic states, can influence nuclear motion and, by extension, their chemistry. Understanding these coupled electron–nuclear phenomena is vital towards understanding mechanisms in photobiology and light harvesting, as well as acting as a step forward in directing chemical reactivity through the control of these superpositions.

Despite significant progress in both experiment and theory, current understanding remains largely confined to small molecular systems. The mechanisms governing the formation and evolution of electronic state superpositions in larger, more complex molecules remain less certain.

This thesis aims to address this gap by employing the semi-classical second-order Ehrenfest (2OE) and fully quantum mechanical Quantum Ehrenfest (Qu-Eh) dynamics methods to investigate coupled electron–nuclear dynamics in medium-sized molecular systems. Pyrazine serves as the principal system of interest due to its well-characterized nonradiative decay from the bright  $\pi\pi^*$  state to the first excited singlet  $n\pi^*$  state via a conical intersection (CoIn); a process recently observed to involve electronic coherence.

With pyrazine, we study how electronic coherences play a role in the decay process. Our results support theoretical arguments that coherences do not form at a CoIn between states of different Abelian point group symmetries at the Franck-Condon region if excited to a pure state. However, we demonstrate that even with a small state mixture (97:3) of the states involved in the CoIn can circumvent this restriction, enabling coherence formation. We also take an in-depth analysis of the effect of the electronic structure method used to model pyrazine on its excited state ordering, rationalizing this effect through the splitting of two pairs of  $n\pi^*$  states.

Finally, this thesis explores the numerical challenges behind the 2OE and Qu-Eh dynamics methods through simulation of various molecular systems and suggest solutions and workarounds for future users of the method.



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# List of Abbreviations

**2OE** Second order Ehrenfest

**ABM** Adams-Bashforth-Moulton

**ADC** Algebraic diagrammatic construction

**AIMS** *Ab initio* multiple spawning

**BLA** Bond length alternation

**BO** Born-Oppenheimer

**CASSCF** Complete active space self-consistent field

**CC** Coupled cluster

**CoIn** Conical intersection

**CI** Configuration interaction

**CSF** Configuration state function

**DD-vMCG** Direct dynamics variational multi-configurational Gaussian

**DFT** Density functional theory

**DFVP** Dirac-Frenkel variational principle

**EOM** Equations of motion

**FC** Franck-Condon

**GGP** Gross Gaussian product

**GVB** General valence bond

**GWP** Gaussian wavepackets

**HF** Hartree-Fock

**KE** Kinetic energy

**LHA** Local harmonic approximation

**LR-TDDFT** Linear response time-dependent density functional theory

**MCSCF** Multi-configurational self-consistent field

**MCTDH** Multi-configurational time-dependent Hartree

**MEP** Minimum energy pathway

**MRCI** Multi-reference configuration interaction

**NM** Normal mode

**PES** Potential energy surface

**PSB** Protonated Schiff base

**Qu-Eh** Quantum Ehrenfest

**RASSCF** Restricted active space self-consistent field

**RK** Runge-Kutta

**SA** State-averaging

**SAC-CI** Symmetry-adapted cluster configuration interaction

**TDSE** Time-dependent Schrödinger equation

**TISE** Time-independent Schrödinger equation

**TR-PES** Time-resolved photoelectron spectroscopy

**TSH** Trajectory surface hopping

**XR-TAS** X-ray transient absorption spectroscopy

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# Chapter 1

## Introduction

The pursuit of ever shorter laser pulses has led to the advent of the attosecond laser pulse, where the width of the pulse envelope is on the same timescale as electronic motion (in the Bohr model of the hydrogen atom it takes an electron  $\sim 150 \times 10^{-18}$  s to do one orbit around the nucleus).<sup>1-6</sup> These pulses are short in time, but wide in frequency due to the time-energy uncertainty principle. As a result, when a molecule interacts with an attosecond pulse, many electronic states can be excited at once, leading to a coherent superposition of states known as an electronic wavepacket.

When electronic wavepackets are produced through an attosecond pulse, this almost always leads to the ionisation of molecular species due to their broad spectral width. However, these wavepackets can also be produced through other means. Electronic state mixtures of neutral systems can be created through the use of multiple UV/Vis pump pulses, for example.<sup>4,7</sup> Electronic coherences can also be formed through the passage of conical intersections (CoIn):<sup>8,9</sup> regions on a potential energy surface where the energy of two or more states are degenerate. These can in theory be found in a plethora of molecular excited state systems, as CoIns are often found, and can occur simply via a UV/Vis pump pulse and the excited state dynamics which follows.

The subsequent electron dynamics, which arise after a superposition of electronic states forms, can manifest as charge migration,<sup>10</sup> where the electronic charge of the molecular system oscil-

lates rapidly from one region to the other. Importantly, this rapid electronic motion has an impact on the nuclear motion, and vice versa, which is mediated through electron-nuclear, also known as nonadiabatic, coupling. In charge migration, for example, the nuclei at the turning points of the charge migration can feel a force exerted upon them by the electrons.<sup>11</sup> From the other side, the nuclei coupling to the electrons can influence and impede electron dynamics, effectively quenching the electronic coherences formed.<sup>5</sup>

Understanding these electron-nuclear coupled interactions, especially around the role of the formation of electronic coherences and their impact on the respective nuclear dynamics, is important for understanding a variety of chemical processes where the motion of electronic charge is crucial, such as photobiological processes including vision,<sup>12,13</sup> light-harvesting and photosynthesis,<sup>14,15</sup> and ultimately to control chemical reactivity through these superpositions.<sup>16,17</sup> While there have been various experimental studies around the electron-nuclear coupled interactions of small molecules such as diatomics,<sup>18–22</sup> the mechanisms that govern how electronic coherences form and impact nuclear motion in medium- to large-sized molecules are not entirely clear. This is in part because the study of electronic coherences experimentally have so far been detected indirectly (this is ultimately a current challenge regardless of the size of the molecular system), and theoretical simulation and prediction of results are crucial to understanding the signals seen experimentally, as well as informing future experimental setups.

There are also key challenges from a theoretical perspective. The electron-nuclear coupled dynamics of molecular systems can be solved through the time-dependent Schrödinger equation (TDSE). The TDSE, however, is only analytically exact for two-body systems. One can numerically solve the TDSE on a grid,<sup>23</sup> yet this is only practical for small systems because computational demand scales exponentially with system size. To study larger systems, approximations are needed, for both the description of the molecular wavefunction itself and/or the forces that govern the dynamics. The challenge then is to balance the level of theory such that one accurately captures the electron-nuclear coupled dynamics, as well as be computationally tractable.

To address this theoretical challenge, this thesis focuses on the electron-nuclear coupled dynam-

ics of medium-sized molecules. More specifically, we aim to better understand how electronic coherences form at CoIns, and additionally, how the theoretical methods chosen can impact the subsequent simulated dynamics. To do this, we principally study the excited state dynamics of the pyrazine molecule. Once excited to the  $\pi\pi^*$  state, pyrazine undergoes nonradiative decay by passing through a CoIn. As of writing, this non-radiative decay has been found experimentally to generate electronic coherences,<sup>8</sup> which disagrees with symmetry-related theoretical arguments.<sup>24</sup> Additionally, the simulated excited state dynamics of pyrazine, particularly regarding the energetic ordering of the excited states, is acutely sensitive to the theoretical methods used. Thus, pyrazine is an interesting and relevant molecule to better the understanding of the electron-nuclear coupled dynamics of coherence formation from a theoretical perspective.

To accurately capture the electron-nuclear coupled dynamics for larger systems, the molecular wavefunction and its corresponding energies can be found through the time-independent Schrödinger equation (TISE). In this work, we employ the complete active space self-consistent field (CASSCF) method,<sup>25</sup> which provides a multiconfigurational description of the electronic wavefunction. This is important in systems where strong nonadiabatic coupling is present, and in conditions where multiple electronic states are populated at the same time. In the first two sections of Chapter 2 of this work, we go in depth into the theory behind solving the TISE, including the Born-Oppenheimer approximation and its subsequent breakdown in regions of strong nonadiabaticity, as well as the various electronic structure methods which can be used and their advantages and disadvantages when describing such regions. Once the electronic wavefunction and the electronic energy have been found, their evolution in time and coupling to the nuclear motion can be determined through approximate nonadiabatic dynamics methods which solve the TDSE. In this thesis we use the semi-classical second order Ehrenfest (2OE)<sup>26</sup> and fully quantum mechanical Quantum Ehrenfest (Qu-Eh) methods,<sup>27</sup> which both treat the electronic motion quantum mechanically, but the nuclear wavefunction differently. The 2OE method treats the nuclear wavefunction as a single classical trajectory, which simplifies the equations of motion (EOM) significantly, allowing for the study of larger systems, but also misses electron-nuclear coupling interactions and decoherence effects, such as the bifurcation of a nuclear wavepacket. The Qu-Eh method treats the nuclei quantum mechanically,

representing the nuclear wavefunction as a set of Gaussian wavepackets (GWPs) which move according to the TDSE, which accurately takes into account the quantum effects lacking in 2OE. An overview of nonadiabatic dynamics methods and their advantages and disadvantages are outlined in the third and final section of Chapter 2. Next, in Chapter 3, we look at the computational implementation of the 2OE and Qu-Eh methods, their numerical challenges and their respective solutions, explored using pyrazine and protonated Schiff base models PSB3 and PSB4 as example systems.

We then begin the study of pyrazine in Chapter 4, where we study the impact of the state ordering of pyrazine for different electronic structure methods. Pyrazine remains a challenging system to model as different electronic structure methods give a different state ordering, which obscures the precise decay mechanism of the system. We rationalise this effect through the splitting of two pairs of  $n\pi^*$  states, using the CASSCF and restricted active space self-consistent field (RASSCF)<sup>28-30</sup> methods as a case study. We then investigate the nonradiative decay using the 2OE and Qu-Eh methods.

In Chapter 5, we turn to the question of coherence formation in pyrazine using the Qu-Eh method. Contrary to recent experimental studies, theory suggests that coherence formation when passing through a CoIn should be small/negligible when the two states involved in the conical intersection have differing Abelian point group symmetries, which is true in the case of pyrazine.<sup>24</sup> We find that in accordance with theory, if pyrazine is excited purely to the  $\pi\pi^*$  state coherences that form are small/negligible. However, if dynamics is initiated with a small mixture of states (97:3 ratio) involved in the conical intersection, this condition is circumvented, and large coherences can form. Finally, in Chapter 6, we summarize the overall conclusions presented in this thesis and discuss further work.

# Chapter 2

## Theory

### 2.1 Introduction

This chapter presents the theoretical framework which is used throughout the thesis for modelling electron-nuclear coupled dynamics.

Section 2.2 begins with the TISE and how the Born-Oppenheimer approximation is used to aid in its solution and how it breaks down in regions of strong nonadiabaticity. The section concludes by giving an overview of the photochemical processes facilitated through this electron-nuclear/nonadiabatic coupling.

Section 2.3 discusses electronic structure methods, which are tasked with solving the TISE and finding the electronic wavefunction, energies, and derivative properties which are required for working with nonadiabatic dynamics methods. This includes the CASSCF method, the principle electronic structure method used in this thesis.

Section 2.4 then examines nonadiabatic dynamics methods and their advantages and disadvantages in modelling electron-nuclear coupled dynamics, including the 2OE and Qu-Eh methods used throughout this work.

## 2.2 Photochemical Concepts

We start this section with the time-independent Schrödinger equation (TISE). This can be represented as:

$$\hat{H}\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}), \quad (2.1)$$

where  $\Psi(\mathbf{r}, \mathbf{R})$  is the total molecular wavefunction,  $E$  is the total molecular energy, and  $\hat{H}$  is the non-relativistic time-independent Hamiltonian. The electronic and nuclear coordinates are given as  $\mathbf{r}$  and  $\mathbf{R}$  respectively. We note that in this thesis, functional dependency will be stated once when a function is introduced, and then suppressed for notational simplicity. The Hamiltonian can be written in atomic coordinates as:

$$\hat{H} = - \underbrace{\sum_i \nabla_i^2}_{\hat{T}^{el}} - \underbrace{\sum_A \frac{1}{2M_A} \nabla_A^2}_{\hat{T}^{nu}} + \underbrace{\sum_{j>i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\hat{V}^{ee}} + \underbrace{\sum_{B>A} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}}_{\hat{V}^{nn}} - \underbrace{\sum_{i,A} \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}_i|}}_{\hat{V}^{en}}, \quad (2.2)$$

where the  $i, j$  and  $A, B$  subscripts denote the electronic and nuclear indices for the molecular system respectively, and  $M_A$  and  $Z_A$  are the mass and charge of the  $A^{th}$  nucleus respectively. The  $\hat{T}^{el}$  and  $\hat{T}^{nu}$  are the kinetic energy (KE) terms for the electronic and nuclear parts of the wavefunction respectively,  $\hat{V}^{ee}$  is the electron-electron repulsion term,  $\hat{V}^{nn}$  is the equivalent nuclear-nuclear repulsion term, and  $\hat{V}^{en}$  is the attractive electron-nuclear term. As previously discussed, the TISE is not analytically solvable for anything larger than a two-particle system. Therefore, for larger systems, approximations must be made to be able to model the molecular wavefunction.

### 2.2.1 The Born-Oppenheimer approximation

A key approximation used to help solve the TISE is the Born-Oppenheimer (BO) approximation,<sup>31</sup> which simplifies the TISE in a profound way that influences how many chemists understand chemistry. This approach begins by expanding the total molecular wavefunction as

orthonormal eigenfunctions,  $\{\psi_i^{el}(\mathbf{r}; \mathbf{R})\}$ , of the electronic Hamiltonian,  $\hat{H}^{el}$ :

$$\Psi = \sum_i \psi_i^{el}(\mathbf{r}; \mathbf{R}) \chi_i(\mathbf{R}), \quad (2.3)$$

$$\hat{H}^{el} = \hat{T}^{el} + \hat{V}^{ee} + \hat{V}^{en} + \hat{V}^{nn}, \quad (2.4)$$

$$\hat{H}^{el} \psi_i^{el} = E_i^{el}(\mathbf{R}) \psi_i^{el}(\mathbf{r}; \mathbf{R}), \quad (2.5)$$

where  $\{E_i^{el}(\mathbf{R})\}$  are the corresponding eigenvalues giving the electronic energies. The nuclear wavefunction,  $\chi_i(\mathbf{R})$ , acts as an ‘amplitude’ for the electronic basis. The amplitudes for these coefficients can be found via the equation:

$$(\hat{T}^{nu} + E_i^{el}) \chi_i = E_i \chi_i, \quad (2.6)$$

where  $E_i$  is the molecular energy corresponding to the nuclear eigenstates. It is worth noting that if not truncated this basis expansion is complete. Solving the TISE with this basis by inserting Eqn 2.3 into Eqn 2.1, multiplying by  $\sum_j \psi_j^{el*}$  on the LHS, and integrating over the electronic coordinates,  $\mathbf{r}$ , we obtain:

$$\sum_{i,j} \langle \psi_j | \hat{H}^{el} | \psi_i \rangle_{\mathbf{r}} \chi_i + \sum_{i,j} \langle \psi_j | \hat{T}^{nu} | \psi_i \rangle \chi_i = \sum_{i,j} E_i \langle \psi_j | \psi_i \rangle \chi_i. \quad (2.7)$$

Rewriting using the orthonormality of the electronic basis gives:

$$\sum_i E_i^{el} \chi_i + \sum_{i,j} \langle \psi_j | \sum_A -\frac{1}{2M_A} \nabla_A^2 | \psi_i \rangle \chi_i = \sum_i E_i \chi_i. \quad (2.8)$$

Through the chain rule, we can expand the second term on the LHS of Eqn 2.8 to give:

$$\sum_i E_i^{el} \chi_i - \sum_{i,j} \sum_A \frac{1}{2M_A} [\nabla_A^2 \langle \psi_j | \psi_i \rangle + 2 \langle \psi_j | \nabla_A \psi_i \rangle + \langle \psi_j | \nabla_A^2 \psi_i \rangle] \chi_i = \sum_i E_i \chi_i, \quad (2.9)$$

simplifying again through the orthonormality of  $\psi$ :

$$\sum_i E_i^{el} \chi_i - \sum_{i,j} \sum_A \frac{1}{2M_A} [\nabla_A^2 + 2F_{ij}(\mathbf{R}) + G_{ij}(\mathbf{R})] \chi_i = \sum_i E_i \chi_i, \quad (2.10)$$

and rewriting gives the convenient form:

$$\sum_i (E_i^{el} + \hat{T}^{nu} - E_i) \chi_i - \sum_{i,j} \sum_A \frac{1}{2M_A} [2F_{ij} + G_{ij}] \chi_i = 0, \quad (2.11)$$

where  $F_{ij}(\mathbf{R}) = \langle \psi_j | \nabla_A \psi_i \rangle$  and  $G_{ij}(\mathbf{R}) = \langle \psi_j | \nabla_A^2 \psi_i \rangle$  are the first- and second-order nonadiabatic coupling terms, often called the derivative coupling and the diagonal BO correction respectively. These are the terms that couple the nuclei and the electrons together, while the first term on the LHS of Eqn 2.11 depends entirely on the nuclear coordinate,  $\mathbf{R}$ .

Because the nuclei are significantly larger than the electrons (a proton is 1,836 times more massive than an electron), the inverse nuclear mass term can be assumed to make the nonadiabatic coupling terms negligibly small, decoupling the motion of the nuclei and the electrons, leading to a less complex set of equations to solve. This is the cornerstone of the BO approximation, and it comes with important consequences.

As the nonadiabatic coupling terms are neglected, electronic states do not ‘talk’ to each other, and so nuclear amplitude does not transfer from one state to another (from a time-dependent perspective). Additionally, the electronic energy depends parametrically on the nuclear coordinate, giving rise to the potential energy surface (PES). Therefore, in the BO picture, the nuclear wavefunction moves and remains on a single PES. For much of chemistry, especially standard organic and inorganic chemistry, where chemical reactions occur solely on the ground state, this picture is useful, and often accurate. The adiabatic approximation is slightly less reductive in its approach, keeping the nonadiabatic coupling terms but removing coupling between states by setting the off-diagonal elements to zero. The adiabatic approximation can be considered as adding corrective nuclear KE terms to the BO approximation, and still exhibits the same picture of the nuclear wavefunction remaining on a single state.

### 2.2.2 Nonadiabaticity: Born-Oppenheimer breakdown

In photochemistry, however, the picture is often different. One can rewrite the derivative coupling between two states  $\psi_i$  and  $\psi_j$  as:

$$F_{ij} = \frac{\langle \psi_j | \nabla \hat{H} | \psi_i \rangle}{E_j - E_i} \quad (2.12)$$

where the term on the denominator is the energy difference between the two states. When these states are well separated in energy, the derivative coupling is small, hence why the BO and adiabatic approximation can be sensible in molecular systems where states are well separated. However, in photochemistry, states are often close together, and in many cases, can be degenerate in energy, in regions known as conical intersections (CoIns), leading to a singularity and ultimately a breakdown of the BO and adiabatic approximation. In these regions, these approximations cannot correctly describe the dynamics of the system,<sup>9,32–37</sup> and these nonadiabatic coupling terms must be taken into account.

### 2.2.3 Adiabatic and diabatic representations

In the adiabatic basis, the electronic states are eigenstates of the BO electronic Hamiltonian, shown in Eqn 2.5. As discussed in the previous section, at CoIns, the derivative coupling terms can become infinitely large, leading in practice to numerical issues in simulation when using adiabatic states. What is often done to bypass this problem is to transform the adiabatic basis via a unitary transformation into one where the nonadiabatic coupling terms are close to zero: this basis is called the diabatic basis.

Strictly speaking, for molecules with 3 or more nuclei there is no transformation which can make these nonadiabatic coupling terms *exactly* zero,<sup>38</sup> hence in practice this basis is known as *quasi-diabatic*, but for sake of simplicity for the rest of the thesis we will discuss these simply as the diabatic basis. In terms of representations, in the adiabatic basis the character of an electronic state can change with respect to the nuclear coordinate, while in the diabatic basis the electronic states do not change character, as shown in Fig. 2.1.

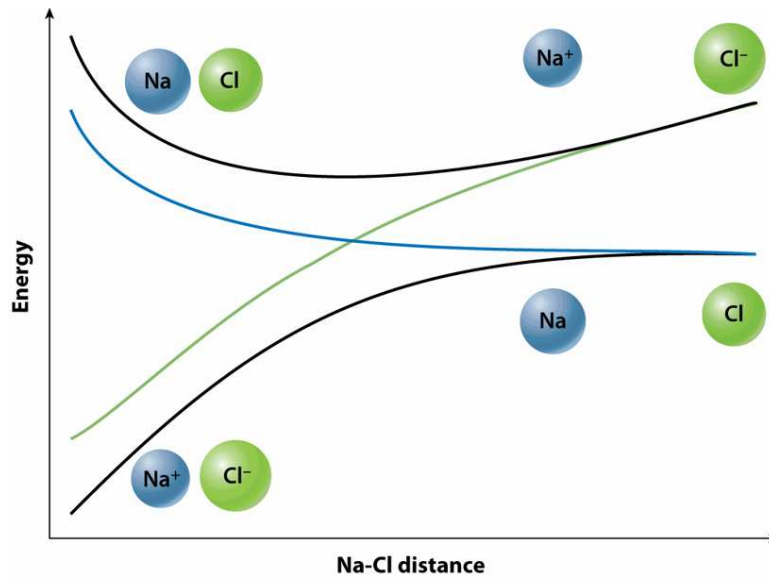


Figure 2.1: Example of potential energy surfaces for NaCl and its dissociation, where the energies of the electronic states vary depending on the nuclear coordinate, in this case the distance between the Na and Cl atoms. As the atoms separate, bond dissociation occurs, which can be ionic or covalent, depicted by the diabatic green and blue curves respectively which do not change electronic character as one moves along either surface. The black lines show the adiabatic states, which do change character along the surfaces. Image taken from T. Van Voorhis *et al.*<sup>39</sup> with permissions.

## 2.2.4 Conical intersections

Conical intersections (CoIns) are regions of phase space where two or more potential energy surfaces are degenerate in energy.<sup>40–43</sup> They are the most extreme cases of nonadiabaticity, leading to ultrafast transfer of nuclear amplitude from one electronic state to another, and are prevalent in many photochemical reactions. In a CoIn between two states there are two coordinates which can lift the degeneracy: these coordinates are known as the branching space, and play a key role in nonadiabatic dynamics when a nuclear wavepacket passes through a CoIn. The branching space is defined by the two vectors:

$$\mathbf{g}_{ij} = \frac{\langle \psi_j | \nabla \hat{H} | \psi_j \rangle - \langle \psi_i | \nabla \hat{H} | \psi_i \rangle}{2}, \quad \mathbf{h}_{ij} = \langle \psi_j | \nabla \hat{H} | \psi_i \rangle, \quad (2.13)$$

where  $\mathbf{g}_{ij}$  is the gradient difference vector and  $\mathbf{h}_{ij}$  is the derivative coupling vector.<sup>42</sup> For a 2-state CoIn, when the electronic energy is shown as a function of the branching space, the shape of the potential surface is a double cone with a single point where the two states are

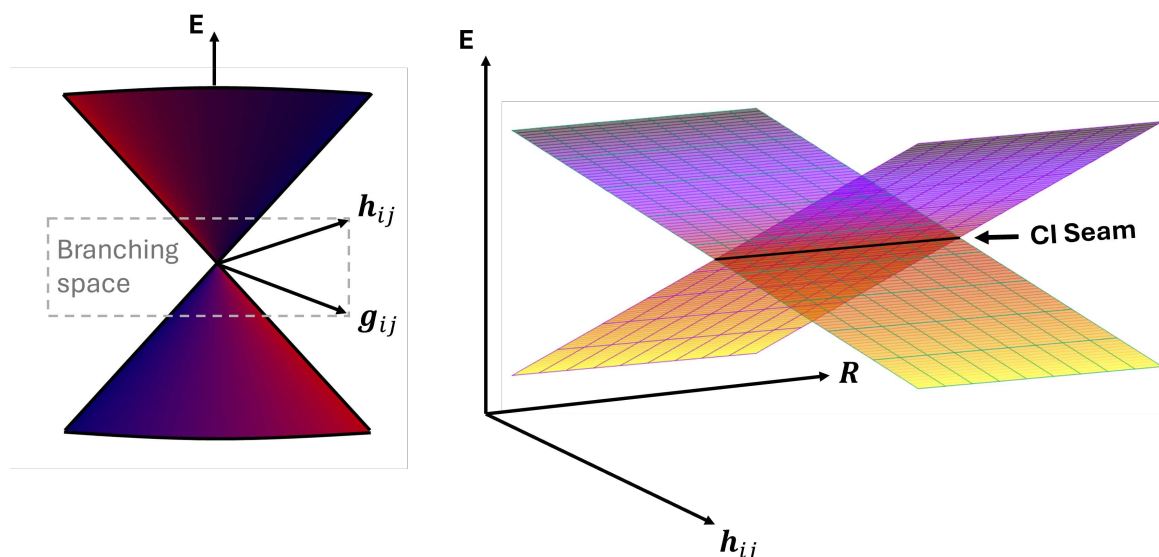


Figure 2.2: Cartoon representations of a conical intersection (CoIn) between two states. The left hand figure shows a CoIn in the branching space; the only two coordinates where the degeneracy between the two states can be lifted. This space consists of the gradient difference vector  $\mathbf{g}_{ij}$  and the derivative coupling vector  $\mathbf{h}_{ij}$ . When the electronic energy is plotted along this space one sees the double cone which this region of space is named for, with a center point where the double cones meet. The right hand figure shows a CoIn with a single branching space vector,  $\mathbf{h}_{ij}$ , and a vector representing the intersection space,  $\mathbf{R}$ , which keeps the degeneracy. In this picture, we see not a single point where the states are degenerate, but a *seam*, where the energy remains degenerate. This space has a  $3N-8$  dimensionality, also noting that the figure is a simplified version, and can be curved rather than a straight line.

degenerate, as shown in the LHS of Fig. 2.2. The degeneracy of the states is then preserved for the other  $3N - 8$  nuclear coordinates, which are known as the intersection space, making a hyper-dimensional seam of points where the two involved states are the same energy. A simple picture of such a seam is shown in the RHS of Fig. 2.2. In terms of topology CoIns can be peaked or sloped, and this can have a significant impact on the excited state decay through a CoIn.<sup>44</sup>

In the adiabatic representation, a real electronic wavefunction undergoes a sign change when encircling a CoIn. This phenomenon, known as the geometric phase, is a fundamental feature of all CoIns. The phenomenon was first recognized by Herzberg and Longuet-Higgins and later generalized by Berry,<sup>45,46</sup> hence is often also referred to in the literature as the Berry phase. The sign change renders the electronic wavefunction double-valued with respect to the nuclear coordinates. Since the total wavefunction must remain single-valued, this introduces a modified boundary condition for the nuclear wavefunction. As a result, the geometric phase

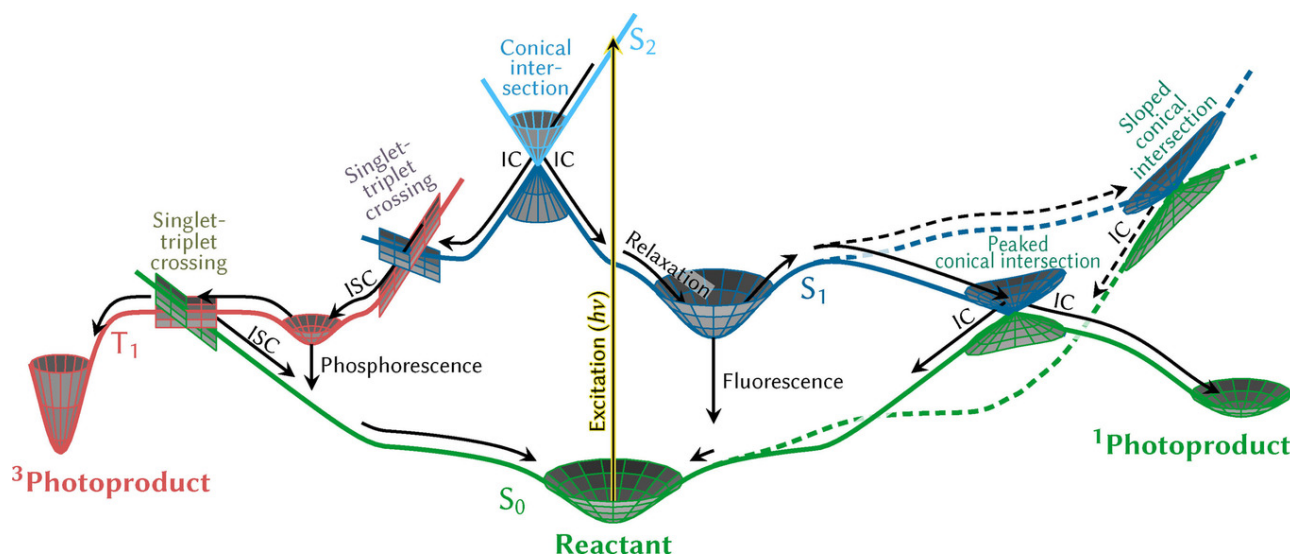


Figure 2.3: A cartoon showing a wide range of photochemical processes which arise on excited state potential energy surfaces. Image released in the public domain by S. Mai and L. Gonzalez.<sup>48</sup>

alters the properties of the nuclear wavefunction and thereby influences its dynamics. These effects are significant and cannot be neglected in the adiabatic representation, as they may impact dynamics even at low energies - where nuclei remain near the minima of the lowest adiabatic potential energy surface (PES) without ever reaching the CoIn.<sup>47</sup>

Different electronic structure methods can generate different CoIn topologies,<sup>44</sup> therefore care must be taken in choosing a method which best matches the topology of a CoIn when it is important in the excited state decay process. In dynamics simulations, due to the singularity for the derivative coupling at CoIns shown in Eqn 2.12, calculations are often performed in the diabatic basis rather than the adiabatic to avoid numerical instabilities.

## 2.2.5 Photochemical processes and summary

With these concepts laid out, we can now picture a general set of excited state processes, as shown in Fig. 2.3, which acts as an effective ‘3D’ Jablonski diagram. A molecule naturally rests in the ground state equilibrium geometry. When a molecule absorbs a photon which corresponds to the energy difference between two electronic eigenvalues, it moves into an excited state. In this excited state the molecule is out-of-equilibrium, and as a result its geometry changes over

time as it moves along the excited state potential energy surface, known as internal vibrational relaxation. There are several mechanisms which can arise to allow the molecule to relax back down to the ground state, and perhaps to a different ground state minimum, turning from reactant to photoproduct. The molecule could relax to the ground state by releasing a photon, known as fluorescence. Relaxation from one state to another can occur non-radiatively through a CoIn, known as internal conversion. There are also similar couplings between states of differing multiplicities, known as intersystem crossing. Radiative decay after intersystem crossing gives rise to phosphorescence.

In this thesis, we are interested in accurately modelling processes which arise at CoIns, specifically related to the singlet states. We do note, however, that versions of the methods we use to model dynamics have a version which can model intersystem crossing.<sup>49,50</sup> The following sections discuss how electronic structure and dynamics methods can describe these interactions.

## 2.3 Electronic Structure

Having established the theory behind photochemical phenomena, we now discuss the electronic structure methods used to compute these potential surfaces and nonadiabatic couplings.

As mentioned previously, electronic structure methods provide approximate solutions to the TISE (Eqn 2.1). This typically begins with a guess or *ansatz* for the electronic wavefunction, which is different for each electronic structure method. How this *ansatz* is chosen impacts how the electron-electron interactions, known as electron correlation, are treated, and therefore impacts the accuracy of the method in how it describes the electronic wavefunction/energy and couplings associated with it. A wavefunction guess is not necessarily the only way to obtain the electronic energy and its respective properties, as we shall see with density functional theory, where all details of the molecular system can be derived from the electron density.

These methods can be generally segregated into single- and multi-reference methods, which take into account whether a wavefunction is constructed beginning from a single electronic configuration or multiple configurations respectively. This is especially important in the calcu-

lation of excited states where some areas of the PES require a multiconfigurational description, such as regions of strong nonadiabaticity like CoIns.

For use in nonadiabatic dynamics methods, there are a set of key prerequisites that electronic structure methods must meet. The first is that it can reliably provide an electronic wavefunction and its respective energies over the course of dynamics (i.e. over a range of different nuclear geometries). This requires being able to correctly describe the electron correlation of the system. Another important aspect in the context of this thesis is being able to accurately describe regions of strong nonadiabaticity such as CoIns, as their topology can greatly impact the electron-nuclear coupled dynamics that occur when passing through one. From a practical perspective, the methods also need to be able to provide at least first derivatives of the electronic energy with respect to the nuclear coordinate, also known as the gradient, and also preferably second derivatives, known as the Hessian. These are required in order to numerically propagate the TDSE forward in time in dynamics methods. Analytical derivatives are preferred over numerical derivatives as they are more efficient and greatly increase numerical accuracy in calculation.<sup>51</sup>

In this section, we will discuss different electronic structure methods, and how they perform with respect to the criteria above.

### 2.3.1 Hartree-Fock theory

Discussion begins with Hartree-Fock (HF) theory,<sup>52–54</sup> a foundational electronic structure method that many other methods are built around, which shall be discussed later. The method uses a guess wavefunction in the form of a single Slater determinant:

$$\psi^{el}(x_1 x_2 \dots x_n) = \begin{vmatrix} \chi_1(x_1) & \cdots & \chi_n(x_1) \\ \vdots & \ddots & \vdots \\ \chi_1(x_n) & \cdots & \chi_n(x_n) \end{vmatrix}, \quad (2.14)$$

where  $\chi_i$  are one-electron molecular orbitals, a function of the spin coordinate  $x_i$  and are approximated by a linear combination of atomic orbitals,  $\{\beta_i\}$ :

$$\chi_i = \sum_j c_j \beta_j, \quad (2.15)$$

which are often Gaussian or Slater-type orbitals, the number and use of which denote the basis set used for a method or a calculation.<sup>55</sup> Use of a Slater determinant in the guess of the wavefunction obeys fermionic antisymmetry as required by the Pauli exclusion principle.

In HF theory, these one-electron molecular orbitals have a corresponding orbital energy,  $\epsilon_i$ , which are found by applying the Fock operator,  $\hat{f}$ , to it:

$$\hat{f}(x_i)\chi_i(x_i) = \epsilon_i\chi_i(x_i), \quad (2.16)$$

$$\hat{f}(x_i) = \hat{h}(x_i) + \sum_j \hat{J}_j(x_i) - \hat{K}_j(x_i), \quad (2.17)$$

$$\hat{h}(x_i) = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}_i|}, \quad (2.18)$$

where  $\hat{h}$  is the one-electron Hamiltonian operator and the two-electron terms are contained within the Coulomb and exchange operators  $\hat{J}$  and  $\hat{K}$  respectively. These can be defined as:

$$\hat{J}_j(x_i) = \int \chi_j^*(x_2) \frac{1}{r_{12}} \chi_j(x_2) dx_2, \quad \hat{K}_j(x_i)\chi_i(x_i) = \left[ \int \chi_j^*(x_2) \frac{1}{r_{12}} \chi_i(x_2) dx_2 \right] \chi_j(x_i). \quad (2.19)$$

The Coulombic operator shows that in HF theory the electron experiences a mean-field Coulombic interaction with all other electrons in the system. This will have consequences for the quality of this method as will be discussed later.

Though a simple method, HF can provide good qualitative descriptions of the ground states of systems at the ground state geometry, given that the system is well-described by a single determinant. The ionisation energies given by HF via Koopmans theorem<sup>56</sup> can also be surprisingly accurate due to a balance in errors due to neglecting orbital relaxation and electron correlation.

### 2.3.1.1 Excited states

The HF method optimises the basis set coefficients to minimise the ground state energy. While the virtual orbitals can be used to calculate properties such as ionisation energies or electron affinities via Koopmans theorem,<sup>56</sup> the virtual orbitals which crudely represent the excited state will be poor. There are methods, such as Time-Dependent Hartree Fock (TDHF) which use first order perturbation theory,<sup>57–59</sup> in other words a linear response in the form of an oscillating potential, to calculate excited states. This approach is also used to find excited state energies for Density Functional Theory (DFT) which shall be discussed later.

### 2.3.1.2 Electron correlation

A key issue with HF theory is that it treats electron-electron interactions in a mean-field manner. This means that HF does not account for electrons instantaneously adjusting to each other's motion. Additionally, as in HF the wavefunction is built of a single Slater determinant, or electron configuration, this can cause issues in describing certain molecular processes, such as bond breaking, or simply certain molecules in their ground state equilibrium geometry, such as ozone, which are best described with multiple electronic configurations.

The energy difference between the exact solution for the electronic energy and the HF solution is known as the correlation energy. This correlation can be split into two parts.<sup>60,61</sup> The first part, dynamic (or external) correlation, is tied to the correlation of electrons instantaneously adjusting to each other, which can be connected to double (or more) excitations of strongly occupied orbitals to correlated weakly occupied orbitals which allow for the description of electrons avoiding those close to one another. The other, static (or internal) correlation, has less to do with instantaneous adjustment of electronic motion with respect to others, and deals with the 'static' molecule, and how a single determinant cannot qualitatively represent a system, such as ozone, where more than one Slater determinant, or electron configuration, is required in order to qualitatively describe it correctly.

Post-HF methods deal with adding the missing electron correlation from HF to the system. This

can be done by adding a perturbative correction to the single-reference Slater determinant, or by adding a linear combination of excited state determinants. These methods are known as *single-reference* methods. However, it is important to note that these methods do not explicitly deal with adding static correlation to the system, only dynamic correlation, as static correlation is concerned with an ansatz that begins with multiple Slater determinant references. These methods are known as *multi-reference*. A high-level overview of these methods will now be discussed, beginning with the full configuration interaction (FCI) method.

### 2.3.2 The Full Configuration Interaction (FCI) method

The configuration interaction (CI) method<sup>62,63</sup> can be considered the ‘brute force’ way to find the correlation energy missing from HF. Instead of using a single Slater determinant as in HF, one uses a linear combination of all possible electronic configurations beginning from a Slater determinant. Alternatively, instead of Slater determinants, which are not in general eigenvalues of the total spin operator,  $\hat{S}^2$ , configuration state functions (CSFs),<sup>64</sup> can be used. CSFs are symmetry-adapted linear combinations of Slater determinants which are eigenvalues of  $\hat{S}^2$ , guaranteeing the purity of the solved states. We can represent the CI wavefunction as:

$$|\psi^{el}\rangle = \sum_i c_i |\phi_i\rangle, \quad (2.20)$$

where  $|\phi_i\rangle$  are Slater determinants, or CSFs, and  $c_i$  are the CI coefficients. For CI the optimal wavefunction is found by variationally minimising the energy with respect to the coefficients for the Slater determinants or CSFs, leading to the matrix eigenvalue equation:

$$\mathbf{H}\mathbf{C}^I = E^I \mathbf{C}^I. \quad (2.21)$$

Here,  $\mathbf{H}$  is the Hamiltonian matrix with elements  $H_{ij} = \langle \phi_i | \hat{H}_e | \phi_j \rangle$ , and  $\mathbf{C}^I$  is a column vector which gives the set of CI coefficients for each SD/CSF for the state I with energy  $E^I$ , giving a picture of which electronic configurations contribute most (or least) to each eigenstate. For the case where all excited state configurations are included for the system, this method is called Full

CI (FCI), and in the basis set limit this method is exact. This method, however, scales rapidly, leaving its current use to small molecules, even at which size requires significant amounts of computational time and power. As FCI considers all excited state electron configurations in its wavefunction construction, it cannot be considered single-reference. Truncated versions of the method, however, can be considered single-reference methods, which are discussed in the next section.

### 2.3.3 Single-reference methods

To overcome the computational expense of the FCI method, truncated CI methods can be used,<sup>62</sup> where instead of adding all excited state configurations to the reference, only all *single*, *double*, or *triple* excitations are considered; these methods are known as CI singles (CIS), CI singles and doubles (CISD), CI singles doubles and triples (CISDT) and so on. The more excitation levels included, the closer the method becomes to FCI. These methods cost less than Full CI and do recover a portion of electron correlation and can describe well the ground state of single-configuration molecules. Analytic first and second derivatives exist for these methods also.<sup>65</sup>

The CIS method is a cheap and accessible method for accessing excited state wavefunctions and their respective energies, especially for larger systems, as it scales similarly to, and improves on, HF ( $N^4$ , where  $N$  is the number of electrons in the system). Adding single excitations to the reference determinant, however, does not begin to recover the majority of electron correlation and is often prone to errors of excitation energy of 1.5 eV and give incorrect ordering of states.<sup>66</sup> The CISD method is a more commonly used method for medium-sized systems, and scales as  $N^6$ , but also suffers (though to a lesser extent) from error, often overestimating excitation energies.<sup>67</sup>

In addition, an important problem that this method will share with other single-reference methods are that these methods cannot correctly describe CoIns between the ground state and the excited state.<sup>44</sup> These methods can, however, model conical intersections between other excited states. For the truncated CI methods, this issue between ground-excited state CoIns

can be overcome by using a multireference extension, known as multi-reference configuration interaction (MRCI),<sup>68</sup> which will be discussed later. Finally, an important general issue with truncated CI methods is that they do not guarantee that the energy of the system will be preserved if the distances between atoms change, also known as size consistency, and also that the method will scale linearly with respect to the number of electrons used, known as size extensivity.

The coupled cluster (CC) family of methods are similar to the truncated CI methods, but remain size extensive and size consistent.<sup>69,70</sup> Similarly to CI, the wave function is built from a single reference determinant,  $|\phi_0\rangle$ , but unlike CI, the excited state determinants are built using an exponential cluster operator,  $e^{\hat{T}}$ :

$$|\psi^{el}\rangle = e^{\hat{T}}|\phi_0\rangle, \quad (2.22)$$

where the operator can be split into a linear combination of smaller operators,  $\hat{T} = \sum_{i=1} t_i \hat{T}_i$ , which will each exchange occupied orbitals with unoccupied orbitals to produce excited state configurations.

In this method, these operators can be grouped into those which produce single, double, triple etc excitations, and from this one can form the truncated CC singles (CCS), doubles (CCSD), triplets (CCSDT) etc methods which act analogously to the truncated CI methods. Similarly, if all possible operators/configurations are included this is equivalent to FCI. The most common methods used are CCSD and CCSD(T), where in the latter the brackets denote that a triple excitation energy correction is added as a perturbative term. These methods are often coined as ‘gold-standard’ single-reference methods, well describing systems with single-configuration ground states. These methods are, however, costly. The CCSD(T) method, for example, scales as  $N^7$  (noting that the CC methods scale similarly to their CI analogues), so can only be used for small to medium-sized molecules. There are different methods which allow CC methods to calculate excited states,<sup>71</sup> such as the symmetry-adapted cluster configuration interaction (SAC-CI),<sup>72</sup> equations of motion CC (EOM-CC),<sup>73,74</sup> and linear-response CCx methods,<sup>75</sup> which perform similarly at their respective levels of excitation.<sup>66</sup> As with all single reference methods,

however, it cannot describe well CoIns between the ground and excited states. Analytic first and second derivatives also exist for this set of methods, but do not have a large improvement in terms of computational efficiency relative to numerical derivatives due to the computational cost of determining the CC amplitudes.<sup>76</sup>

Another popular set of single-reference methods are the Algebraic Diagrammatic Construction (ADC(x)) methods.<sup>77,78</sup> These methods build on the ground state post-HF Moller-Plesset (MPx) method<sup>79,80</sup> to approximate excited states. In MPx methods, a perturbational term is added to the Hamiltonian or Fock matrix to recover electron correlation:  $\hat{H}_e = \hat{H}_0^{el} + \lambda V$ . The wavefunction and energies can then be expressed as a Taylor expansion with respect to this perturbation:

$$\psi^{el} = \lim_{m \rightarrow \infty} \sum_{i=0}^m \lambda^i (\psi^{el})^i, \quad (2.23)$$

$$E^{el} = \lim_{m \rightarrow \infty} \sum_{i=0}^m \lambda^i (E^{el})^i. \quad (2.24)$$

The HF energy is the sum of the zeroth and first order perturbations, so the first correction comes from second order upward  $E^{corr} = E^{(2)} + E^{(3)} + E^{(4)} + \dots$ . In ADC(x), to then approximate the excited state based on the Green's function, the system has a linear time-dependent oscillating electric field applied to it, at a specific frequency. The excitation energies can be extracted by finding the poles of ground-state polarisability. The x in ADC(x) relates to which order of the MP reference is used. The most often used method is the ADC(2) method, which uses an MP2 reference wavefunction. This also shares similarities with the CC2 method. The method is black-box and can work well for calculating excited states for single-reference systems. It scales as  $N^5$ , which makes it useful for medium-sized molecules, and analytical first derivatives do exist for this method.<sup>81</sup> However, like other single-reference methods, it does not recover static correlation well, and can fail to describe specific systems, such as CoIns between the ground and excited state, noting a specific case for organic molecules with a carbonyl group attached.<sup>82</sup>

### 2.3.3.1 Linear response density functional theory (LR-TDDFT)

In prior discussion, the electronic structure methods mentioned were wavefunction-based methods, where a guess wavefunction is used to describe the whole molecular system. In density functional theory (DFT),<sup>83,84</sup> the system is described in its entirety by the electron density, and was proved so by the Hohenberg-Kohn theorem.<sup>83</sup> The electron density can be described as the square of the wavefunction integrated over all space bar a single spatial coordinate:

$$\rho(r_1) = N \int \cdots \int |\psi(x_1, x_2, \cdots, x_N)|^2 ds_1 dx_2 \cdots dx_N, \quad (2.25)$$

where  $s_1$  is the spin coordinate of  $x_1$ , and the energy can be obtained as a functional of the density,  $E[\rho]$ . In practice, this is done via the Kohn-Sham equations,<sup>84</sup> which uses a system of non-interacting electrons under an effective potential which yields the total energy of the real system. In the Kohn-Sham method, the energy is written as:

$$E[\rho] = \sum_i \langle \theta_i | -\frac{1}{2} \nabla^2 | \theta_i \rangle + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} + J[\rho] + E_{XC}[\rho], \quad (2.26)$$

where  $\theta_i$  are the Kohn-Sham orbitals. The first term on the RHS is the KE term for the system of non-interacting electrons, the second term is the electron-nuclear interaction, the third term,  $J[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$ , is the classical coulomb repulsion of the density, and  $E_{XC}[\rho]$  is the exchange-correlation energy functional. This term contains the terms which correct for the non-interacting system, including the KE and electron-electron repulsion terms. The variation of the form of this functional, of which there are many,<sup>85</sup> is what defines which ‘functional’ is used in DFT.

DFT is a ground state theory. To find excited state energies one moves to time-dependent DFT (TDDFT),<sup>86,87</sup> where the Runge-Gross theorem,<sup>86</sup> the excited state analogue of the Hohenberg-Kohn theorem, says there is a one-to-one mapping of the electron density to an external potential. This allows for excited state energies and transition dipole moments to be extracted in a propagator-based linear response (LR-) manner.

LR-TDDFT is a single-reference method, scales very well ( $N^{3-4}$  depending on functional type) and therefore can be applied to larger systems.<sup>59</sup> It is a single reference method and, therefore, fails to describe multi-configurational systems. It is known to incorrectly describe CoIns between the ground and excited state, forming so-called ‘linear intersections’,<sup>88</sup> as well as poorly describe bond-breaking,<sup>89</sup> charge transfer states,<sup>90</sup> states with double and higher excitations,<sup>91</sup> and high-energy states.<sup>92</sup> Analytical first and second derivatives have been found for DFT, however, if using a local exchange-correlation functional, the exchange correlation energy must be found numerically, which can impact the quality of the first, and especially second, derivatives.<sup>51</sup>

It is worth noting that with certain functionals some of these symptoms can be remedied, for example, the CAM-B3LYP functional can work well for charge transfer states.<sup>93</sup> However, this also reflects a deeper issue within LR-TDDFT; depending on the functional used, the calculated result can change significantly. This leads to benchmarking multiple functionals at once, and choosing the functional which best suits the problem at hand. Therefore, while TDDFT is a powerful black box method for single-reference systems, it has an uncertain future in terms of its accuracy and predictability.

### 2.3.4 Multi-configurational self-consistent field (MCSCF) methods

The multi-configurational self consistent field (MCSCF) methods<sup>68,94</sup> are a set of multi-reference methods that aim to practically include the configurations which are most important, or hold the most weight/contribution to the total wavefunction, in a calculation by partitioning the configurational space into two main sections: one section which is treated to a FCI (or some form of truncated CI) expansion, called the *active space*, and another where the configurations have a HF treatment, known as the *inactive space*. In this method, both the CI coefficients and the orbitals are variationally optimised to find the minimum energy of the system. The MCSCF wavefunction can be written as:

$$|\psi_{MCSCF}^{el}\rangle = e^{-\hat{\kappa}} \sum_i c_i |\phi_i\rangle, \quad (2.27)$$

where  $\hat{\kappa}$  is the orbital rotation matrix and  $|\phi_i\rangle$  are Slater determinants or their spin-adapted CSF equivalents. Within this formalism, both  $\hat{\kappa}$  and  $\{c_i\}$  are optimised to minimise the energy of the system.

#### 2.3.4.1 Complete active space self-consistent field (CASSCF) method and other MCSCF variants

The complete active space self-consistent field (CASSCF) method<sup>25</sup> is one of the most popular MCSCF methods. In CASSCF, the active space, which is a chosen set of  $N$  electrons and  $n$  orbitals, is treated to a FCI expansion, while the inactive space is given a HF treatment. This set is often denoted as an  $(N,n)$  active space in the literature. An example of the method in practice is given in Fig. 2.3.4.1 for a (6,6) active space. From a practical perspective, the number of CSFs (in other words configurations) generated is given by Weyl's formula:

$$N_{CSF} = \frac{2S+1}{n+1} \binom{n+1}{\frac{N}{2}-S} \binom{n+1}{\frac{N}{2}+S+1}, \quad (2.28)$$

where  $S$  is the spin quantum number of the system. Computationally, it is not advisable, or computationally feasible, to use anything larger than a (20,20) active space. There are methods, however, such as the DMRG<sup>95,96</sup> and ICE-CI methods,<sup>97</sup> which use tensor approaches to simplify calculations to allow for larger active spaces. To perform excited state calculations with CASSCF,<sup>94</sup> individual states can be optimised, known as state-specific (SS-) CASSCF. Using this method to compare with different excited states is not desirable, however, as in this approach the optimised state can be contaminated with those that it wants to be compared with. One approach which aims to overcome this is known as state-averaging (SA-) CASSCF,<sup>98,99</sup> where the weight-averaged one- and two-electron reduced density matrices are optimised to minimise the average of the states of interest.

It is also worth noting that there is a version of CASSCF where only the CI coefficients are optimised and not the orbitals. This method is known as CAS-CI, and is also used in the 2OE and Qu-Eh dynamics methods from a technical perspective, alongside CASSCF, which will be

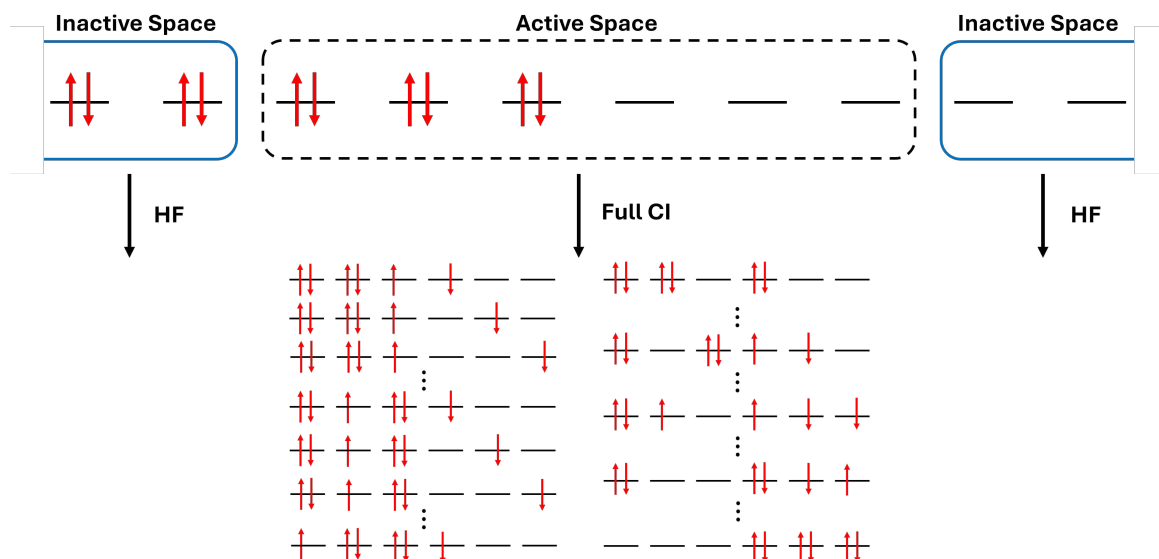


Figure 2.4: Cartoon of how CASSCF applies to a 6 electron 6 orbital (6,6) active space. The orbitals within the active space are treated to a Full CI expansion, shown by the various sets of configurations in the centre of the figure. According to Weyl’s formula (Eqn 2.28), there are 175 CSFs generated from this active space. The inactive space is given a HF treatment.

later explained in Section 2.4.2.2.

One benefit of the CASSCF method, like other MCSCF methods, is that it can better describe multi-reference systems, which single-reference methods are unable to do. This includes regions of the PES where multiconfigurational character changes, such as CoIns. Additionally, unlike single-reference methods, it can correctly qualitatively describe CoIns between the ground and the excited state.<sup>44</sup> It is a method which is known to recover static correlation well, particularly within the active space, and also in the inactive space through orbital rotations, which puts the method in a good position to correctly qualitatively describe bond-breaking and formation. The CASSCF method also has access to analytical first and second derivatives, which can be found by solving the coupled-perturbed MCSCF equations.<sup>100,101</sup>

However, the CASSCF method is known not to recover dynamic correlation well, unlike single-reference methods. This is down to configurations not included within the active space; double excitations to correlated virtual orbitals which are important to capture dynamic correlation. This can lead to imbalanced descriptions of electronic states, for example, in systems where there are ionic states.<sup>102–104</sup> There are two main approaches to recover this correlation in CASSCF. Firstly, the active space could be enlarged, but as discussed before with Weyl’s

formula (Eqn 2.28) this quickly becomes impractical. Another approach in line with enlarging the number of configurations is to use the Restricted Active Space Self Consistent Field Method (RASSCF),<sup>28–30</sup> which divides configurations into further subsets. The RAS1 and RAS3 spaces are for occupied and virtual orbitals respectively, where only a few excitations (or holes) are allowed (usually 1 or 2), and the RAS2 space, the same as the active space in CASSCF where a FCI expansion is applied. This approach allows for the inclusion of additional configurations, without such a large combinatoric increase shown in CASSCF. The generalised valence bond (GVB-) CASSCF method<sup>105</sup> takes this one step further, where occupied and virtual orbital pairs add two GVB configurations (one orbital is unoccupied and one is double occupied) to the active space. These methods, and others which work along these lines, such as GASSCF,<sup>106</sup> for example, are discussed in further detail in the following review articles.<sup>62,68,107</sup>

The second way to incorporate dynamic correlation to CASSCF is by adding a perturbative correction. The most popular method which does this is known as CASPT2<sup>108,109</sup> (higher order methods, such as CASPT3,<sup>110</sup> also exist) where a second order perturbative correction is added to balance dynamic correlation. Unlike the RASSCF-type approach, where a choice must be made about which orbitals are added to the RAS1 and RAS3 spaces, the PT2 or PT3 correction is ‘black-box’, and hence more user-friendly. These methods are popular and can yield good agreement with experimental values,<sup>111</sup> and has access to analytical first derivatives,<sup>112</sup> albeit the method is more costly than the CASSCF method. CASPT2 does, however, have its own issues. As the method is perturbational, it is no longer variational and hence convergence and extent of perturbative correction cannot be assessed. The method also suffers from intruder states, where states can have energies close to or below the reference state, as well as have systematic errors when simulating open-shell systems. An empirical shift, known as the IPEA shift, is used to correct for these issues, though there is some discussion about whether this shift is justified for certain systems, such as small- to medium-sized organic chromophores.<sup>113</sup> The multi-state (MS-) CASPT2 method<sup>114</sup> can be considered the analogue perturbative correction case for SA-CASSCF, with additional methods such as extended MS-CASPT2 (XMS-CASPT2),<sup>112</sup> and extended multi-configuration quasi-degenerate perturbation theory (XMQCDPT2)<sup>115</sup> methods which add further corrections to the perturbative method.

The final key practical issue within CASSCF, and MCSCF methods in general, is that the active space must be chosen, and that there is no definitive method which dictates how this is done. For most CASSCF users, chemical intuition is used to choose the active space,<sup>116</sup> the set of key orbitals which are expected to be important when studying the photochemical process. This does by principle add bias to the calculation. There are automated methods which have been developed to tackle this issue,<sup>117–119</sup> though are not universal in practice.<sup>116</sup>

### 2.3.5 Multi-reference and spin flip methods

As discussed previously, single-reference methods fail to describe systems where the ground state has more than one primary configuration. There are methods that augment so-called single-reference methods to overcome this. The first are known as multi-reference (MR-) methods.<sup>68</sup> These are methods where instead of using a single reference, a chosen set of reference Slater determinants or CSFs are used. The truncated MR-CI methods are a prime example,<sup>120</sup> where now a CI expansion occurs from multiple references instead of one. The MR-CI method does still suffer from not being size-extensive, however, much like the single-reference truncated CI methods. Similar analogues, such as MR-CC,<sup>121</sup> also exist. Note that for the MR- methods the set of reference determinants or CSFs must be chosen *a priori*, and therefore share a similar dilemma as choosing the subspaces in MCSCF methods.

The spin-flip (SF-) methods are another set of methods which aim to solve issues related to being single-reference.<sup>122</sup> If looking at singlet states, for example, the spin-flip method uses a triplet reference, and obtains the singlet state through a ‘spin-flip’ de-excitation. Through this method, configurations which are inaccessible through single-reference methods alone can be obtained. This approach has been extended to many methods, including truncated CI methods, EOM-CCSD and TD-DFT, which allow these otherwise unfavourable methods to correctly describe ground state/excited state CoIns.<sup>44</sup> A common issue with these methods relate to spin contamination which can be caused by spin-contaminated references or an incomplete level of excitation, which can occur in SF-CIS, or SF-TD-DFT for example.

### 2.3.6 Summary

In this section, we have looked at a range of different electronic structure methods and their advantages and disadvantages as potential suitors for nonadiabatic dynamics methods.

We started with HF theory, the simplest electronic structure method, which approximates the electronic wavefunction as a single Slater determinant, and how its mean-field treatment misses the important instantaneous interaction of electrons (electron correlation). The difference between the true energy of the system and the HF energy of the system is known as the correlation energy, and post-HF methods then try to recover this correlation energy.

The Full CI (FCI) method totally recovers this correlation energy (within the basis set limit), using a linear combination of all possible excited state determinants as an ansatz. This method, however, is extremely expensive and only possible to use for the smallest systems.

This leads to a set of single-reference methods - truncated CI, coupled cluster (CC), ADC(x) methods, and LR-TDDFT - which aim to recover the majority of the dynamic electron correlation in these systems without the expense of FCI, using a single reference determinant as a base. These methods, such as the CC methods, can perform well in studying systems with a dominant electronic configuration, including excited states and CIs that lie between them. Methods such as LR-TDDFT scale and can perform very well and hence are often used to study the excited states (and electron-nuclear coupled dynamics) of large systems. However, these methods systematically struggle when static correlation needs to be described, for instance, with bond breaking. Furthermore, these methods cannot correctly describe conical intersections between the ground state and excited states. This can be remedied in the majority of these methods by using the spin-flip formulation.

Multi-reference methods, such as MCSCF, and its variants CASSCF, RASSCF, etc, capture this static electron correlation by using a reference determinant which is a linear combination of electronic configurations (either Slater determinants or CSFs). Multi-reference versions of single-reference methods also exist. These methods can well describe PESs which have multi-configurational character, such as CoIns, including those between the ground and excited states.

Methods such as CASSCF do suffer, however from not fully recovering dynamic correlation. This can be remedied by including more configurations within the active space, which RASSCF can do, or by using perturbational corrections, such as CASPT2, albeit at higher computational cost. The major challenges with these methods include the previous issue of balancing electron correlation, alongside choosing an appropriate active space and typically higher computational costs relative to commonly used single-reference methods.

All methods discussed in this section have access to analytical first derivatives, however, not all methods have access to analytical second derivatives. This is important to note later on, as some nonadiabatic dynamics methods, including the 2OE and Qu-Eh methods used in this work, require them in their propagation. It would be beneficial to see more progress in developing analytical second derivatives in future for some these methods, albeit noting the difficulty which comes with implementing these, as well as the computational challenge of having enough memory to calculate these values.

With this wide range of methods discussed, we move on to examine the nonadiabatic dynamics methods that these electronic structure methods aim to assist.

## 2.4 Nonadiabatic Dynamics

In the previous section, we discussed the electronic structure methods used to approximately solve the time-independent Schrödinger equation (TISE) and calculate observables after finding the wavefunction and its respective eigenvalues (or energies). In this chapter, we shift our focus to the time-dependent Schrödinger equation (TDSE) and explore the methods used to approximately solve it, particularly in the context of electron-nuclear coupled (or nonadiabatic) dynamics.

In most cases, the TDSE cannot be solved exactly analytically. Some methods aim to solve this numerically, such as exact grid quantum dynamics and multi-configurational time-dependent Hartree (MCTDH) methods, but suffer due to computational expense and can only simulate small systems or reduced dimensionality. These methods often have to pre-compute their

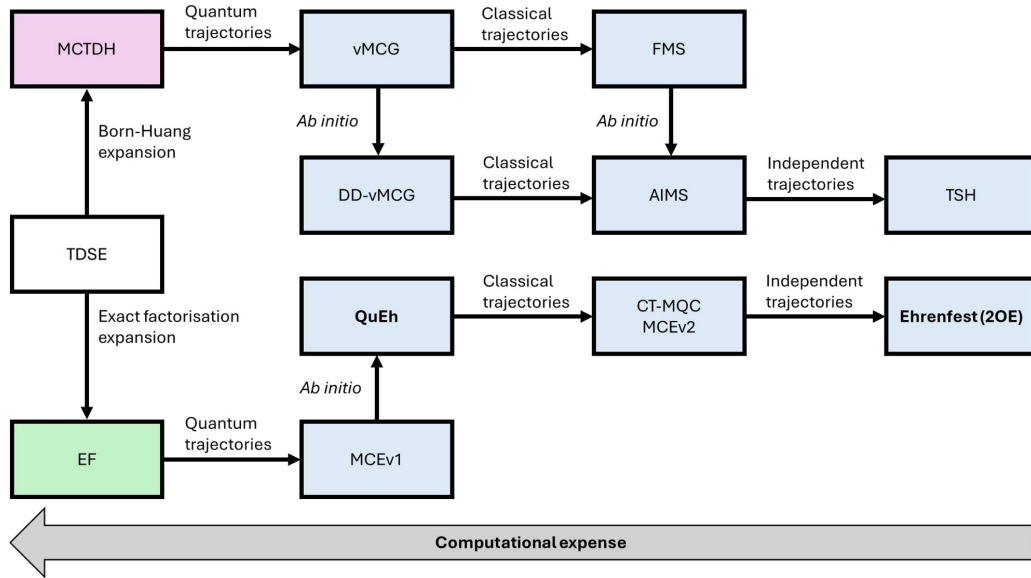


Figure 2.5: Flow chart showing how different nonadiabatic dynamic methods relate to one another, all beginning from the TDSE under which representation of the wavefunction ansatz one takes (whether Born-Huang, or exact factorisation), whether nuclear trajectories are propagated quantum mechanically or classically, if these trajectories are coupled to one another, and if dynamics requires a pre-computed potential surface or if they can be done *ab initio*/on-the fly. With additional approximations, the computational expense decreases, as shown by the arrow in the figure. In this thesis, the dynamics methods used are Qu-Eh and 2OE, as shown in **bold**.

potential surfaces which then simulate the motion of the nuclear wavepacket on them, which can be tedious. This has led to the development of *ab initio* trajectory-based methods, which calculate electronic structure properties on-the-fly, when they are required in simulation.

To make simulations of larger systems feasible, many of these on-the-fly methods introduce approximations. A high-level overview of these methods and how they relate to one another can be seen in Fig. 2.5. A common approach is to treat the nuclei classically while treating the electrons quantum mechanically, which leads to the family of semi-classical dynamics methods. These methods require a mediation between the classical and quantum parts of the simulation, nonadiabatic coupling being a prime example. Among them, trajectory surface hopping (TSH) allows stochastic transitions between adiabatic potential energy surfaces, while the Ehrenfest method describes motion along a single ‘mean-field’, time-dependent potential surface. However, such trajectory-based methods - using independent, non-interacting point trajectories - often struggle to describe key nonadiabatic processes such as wavepacket bifurcation and decoherence.

To overcome these limitations, more sophisticated methods have been developed that couple trajectories, often represented as Gaussian wavepackets (GWPs). Techniques such as *ab initio* multiple spawning (AIMS) and multiconfigurational Ehrenfest (MCE) improve the description of nonadiabatic dynamics by allowing interaction between trajectories. Similarly, coupling through quantum forces is implemented in the coupled-trajectory mixed quantum–classical (CT-MQC) method.

In certain phenomena, such as attochemistry or the formation of electronic coherences, accurate treatment of electron–nuclear coupling is crucial, and the classical treatment of nuclei may fail to capture the essential physics. To address this, methods such as the direct-dynamics variational multiconfigurational Gaussian (DD-vMCG) and Quantum Ehrenfest (Qu-Eh) approaches treat the nuclei quantum mechanically as coupled GWPs evolving on diabatic and Ehrenfest surfaces, respectively.

With the increased level of detail and physical accuracy in these methods comes greater computational cost. Thus, the choice of an appropriate approach depends on the balance between practicality and the level of detail required to capture the photochemical process of interest.

In the following section, we derive the second-order Ehrenfest (2OE) and Quantum Ehrenfest (Qu-Eh) methods, which will be employed in the subsequent chapters of this thesis. These methods offer an accurate framework for modeling nonadiabatic dynamics, and we will compare them with other approaches to highlight how their respective approximations and implementations influence the simulation of photochemical systems.

### 2.4.1 The TDSE

In time-dependent quantum mechanics, the molecular system evolves according to the time-dependent Schrödinger equation (TDSE):

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, \mathbf{R}, t) = \hat{H} \Psi(\mathbf{r}, \mathbf{R}, t). \quad (2.29)$$

The TDSE can only be solved analytically for very small systems (the hydrogen atom, for example). For larger systems, such as molecules, numerically exact solutions are possible by describing the nuclear wavepacket in a discrete basis such as a grid with  $N$  points, for  $d$  the number of degrees of freedom for the molecule.<sup>123</sup> However, this exact quantum dynamics approach scales in terms of computational expense as  $N^d$ . Practically, this means that numerically exact solutions are only possible for systems with a small number of degrees of freedom. Methods such as multi-configurational time-dependent Hartree (MCTDH)<sup>124,125</sup> can reduce this number of DOFs by making their discrete basis time dependent, and pairing strongly correlated degrees of freedom together, allowing for grid-based numerical simulations of larger systems; however, there is still an exponential increase with respect to the number of DOF. In addition, in these methods, the potential energy surfaces at these grid points must be calculated and fitted prior to simulation. In this section, we will discuss on-the-fly nonadiabatic dynamics methods, which aim to tackle the issues encountered by these grid based methods, principally:

- (i) simulation of high-number DOF systems such as medium-sized molecules ( $\geq 10$  atoms) and
- (ii) on-the-fly calculation of electronic structure information as required in dynamics. The first step of developing these methods involves providing an *ansatz* for the molecular wavefunction. This can be done in many ways, but for now we will use the exact factorisation (EF, a.k.a product) *ansatz*<sup>126</sup> which uses a product of a time-dependent electronic wavefunction that is parametrically dependent on the nuclei,  $\psi(\mathbf{r}, t; \mathbf{R})$ , and a time-dependent nuclear wavefunction,  $\chi(\mathbf{R}, t)$ :

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \chi(\mathbf{R}, t)\psi(\mathbf{r}, t; \mathbf{R}). \quad (2.30)$$

Another *ansatz* for the wavefunction is the Born-Huang representation,<sup>127</sup> where one has time-dependent nuclear coefficients,  $\chi_i(\mathbf{R}, t)$ , connected to time-independent electronic wavefunctions,  $\phi_i(\mathbf{r}; \mathbf{R})$ :

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_i \chi_i(\mathbf{R}, t)\phi_i(\mathbf{r}; \mathbf{R}). \quad (2.31)$$

This is an often used ansatz for dynamics methods<sup>128</sup> which will be encountered and discussed later. We first discuss the Ehrenfest method and its derivation.

### 2.4.2 The Ehrenfest method

The equations of motion for the electronic and nuclear parts of the Ehrenfest method<sup>129–132</sup> can be derived from the EF ansatz shown in Eqn 2.31 by using the Dirac-Frenkel variational principle (DFVP).<sup>57,58</sup> The DFVP allows us to obtain an optimal time evolution of an approximate wavefunction:

$$\langle \delta\Psi | i\frac{\partial}{\partial t} - \hat{H} | \Psi \rangle = 0. \quad (2.32)$$

The following derivation takes the same route as the work of M. Vacher *et al.*<sup>133,134</sup> Before deriving, an additional phase term is added to the ansatz to simplify later equations:

$$\Psi = \chi\psi \exp\left(\frac{i}{\hbar} \int^t E(t') dt'\right), \quad (2.33)$$

alongside internal phase factors for the nuclear and electronic parts of the wavefunction ansatz:

$$i\hbar\langle\chi|\dot{\chi}\rangle_{\mathbf{R}} = \langle\Psi|\hat{H}|\Psi\rangle_{\mathbf{r},\mathbf{R}} = E_{tot}, \quad (2.34)$$

$$i\hbar\langle\psi|\dot{\psi}\rangle_{\mathbf{r}} = \langle\Psi|\hat{H}_e|\Psi\rangle_{\mathbf{r},\mathbf{R}} = E(t), \quad (2.35)$$

where we introduce the  $\dot{\phantom{x}}$  superscript to denote a function which is being acted upon by  $\frac{\partial}{\partial t}$ . To obtain the electronic part of the EOM, we use the DFVP by varying with respect to the electronic wavefunction:

$$\langle \delta\Psi | \hat{H} | \Psi \rangle_{\mathbf{R}} = i\hbar\langle \delta\Psi | \dot{\Psi} \rangle_{\mathbf{R}}. \quad (2.36)$$

We first expand the LHS of Eqn 2.36:

$$\begin{aligned} \langle \delta\Psi | \hat{H} | \Psi \rangle_{\mathbf{R}} &= \langle \chi | \hat{H} | \psi \chi \rangle_{\mathbf{R}} \\ &= \langle \chi | \hat{T}_N + \hat{T}_e + \hat{V}_{N-e} | \chi \rangle_{\mathbf{R}} \psi \\ &= \left[ \langle \chi | \hat{T}_N | \chi \rangle_{\mathbf{R}} + \hat{T}_e + \langle \chi | \hat{V}_{N-e} | \chi \rangle_{\mathbf{R}} \right] \psi, \end{aligned} \quad (2.37)$$

followed by the RHS:

$$\begin{aligned}
i\hbar\langle\delta\Psi|\dot{\Psi}\rangle_{\mathbf{R}} &= i\hbar\langle\chi|\dot{\psi}\chi + \dot{\chi}\psi + \frac{i}{\hbar}E(t)\chi\psi\rangle_{\mathbf{R}} \\
&= i\hbar\langle\chi|\chi\rangle_{\mathbf{R}}\dot{\psi} + i\hbar\langle\chi|\dot{\chi}\rangle_{\mathbf{R}}\psi - E(t)\langle\chi|\chi\rangle_{\mathbf{R}}\psi \\
&= i\hbar\dot{\psi} + (E_{tot} + E(t))\psi.
\end{aligned} \tag{2.38}$$

We now insert Eqn 2.37 and Eqn 2.38 into Eqn 2.36 to give:

$$\begin{aligned}
i\hbar\dot{\psi} &= [\langle\chi|\hat{T}_N|\chi\rangle_{\mathbf{R}} + \hat{T}_e + \langle\chi|\hat{V}_{N-e}|\chi\rangle_{\mathbf{R}}]\psi - (E_{tot} + E(t))\psi \\
&= \left[\hat{T}_e + \langle\chi|\hat{V}_{N-e}|\chi\rangle_{\mathbf{R}}\right]\psi.
\end{aligned} \tag{2.39}$$

In explicit form, this is:

$$i\hbar\frac{\partial\psi(\mathbf{r}, t; \mathbf{R})}{\partial t} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 \psi(\mathbf{r}, t; \mathbf{R}) + \langle\chi(\mathbf{R}, t)|\hat{V}_{N-e}(\mathbf{r}, \mathbf{R})|\chi(\mathbf{R}, t)\rangle_{\mathbf{R}} \cdot \psi(\mathbf{r}, t; \mathbf{R}). \tag{2.40}$$

Similarly, we now obtain the EOM for the nuclear part by using the DFVP and varying with respect to the nuclear part of the wavefunction:

$$\langle\delta\Psi|\hat{H}|\Psi\rangle_{\mathbf{r}} = i\hbar\langle\delta\Psi|\dot{\Psi}\rangle_{\mathbf{r}}. \tag{2.41}$$

For the LHS:

$$\begin{aligned}
\langle\delta\Psi|\hat{H}|\Psi\rangle_{\mathbf{r}} &= \langle\psi|\hat{H}|\psi\chi\rangle_{\mathbf{r}} \\
&= \langle\psi|\hat{T}_N + \hat{H}_e|\psi\rangle_{\mathbf{r}}\chi \\
&= \left[\hat{T}_N + \langle\psi|\hat{H}_e|\psi\rangle_{\mathbf{r}}\right]\chi,
\end{aligned} \tag{2.42}$$

and for the RHS:

$$\begin{aligned}
 i\hbar\langle\delta\Psi|\dot{\Psi}\rangle_{\mathbf{R}} &= i\hbar\langle\psi|\dot{\psi}\chi + \psi\dot{\chi} + \frac{i}{\hbar}E(t)\chi\psi\rangle_{\mathbf{r}} \\
 &= i\hbar\langle\psi|\dot{\psi}\rangle_{\mathbf{r}}\chi + i\hbar\langle\psi|\psi\rangle_{\mathbf{r}}\dot{\chi} - E(t)\langle\psi|\psi\rangle_{\mathbf{r}}\chi \\
 &= i\hbar\dot{\chi}.
 \end{aligned} \tag{2.43}$$

Again, we insert Eqn 2.42 and Eqn 2.43 into Eqn 2.41 to give:

$$i\hbar\dot{\chi} = \left[ \hat{T}_N + \langle\psi|\hat{H}_e|\psi\rangle_{\mathbf{r}} \right] \chi. \tag{2.44}$$

Explicitly, this is written as:

$$i\hbar\frac{\partial\chi(\mathbf{R},t)}{\partial t} = -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 \chi(\mathbf{R},t) + \langle\psi(\mathbf{r},t;\mathbf{R})|\hat{H}_e(\mathbf{r};\mathbf{R})|\psi(\mathbf{r},t;\mathbf{R})\rangle_{\mathbf{r}} \cdot \chi(\mathbf{R},t). \tag{2.45}$$

The Eqns 2.40 and 2.45 correspond to the time-dependent Hartree method.<sup>135</sup> To move from this to the Ehrenfest method, Eqns 2.40 and 2.45 must be taken to the classical limit. To do this, the nuclear wavefunction is expressed as:

$$\chi = \exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right), \tag{2.46}$$

where  $S(\mathbf{R},t)$  is a complex phase factor. Inserting this into Eqn 2.45 gives:

$$\frac{\partial S}{\partial t} + \sum_I \frac{1}{2M_I} \left(\vec{\nabla}_I S\right)^2 + \langle\psi|\hat{H}_e|\psi\rangle_{\mathbf{r}} = \hbar^2 \sum_I \frac{1}{2M_I} \nabla_I^2 S. \tag{2.47}$$

Taking the classical limit  $\hbar \rightarrow 0$  and defining the Newtonian momentum as  $\mathbf{P} = \vec{\nabla}_I S$  then gives:

$$\mathbf{F}_I = \frac{d\mathbf{P}_I}{dt} = -\vec{\nabla}_I \langle\psi|\hat{H}_e|\psi\rangle_{\mathbf{r}}, \tag{2.48}$$

which is the nuclear force for the Ehrenfest method. For the electronic part, the nuclear wave function in Eqn 2.40 is treated as a delta function to give:

$$i\hbar \frac{\partial \psi}{\partial t} = \left( -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 + \hat{V}_{n-e} \right) \psi = \hat{H}_e \cdot \psi. \quad (2.49)$$

Generally, the above Eqns 2.48 and 2.49 define the Ehrenfest method.

As an aside, if the electronic wavefunction is described in a basis of time-independent adiabatic states,  $\phi^{ad}(\mathbf{r}; \mathbf{R})$ , and corresponding energies  $E^{ad}(\mathbf{R})$  with time-dependent coefficients,  $c_i(t)$ :

$$\psi = \sum_i c_i(t) \phi_i^{ad}(\mathbf{r}; \mathbf{R}). \quad (2.50)$$

Inserting this into Eqn 2.48 gives:

$$\mathbf{F}_I = -\sum_i |c_i|^2 \frac{\partial E_i^{ad}}{\partial \mathbf{R}_I} + \sum_{i,j} c_i^* c_j \langle \phi_i^{ad} | \frac{\partial}{\partial \mathbf{R}_I} \phi_j^{ad} \rangle_{\mathbf{r}} (E_j^{ad} - E_i^{ad}). \quad (2.51)$$

In this representation, the force is dependent on the first term, which corresponds to the average of the gradient of the adiabatic state weighted by their state population, and also an additional nonadiabatic inter-state gradient contribution which is weighted by the energy difference between states, as well as the product of their respective state populations. In the adiabatic basis, inserting Eqn 2.50 into Eqn 2.49, and applying the chain rule gives:

$$i\hbar \frac{\partial c_i}{\partial t} = c_i E_i^{ad}(\mathbf{R}) - i\hbar \sum_{i \neq j} c_j \langle \phi_i^{ad} | \partial_{\mathbf{R}} \phi_j^{ad} \rangle_{\mathbf{r}} \cdot \frac{\partial \mathbf{R}}{\partial t}, \quad (2.52)$$

where we begin to see time-dependent nonadiabatic couplings, similar to those in time-independent form in Eqn 2.11.

### 2.4.2.1 Implications of the Ehrenfest method

According to Eqn 2.48, the force the nuclei experience is the expectation value of the electronic Hamiltonian with respect to the electronic wavefunction. In other words, the nuclei move ac-

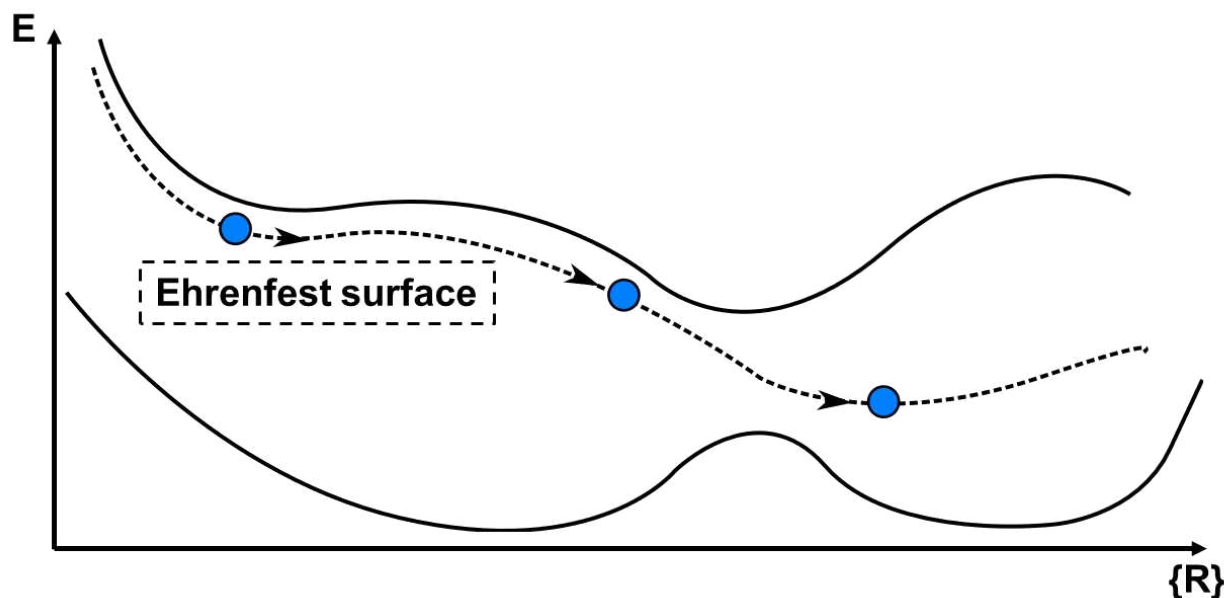


Figure 2.6: Cartoon for the Ehrenfest method, where a single point trajectory moves classically along an Ehrenfest ‘mean-field’ potential surface, constructed from a set of states (in the case of this cartoon, adiabatic states).

cording to the electrons in a ‘mean-field’ fashion. In conjunction with the nuclear wavefunction being treated as delta functions from Eqn 2.49, the Ehrenfest method can be considered as point trajectories moving classically along an effective single time-dependent potential energy surface (or Ehrenfest surface) (Fig. 2.6). This ‘mean-field’ approach is useful in describing regions of strong nonadiabaticity where electronic states are close or equal to each other,<sup>136–138</sup> such as conical intersections or avoided crossings, where other methods, such as surface hopping (which is discussed further in Section 2.4.3),<sup>139</sup> require some *ad hoc* criterion to determine when to hop over to another state. The Ehrenfest method, on the other hand, can smoothly cross through. However, this mean-field approach also means that when the topology of PESs strongly differ that the nuclear trajectories can become artificial. Additionally, a result of the Ehrenfest method leads to a lack of detailed balance for properties such as electronic state populations.<sup>140,141</sup> An important point is that as the Ehrenfest method propagates a single point trajectory, modelling the decoherence or bifurcation of a nuclear wavepacket is not possible unless it is accounted for by using an ensemble of trajectories to approximate it. Various sampling methods are available when creating such an ensemble, each with advantages and disadvantages.<sup>142–146</sup> However, these trajectories will not interact and couple with each other, resulting

in a lack of coupling between different motions within the system. Specifically, motion along the derivative coupling of the system will not be properly described, which is an important level of detail when studying coupled electron-nuclear phenomena such as electron dynamics and coherences.<sup>147</sup> Though it is worth noting that despite this semi-classical methods such as Ehrenfest and surface hopping have been successfully used to study the electron nuclear-coupled dynamics of a range of molecular systems, and study attochemical phenomena such as electronic coherences and their influences on dynamics.<sup>148–150</sup> This includes the second order Ehrenfest (2OE) method used in this thesis which shall be shortly discussed.<sup>49,151–161</sup> In more general terms, this lack of interaction can lead to decoherence/overcoherence issues in nonadiabatic dynamics.<sup>162,163</sup> These issues can be circumvented by coupling trajectories together, often at higher computational cost, which is done in other methods which shall be discussed later, such as multiconfigurational Ehrenfest (MCE),<sup>164–166</sup> *ab initio* multiple spawning (AIMS),<sup>167,168</sup> Quantum Ehrenfest (Qu-Eh),<sup>27</sup> and others.

#### 2.4.2.2 The second order Ehrenfest (2OE) method

How the Ehrenfest method is implemented in practice changes depending on the developer. In the present work, the second order Ehrenfest method (2OE)<sup>26</sup> is used, which differs from other Ehrenfest methods which only use first derivatives for propagation<sup>169</sup> by using analytical second derivatives which allow for longer and more numerically stable time steps. In 2OE, the dynamics method is intertwined with the CASSCF electronic structure method,<sup>†</sup> where the electronic wavefunction is described in basis of CSFs. These CSFs are quasi-diabatic, and can be related to the adiabatic basis via a unitary transformation  $\mathbf{U}$ . As discussed in Section 2.2.3, within this basis the nonadiabatic coupling vectors are approximately zero, leading to a similar form of the EOM for the electronic part in Eqn 2.52 but with the second RHS term removed:

$$i\hbar \frac{\partial c_i^{CSF}(t)}{\partial t} = c_i^{CSF}(t) E_i(\mathbf{R}), \quad (2.53)$$

---

<sup>†</sup>It is worth noting that there is also a TDDFT-ED method which intertwines the Ehrenfest method with TDDFT formalism, and is also used to study attosecond dynamics.<sup>148,170,171</sup>

where  $c_i^{CSF}(t)$  is the time-dependent CSF expansion coefficient. In practice, the coefficients for the CSFs at a given time step  $t_n$  can be represented by a column vector  $\mathbf{A}(t_n)$ , and Eqn 2.53 becomes:

$$\mathbf{A}(t_n) = \mathbf{U}(t_n) \exp \left( -\frac{i}{\hbar} \mathbf{H}_e^{ad}(t_n)(t_n - t_{n-1}) \right) \mathbf{U}^\dagger(t_n) \mathbf{A}(t_{n-1}), \quad (2.54)$$

where the nuclei are propagated via a Hessian-based predictor-corrector scheme developed by Hase and Shlegel.<sup>172</sup> This requires the electronic energy of the Ehrenfest potential, and its first and second derivatives with respect to the nuclear coordinate,  $\mathbf{R}$ . The 2OE method uses CAS-CI to generate the energies and computes the gradient and Hessian analytically in a form derived from Almlöf and Taylor.<sup>101</sup> At each time step, the orbitals are re-orthogonalized and treated to a single SCF cycle to follow the evolving nuclear geometry, ensuring that the (quasi-)diabatic CASSCF electronic basis remains effectively unchanged throughout the dynamics. The 2OE dynamics method is performed with a development version of the GAUSSIAN software package.<sup>173</sup> Initial conditions for the nuclei in 2OE are straightforward, in the sense that trajectories begin with an initial geometry and momentum either along either a cartesian vector or a normal mode (NM). The electronic wavefunction in 2OE, as well as Qu-Eh which will be discussed later, can also be initiated in a number of ways. Dynamics can be initiated on pure adiabatic or diabatic states, according to specific CI or CSF vectors from the CASSCF wavefunction. Additionally, dynamics can be initiated with an electronic wavefunction,  $\Theta$ , which is a superposition of two electronic states,  $\phi_I$  and  $\phi_{II}$ , according to the equation:

$$|\Theta\rangle = \cos\left(\frac{\theta}{2}\right) |\phi_I\rangle + \sin\left(\frac{\theta}{2}\right) e^{i\epsilon} |\phi_{II}\rangle, \quad (2.55)$$

where the two inputs,  $\theta$  and  $\phi$ , control the relative composition of the mixture and the relative phase between the two states respectively.

Additionally, in 2OE (as well as in Qu-Eh which will be discussed later) the first-order effect of a laser pulse within the dipole approximation can be implemented into the code.<sup>174,175</sup> The electric field of implemented pulse has the form:

$$\mathbf{E}(t) = E_0 \cdot \cos(\omega(t - t_0) + \gamma) \cdot e^{-\sigma(t-t_0)^2}, \quad (2.56)$$

where  $E_0 = \sqrt{E_x^2 + E_y^2 + E_z^2}$  is the maximum value of the amplitude of the electric field,  $\omega$  is the frequency of the pulse,  $t_0 = \frac{t_{\text{on}} - t_{\text{off}}}{2}$  where  $t_{\text{on}}$  and  $t_{\text{off}}$  refer to the times at which the pulse is switched on and switched off in simulation,  $\gamma$  is the carrier envelope phase (CEP) and  $\sigma = \frac{\sqrt{2\ln(2)}}{\text{FWHM}}$  where FWHM = full-width half-maximum of the pulse. The pulse is modelled by including the time-dependent interaction of the electric field of the laser pulse and the dipole moment of the molecular system, which is added into the one-electron Hamiltonian:

$$\hat{h}_{el}(t) = \langle i | \hat{h}_0 | j \rangle + \langle i | \vec{\mu} | j \rangle \cdot \mathbf{E}(t), \quad (2.57)$$

where  $|i\rangle$  is the orbital basis,  $\hat{h}_0$  is the one electron Hamiltonian operator, and  $\vec{\mu}$  is the transition dipole moment.

### 2.4.3 Trajectory surface hopping

Trajectory surface hopping (TSH)<sup>139</sup> (Fig. 2.7) is a dynamics method similar to that of the Ehrenfest method, where a nuclear single point trajectory moves along a potential surface according to classical forces. The difference lies in that in TSH there is no Ehrenfest surface. In TSH, there are many adiabatic states and the trajectory moves along one of these at a time – the current one being the ‘active’ state. Because of this, however, nonadiabatic effects, such as decay onto another state, and/or passing through a CI, have to be implemented in an *ad hoc* manner. This is done through a ‘hop’ determined by some criterion. The most popular method is known as the fewest switches algorithm developed by Tully,<sup>139</sup> where if a random number is smaller than a property proportional to the nonadiabatic coupling, then a ‘hop’ will be made to the next state. When a hop occurs and the trajectory changes state, energy must be conserved and hence another criterion for this purpose is necessary. This is typically implemented by rescaling the velocity of a trajectory along the directions of the nonadiabatic coupling vectors.<sup>176</sup> The *ad hoc* hopping criterion can cause issues. Frustrated hops are an example, which are hops that have been accepted but cannot occur as they would break energy conservation.<sup>177</sup>

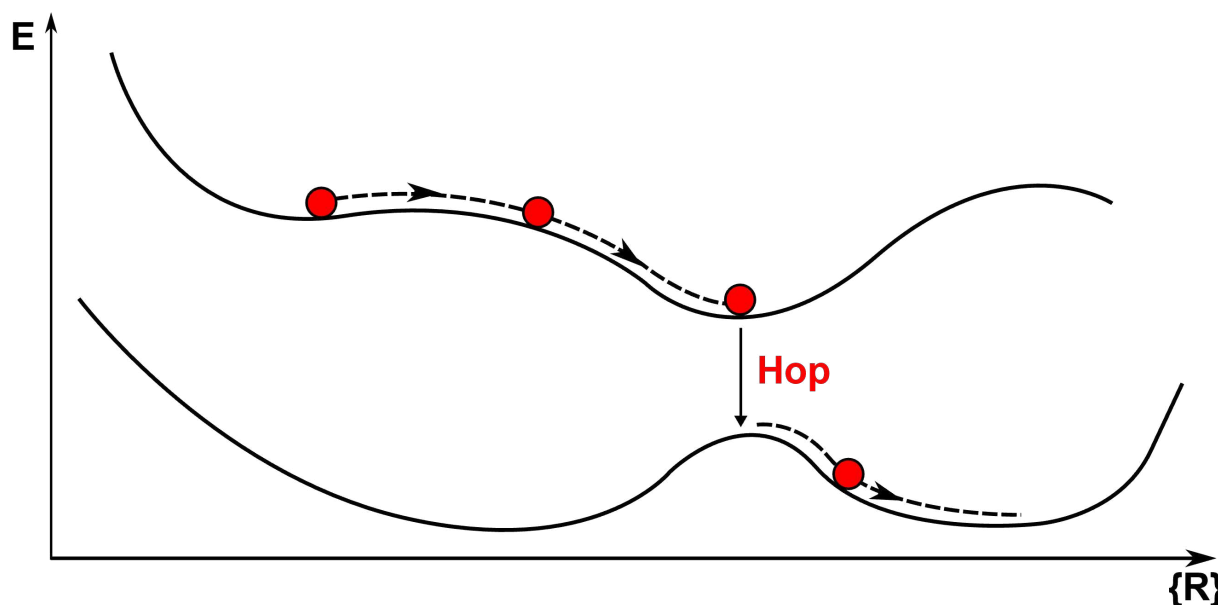


Figure 2.7: A cartoon of a trajectory surface hopping (TSH) nuclear point trajectory moving classically along an adiabatic potential surface. An *ad hoc* criterion (usually linked to the nonadiabatic coupling) is used to allow the trajectory to hop from one state to another, which allows nonadiabatic coupling to be modelled for the system.

An issue TSH shares with classical Ehrenfest methods is that trajectories do not couple to each other, hence overcoherence arises.<sup>177,178</sup> This can be addressed in various forms of decoherence correction in TSH,<sup>179</sup> and similar corrections also exist for the Ehrenfest method.<sup>180</sup> In systems where there is a coherent superposition of electronic states, the initialisation of the electron dynamics is important. It has been shown that for the classical Ehrenfest and TSH methods, both can struggle to capture the correct dynamics for electronic state superposed systems due to issues related to coherence and for mean-field effects for Ehrenfest.<sup>181</sup> Using a spin mapping approach for both methods can improve this, however these methods can still fail to capture some electron-nuclear coupled phenomena due to the restriction that the nuclei follow classical trajectories.<sup>182–187</sup>

#### 2.4.4 Coupled trajectory methods

The full multiple spawning (FMS)<sup>188</sup> approach can be considered a linker between the independent trajectory Ehrenfest and TSH methods and the fully quantum dynamics methods such as Qu-Eh and DD-vMCG to be discussed later. In FMS, the nuclear wavepacket is described

by a basis of frozen Gaussian wavepackets (GWPs), which move classically across typically adiabatic potential surfaces, like that of surface hopping. When the GWPs approach a region of strong nonadiabaticity, there is a criterion related to the nonadiabatic coupling vectors which if passed ‘spawns’ a child GWP on the other PES. In dynamics, these ‘parent’ and child GWPs are coupled to each other and given a large enough basis and all matrix elements are calculated exactly, the FMS method is formally exact. In practice, however, one would need a precomputed potential surface to perform such dynamics.

The *ab initio* multiple spawning (AIMS)<sup>167</sup> method enables an on-the-fly version of this approach through two key approximations: (i) a zero-order saddle point approximation which allows for calculation of matrix elements on the fly and (ii) an initial first generation (IFG) approximation, which assumes that as a nuclear wavepacket decoheres very quickly after dynamics initiates, the initial GWPs are uncoupled from  $t=0$  (but do couple to their child-GWPs). In the AIMS method, there is the advantage that parent and child GWPs are coupled and that the basis is adaptive, unlike those in Ehrenfest and surface hopping where trajectories are entirely independent. This allows for a more effective treatment of nonadiabatic scenarios where, for example, a nuclear wavepacket bifurcates. The method, however, does suffer from a finite basis, as well as from the approximations which make it an *ab initio* method, and ultimately, as the nuclei are propagated classically will not capture electron-nuclear coupled dynamics entirely.<sup>147,182</sup> The dynamics method is also more computationally costly than Ehrenfest and surface hopping methods. As more GWPs spawn, more electronic structure calculations are needed, hence becomes more costly over the course of dynamics, though an adapted method called AIMSWISS aims to cut this down via a stochastic algorithm.<sup>189</sup>

The multiconfigurational Ehrenfest method MCEv2 developed by Shalishilin *et al.*,<sup>165</sup> can be considered the ‘AIMS-like’ version of the Ehrenfest method, where the nuclear wavepacket is described by a set of coupled GWPs which each move classically along individual Ehrenfest potential surfaces. As we will see later, this is like the Qu-Eh method if the nuclei were treated classically. We note that in MCEv2 the basis is not adaptive. There is a version of this method known as Ab Initio Multiple Cloning (AIMC),<sup>166</sup> which solves an issue wherein MCE fails to sample phase space correctly due to artificial Ehrenfest surfaces trapping GWPs in

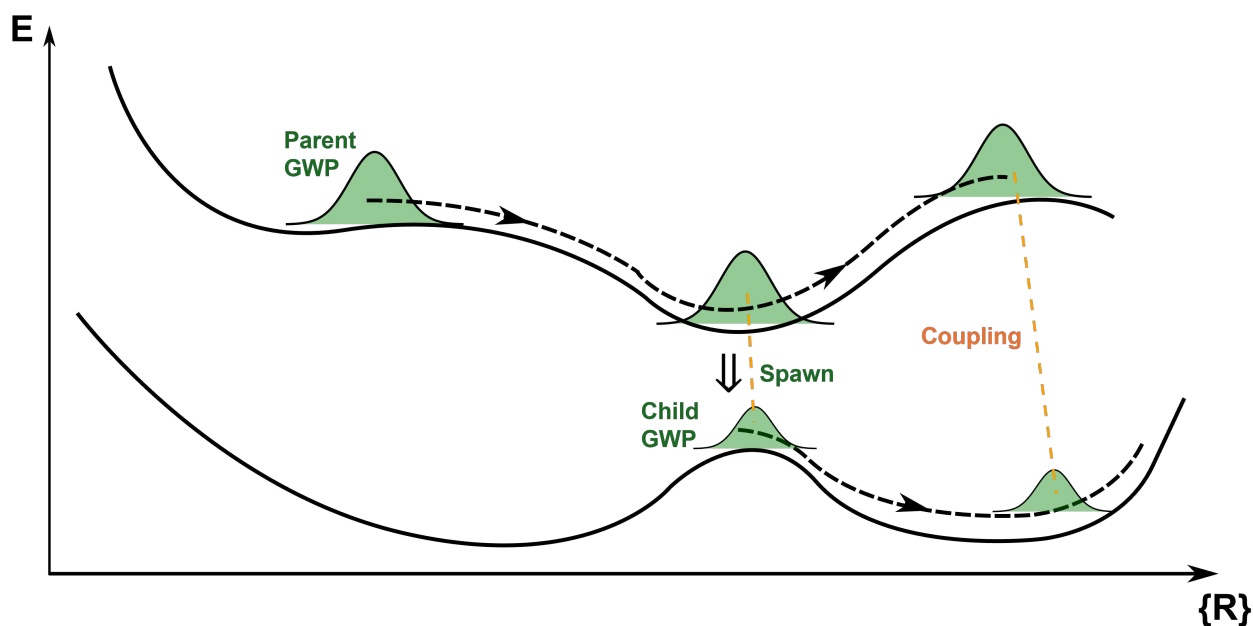


Figure 2.8: Cartoon of full multiple spawning (FMS) and *ab initio* multiple spawning (AIMS) methods. Both FMS and AIMS use frozen GWPs which move classically along an excited state potential surface. A spawning algorithm creates a child GWP which couples to the parent GWP when in a region of strong nonadiabaticity, allowing for a more accurate modelling of wavepacket bifurcation than standard Ehrenfest and TSH methods.

regions where it should physically be able to access, and so spawns child GWPs onto adiabatic potential surfaces. Given a sufficient number of GWPs, both methods should converge to the same result.<sup>168</sup>

In a similar vein to MCE, the coupled-trajectory mixed quantum-classical (CT-MQC) method of Agostini *et al.*<sup>190–192</sup> has classical coupled trajectories moving along a time-dependent potential energy surface, with the primary difference being that the forces are derived by different terms defined by the EF ansatz. In CT-MQC, a time-dependent vector potential term determines the forces for the trajectories, where in the EOM a quantum momentum term allows for the coupling and overcoherence correction which is similar in MCE. When this term is neglected, this method reduces down to the Ehrenfest method. CT-MQC as a method appears to perform better in describing an initial coherent superposition of electronic states than the Ehrenfest method or TSH,<sup>181</sup> but still misses detail, most likely due to classical nuclear motion.

### 2.4.5 Quantum Ehrenfest (Qu-Eh)

For the Qu-Eh method,<sup>27</sup> we take the EF ansatz from Eqn 2.31, and, as done in the DD-vMCG method,<sup>193</sup> we expand the nuclear wavefunction as a set of frozen time-dependent GWPs,  $g_i(\mathbf{R}, t)$ :

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_i A_i(t) g_i(\mathbf{R}, t) \psi(\mathbf{r}, t; \mathbf{R}), \quad (2.58)$$

where  $A_i(t)$  are time-dependent coefficients for the GWPs. Then, similar to the approach for deriving the time-dependent Hartree and Ehrenfest methods in Section 2.4.2, we apply the DFVP (Eqn 2.32) to this ansatz (Eqn 2.58) to find the EOMs. First, we vary the wavefunction with respect to the coefficients,  $\delta\Psi = g_i\psi\delta A_i$ , alongside the normalisation conditions required in the EF formalism,  $\langle\psi|\psi\rangle_{\mathbf{r},\mathbf{R}} = 1$  and  $i\langle\psi|\dot{\psi}\rangle_{\mathbf{r},\mathbf{R}} = \Theta(\mathbf{R})$ , where  $\Theta(\mathbf{R})$  is some arbitrary real function. This leads to the EOM:

$$i\dot{A}_k = \sum_{i,j} S_{ki}^{-1} (H_{ij} - i\tau_{ij} - T_{ij}) A_j, \quad (2.59)$$

where  $S_{ij} = \langle g_i | g_j \rangle_{\mathbf{r},\mathbf{R}}$  is the GWP overlap,  $H_{ij} = \langle g_i \psi | \hat{H} | g_j \psi \rangle_{\mathbf{r},\mathbf{R}}$  is the Hamiltonian, and  $\tau_{ij} = \langle g_i | \dot{g}_j \rangle_{\mathbf{R}}$  is the time-derivative GWP overlap matrix terms, and  $T_{ij} = \langle g_i | \Theta | g_j \rangle_{\mathbf{R}}$ . Next, the DFVP is applied to the time-dependent parameters, where  $\lambda_i^\alpha$  is the  $\alpha$ th parameter of the  $i$ th GWP. This variation yields:

$$i\dot{\lambda}_{\beta k} = \sum_{\alpha,i,j} C_{\beta k \alpha i}^{-1} \rho_{ij} \left( H_{ij}^{\alpha 0} - T_{ij}^{\alpha 0} - \sum_{l,m} S_{il}^{\alpha 0} S_{lm}^{-1} (H_{mj} - T_{mj}) \right), \quad (2.60)$$

where S, H, and T denote various derivative overlap matrix terms:

$$\begin{aligned} H_{ij}^{\alpha 0} &= \left\langle \frac{\partial g_i}{\partial \lambda_i^\alpha} \psi \middle| \hat{H} \middle| g_j \psi \right\rangle_{\mathbf{r},\mathbf{R}}, & S_{ij}^{\alpha 0} &= \left\langle \frac{\partial g_i}{\partial \lambda_i^\alpha} \middle| g_j \right\rangle_{\mathbf{R}}, \\ S_{ij}^{\alpha \beta} &= \left\langle \frac{\partial g_i}{\partial \lambda_i^\alpha} \middle| \frac{\partial g_j}{\partial \lambda_j^\beta} \right\rangle_{\mathbf{R}}, & T_{ij}^{\alpha 0} &= \left\langle \frac{\partial g_i}{\partial \lambda_i^\alpha} \middle| \Theta \middle| g_j \right\rangle_{\mathbf{R}}. \end{aligned} \quad (2.61)$$

The C-matrix,  $C_{\beta k \alpha i} = \rho_{ij} \left( S_{ij}^{\alpha \beta} - \sum_{l,m} S_{il}^{\alpha 0} S_{lm}^{-1} (H_{mj} - T_{mj}) \right)$ , is a matrix involving various parameter-derivative overlaps as shown above, and  $\rho_{ij} = A_i^* A_j$  corresponds to the nuclear

density matrix.

The final EOM is derived by varying the wavefunction with respect to the electronic wavefunction,  $\psi$ , at a specific nuclear coordinate,  $\mathbf{R}$  (which we will show functional dependence for in this section for clarity), which gives:

$$i|\dot{\psi}\rangle_{\mathbf{R}} = [\rho(\mathbf{R})]^{-1} \left( \sum_{i,j} A_i^* H_{ij}^g(\mathbf{R}) A_j - A_i^* H_{ij}(\mathbf{R}) A_j + A_i^* T_{ij}(\mathbf{R}) A_j \right) |\psi\rangle_{\mathbf{R}}, \quad (2.62)$$

where  $\rho(\mathbf{R})$  is the nuclear density at nuclear coordinate  $\mathbf{R}$  given by:

$$\rho(\mathbf{R}) = \sum_{i,j} A_i^* \langle g_i | g_j \rangle_{\mathbf{R}} A_j, \quad (2.63)$$

and  $H_{ij}^g(\mathbf{R}) = \langle g_i | \hat{H} | g_j \rangle_{\mathbf{R}}$ .

The Eqns 2.59, 2.60, and 2.62 give a coupled set of EOMs for the GWP coefficients, parameters, and the electronic wavefunction respectively for our ansatz. A few more terms are now defined to rearrange these equations to arrive at the Qu-Eh method.

We start with the electronic part by explicitly writing out and then rewriting the Hamiltonian matrix element at a given nuclear coordinate  $\mathbf{R}$ ,  $H_{ij}(\mathbf{R})$ :

$$\begin{aligned} H_{ij}(\mathbf{R}) &= \langle g_i \psi | \hat{T}_N + \hat{H}_{el} | g_j \psi \rangle_{\mathbf{R}} \\ &= g_i^*(\mathbf{R}) \langle \psi | \hat{T}_N | \psi \rangle_{\mathbf{R}} g_j(\mathbf{R}) + S_{ij}(\mathbf{R}) V(\mathbf{R}), \end{aligned} \quad (2.64)$$

where  $\hat{T}_N$  is the nuclear KE operator,  $\hat{H}_{el}$  is the electronic Hamiltonian operator,  $S_{ij}(\mathbf{R}) = \langle g_i | g_j \rangle_{\mathbf{R}}$  is the GWP overlap term, and  $V(\mathbf{R})$  defines our time-dependent Ehrenfest potential term:

$$V(\mathbf{R}) = \langle \psi | \hat{H} | \psi \rangle_{\mathbf{R}}. \quad (2.65)$$

This brings in the characteristic of the coupled GWPs moving according to the TDSE along an Ehrenfest potential surface. If written in mass-weighted coordinates, where  $\hat{T}_N = -\frac{1}{2} \nabla \cdot \nabla$ ,

then:

$$\langle \psi | \hat{T}_N | \psi \rangle_{\mathbf{R}} = -\frac{1}{2} \nabla^2 - \langle \psi | \nabla \psi \rangle_{\mathbf{R}} \cdot \nabla - \frac{1}{2} \langle \psi | \nabla^2 \psi \rangle_{\mathbf{R}} = \hat{T}_N + 2\mathbf{F}(\mathbf{R}) \cdot \nabla + G(\mathbf{R}), \quad (2.66)$$

where  $\mathbf{F}(\mathbf{R})$  is a vector derivative term and  $G(\mathbf{R})$  is a scalar derivative term. Now, we can insert this into Eqn 2.64 to give:

$$H_{ij}(\mathbf{R}) = \langle g_i | \hat{T}_N g_j \rangle_{\mathbf{R}} + 2\mathbf{F}(\mathbf{R}) \cdot \langle g_i | \nabla g_j \rangle_{\mathbf{R}} + S_{ij}(\mathbf{R})G(\mathbf{R}) + S_{ij}V(\mathbf{R}), \quad (2.67)$$

where on the RHS the first term corresponds to the GWP nuclear KE, the second term couples the electronic and nuclear motion via an Ehrenfest derivative coupling, and the third term acts as a nonadiabatic correction to the Ehrenfest potential. The next term which has yet to be defined is  $\Theta(\mathbf{R})$ , which we shall set to:

$$\Theta(\mathbf{R}) = 2 \sum_{i,j} A_i^* \frac{\mathbf{F}(\mathbf{R}) \cdot \langle g_i | \nabla g_j \rangle_{\mathbf{R}}}{\rho(\mathbf{R})} A_j + G(\mathbf{R}). \quad (2.68)$$

This is done for the purpose of changing the EOMs of Eqns 2.59, 2.60, and 2.62 into the more pragmatically useful forms:

$$i\dot{A}_k = \sum_{i,j} S_{ki}^{-1} (H_{ij}^N - i\tau_{ij}) A_j, \quad (2.69)$$

$$i\dot{\lambda}_{\beta k} = \sum_{\alpha, i, j} C_{\beta k \alpha i}^{-1} \rho_{ij} \left( H_{ij}^{N(\alpha 0)} - \sum_{l, m} S_{il}^{(\alpha 0)} S_{lm}^{-1} H_{mj}^N \right), \quad (2.70)$$

$$i|\dot{\psi}\rangle_{\mathbf{R}} = \left( \hat{H}_{el}(\mathbf{R}) - V(\mathbf{R}) - \frac{1}{2} \nabla^2 + [\rho(\mathbf{R})]^{-1} i\mathbf{P}(\mathbf{R}) \cdot \nabla \right) |\psi\rangle_{\mathbf{R}}, \quad (2.71)$$

where  $H_{ij}^N$  is defined as the nuclear Hamiltonian matrix term:

$$H_{ij}^N = \langle g_i | \hat{T}_N g_j \rangle_{\mathbf{R}} + \langle g_i | V | g_j \rangle_{\mathbf{R}} + 2\mathbf{F}(\mathbf{R}) \cdot \langle g_i | \nabla g_j \rangle_{\mathbf{R}} - 2 \sum_{i,j} A_i^* \frac{\mathbf{F}(\mathbf{R}) \cdot \langle g_i | \nabla g_j \rangle_{\mathbf{R}}}{\rho(\mathbf{R})} A_j, \quad (2.72)$$

and  $\mathbf{P}(\mathbf{R}) = -i \sum_{i,j} A_i^* \langle g_i | \vec{\nabla} g_j \rangle_{\mathbf{R}} A_j$  is the nuclear momentum at  $\mathbf{R}$ . Up to this point the EOMs are formally exact, but practically difficult to solve. The final change made now is to expand the electronic wavefunction,  $\psi(\mathbf{r}, t; \mathbf{R})$ , into a basis of orthonormal time-independent electronic

functions,  $\phi_i(\mathbf{r}; \mathbf{R})$ ;

$$|\psi(\mathbf{r}, t; \mathbf{R})\rangle = \sum_i c_i(t) |\phi_i(\mathbf{r}; \mathbf{R})\rangle. \quad (2.73)$$

Inserting this into Eqn 2.71, and accounting for orthonormality yields:

$$i\dot{c}_i = \sum_j \left( H_{el,ij}(\mathbf{R}) - \delta_{ij} V(\mathbf{R}) - \frac{1}{2} G_{ij}(\mathbf{R}) + [\rho(\mathbf{R})]^{-1} i\mathbf{P}(\mathbf{R}) \cdot D_{ij}(\mathbf{R}) \right) c_j, \quad (2.74)$$

where  $D_{ij}(\mathbf{R}) = \langle \phi_i | \nabla \phi_j \rangle_{\mathbf{R}}$  and  $G_{ij}(\mathbf{R}) = \langle \phi_i | \nabla^2 \phi_j \rangle_{\mathbf{R}}$  are the derivative coupling matrices. In the Qu-Eh method, similar to that of the 2OE method, the basis of the time-independent electronic states are in the CSF basis, which are quasi-diabatic. As a result, these derivative coupling matrices are also approximately zero. This leads to the final EOMs which define the Qu-Eh method:

$$i\dot{A}_k = \sum_{i,j} S_{ki}^{-1} (H_{ij}^N - i\tau_{ij}) A_j, \quad (2.75)$$

$$i\dot{\lambda}_{\beta k} = \sum_{\alpha, i, j} C_{\beta k \alpha i}^{-1} \rho_{ij} \left( H_{ij}^{N(\alpha 0)} - \sum_{l, m} S_{il}^{\alpha 0} S_{lm}^{-1} H_{mj}^N \right), \quad (2.76)$$

$$i\dot{c}_i = \sum_j (H_{el,ij}(\mathbf{R}) - \delta_{ij} V(\mathbf{R})) c_j, \quad (2.77)$$

where  $H_{el,ij}(\mathbf{R}) = \langle g_i | \hat{T}_N | g_j \rangle_{\mathbf{R}} + \langle g_i | V | g_j \rangle_{\mathbf{R}}$  and  $V = \sum_{i,j} c_i^* H_{el,ij} c_j$  is the Ehrenfest potential.

## 2.4.6 Qu-Eh Implementation

### 2.4.6.1 Propagation

Qu-Eh follows similar implementation to that of 2OE,<sup>26</sup> where the method is intertwined with the CASSCF method and the electronic wavefunction propagation is done via a column vector with all of the coefficients for the CSFs, as shown in Eqn 2.54. As in 2OE, the calculation of the electronic structure and electronic wavefunction propagation is performed through a development version of the GAUSSIAN software package.<sup>173</sup> The nuclear propagation is performed with a DD-vMCG code in the Quantics software package,<sup>194</sup> where the two software packages call to each other after each propagation step to define the Qu-Eh method in practical

implementation.

Much like DD-vMCG, Qu-Eh is an on-the-fly method, which means it does not have access to the full potential surface. This is accounted for by applying the local harmonic approximation for each GWP in dynamics:

$$V(\mathbf{R}) = V^i + \mathbf{G}^i(\mathbf{R}) \cdot (\mathbf{R} - \mathbf{R}^i) + \frac{1}{2}(\mathbf{R} - \mathbf{R}^i)^\dagger \cdot \mathbf{H}^i \cdot (\mathbf{R} - \mathbf{R}^i), \quad (2.78)$$

where  $V^i = V(\mathbf{R}_i)$ ,  $\mathbf{G}^i = \frac{dV(\mathbf{R})}{d\mathbf{R}}|_{\mathbf{R}_i}$ , and  $\mathbf{H}^i = \frac{d^2V(\mathbf{R})}{d\mathbf{R}^2}|_{\mathbf{R}_i}$  are the Ehrenfest potential, gradient and Hessian respectively, and are all calculated via CAS-CI as in 2OE as discussed in Section 2.4.2.2. This means that each GWP moves along its own effective potential surface and is coupled to every other GWP, which is conceptualised in Fig. 2.9, therefore there is an electronic structure calculation for each GWP at every time step.

#### 2.4.6.2 The nuclear basis

Because the Qu-Eh method is a fully quantum mechanical method, the computational cost is more expensive than that of semi-classical methods such as 2OE, TSH or AIMS. Often, from a practical perspective, this means that dynamics must be performed in reduced dimensionality. This is done by sending GWPs along selected NMs of a molecule, where GWP coordinates are defined in terms of mass- and frequency-scaled NM vectors obtained from a ground state Franck-Condon point frequency calculation. All GWPs begin dynamics placed at the same geometry (in the case of this thesis, all simulations begin at the FC geometry), and velocities are assigned to each GWP. Typically in Qu-Eh, for each NM, 2 GWPs are assigned, where their initial momentum is sent in the  $+$  and  $-$  directions of the assigned NM respectively. Alongside this, there is an additional GWP which has no initial momentum, denoted as the centroid GWP, and its motion is dictated through the coupling of all other GWPs, and acts as an effective minimum energy pathway (MEP) trajectory for dynamics. At  $t = 0$ , only the centroid GWP is initially populated, and over the time of the simulation the GWPs moving along the NMs become populated as required for the simulation. Therefore, for  $N$  number of

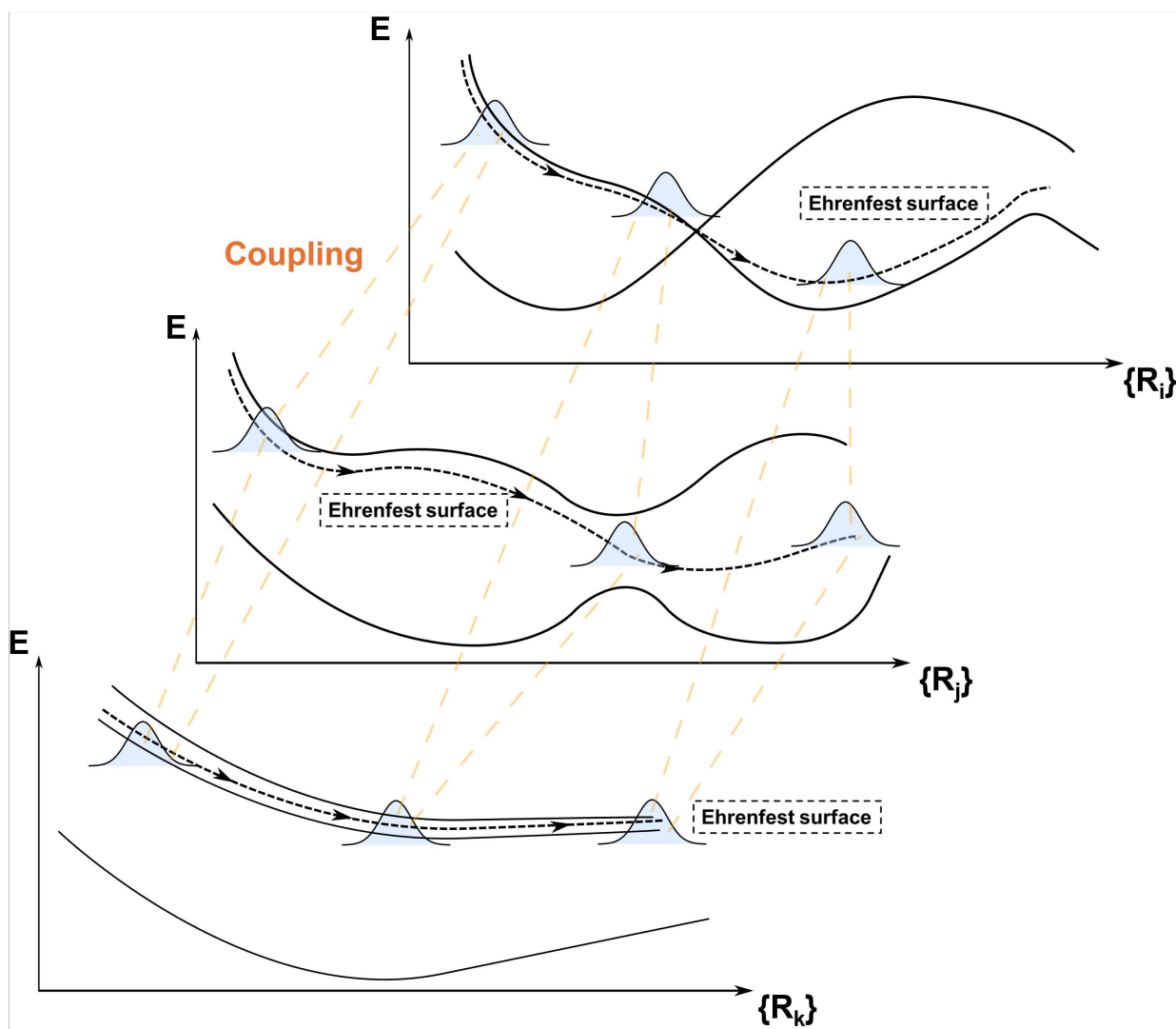


Figure 2.9: Cartoon for the Qu-Eh method. GWPs are sent along different regions of phase space,  $\{R_{i-k}\}$ , and each move along a time-dependent Ehrenfest potential surface. Unlike 2OE, the GWPs move according to the TDSE, and are coupled to each other, indicated by the dashed orange lines.

NMs selected for reduced dimensionality study, there will be  $2N + 1$  GWPs. An example of how 5 GWPs are initialised for a 2-mode Qu-Eh simulation of pyrazine is shown in Fig. 2.10.

### 2.4.6.3 Calculating properties

In Qu-Eh, the Gaussian basis functions are non-orthogonal, therefore when looking at average properties one cannot define the weight of a Gaussian wavepacket solely by the magnitude of its coefficient,  $|A_i|^2$ . One way to get around this is to define an ‘effective’ weight in a similar process to that of calculating the Mulliken populations<sup>195</sup> which takes into account the overlap

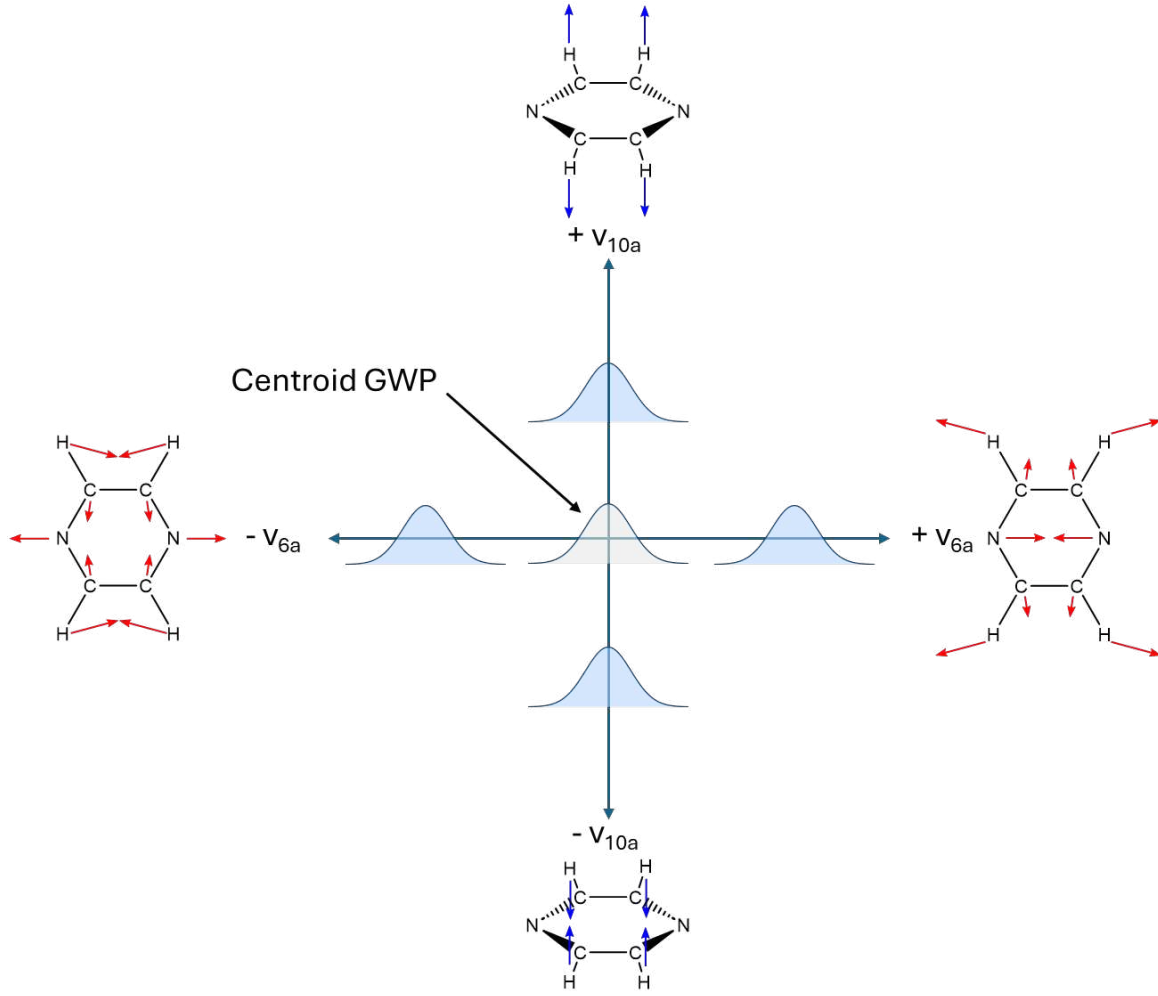


Figure 2.10: Example for how the nuclear basis set is initialised for a 2-mode simulation for pyrazine along  $\nu_{6a}$  and  $\nu_{10a}$ . As Qu-Eh uses  $2N+1$  GWPs where  $N$  is the number of NMs, we have 5 GWPs in this simulation. The axes represent the momentum space, where in position space all GWPs begin from the FC geometry. The first GWP is the centroid GWP (grey Gaussian) which has no initial momentum in any direction, the other 4 NMs are sent along the positive and negative directions of the NMs included in the calculation, in this case the  $+$  and  $-$  direction of  $\nu_{6a}$  and  $\nu_{10a}$ .

of respective Gaussian wavepackets known as the gross Gaussian product (GGP):<sup>196</sup>

$$GGP_i(t) = \text{Re} \left\{ \sum_j S_{ij}(t) A_j(t) A_i(t) \right\}, \quad (2.79)$$

where  $S_{ij}(t) = \int g_i^*(\mathbf{R}, t) g_j(\mathbf{R}, t) d\mathbf{R}$  is the GWP overlap matrix. Therefore, for any observable property ( $O$ ) we can find the expectation value by using the weights calculated by the GGP:

$$\langle O(t) \rangle \approx \sum_i GGP_i(t) \cdot O_i(t). \quad (2.80)$$

The GGP values are calculated by the Quantics software package, and this is extracted by a code developed by D. Danilov,<sup>50</sup> alongside observables of interest (CI and CSF state populations, NM excitations, Mulliken populations, bond lengths/angles/dihedrals, etc), which allows us to calculate GGP average properties. It is worth noting that while the GGP average provides a useful form of analysis for the overall dynamics of these simulations, in a similar vein to that of Mulliken analysis, it should be understood as an approximation rather than an exact representation. At certain isolated points, for example, it may yield slightly unphysical values such as a negative adiabatic state population.

### 2.4.7 DD-vMCG and MCEv2

The DD-vMCG method<sup>193,197</sup> is very similar to Qu-Eh. Indeed, it shares the same code which propagates their respective nuclei. In line with being a fully quantum mechanical method, DD-vMCG has been found to perform better in modelling dynamics involving excited state superpositions than semi-classical methods such as classical Ehrenfest or TSH.<sup>147</sup> The principle difference between DD-vMCG and Qu-Eh lies in the fact that in DD-vMCG the GWPs move along many diabatic potential surfaces rather than single time-dependent Ehrenfest potential surfaces. Each of these approaches, which are called multi-set and single-set respectively, have advantages and disadvantages. As discussed previously in Section 2.4.2.1, the Ehrenfest potential surface can become unphysical when the adiabatic potential surfaces which construct it strongly differ topologically. In DD-vMCG, this is not an issue. However, DD-vMCG does use diabatic surfaces, which if not constructed correctly can lead to unphysical dynamics in their own right.

In Qu-Eh, because we use only a single Ehrenfest potential surface, only one electronic structure calculation is required for each GWP at any point in time. For DD-vMCG, a calculation is required for each excited state potential surface used for each GWP, which does add computational cost. DD-vMCG can circumvent this as it generates a database of electronic structure properties at each geometry, and if a point is close enough to one of these database points in dynamics, an interpolation is performed, reducing the number of electronic structure calculations

required.<sup>198</sup> Access to this database is not possible for Qu-Eh.

One disadvantage Qu-Eh does have, however, compared to DD-vMCG, is that the dynamics method is intertwined, and hence limited to the CASSCF electronic structure method. In DD-vMCG, one can use different electronic structure methods, given the first and second derivatives are available.

Another method which is similar to Qu-Eh is the multiconfigurational Ehrenfest method MCEv1,<sup>199</sup> which is similar to MCEv2 and variants except the nuclei move according to the TDSE i.e. fully quantum mechanically. The key differences between these methods are that much like DD-vMCG, MCEv1 is not restricted to the CASSCF method like Qu-Eh is. However, unlike DD-vMCG and Qu-Eh, this method is not on-the-fly, as a pre-computed potential surface is required to run dynamics.

### 2.4.8 Summary

To conclude, in this section, we have looked at various methods which aim to model time-dependent electron-nuclear coupled dynamics in chemistry. These methods arise in order to overcome the difficulty of solving the complex time-dependent Schrödinger equation (TDSE). As only a few small systems can be solved analytically for the TDSE, a key next step is to solve the problem numerically. This can be done exactly using grid-based methods such as the ‘standard method’ or MCTDH; however, the exponential computational cost scaling with increasing degrees of freedom limits these approaches to only small or reduced-dimensionality systems, often requiring pre-computed potential energy surfaces in order for simulations to run.

On-the-fly dynamics methods aim to tackle larger systems, where electronic structure information is computed only when needed, often along a trajectory of some function. The simplest of these methods, known as semi-classical methods, propagate the nuclei classically and the electrons quantum mechanically. This gives the picture of point trajectories moving along many adiabatic (or diabatic) potential surfaces and applying *ad hoc* measures such as ‘hopping’ between states to model nonadiabatic behaviour, as in TSH. Alternatively, one can propagate

along a single time-dependent potential surface, as derived in the Ehrenfest method (such as the 2OE method), which circumvents this ad hoc criterion but can produce nonphysical potential surfaces in specific circumstances.

Each of these methods has been used to study nonadiabatic dynamics but suffer from overcoherence, as trajectories are not coupled. The next step moves to methods such as AIMS and MCEv2, where one has Gaussian wave packets (GWPs) which move classically but are coupled to one another. This additional coupling brings higher detail to model electron–nuclear dynamics but also increases computational expense.

Classical nuclei can miss important electron–nuclear coupling detail, principally in describing motion along the nonadiabatic coupling vector, and hence on-the-fly methods which treat the nuclei quantum mechanically have been developed to tackle this issue. The DD-vMCG method, using coupled GWPs which move along diabatic potential surfaces according to the TDSE (i.e., fully quantum mechanically), has been successfully used to study nonadiabatic dynamics. The Qu-Eh method can be considered equivalent to the DD-vMCG method, with the key difference that GWPs move along single time-dependent potential energy surfaces, rather than many diabatic potential surfaces.

Both the 2OE and Qu-Eh methods offer a practical and accurate framework for describing nonadiabatic dynamics, providing a good balance between computational efficiency and physical realism. These methods have also been successfully applied in previous studies to capture key nonadiabatic effects,<sup>11,49,151–161,175,200</sup> motivating their use in this work.

There is considerable effort in the nonadiabatic dynamics community to create a framework to compare dynamics methods (and the electronic structure methods they use in conjunction) across different excited-state phenomena. While DD-vMCG can, and has, been used for such comparisons,<sup>147</sup> the Qu-Eh method should be equally viable and should be used alongside other approaches for it to be better recognised and appreciated by the community.

In the coming chapters, the 2OE and Qu-Eh methods derived in this chapter will be used to study electron-nuclear coupled dynamics, specifically towards excited state decay and formation

of electronic coherences through CoIns.

## 2.5 Chapter Summary

In this chapter, we have outlined the theoretical framework needed to understand the methods used throughout this work, and the electron-nuclear coupled dynamics we intend to model. In the following chapter, we will discuss the specific numerical challenges associated with the 2OE and Qu-Eh methods, and how these can be overcome.

# Chapter 3

## Numerical Challenges

### 3.1 Introduction

The dynamics methods which are used in the present work, 2OE and Qu-Eh, are currently implemented in a development version of GAUSSIAN,<sup>201</sup> and in the case of Qu-Eh is interfaced with the QUANTICS software package.<sup>194</sup> While the 2OE and Qu-Eh methods has been established since 2014 and 2018 respectively,<sup>26,27</sup> and new versions of these methods exist,<sup>159</sup> including in spin-orbit coupling interactions,<sup>49</sup> the code remains closed source and numerical issues present from the beginning of implementation still remain.

This chapter details the key numerical challenges. Some numerical issues arise from the propagation of the electronic wavefunction, which for 2OE and Qu-Eh are the same, and are tied to the updating of the orbitals and loss of the active space over the course of dynamics. The 2OE and Qu-Eh methods have different procedures for nuclear propagation, but share in challenges related to the choice of integration method for nuclear propagation and the size of the timestep used. Due to the non-orthogonal nuclear basis used in Qu-Eh, the method also suffers from linear dependence issues. In addition to this, as discussed in Section 2.4.2.2, 2OE and Qu-Eh can be implemented with a few-cycle laser pulse, and this also comes with issues of its own related to both orbital updating and how the nuclei are propagated.

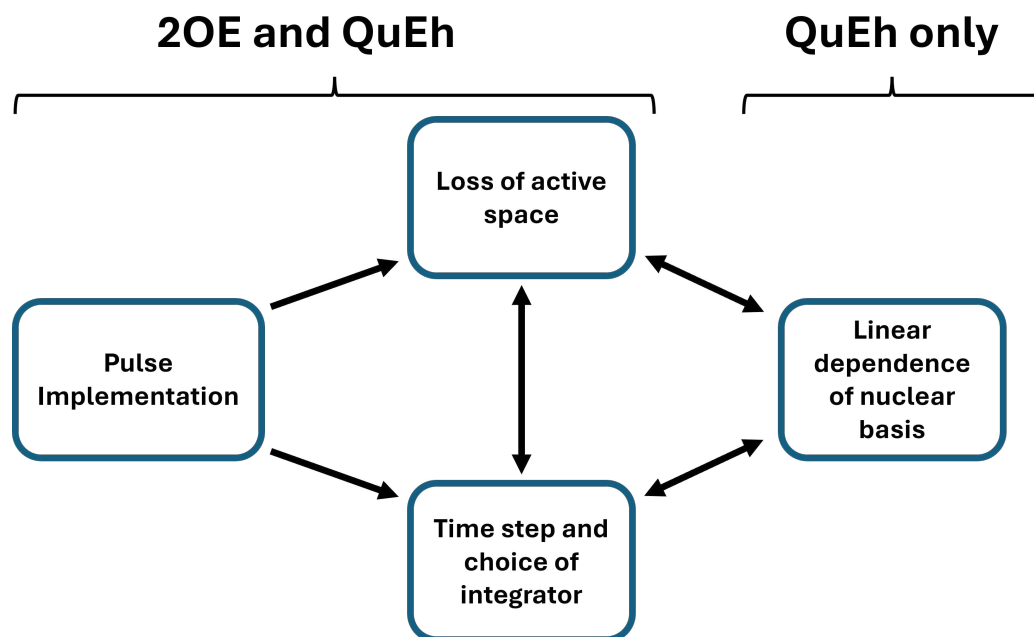


Figure 3.1: Main numerical issues encountered in dynamics, each of which are often closely interconnected.

It is worth noting that in simulation these issues can become closely related and link together (Fig. 3.1), where often a sole problem cannot be determined with complete certainty. Nonetheless, solutions and procedures exist for each of these issues, which shall be subsequently discussed.

## 3.2 Loss of the Active Space in Dynamics

For both the 2OE and Qu-Eh dynamics methods, the electron propagation is performed in practice according to Eqn 2.54, where the CSF coefficients are updated at every time step. The orbitals, on the other hand, are re-orthogonalised and treated to a single SCF cycle to keep the orbitals ‘in track’ with the nuclei throughout dynamics. During a simulation, monitoring the convergence of these orbitals at each time step is crucial. If the orbitals do not converge well, this means the orbitals are not ‘in track’ with the nuclei and the active space is lost, resulting in a poorly described electronic wavefunction. This can lead to spikes in the Ehrenfest gradient, poor conservation in total energy, and unphysical dynamics.

A key example of this issue can be shown in a preliminary study of the excited state dynamics

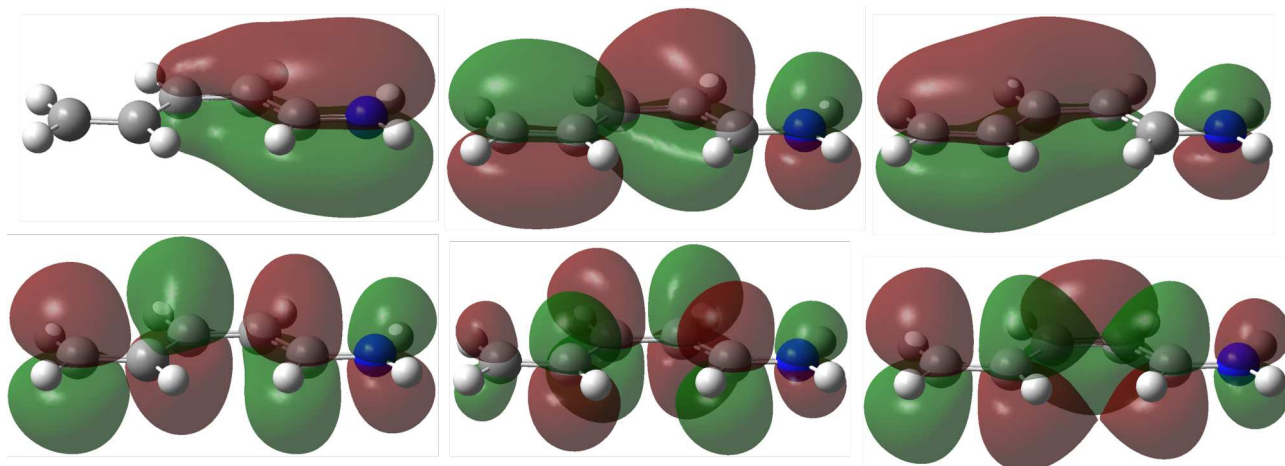


Figure 3.2: The (6,6) active space orbitals used in CASSCF calculations for PSB3 using the  $\pi$  and  $\pi^*$  orbitals of its conjugated double bond system.

of retinal protonated Schiff base model PSB3. Once excited to the  $S_1$  state, PSB3 undergoes *cis*→*trans* photoisomerization by passing through a  $S_0$ - $S_1$  CoIn. We ran dynamics beginning from a well-known transition state which lies close to the CoIn to study dynamics near and passing through the crossing. The active space for PSB3 consists of 6 electrons and 6 orbitals, including the  $\pi$  and  $\pi^*$  bonds of the conjugated double bonds in the molecule shown in Fig. 3.2. In dynamics we found that the total energy was conserved, however, around 30 fs into simulation a spike in the gradient (black line in Fig. 3.3(c)) created an artificial extension in the C-N bond (purple line in Fig. 3.3(c)). This was likely caused by the active space not being able to accommodate the dihedral torsion which occurs as PSB3 approaches and passes through the CoIn, as shown by the CAS convergence (solid green line) and dihedral angle (solid purple line) in Fig. 3.3(a). We found that this could be fixed by including more CSFs in the MCSCF wavefunction through the CAS-GVB method, including the  $\sigma$  and  $\sigma^*$  orbitals of the C-N bond as a GVB pair.

The results for these simulations are shown in Fig. 3.3(a) and Fig. 3.3(d), where in Fig. 3.3(a) while the dihedral angle in the GVB-CAS simulation is not as large (dashed purple line), the convergence for the same angle values using CASSCF are much better (dashed green line). The bond length changes over time shown in Fig. 3.3(d) for GVB-CAS are qualitatively similar to that of CASSCF(6,6) (Fig. 3.3(c)), but this time there is no extension in the C-N bond or gradient spike. The downside for using this method, however, is that in GAUSSIAN the GVB-

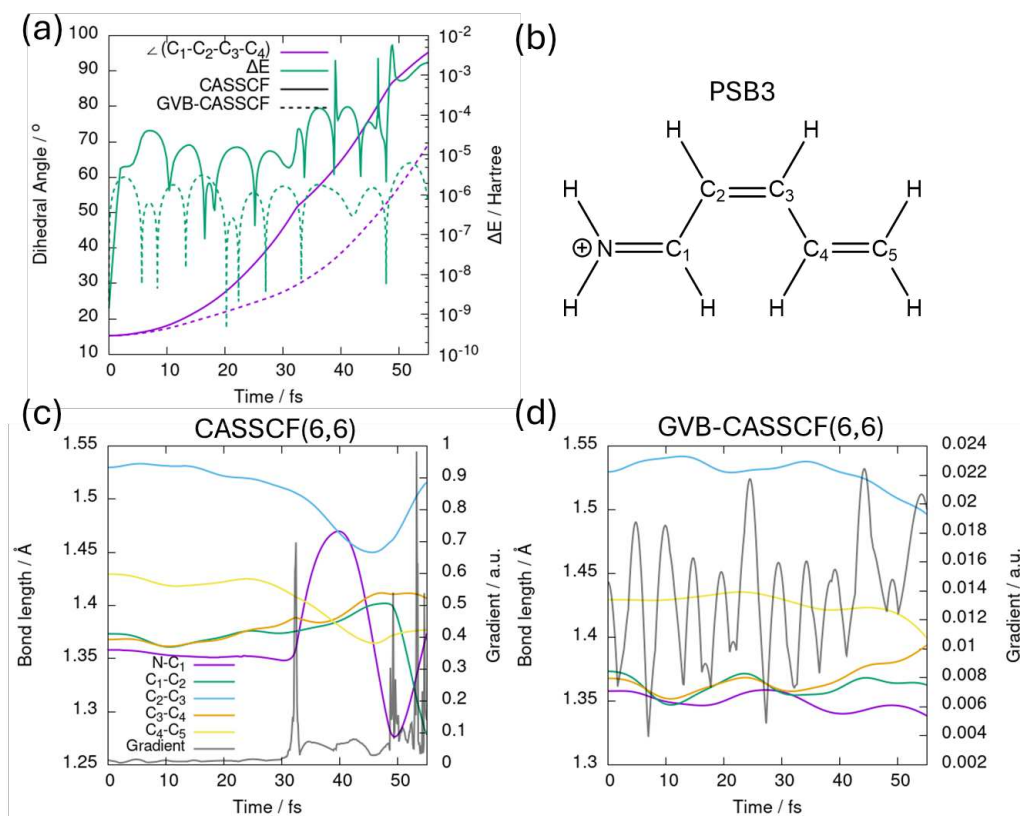


Figure 3.3: Results from two 2OE trajectories modelling the excited state dynamics of PSB3 beginning from a transition state on the  $S_1$  state which lies close to a  $S_0$ - $S_1$  CoIn that PSB3 passes through to photoisomerise. One trajectory uses SA(3)-CASSCF(6,6), and the other uses SA(3)-GVB-CASSCF(6,6). (a) shows the dihedral angle  $C_1$ - $C_2$ - $C_3$ - $C_4$ , with number labels shown in (b), and the SCF convergence over time for both trajectories. (c) shows N-C and C-C bond lengths and the magnitude of the nuclear gradient over time for the CASSCF(6,6) trajectory, showing a spike in gradient and unphysical C-N extension at around 30 fs. (d) shows the same bond lengths and gradients over time as (c), but for the GVB-CASSCF(6,6) trajectory, which includes twice the configurations as CASSCF(6,6) and avoids the gradient spike issue shown in (c).

CASSCF method does not have access to second derivatives, of which would require significant effort to develop and obtain. This means that the nuclear dynamics were propagated with the gradient only, which does result in qualitative differences in dihedral angle over time, as shown in Fig. 3.3(a), and bond length changes over time when comparing Fig. 3.3(c) and 3.3(d). In general, using a larger active space does reduce the likelihood of its loss during dynamics, however this does come with near-exponentially more costly electronic structure calculations, which are the rate-determining step in these simulations. This is why GVB-CASSCF in this study was preferred over CAS(8,8).

In Qu-Eh, GWPs are sent along the positive and negative directions of NMs. Some of these

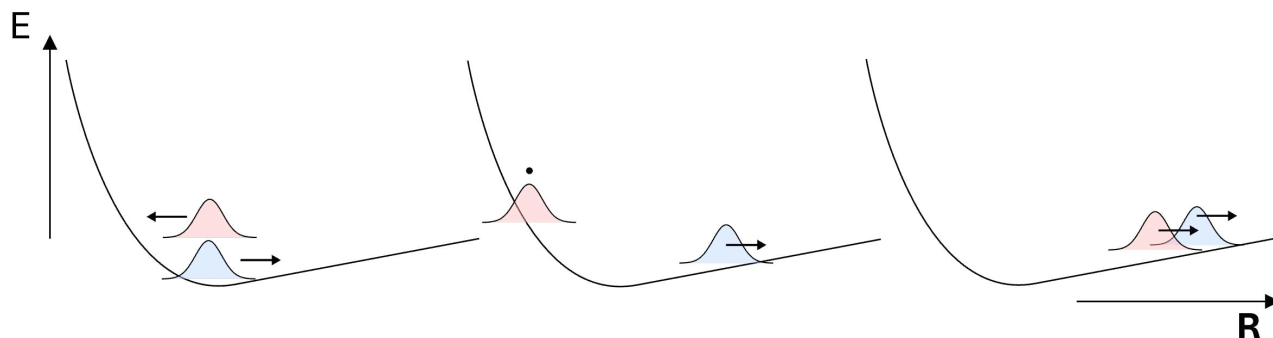


Figure 3.4: Example of a scenario which causes linear dependence in the Qu-Eh method. Two GWPs are sent in opposing directions along a totally symmetric mode,  $\mathbf{R}$ , where the curvature of the potential,  $E$ , differs in the  $+$  and  $-$  directions. In this scenario the  $-$  side is steeper than the  $+$  side. The GWP sent along the steeper potential will move along it, decelerate, and quickly reverse, then moving in the same direction as the GWP moving along the shallower potential on the  $+$  side. This leads to two GWPs which are moving in very similar ways in the same region of space, leading to linear dependence for these two GWPs.

NMs can not be well described by the active space. For example, when CASSCF is used to study pyrazine, as will be discussed in Chapters 4 and 5, a 10 electron 8 orbital active space is typically used,<sup>202,203</sup> which includes the lone pairs of the N atoms and the  $\pi$  and  $\pi^*$  orbitals of the aromatic ring. Out-of-plane modes for pyrazine can distort the  $\pi$  bonding and lead to the loss of the active space. In the case of our simulations, this meant that NMs had to be carefully selected to be able to both correctly describe the nonadiabatic dynamics, but also not lead to the loss of the active space. Specifically, this meant including important out of plane modes, such as  $v_{10a}$  which is related to the derivative coupling vector, but also excluding modes which lead to the loss of the active space.

### 3.3 Linear Dependence in Nuclear Basis

In theory, Qu-Eh should be able to run simulations of full dimensionality by sending GWPs along the positive and negative directions of all NMs within a molecular system. However, in practice the EOMs which determine the coefficients and parameters of these GWPs make this full-dimensionality scenario challenging due to the effect of linear dependence on the non-orthogonal nuclear basis.

Linear dependence arises when GWPs occupy the same part of space, where GWP overlap is

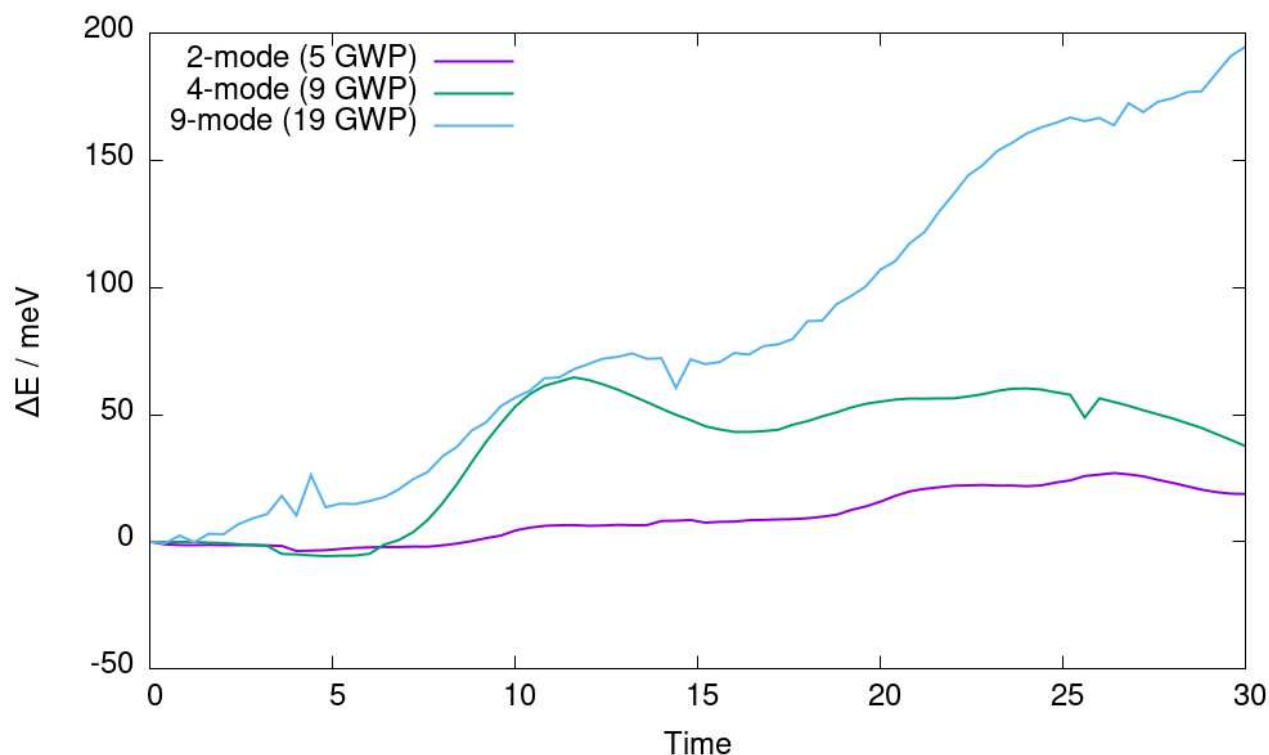


Figure 3.5: Deviation in total energy,  $\Delta E$ , over time for Qu-Eh simulations modelling the excited state decay of pyrazine beginning from the FC geometry of the  $S_2$  state using SA(6)-CASSCF(10,8) for 2 modes (purple line), 4 modes (green line), and 9 modes (blue line). The plot shows that total energy deviates more as more NMs are included in simulation.

high. This will lead to very small eigenvalues in the GWP overlap matrix,  $S$ , which, when inversed in the EOMs for the coefficients for the GWPs shown in Eqn 2.75, and for the centre positions of the GWPs in Eqn 2.76, will lead to numerical singularities which manifest in poor energy conservation in dynamics. A hypothetical example is illustrated in Fig. 3.4, wherein two GWPs are sent along a totally symmetric mode where one side of the potential is steep. In this scenario the GWP moving in the direction of the steep potential will reverse direction and will then move similarly to the GWP sent in the other direction, as well as be in the same region of space, leading to linear dependence.

In Qu-Eh, a medium-sized system such as pyrazine could be modelled in full dimensionality with 49 GWPs along 24 NMs. However, issues related to linear dependence (alongside modes which disrupt the active space as discussed in Section 3.2) lead to poor energy conservation within a few fs, leading to unphysical dynamics. In practice, this can be avoided by running dynamics in reduced dimensionality and using a smaller number of NMs, though the more modes included

can increase the likelihood of issues related to linear dependence. This can be seen in Fig. 3.5, which shows the change in total energy for Qu-Eh simulations for the  $S_2$  excited state decay of pyrazine including different amounts of NMs (2, 4 and 9), and therefore GWP (5, 9, and 19). As the number of NMs increase, energy conservation becomes worse, though remaining under an acceptable threshold for dynamics. Pyrazine is an example of a system where a small number of modes can describe a vast majority of the nonadiabatic dynamics, which has been shown previously using small to many mode simulations,<sup>203–205</sup> and will subsequently be shown in Qu-Eh simulations in Chapter 5. This is not the case for all systems, however. Another option is to shorten the width of the GWPs themselves to avoid large GWP overlaps, which has been used as a solution in previous Qu-Eh simulations to avoid linear dependence issues.<sup>200</sup> This does, however, mean that GWPs interact and couple with each other less, which leads to slightly more ‘classical’ dynamics, and more GWPs may be required to reach a convergent result. We note that in this thesis all Qu-Eh simulations have GWP that are kept at  $1/\sqrt{2}$  which is the width of the ground state vibrational wavefunction in the harmonic approximation.

## 3.4 Choice of Integrator and Time Step in Propagating the Nuclear Wavefunction

The choice of time step and integrator used to propagate the nuclei in nonadiabatic dynamics simulations can have an impact on the results of dynamics, especially in respect to numerical stability. This section will discuss which nuclear propagation methods are used, and what numerical challenges are associated with each of them.

### 3.4.1 2OE method integrator and time step

In the 2OE method, the nuclei are propagated according to the fifth-order fitting procedure developed by Hase and Schlegel,<sup>172</sup> which allows for much larger time steps to be taken while also preserving total energy conservation. A full time step of the method works as follows (and

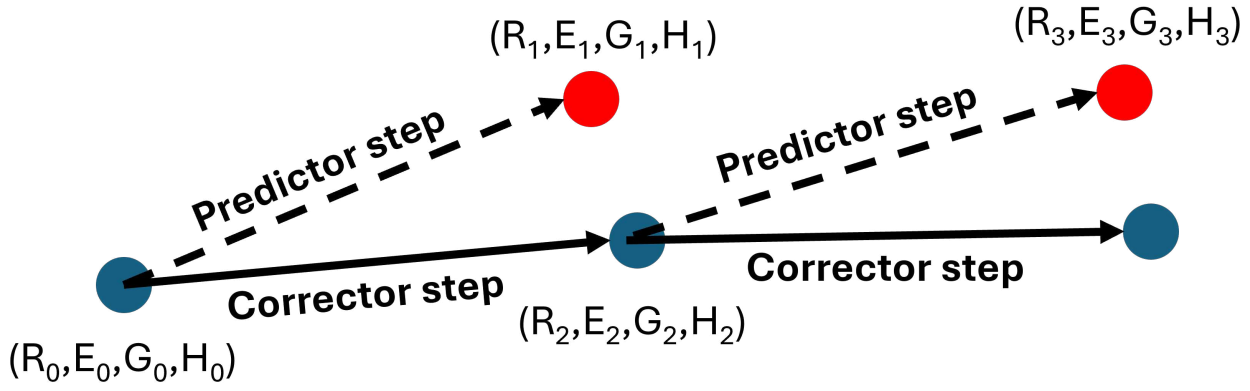


Figure 3.6: A schematic showing the predictor-corrector scheme. 1) The energy, position, gradient, and Hessian are computed at the first point. 2) The energy of the next time step is computed using a second-order fit, and the position, gradient, and Hessian are all recomputed at this new point. This is the predictor step. 3) A more accurate 5th order fit is then utilized using the information from the gradients and Hessians of the points at 1 and 2 to better fit the path to the true PES, generating the corrector step. This process is repeated in steps 4) and 5).

is illustrated in Fig. 3.6):

1. The energy of the next time step is estimated by performing a second order Taylor expansion:  $E(R) = E^0 + G^0 \cdot (R - R^0) + 1/2 (R - R^0)^\dagger \cdot H^0 \cdot (R - R^0)$ , where  $E^0$ ,  $G^0$ , and  $H^0$  are the energy, gradient, and Hessian of the Ehrenfest potential surface respectively, calculated at the CAS-CI level at the current geometry. The force can be found by differentiating the above equation with respect to the nuclear coordinate  $R_I$ :  $F_I = \frac{dP_I}{dt} = -G_I^0 - \sum_J H_{IJ}^0 \cdot (R_J - R_J^0)$ .
2. With this information a predictor step can be performed using the energy and gradient determined from the second order fit. The step size made depends on a trust radius which is set prior to dynamics, hence the step size can vary at each step.
3. The energy, gradient and Hessian,  $E^0$ ,  $G^0$ , and  $H^0$  at the new geometry found by the predictor step are calculated.
4. The  $E^0$ ,  $G^0$ , and  $H^0$  values from the initial step in (1) and the predictor step in (3) are fitted to a 5th order polynomial to provide a more accurate potential surface and using this to take the next step. This is known as the corrector step.

This method suffers, however, when very small step sizes are used. In the corrector step, when two points are taken close to one another, the values of the Hessians can become very small, and are not well described by the fifth order fitting procedure, leading to error. In these cases the fifth order fitting procedure can be turned off, however now the time step is only the predictor step in (1), where smaller time steps must then be taken to accommodate the less accurate fit. Energy conservation in this case is less stable. An example is shown again for the PSB3 molecule in Fig. 3.7, where 2OE dynamics is ran both with and without the fifth order fit. Comparing the dynamics through the BLA coordinate for the simulation with the corrector step (Fig. 3.7(a)) and only the predictor step (Fig. 3.7(b)), dynamics show qualitative similarity, noting how both have the same artificial C-N bond extension as discussed in Section 3.2, though with the no-fit simulation this extension is larger. However, the energy conservation in the no-fit simulation is significantly larger than that of the fifth order fit case, unable to maintain energy conservation with the spike in the gradient at 30 fs (see Fig. 3.3(c)) as shown in Fig. 3.7(c).

### 3.4.2 Qu-Eh method integrator and time step

In the Qu-Eh method, there is more flexibility in the integration method used which propagates the nuclei as there are more options available within the QUANTICS software package responsible for the nuclear propagation. Both the order and the type of integrator can impact the propagation of dynamics, so the integration method must be chosen carefully, and alongside this the step size must also be tested.

An illustrative example is in the excited state decay of pyrazine. In the specific case where dynamics was ran using 9 NMs (and 19 GWPs), the Runge Kutta 5th order (RK5) method to was initially used and had acceptable energy conservation, however experienced sharp variations and plateaus in NM excitation in dynamics, as seen in Fig. 3.8(a). Additionally, non-totally symmetric modes, such as  $\nu_{14}$  (red line) and  $\nu_{10a}$  (black line) which should be approximately zero in the average, are not, which is a major issue if trying to monitor electronic coherences as shall be discussed in Chapter 5. Using the Adams-Bashforth-Moulton (ABM) integrator removes these sharp variations resulting in smooth dynamics, shown in Fig. 3.8(b), and preserves

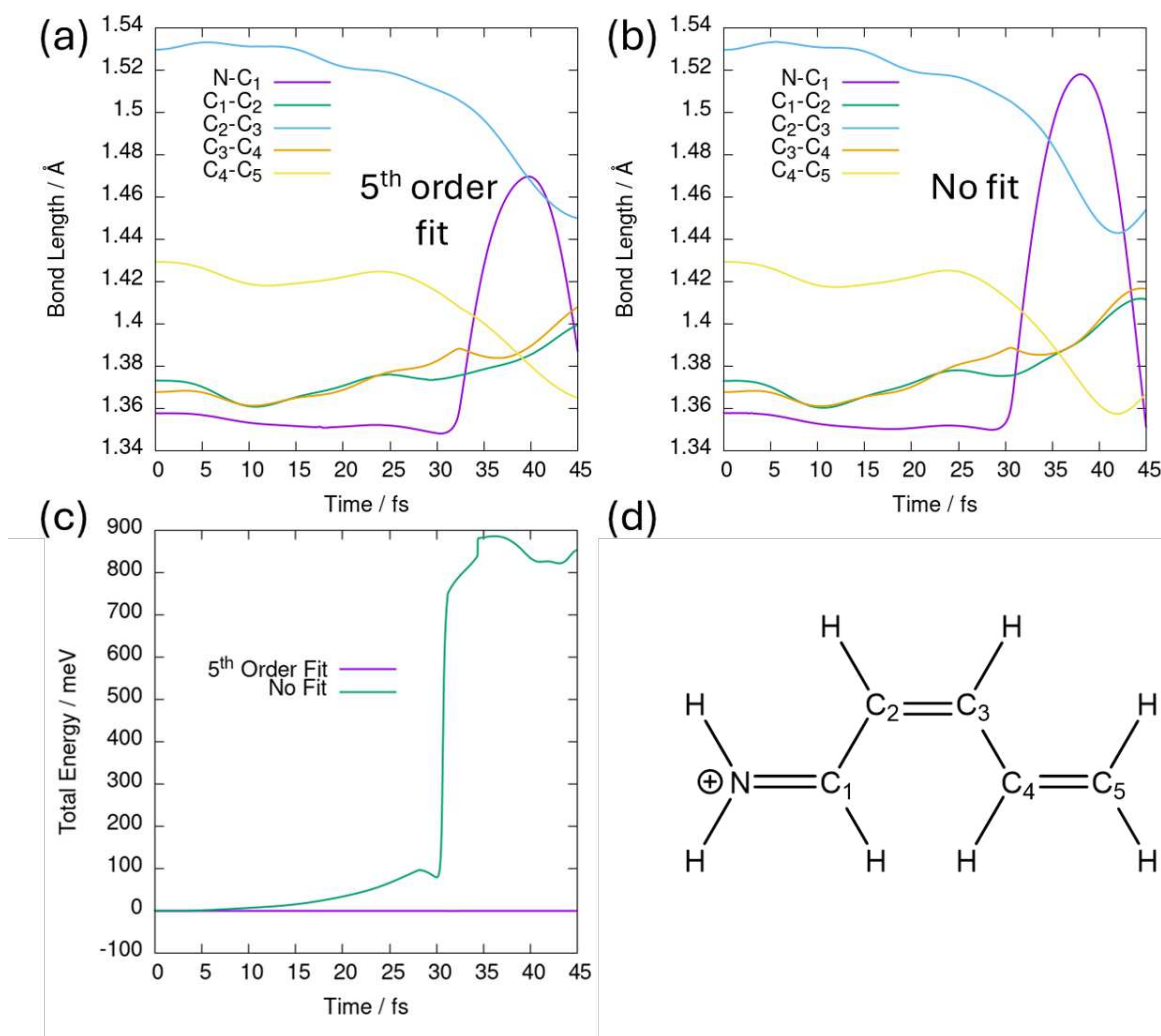


Figure 3.7: Results from the SA(3)-CASSCF(6,6) 2OE trajectory modelling the excited state dynamics of PSB3 initiated from the transition state on the  $S_1$  state located close to the  $S_0$ - $S_1$  CoIn as discussed in Fig. 3.3. (a) and (b) show the N-C and C-C bond lengths over time for simulations using a fifth order fitting corrector step and without respectively, with labelling shown in (d). (c) shows the conservation of total energy over time for each simulation in meV.

near zero averages for the non-totally symmetric modes, giving similar (acceptable) energy conservation as shown in Fig. 3.8(c). The change in the ‘quality’ in dynamics may be due to the fact that the ABM method is a predictor-corrector method, meanwhile RK is not, and that the ABM method used in dynamics was an order higher than RK5, leading to less error. For more details about each integration method, see Appendix Sections A.1 and A.2.

In Qu-Eh, there is a timestep associated to the updating of the electronic wavefunction, where at each point the energy, gradient, and Hessian are evaluated to form a LHA surface as discussed in 2.4.6.1, and a timestep associated with the nuclear integration which takes place on this

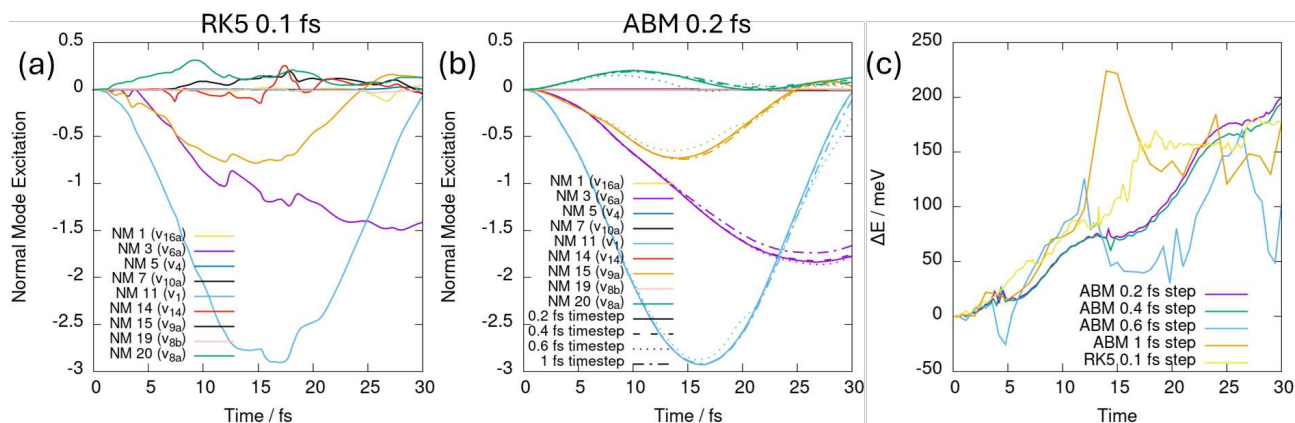


Figure 3.8: Qu-Eh dynamics information for the  $S_2$  state decay of pyrazine using SA(6)-CASSCF(10,8) and 9 NMs beginning from the FC geometry on the  $S_2$  state. (a) and (b) show the GGP averaged NM excitation over time for simulations using the RK5 integrator & 0.1 fs timestep and the ABM integrator & 0.2 fs timestep. In (b) the dashed green, orange, purple and light blue lines show the NM excitations for the totally symmetric NMs for larger timesteps, as an indicator of convergence in dynamics with respect to the time step. (c) shows the change in total energy over time for all simulations.

constructed surface. The time steps within nuclear integration are small, with timesteps ranging from  $10^{-4}$  to  $10^{-1}$  fs. The timesteps associated to the electronic wavefunction are constant and must be tested to ensure convergence in dynamics. For example, simulations ran using the ABM integrator in pyrazine with wavefunction timesteps of 0.2 fs, 0.4 fs, 0.6 fs and 1 fs show qualitative similarity in dynamics, shown in the totally symmetric modes  $\nu_{6a}$ ,  $\nu_1$ ,  $\nu_{9a}$  and  $\nu_{8a}$  in Fig. 3.8(b) (purple, light blue, orange and green respectively, step size shown by dashed lines). Convergence in results occurs by 0.4 fs, matching the 0.2 fs result shown in Fig. 3.8(b) by NM excitation and also in energy conservation in Fig. 3.8(c). Also note that in Fig. 3.8(c) the energy conservation does not improve with respect to time step, suggesting that linear dependence issues previously discussed are the cause of the drift in total energy.

### 3.5 Using a Few-Cycle Laser Pulse

The 2OE and Qu-Eh methods can be used to study nonadiabatic dynamics in the presence of a few-cycle laser pulse,<sup>174</sup> using the implemented laser pulse discussed in Section 2.4.2.2. This has been used to show how a few-cycle laser pulse can be used to generate excited state mixtures and therefore influence excited state dynamics.<sup>174</sup> There are, however, numerical challenges

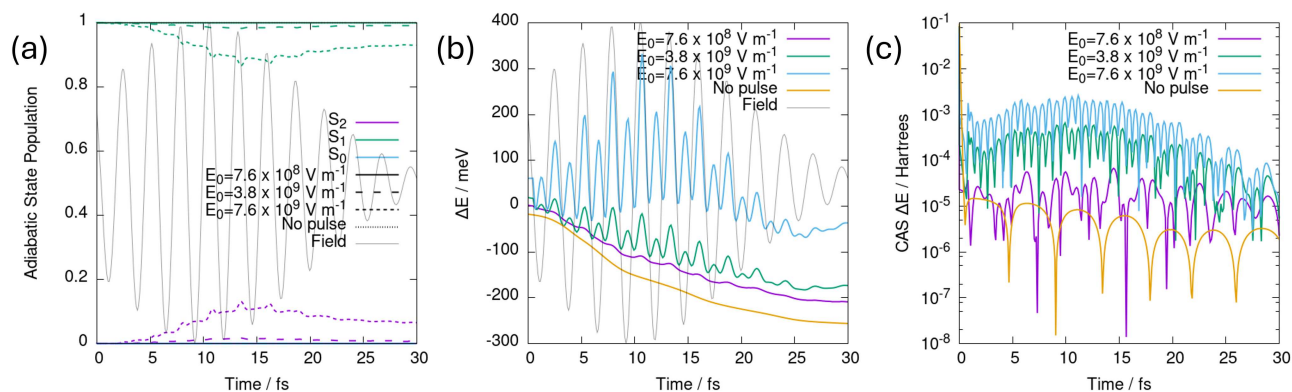


Figure 3.9: 2OE trajectory information for excited state dynamics of PSB4 using SA(3)-CASSCF(8,8) beginning from the FC geometry on the  $S_1$  state and no initial momentum with a laser pulse using different electric field intensities. (a) shows the  $S_0$ - $S_2$  adiabatic state populations over time for simulations using different pulse intensities (or no pulse at all), alongside the shape of the laser field (grey). (b) shows the total energy over time for these simulations, alongside the shape of the laser field. (c) shows the CAS convergence over time for these simulations.

associated with this pulse implementation. These issues will be explained using single 2OE trajectories with pulse implementation for the retinal protonated Schiff base model PSB4, which contains an additional conjugated double bond with respect to PSB3. PSB4 similarly undergoes photoisomerization by passing through a  $S_1$ - $S_2$  CoIn, though in this case there is no TS which lies close to the CoIn, so 2OE simulations begin at the FC region on the  $S_1$  state with no initial momentum. The few-cycle laser pulse is applied from the beginning of dynamics at a frequency resonant to the  $S_1$ - $S_2$  energy gap in order to populate the  $S_2$  state. The first issue is that the laser pulse creates near-instant energy conservation issues when using the Hase and Schlegel predictor-corrector scheme in 2OE. This means that only the second-order predictor step could be used, which as previously discussed in Section 3.4.1 leads to smaller time steps required and poorer energy conservation.

The second issue is that the stronger the interaction between the pulse and the molecular system, the more unstable the energy conservation is in dynamics. In this context, a stronger interaction corresponds to a higher pulse intensity and a resonance between the pulse frequency and energy gaps between the excited state(s) of interest. This is demonstrated in Fig. 3.9, where 2OE trajectories for PSB4 are ran and the pulse shape, shown in Fig. 3.9(a) and 3.9(c), is kept the same but the pulse intensity is varied ( $7.6 \times 10^7$ ,  $3.8 \times 10^9$ ,  $7.6 \times 10^9$  V m $^{-1}$ ). The adiabatic

state populations for  $S_0$ - $S_2$  are shown for these simulations in Fig. 3.9(a), where it is clear that with a higher pulse intensity that there is more population transfer into the  $S_2$  state, with only the most intense pulse (dashed purple line) transferring a significant amount. The population transfer lines up with the pulse shape, where peaks in the  $S_2$  population correspond to the maxima and minima of the pulse (grey line). However, with this increase in intensity comes an increase in the deviation of total energy, which is shown in Fig. 3.9(b). The blue line in Fig. 3.9(b) shows the total energy for the strongest intensity pulse, which shows deviation up to 350 meV, while the other pulses (green and purple lines), orders of magnitude weaker in terms of intensity, do not distort the total energy as significantly. This total energy deviation can be connected to poorer CAS convergence as the electric field distorts the orbitals rapidly over time. Fig. 3.9(c) shows the CAS convergence over time for these simulations, where the stronger the pulse, the poorer the CAS convergence is. As discussed in Section 3.2, this poor energy conservation and CAS convergence can lead to unphysical dynamics. In practice, this means that a laser pulse must be chosen such that it is strong enough to significantly impact the molecular system, but not be so strong that it generates poor energy conservation.

## 3.6 Summary

In this chapter, we have looked at some of the key numerical challenges which can occur with the 2OE and Qu-Eh dynamics methods used in this thesis. We first discussed how the loss of the active space during dynamics can lead to gradient spikes, poor energy conservation, and ultimately unphysical dynamics. We show that these issues can be circumvented by enlarging or modifying the active space (via GVB-CASSCF or RASSCF, for example), though noting this does mean more computational cost, as well as being selective in the modes chosen in running Qu-Eh simulations. Secondly, the impact of linear dependence on the non-orthogonal GWP basis of Qu-Eh was explained, which becomes more of an issue as more modes are included in simulation and can restrict the dimensionality of a calculation. This can be avoided by using narrower GWPs, but this can also lead to more ‘classical’ dynamics. This is a challenge which should be fixed in the next version Qu-Eh implementation.

Additionally, the choice of nuclear integrator and step size was also reviewed. For 2OE, the predictor-corrector scheme allows for large time steps however becomes unreliable when smaller time steps are used, which can be solved by using a second order fit consisting of only the predictor step, noting poorer energy conservation comes with this. In Qu-Eh, more options of nuclear integrator are available, and testing of different integrators is advised. To highlight this, we give a case study showing that the Adams-Bashforth-Moulton predictor-corrector integrator performs better for simulating the excited state dynamics of pyrazine than the Runge-Kutta 5th order integrator. Through this we also show that the convergence of dynamics with respect to the electronic/wavefunction evaluation time step is also important to monitor. Finally, we also explore the challenges of using few-cycle laser pulse implementation in the 2OE dynamics method, where strong electric fields can poorly impact CAS convergence and energy conservation.

These issues show the current practical limits of the 2OE and Qu-Eh methods in this thesis, and also guide the computational methodological choices made in subsequent results chapters.

## Chapter 4

# Relationship of the $n\pi^*$ States and its Impact on the Radiationless $S_2$ Decay of Pyrazine

*Note: some material in this chapter is derived from Moore et al.<sup>206</sup> The dissertation author was the primary researcher and author of this paper.*

### 4.1 Introduction

Pyrazine is a medium-sized molecule of  $D_{2h}$  point group symmetry - akin to benzene but with two opposing C atoms replaced by N atoms. For decades, pyrazine has been used for benchmarking purposes within computational chemistry, both in single-point calculations for comparisons of vertical excitation energies and simulating UV/Vis spectra, and also in nonadiabatic dynamics for modelling the non-radiative decay of the  $S_2$  state down to the ground state.

Pyrazine has many low-lying states, however, in this study we focus on the first 5 excited singlet states:  $S_1$ - $S_5$ . These consist of one  $\pi\pi^*$  state of  $^1B_{2u}$  symmetry and two pairs of  $n\pi^*$  states,

$^1B_{3u}$  &  $^1B_{2g}$  and  $^1A_u$  &  $^1B_{1g}$ , which are related through valence bond structures which we shall discuss later. Historically, the  $S_2$  state was identified as the  $\pi\pi^*$  state of  $^1B_{2u}$  symmetry, and the  $S_1$  state was identified as the  $n\pi^*$  state of  $^1B_{3u}$  symmetry. We will continue to refer to the states as such and later explain why this is in contention.

To set the scene for pyrazine’s historical computational perspective, a conical intersection between the  $S_2$  and  $S_1$  states was found computationally in the late 1980s Schneider *et al.*<sup>204</sup> This was later supported by experimental observations of ultrafast relaxation from the  $S_2$  state to the  $S_1$  state in time-resolved photoelectron spectroscopy (TR-PES) studies in the late 90s to early 00s, with decay from the  $S_2$  state occurring in around 22 fs,<sup>207</sup> which has been confirmed in later experiments.<sup>208,209</sup> Only recently has a new, shorter time of around 13 fs been observed using higher resolution TR-PES measurements.<sup>210</sup> Both grid-based and MCTDH quantum dynamics studies using a 2-state, 3/4-mode model could replicate these decay lifetimes,<sup>211,212</sup> hence for decades the mechanism for pyrazine was considered solved, with a  $^1B_{2u}$ - $^1B_{3u}$  conical intersection causing the ultrafast decay to the ground state.

However, since 2008, from a computational study by Werner *et al.*,<sup>213</sup> some have suggested that the higher lying dark  $^1B_{2g}$  and  $^1A_u$  states play a role in the decay, and at points become the  $S_2$  state during this process. This was later supported by Sala *et al.*,<sup>214,215</sup> whose quantum dynamics simulations suggest the involvement of the  $^1A_u$  state in the decay, and by Tsuru *et al.* in a TR-NEXRAFS simulation using MCTDH EOM-CCSD.<sup>216</sup>

This hypothesis has been in contention since with arguments from Kanno *et al.*<sup>217</sup> who performed MRCISD quantum dynamics and found little to no involvement of  $^1A_u$  and  $^1B_{2g}$  states, as well as B. Mignolet *et al.*<sup>218</sup> who calculated the vacuum PES spectra of pyrazine using MRCI using the four lowest excited states and found no involvement of these dark states in the  $S_2$  decay.

From an experimental perspective, prior studies focused on obtaining the decay from  $S_2$  to  $S_1$  and/or  $S_2$  to the ground state, with no direct focus on involvement from a higher lying dark  $^1A_u$  state.<sup>204,207,208</sup> In 2016, a time-resolved photoelectron imaging (TR-PEI) study by Horio *et al.*<sup>209</sup> did not observe the involvement of the  $^1A_u$  state in the decay from the  $S_2$  state. In 2021,

an X-ray transient absorption spectroscopy (XR-TAS) study by Scutelnic *et al.*<sup>219</sup> reported that the  $^1A_u$  state had been observed after becoming populated after  $200 \pm 50$  fs with supporting TDDFT/B3LYP/cc-pVDZ FSSH simulations. More recently, a study by Chang *et al.*<sup>8</sup> observe with XR-TAS that not only is the  $^1A_u$  state populated within the first tens of fs, but also that electron dynamics are generated via the passing of a conical intersection, with oscillations in population between the  $^1A_u$  state and the  $^1B_{3u}$  state. This specific aspect of pyrazine will be discussed further in Chapter 5.

The issue with confirmation of the precise mechanism of the  $S_2$  decay is that depending on the electronic structure method, the ordering of the states change. Variational methods such as CASSCF,<sup>220–222</sup> RASSCF,<sup>30</sup> and MRCI<sup>214</sup> agree with the historical ordering of states where  $S_1$  is the  $^1B_{3u} n\pi^*$  state and  $S_2$  is the  $^1B_{2u} \pi\pi^*$  state, and show no sign of involvement of the higher lying  $^1B_{2g}$  and  $^1A_u$  states in the decay from the  $S_2$  state. In response methods such as TDDFT and CASPT2, the  $^1A_u$  state lies below the  $^1B_{2u}$  state and becomes the  $S_2$  state.<sup>220,221,223</sup> In coupled cluster methods, the  $^1A_u$  state and  $^1B_{2g}$  state are near to degenerate with the historical  $^1B_{2u}$  state.<sup>220,224</sup> Therefore, there are still questions and uncertainties over the state ordering and hence over the decay mechanism of pyrazine, with a need for both new experimental and computational studies to better understand the  $S_2$  decay mechanism.

In this chapter we study the excited state potential surfaces of the well-known  $^1B_{2u}$  and  $^1B_{3u}$  states, often known as the  $S_1$  and  $S_2$  states respectively, as well as the higher lying dark states  $^1B_{2g}$  and  $^1A_u$  to observe how these states interact with each other from a statics perspective. This will then be followed with a dynamics perspective, to see how the system evolves through time in the excited state after photoexcitation. In our dynamics simulations, we use the semi-classical 2OE<sup>26</sup> and fully quantum method Qu-Eh<sup>27</sup> to describe the electron-nuclear coupled dynamics involved in the excited state decay. This is paired with the SA-CASSCF method, which, while not as accurate in describing the vertical excitation energies as other methods, we show to be qualitatively faithful to the RASSCF description of pyrazine, a method that should in principle recover a large amount of the electron correlation missing in CASSCF.<sup>30</sup>

## 4.2 Computational Details

### 4.2.1 Statics

For calculating vertical excitation energies to compare different electronic structure methods, the Gaussian16 software package<sup>201</sup> was used for the TDDFT/B3LYP, CIS, EOM-CCSD, and SA-CASSCF methods. All methods employed a 6-31G\* basis set. Other basis sets, such as cc-pVDZ, were also used to both compare with other computational studies, and also to improve basis set error for the CIS calculations.

For CASSCF calculations, a 10 electron 8 orbital active space was used, consisting of two n orbitals which are the lone pairs on each N atom, and three  $\pi$  and  $\pi^*$  orbitals around the pyrazine ring. This active space has a useful balance of size and accuracy compared to other active spaces when comparing to vertical excitation energies,<sup>221</sup> and has also been used to simulate spectra for pyrazine in dynamics simulations.<sup>202,203</sup> For the corresponding active space for the RASSCF calculations, the RAS2 space is the same as the previously used 10 electron 8 orbital active space, and the RAS1 and RAS3 spaces consisted of the C-C and C-N  $\sigma$  and  $\sigma^*$  orbitals of the ring respectively. The active space orbitals used for both CASSCF and RASSCF are shown in Fig. 4.1. Ground state optimisation calculations were performed with these methods, and the bond lengths and angles of these optimised geometries can be shown in Table 4.1. B3LYP geometries are largely consistent with previous computational studies when comparable basis sets are used, with small deviations mainly arising from differences in optimisation protocols and convergence criteria.<sup>225</sup> MP2 results show somewhat larger discrepancies that depend strongly on basis set choice,<sup>214,226,227</sup> while CASSCF and CASPT2<sup>228</sup> are in close agreement with other methods, aside from slightly shorter C-H bond lengths. Compared with the available electron diffraction data,<sup>229</sup> which lack reported uncertainties, most methods reproduce C-N bond lengths and key bond angles well but tend to underestimate C-C bond lengths and overestimate C-H and N-C-H values. Nonetheless, the variations across methods are minor, hence in our calculations the optimised B3LYP/6-31G\* geometry is used across all electronic structure methods as the FC geometry for vertical excitation calculations.

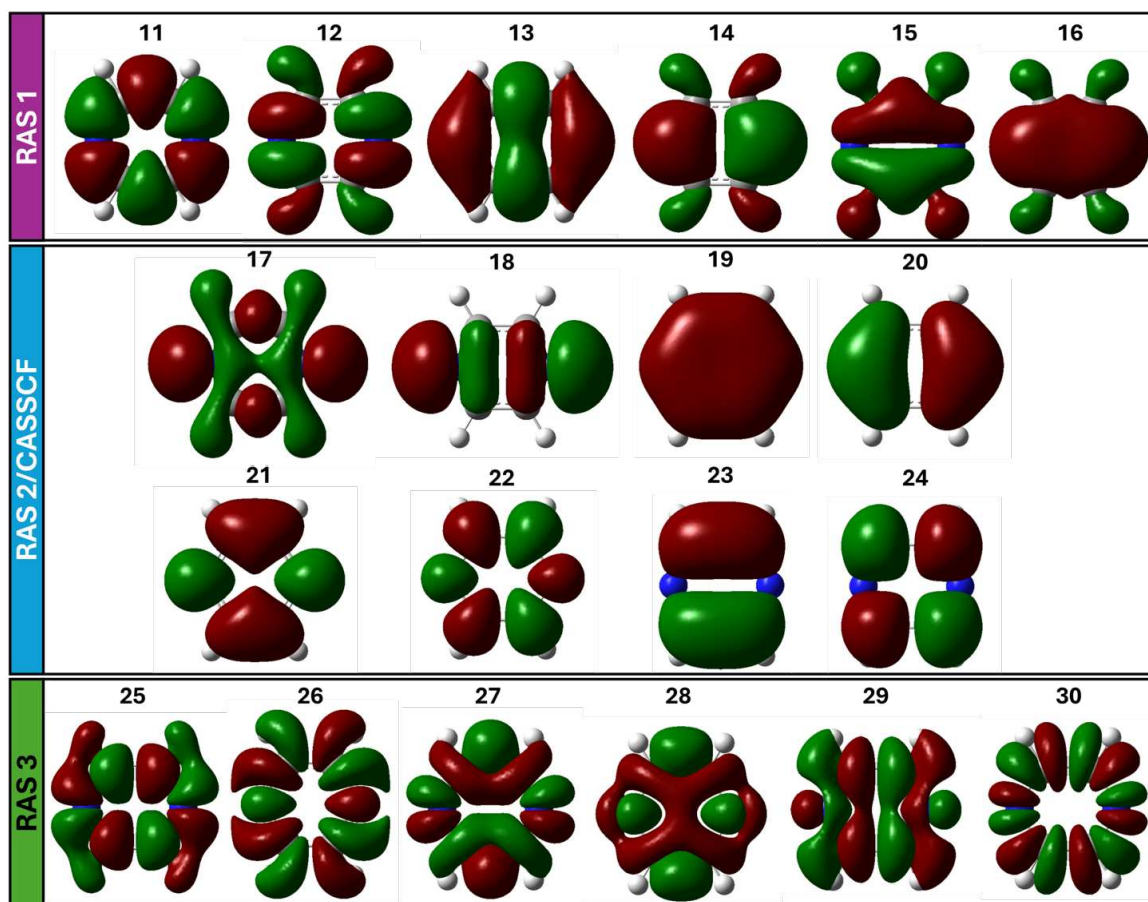


Figure 4.1: Active space orbitals used both in the CASSCF(10,8) and RASSCF(6,8,6) calculations. The labels denote the RAS1, RAS2 (in this case the 10 electron 8 orbital active space for CASSCF), and RAS3 spaces for the RASSCF calculations.

Table 4.1: Bond lengths (Å) and bond angles (°) of optimised ground state geometries of pyrazine for different electronic structure methods and basis sets.

| Method                            | C-C   | C-H   | C-N   | C-C-N | C-N-C | N-C-H |
|-----------------------------------|-------|-------|-------|-------|-------|-------|
| B3LYP/6-31G*                      | 1.397 | 1.088 | 1.338 | 122.1 | 115.8 | 117.0 |
| B3LYP/cc-pVDZ                     | 1.399 | 1.095 | 1.339 | 122.2 | 115.5 | 117.0 |
| B3LYP/cc-pVTZ                     | 1.391 | 1.084 | 1.332 | 122.0 | 116.1 | 117.2 |
| B3LYP/cc-pVDZ <sup>225</sup>      | 1.399 | 1.095 | 1.339 | 122.2 | 115.5 | 117.0 |
| B3LYP/cc-pVTZ <sup>225</sup>      | 1.391 | 1.084 | 1.332 | 122.0 | 116.1 | 117.2 |
| MP2/6-31G*                        | 1.396 | 1.088 | 1.345 | 122.4 | 115.3 | 116.8 |
| MP2/aug-cc-pVDZ                   | 1.407 | 1.095 | 1.351 | 122.2 | 115.2 | 116.8 |
| MP2/6-31G* <sup>226</sup>         | 1.402 | 1.085 | 1.346 | 122.3 | 115.3 | 116.8 |
| MP2/aug-cc-pVDZ <sup>214</sup>    | 1.393 | 1.083 | 1.339 | 122.3 | 115.4 | 117.0 |
| MP2/DZP <sup>227</sup>            | 1.402 | 1.085 | 1.342 | 122.3 | 115.3 | 116.8 |
| CCSD/6-31G*                       | 1.397 | 1.089 | 1.341 | 122.3 | 115.4 | 116.8 |
| CCSD/cc-pVTZ <sup>230</sup>       | 1.392 | 1.082 | 1.333 | —     | —     | —     |
| CASSCF(10,8)/6-31G*               | 1.395 | 1.075 | 1.331 | 122.0 | 116.0 | 117.1 |
| CASPT2/aug-cc-pVTZ <sup>228</sup> | 1.396 | 1.081 | 1.341 | 122.4 | 115.3 | 116.9 |
| Experiment <sup>229</sup>         | 1.403 | 1.115 | 1.339 | 122.2 | 115.6 | 113.9 |

### 4.2.2 Dynamics

In dynamics simulations, the semi-classical 2OE method,<sup>26</sup> where the electrons are propagated according to the TDSE and the nuclei are propagated classically, and fully quantum Qu-Eh method,<sup>27</sup> where the nuclei also move according to the TDSE, are used. For both 2OE and Qu-Eh, the nuclear trajectory and each individual GWP which makes up the nuclear wavepacket respectively move along a single time-dependent ‘Ehrenfest’ potential energy surface, which well-describes regions where strong nonadiabatic coupling is present, such as pyrazine’s  $S_1$ - $S_2$  CoIn. Importantly, both methods use SA(6)-CAS(10,8)-CI to calculate the electronic energy and first and second derivatives required to propagate the nuclei and electrons forward in time.<sup>101</sup>

In 2OE simulations, dynamics consist of a single classical nuclear trajectory beginning from the FC region (using the same B3LYP/6-31G\* optimised geometry used in static calculations) from the pure  $S_2$  state with no initial momentum. The average time step for dynamics is  $\sim 0.1$  fs and was ran for 30 fs. It is worth noting that this is indeed a single point trajectory and does not resemble a nuclear ensemble that will have momentum and can bifurcate. Therefore, the 2OE trajectory acts similarly to an MEP but has memory of its gained momentum, hence ultimately yields information as an effective potential reaction path on the excited state.

The Qu-Eh method, on the other hand, does model the full nuclear wavepacket. For the Qu-Eh dynamics simulations, all GWPs are initiated from the same B3LYP/6-31G\* optimised FC geometry as 2OE and statics calculations, where 9 GWPs are sent along 4 NMs and are propagated for 30 fs with 1 fs timesteps. The GWP coordinates are defined in terms of mass- and frequency-scaled NM vectors obtained from a ground state FC point frequency calculation performed at the B3LYP/6-31G\* level of theory. The NMs chosen are those shown in the top of Fig. 4.2. These modes span the derivative coupling vector  $\nu_{10a}$  and three totally symmetry modes which span the gradient difference vector of the  $S_1$ - $S_2$  conical intersection, ( $\nu_{6a}$ ,  $\nu_1$ ,  $\nu_{9a}$ ), which are shown at the bottom of Fig. 4.2. From the Qu-Eh simulations, snapshots of the geometries along the centroid GWP were taken at different times. These geometries were used to calculate SA(6)-RASSCF[1,1](6,8,6)/6-31G\* energies. This allowed for a study on the

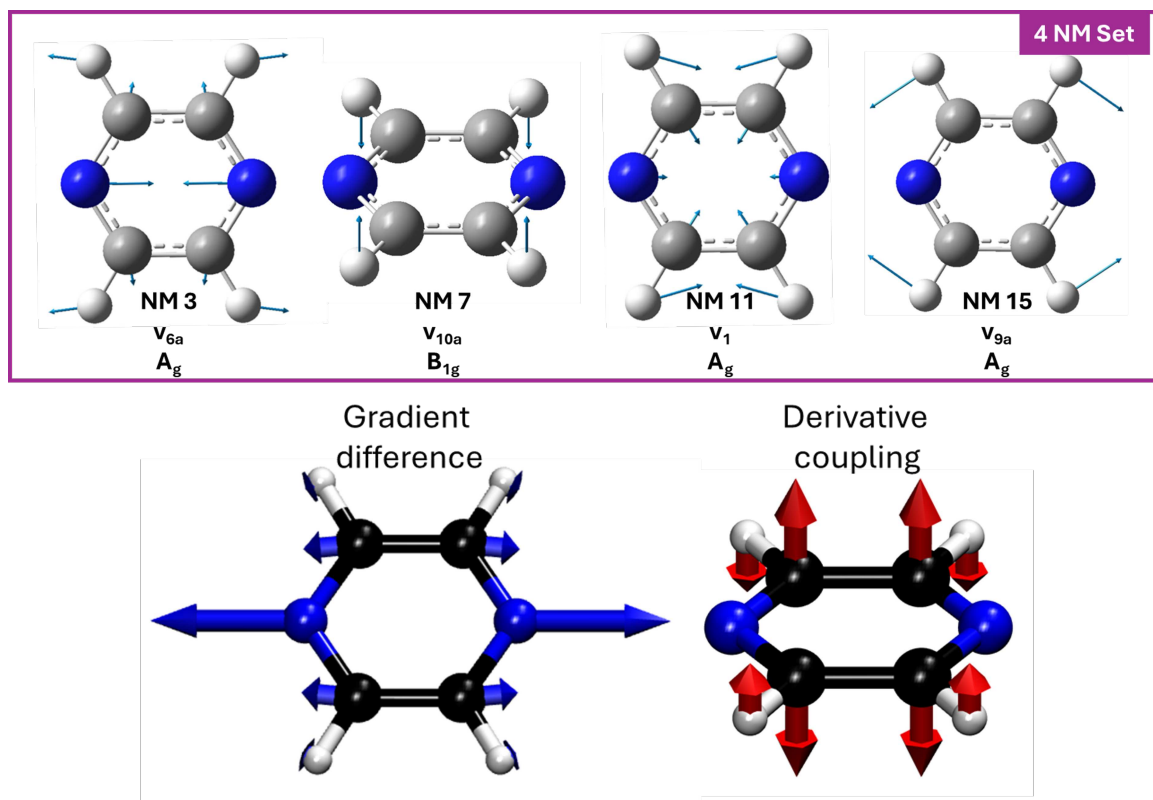


Figure 4.2: (Top) The NMs of pyrazine, calculated at B3LYP/6-31G\* level of theory, used in the 4-mode 6-state Qu-Eh simulation in this study. (Bottom) The branching space of the  $S_1$ - $S_2$  conical intersection which pyrazine decays through in the historical model. The NMs chosen aim to describe the motion along the branching space shown.

impact of electron correlation through a comparison of SA-CASSCF and SA-RASSCF energies and state orderings along an approximate reaction pathway, which shall be discussed later.

## 4.3 Results and Discussion

### 4.3.1 Comparison of excitation energies from different electronic structure methods

Discussion begins with a comparison of the vertical excitation energies for the low-lying excited states of pyrazine from the Franck-Condon (FC) region for different electronic structure methods and experimental values, shown in Table 4.2. It is worth noting that the CASSCF- and CASPT2-based methods in this chapter, both calculated and cited from the literature, use the

10 electron 8 orbital active space consisting of the lone pairs of the N atoms, and the  $\pi$  and  $\pi^*$  bonds of the ring.

Across all methods compared, including experiment, the  $S_1$  state has  $^1B_{3u}$  symmetry at the equilibrium ground state geometry. This may change as one evolves on the excited state, which we will explore in Section 4.3.2. Most methods, including SA(6)-CASSCF,<sup>220–222</sup> overestimate the vertical excitation energy for this state. The CASPT2,<sup>220,221,223</sup> XMCQDPT2,<sup>214</sup> EOM-CCD(T),<sup>231</sup> and B3LYP/TDDFT methods<sup>221,232</sup> reproduce the states vertical excitation energy best.

The  $S_2$  state shows more disagreement. Most methods consider the  $S_2$  state to have  $^1B_{2u}$  symmetry, however, the CASPT2,<sup>220,221,223</sup> XMCQDPT2,<sup>214</sup> and TDDFT<sup>221,232</sup> methods consistently show the  $S_2$  state having  $^1A_u$  symmetry, where the  $S_3$  state now has  $^1B_{2u}$  symmetry, or even for TDDFT/LB94 where now the  $S_4$  state has  $^1B_{2u}$  symmetry.<sup>233</sup> Other methods, such as CASPT3,<sup>221,222,234</sup> EOM-CCSD and -CCSD(T) methods<sup>224,231</sup> show that the  $S_2$  state is  $^1B_{2u}$ , but is very close or degenerate to the  $S_3$  state of  $^1A_u$  symmetry. Despite this, most methods are close to the experimental values of the vertical excitation energy for this state. The CASSCF, CASPT3, TDDFT and CC methods seem to overestimate this value, while CASPT2 lies close to the experimental values, as well as SAC-CI.<sup>235</sup> For CASSCF methods with a (10,8) active space, the majority show that the  $S_2$  state has  $^1B_{2u}$  symmetry, followed by  $S_3$  with  $^1B_{2g}$  symmetry, and then  $S_4$  with  $^1A_u$  symmetry.<sup>220–222</sup>

The  $^1A_u$  state is more difficult to compare to, with a single experimental value which is an estimate from an electron energy loss spectroscopy (EELS) study.<sup>232</sup> Along with two values for the  $^1B_{2g}$  state, it is difficult to discern which state lies above which at the equilibrium geometry from experiment alone, and indeed the same case applies to whether the  $^1A_u$  state lies above the  $^1B_{2u}$  state or otherwise. It is worth noting that in transient absorption X-ray spectroscopy (XR-TAS) studies, the  $^1A_u$  state has been detected and its role in the observed spectra has suggested that the  $^1A_u$  state lies close to or below the  $^1B_{2u}$  state.<sup>8,219</sup>



These studies, however, alongside simulation, predict excited state decay times which disagree with recent time-resolved photoelectron spectroscopy (TR-PES) results.<sup>210</sup> Regardless, further experimental study is required to better resolve the understanding around pyrazine's decay mechanism, given that, as Table 4.2 shows, different electronic structure methods yield differing state orderings.

Considering the CASSCF family of methods, one can see that the perturbative correction added in CASPT2 has a large impact on the  $n\pi^*$  states  $^1B_{3u}$ ,  $^1A_u$ , and  $^1B_{2g}$ , with energy changes of roughly 1 eV, 1.5 eV, and 0.3 eV respectively (Table 4.2). However, if we consider the SA(5)-RASSCF[1,1](6,8,6) calculations of T. Tran *et al.*,<sup>30</sup> we observe that the state ordering between RAS and CAS changes only in that the  $^1B_{2g}$  state lies above the  $^1A_u$  state but remains above the  $^1B_{2u}$  state. The energy difference between the  $^1B_{2u}$  and  $^1B_{3u}$  states is also closer to experiment (0.2 eV for CASSCF and 0.64 eV for RASSCF, and  $\sim 1$  eV for experiment). In addition, looking at higher order perturbative corrections in CASPT3 calculations<sup>221,222,234</sup> show that the  $^1A_u$  state lies above the  $^1B_{2u}$  state and is near degenerate rather than lying below it. The  $^1B_{2g}$  state lies above the  $^1A_u$  state in this case, unlike CASSCF where it lies below and is near degenerate with the latter state.

The various electronic structure methods used to study the electronic state orderings of pyrazine differ mainly in the position of the  $^1A_u$  state (i.e. above or below the  $S_2 \pi\pi^*$  state). The theoretical basis for this can be understood from the Valence Bond (VB) analysis of the 5 low-lying states of pyrazine derived from the early work of Dunning and Goddard.<sup>240</sup>

The  $n\pi^*$  states for pyrazine are single excitations from the lone pairs to vacant p orbitals (Fig. 4.3 b and b'). They consist of two pairs of states shown in Fig. 4.3:  $a \pm a'$  to give  $^1B_{3u}$  (+) and  $^1B_{2g}$  (−) and  $c \pm c'$  to give  $^1A_u$  (+) and  $^1B_{1g}$  (−). The two pairs of  $n\pi^*$  states only differ by different couplings between C atoms ( $a/a'$  versus  $c/c'$  in Fig. 4.3). The states  $a$  and  $a'$  are derived from excitation from the ground state Kekulé-like structure while  $c$  and  $c'$  are derived from an excited Dewar structure and should be higher in energy. The ground and  $\pi\pi^*$  states are like the Kekulé and anti-Kekulé states of benzene. The various theoretical computations differ mainly in the splitting of  $a \pm a'$  versus  $c \pm c'$  and the possibilities are summarized in

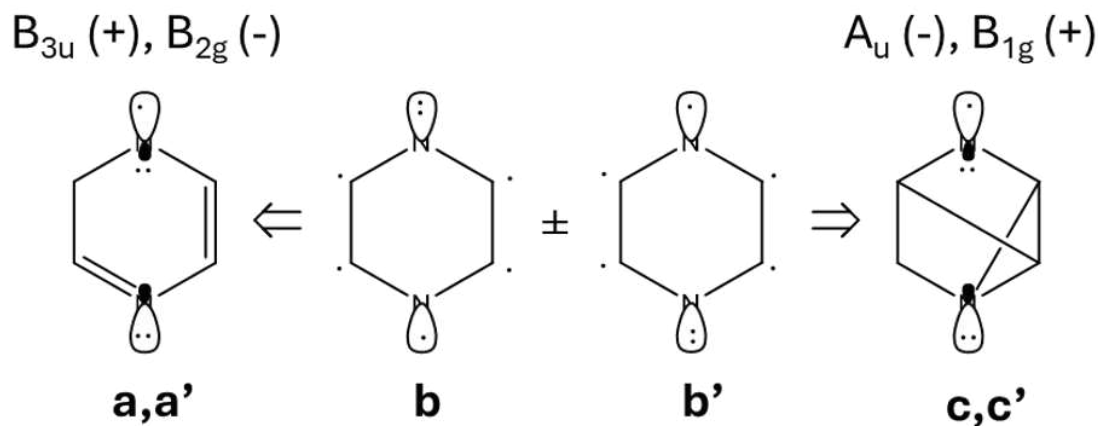


Figure 4.3: VB representation of the two pair of  $n\pi^*$  states.<sup>240</sup> The  ${}^1B_{3u}$  and  ${}^1B_{2g}$  states are  $a \pm a'$ , where  $a'$  is a rotated through 180 degrees ( $'$  notation is the same throughout the scheme). The  ${}^1A_u$  and  ${}^1B_{1g}$  states are  $c \pm c'$ . In  $b$  and  $b'$  we show the 2 configurations of the lone pairs only, where the spin coupling of the remaining  $\pi$  electrons is the same but not given. The  ${}^1B_{3u}$  state is the sum of these components and the  ${}^1B_{2g}$  state is the difference with the spin coupling shown in  $a$  or  $a'$ . Similarly, one component of the state  ${}^1A_u$  is  $b+b'$  with the spin coupling given  $c$  and  $c'$ , while the  ${}^1B_{1g}$  state is  $b-b'$ .

Fig. 4.4, which shows the state ordering obtained with various theoretical methods along with the splittings  $a \pm a'$  ( $\Delta E ({}^1B_{2g} - {}^1B_{3u})$ ) versus  $c \pm c'$  ( $\Delta E ({}^1B_{1g} - {}^1A_u)$ ).

The computed splittings (Table 4.2) are much larger (Fig. 4.4 RHS) for CASPT2 than CASSCF (Fig. 4.4 LHS). In RASSCF, the splitting lies in-between the two (Fig. 4.4 centre); larger than CASSCF splittings but lesser than those of CASPT2. As shown by Dunning,<sup>240</sup> the splitting  $a \pm a'$  or  $c \pm c'$  is proportional to the lone pair overlap which should be small and positive (so for  ${}^1B_{3u}$  state is lowest for the pair  $a \pm a'$ ). Since the effect of the spin coupling in the ring (linker) should be small, one would expect the splitting of both pairs of  $n\pi^*$  states (ie within LHS or within RHS) to be equal. The splittings obtained with CASPT2 etc (Fig. 4.4 RHS) are consistently larger than with variational methods in which the two splittings are more similar in magnitude. Thus, the origin of the discrepancy between methods like CASPT2 and CASSCF/RASSCF lies in energy difference splitting between  ${}^1B_{3u}$ - ${}^1B_{2g}$  (Fig. 4.3a  $\pm a'$ ) and  ${}^1A_u$ - ${}^1B_{1g}$  (Fig. 4.3c  $\pm c'$ ) that must arise from the different internal C-C spin coupling. But this is internal and semi-internal correlation (referring to a double excitation in which an active electron is excited within the active space at the same time that an inactive electron is promoted to the virtual space),<sup>30,241,242</sup> which we compute to infinite order in CASSCF, not

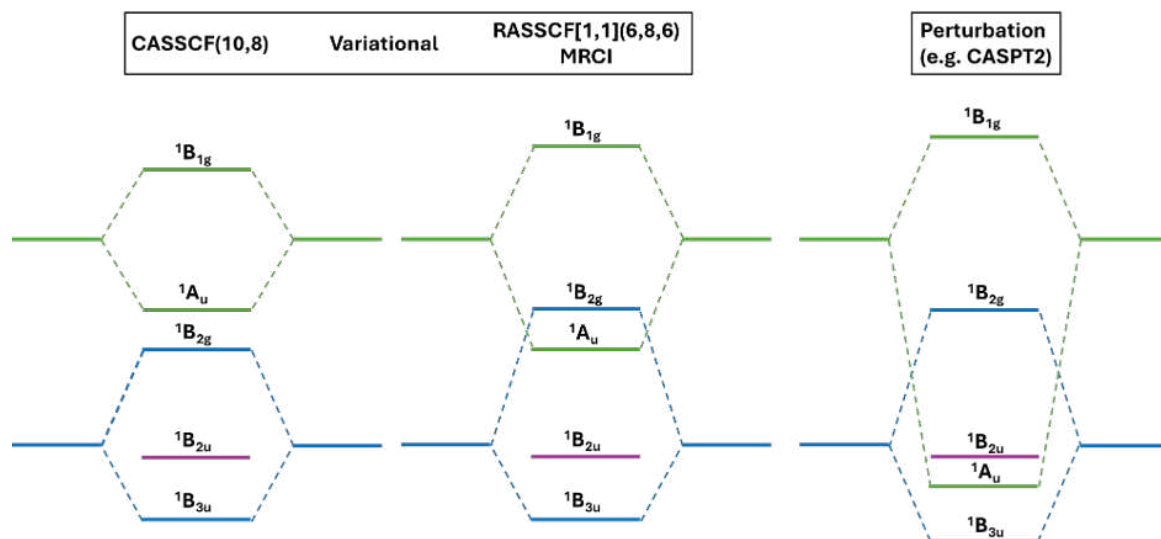


Figure 4.4: Energy level diagrams for the  ${}^1B_{2u}$   $\pi\pi^*$  state and two pairs of  $n\pi^*$  states ( ${}^1B_{3u}$ - ${}^1B_{2g}$  and  ${}^1A_u$ - ${}^1B_{1g}$ ) for variational and perturbation based electronic structure methods. The splitting of the  $n\pi^*$  state pairs determines the energy ordering of the states.

external correlation which is computed to 2nd order in CASPT2 and 3rd order in CASPT3 (which gets the same energy order as RASSCF). The  $n\pi^*$  state is a single excitation from the lone pair to a vacant p orbital. Dynamic correlation involves the double excitations of the inactive or active orbitals into the virtual space. CASPT2 adds the dynamic correlation from outside the active space, therefore we shouldn't expect that the  $n\pi^*$  states should lower in energy as much as they do in CASPT2 to give the state ordering that  ${}^1A_u$  is below  ${}^1B_{2u}$ . RASSCF[1,1] recovers the semi-internal correlation which involves the 'double' excitation of an active and inactive electron into the virtual space, and we see that recovery of semi-internal correlation generally preserves the state ordering of CASSCF (bar the  ${}^1A_u$  state being lower than the  ${}^1B_{2g}$  state). In the next section, show that this indeed is the case over the range of geometries which occur on pyrazine's excited state decay pathway.

### 4.3.2 Excited state pathway comparison (CASSCF vs RASSCF)

We now test the reliability of the CASSCF method against the RASSCF method for pyrazine. As discussed in Section 2.3.4.1, CASSCF does not entirely recover dynamic correlation effectively. We can use RASSCF as an extension of CASSCF to recover some of this dynamic correlation. Specifically, within this study, the RASSCF[1,1] method is used wherein we only

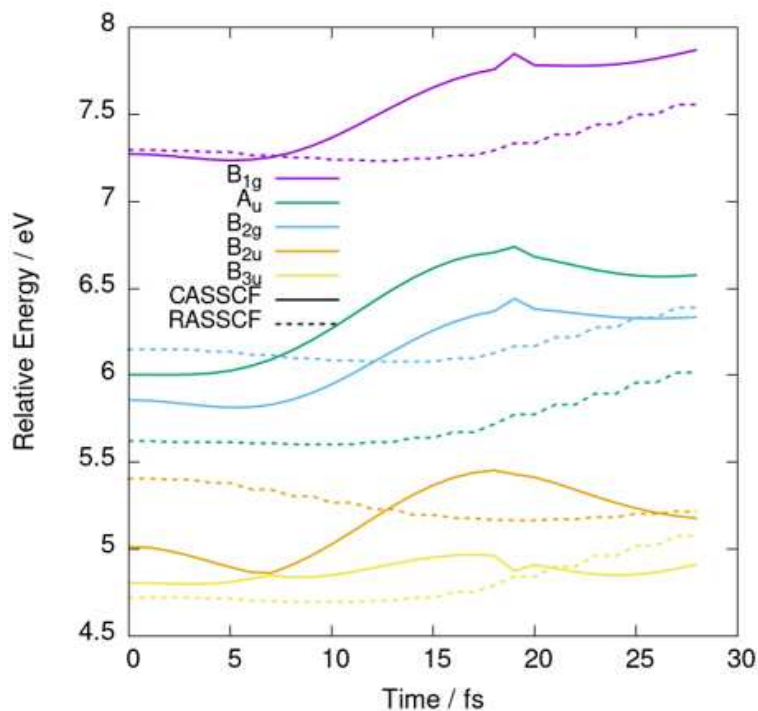


Figure 4.5: The state energies of SA(6)-CASSCF(10,8) over time in the centroid GWP of a 4-mode 6-state Qu-Eh run of pyrazine beginning at the FC geometry on the  $S_2$  ( $^1B_{2u}$ ) state, alongside SA(6)-RASSCF[1,1](6,8,6) state energies using geometries along the trajectory of the GWP at regular timesteps.

include one hole in RAS1 and one particle in RAS3 which recovers the semi-internal correlation which involves the ‘double’ excitation of an active and an inactive electron into the virtual space.<sup>30,241,242</sup>

We track the RASSCF[1,1](6,8,6) state energies using geometries from a centroid GWP from a 4-mode 6-state Quantum Ehrenfest calculation (Fig. 4.5) which acts similarly to a minimum energy pathway (MEP). This centroid GWP begins at the FC geometry on the pure  $S_2$   $^1B_{2u}$   $\pi\pi^*$  state. Here we see that the GWP, with CASSCF, from the  $S_2$   $^1B_{2u}$   $\pi\pi^*$  state reaches the  $S_1$   $^1B_{3u}$   $n\pi^*$  state via a  $S_1$ - $S_2$  CoIn by around 7 fs. However, with RASSCF, we see that the two states at 7 fs maintain a larger energy gap. We do begin to see the  $S_1$  and  $S_2$  states come close to degeneracy by around 16 fs. We note that for RASSCF that the  $^1A_u$  state is  $S_3$  and the  $^1B_{2g}$  state is  $S_4$ , where compared to CASSCF these states are the other way around. This can be explained in terms of splittings between  $n\pi^*$  state pairs, as discussed previously. The most significant result is that the higher lying  $n\pi^*$  states such as  $S_3$   $^1B_{2g}$  and  $S_4$   $^1A_u$  do not appear

to interact with the lower lying states along this path for RASSCF, and that for RASSCF the energy orderings of the states are generally preserved.

These results highlight that while CASSCF does not recover dynamic correlation explicitly, it mostly retains the correct state ordering and qualitative features of the dynamics. The inclusion of semi-internal correlation via RASSCF confirms that the missing dynamic correlation does not significantly affect the excited state dynamics of pyrazine. This suggests that CASSCF can provide a qualitatively consistent picture of dynamics to that of RASSCF in the present study.

### 4.3.3 Excited state dynamics

The summary of all dynamics results can be seen in Fig. 4.6, where comparisons can be seen for the single 2OE trajectory initiated from the pure  $S_2$  at the FC geometry with no initial momentum, and the GGP-averaged results of the 4-mode 6-state Qu-Eh simulation.

Firstly, looking at NM excitations over time for 2OE in Fig. 4.6(a), we note that all the NMs which are excited are all totally symmetric modes:  $\nu_{6a}$ ,  $\nu_1$ ,  $\nu_{9a}$ ,  $\nu_{8a}$ , and  $\nu_2$ . The  $\nu_1$  and  $\nu_{6a}$  modes are excited the most, acting as the central drivers of dynamics. All these modes, particularly  $\nu_{6a}$ , connect to the gradient difference vector for the  $S_1$ - $S_2$  CoIn seen in Fig. 4.2 and drive the molecule towards this CoIn. In comparison to the Qu-Eh simulation, NM excitation occurs only along the 4 chosen modes:  $\nu_{6a}$ ,  $\nu_{10a}$ ,  $\nu_1$ , and  $\nu_{9a}$ . The modes which both simulations share,  $\nu_{6a}$  (purple line),  $\nu_1$  (light blue line), and  $\nu_{9a}$  (orange line), in Fig. 4.6(a) for 2OE and Fig. 4.6(b) for Qu-Eh, are very similar in terms of magnitude, as well as where their minima/maxima lie. In both simulations, the  $\nu_{10a}$  mode (green line) show zero NM excitation. In 2OE, this is because dynamics moves only along the totally symmetric modes. In Qu-Eh, GWPs are moving along the  $\nu_{10a}$  mode, but the motion is equal and opposite in both directions, and so cancels out in the GGP average. This is discussed in more detail in Section 5.4.1.2.

Similarities in the nuclear dynamics between simulations are reflected in the adiabatic state populations seen in Fig. 4.6(c) and 4.6(d), where both 2OE and Qu-Eh reach the  $S_1$ - $S_2$  CoIn by around 7 fs and decays to the  $S_1$  state in a ‘step-change’ like manner, with a slight resurgence

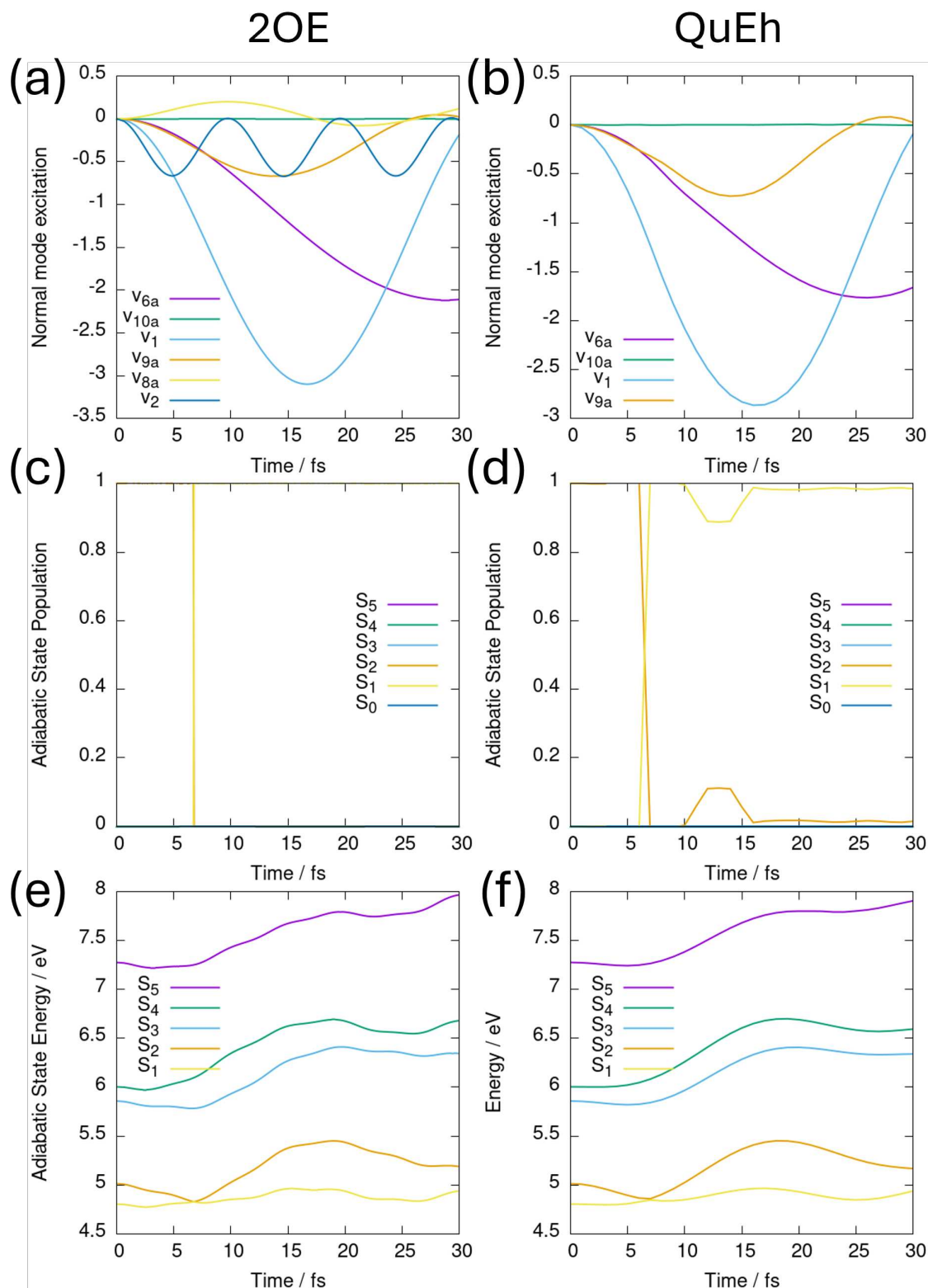


Figure 4.6: Results for 2OE trajectory (left column) and 4-mode 6-state Qu-Eh simulation (right column) modelling the excited state decay of pyrazine. Both simulations are initiated from the FC geometry on the  $S_2$  state and use SA(6)-CASSCF(10,8), where the 2OE trajectory has no initial momentum. The Qu-Eh plots show the GGP-average bar (f), which is taken from the centroid GWP. (a) and (b) show the NM excitations over time, (c) and (d) show the adiabatic state populations for  $S_0$ - $S_5$  over time, and (e) and (f) show the adiabatic state energies over time for the respective simulations.

in the Qu-Eh result as an effect of the GGP average. This can also be seen by looking at the adiabatic state energies for 2OE and Qu-Eh simulations shown in Fig. 4.6(e) and 4.6(f) respectively, where the crossing point of the  $S_1$  (yellow line) and  $S_2$  (orange line) adiabatic states occurs around the same time ( $\sim 7$  fs). In 2OE, the decay occurs diabatically, where the diabatic state population remains constant over time. In Qu-Eh, this is also generally true but does have a slight amount of mixing caused by the  $\nu_{10a}$  derivative coupling mode, which will be discussed in more detail in Chapter 5.

The fast decay indicates that the FC geometry lies very close to the CoIn seam over time, in the catchment area of the  $S_1$ - $S_2$  CoIn. This decay is much faster than what is typically found with nonadiabatic dynamics using the well-known 2-mode 3-state vibronic coupling model potential surfaces for pyrazine,<sup>204</sup> as well as higher mode models,<sup>203,205</sup> where the majority of adiabatic state population transfer passes through the CoIn in around 30 fs. *Ab initio* dynamics, such as ADC(2)<sup>243-246</sup> and TDDFT<sup>213</sup> surface hopping results also give some qualitative similarity to these results, albeit there are differences in which diabatic states are populated over time due to the involvement of the dark  $n\pi^*$  states. The reason for this is that the CASSCF method places the  $S_1$  and  $S_2$  states much closer together than the 3-state model - 4.81 and 5.01 eV respectively in SA(6)-CASSCF versus 3.94 and 4.84 eV respectively in the original model developed by Schneider and Domcke using the INDO/S CI method.<sup>204</sup> In CASSCF this puts pyrazine in the catchment area of the conical intersection once in the excited state, leading to rapid decay to the  $S_1$  state, expectedly faster than that of the iconic 2-state 3-mode model. Comparing to experimental studies, the most recent high-resolution TR-PES study from Karashima *et al.* found full decay from the  $\pi\pi^*$  state to occur within 13 fs,<sup>210</sup> while the XR-TAS work of Scutelnic *et al.* found decay from the  $\pi\pi^*$  state to be  $90 \pm 70$  fs.<sup>219</sup> Another recent XR-TAS study, from the work of Chang *et al.*, state no experimental decay time, but have supporting ADC(2) surface hopping and MCTDH simulations which found full decay occurring in around 50 fs.<sup>8</sup> Therefore, we note that while our results are in reasonable agreement with the TR-PES study, there is still uncertainty and disagreement from excited state decay times found from XR-TAS studies, and the simulations that support them. It is worth noting that in these simulations there is no population transfer to the higher lying  $n\pi^*$  states. This is further reflected in the adiabatic

state energies for 2OE and Qu-Eh simulations shown in Fig. 4.6(e) and 4.6(f) respectively, where the higher lying  $n\pi^*$  states show no crossings or close interactions with the lower lying states, lying at least 1 eV above these states over the entire course of dynamics.

It is surprising to see that a single point classical Ehrenfest trajectory, as shown by the 2OE result, can share much with the 4-mode Qu-Eh simulation, which treats the nuclei quantum mechanically, and also resemble a nuclear wavepacket. This is most likely due to the fact that dynamics begins within the catchment region of the  $S_1$ - $S_2$  CoIn, therefore dynamics is dominated by the branching space, specifically the gradient difference vector. Both 2OE and Qu-Eh simulations cover these spaces well, and as a result we see similar dynamics. It is worth noting that because 2OE is a classical nuclei method, it does not fully describe the motion along the derivative coupling, which is true for the Qu-Eh method. Regardless, decay in either method is shown to be diabatic, where the gradient difference acts as the important vector of motion for dynamics. In the next chapter, the derivative coupling plays a more crucial role in the mixing of states and formation of electronic coherences, which only the Qu-Eh method can describe correctly.

## 4.4 Conclusion

In this chapter, we have studied the radiationless decay of the  $S_2$   $\pi\pi^*$  state in pyrazine both from a static and dynamic perspective using CASSCF and the semi-classical 2OE and fully quantum Qu-Eh method.

Analysis of pyrazine’s electronic structure shows that different electronic structure methods lead to different state orderings, particularly around the optically bright  $^1B_{2u}$  state and the dark  $^1A_u$  state. We show that from a valence bond perspective these differences can arise due to different splittings of the  $n\pi^*$  state pairs,  $^1B_{3u}$  &  $^1B_{2g}$ , and  $^1A_u$  &  $^1B_{1g}$ . These splittings arise from internal spin coupling which should come from internal and semi-internal electron correlation. We find that variational methods such as CASSCF and MRCI split these states less than perturbational methods such as CASPT2 and ADC(2), which lead to different state

orderings. The CASSCF method was also compared with the RASSCF method, to see if recovering semi-internal electron correlation would significantly change the state ordering over a number of geometries from the centroid GWP of a Qu-Eh simulation acting as a minimum energy pathway. We found that both CASSCF and RASSCF generally preserved this state ordering over the effective MEP.

Dynamics simulations for 2OE and Qu-Eh beginning at the pure  $S_2$  state at the FC geometry reinforced the conclusions of the effective MEP. Both semi-classical 2OE and fully quantum mechanical Qu-Eh simulations show rapid internal conversion from the  $S_2$  ( $^1B_{2u}$ ) to the  $S_1$  ( $^1B_{3u}$ ) state within approximately 7 fs, closely matching the fastest timescales observed in high-resolution TR-PES experiments.<sup>210</sup> Though noting less agreement with recent XR-TAS results<sup>8,219</sup> and supporting simulations.<sup>214,243,246</sup> Importantly, neither simulation shows involvement of the higher-lying  $^1A_u$  or  $^1B_{2g}$  states during this ultrafast decay, suggesting that these states do not contribute to the primary decay pathway under the conditions studied. Both dynamics methods showed similar dynamics and decay times, despite the fact that some modes in the 2OE trajectory were not present in the Qu-Eh simulations. This is likely because dynamics begins in the catchment region of the CoIn, so motion is dominated within the gradient difference vector of the branching space, in this case modes  $\nu_{6a}$  and  $\nu_1$ , both of which are present in the 2OE and Qu-Eh simulations.

Our results show that the CASSCF method is at least qualitatively faithful to the RASSCF description of pyrazine, and supports the historical decay mechanism of pyrazine. We note that in terms of the current literature, the involvement of the dark  $n\pi^*$  states is the leading theory as of writing due to recent XR-TAS experiments. Nonetheless, this study highlights the vast range of state orderings that pyrazine can garner using differing electronic structure methods, and that there is currently an experimental disagreement in terms of decay rate between TR-PES and XR-TAS methods. Given the sensitivity of state ordering to both electronic structure method and nuclear geometry, continued high-resolution experimental investigations - and supporting computational simulations - will be essential to definitively resolve the mechanistic details.

In the next chapter, we will study in more detail the role that electronic coherences play within

the excited state decay mechanism of pyrazine using Qu-Eh simulations and the CASSCF method.

# Chapter 5

## Electronic Coherence Formation in the Radiationless $S_2$ Decay of Pyrazine

*Note: the material in this chapter is derived from Moore et al.<sup>206</sup> The dissertation author was the primary researcher and author of this paper.*

### 5.1 Introduction

An ongoing challenge in the study of electron-nuclear coupled dynamics, especially concerning electron dynamics, is characterizing experimentally the coherences formed when passing through a CoIn. The first experimental evidence of coherences generated by CoIns was suggested to have been found in the excited state decay from the  $^1B_{2u} \pi\pi^*$  state ( $D_{2h}$ ) of pyrazine in an X-ray transient absorption spectroscopy (XR-TAS) study.<sup>8</sup> Experimentally, two-dimensional electronic spectroscopy (2DES),<sup>247</sup> XR-TAS,<sup>8</sup> and time resolved photoelectron spectroscopy (TR-PES) studies<sup>248</sup> have been used to probe electronic coherences in molecular systems. Direct observation of electronic coherences remains difficult due to either a lack of signal information in 1-dimensional spectroscopic methods, or in the case of 2DES spectra difficulty of distinguishing the roles of electronic, vibronic, and vibrational degrees of freedom within studies.<sup>247</sup> There are proposed experiments, such as TRUECARS, which may be able to directly observe

electronic coherences,<sup>249,250</sup> but have not yet been implemented. Neville *et al.*<sup>24</sup> have discussed the symmetry aspects for the creation of coherences at a CoIn. They show that a coherence cannot be generated by passing through a CoIn if the two states involved at the crossing have different Abelian point group symmetries at the Franck-Condon (FC) region, and show this to be the case for pyrazine in quantum dynamics simulations.<sup>24</sup> As we will discuss subsequently, this is not true if the state is mixed with the other state connected to the CoIn.

In the vicinity of a CoIn, the nonadiabatic electron-nuclear coupling (derivative coupling) plays an essential role. The behaviour of electronic coherences depends on the interactions/coupling between the nuclear wavefunction and the electronic wavefunction,<sup>4</sup> hence in a simulation a correct description of the electron-nuclear coupled dynamics is key to understanding these processes. Thus, the method used for the electronic structure calculation must be capable of allowing the correct description of superpositions of electronic states, and the dynamics method used must be able to describe the electron-nuclear interactions through time. As discussed in Section 2.4, dynamics methods such as the grid-based MCTDH,<sup>124</sup> and trajectory-based methods such as DD-vMCG<sup>197</sup> and Qu-Eh,<sup>27</sup> where the nuclei are treated quantum mechanically, have been found to best describe this type of dynamics.<sup>147,251</sup>

As discussed in Chapter 4, there is an ongoing discussion around the state ordering of pyrazine, and therefore its decay mechanism.<sup>8,209,213,214,217–219</sup> In this study we consider the previously established three-state decay model where the  $S_1$  state is the  $^1B_{3u}$   $n\pi^*$  state and the  $S_2$  state is the  $^1B_{2u}$  state, using the variational SA-CASSCF method. An alternative model states that a dark  $n\pi^*$   $^1A_u$  state lies below the  $^1B_{2u}$  state, where initial radiationless decay occurs, followed by radiationless decay from the  $^1A_u$  state to the  $^1B_{3u}$  state, which can be found with perturbation theory electronic structure methods such as ADC(2) or CASPT2.<sup>8,221,223</sup> This model is additionally the one used to explain coherences seen in a recent experiment.<sup>8</sup> The principles of the formation of coherences and symmetry discussed here are the same for either state ordering. We will show that upon excitation to the bright  $S_2$  state in pyrazine, that one lies within the catchment region of the  $S_1$ - $S_2$  CoIn, and electronic coherences will form due to the normal mode (NM) corresponding to the derivative coupling,  $\nu_{10a}$ , from the outset. This can be understood by looking at Fig. 5.1, which is a cartoon of the CoIn of pyrazine,

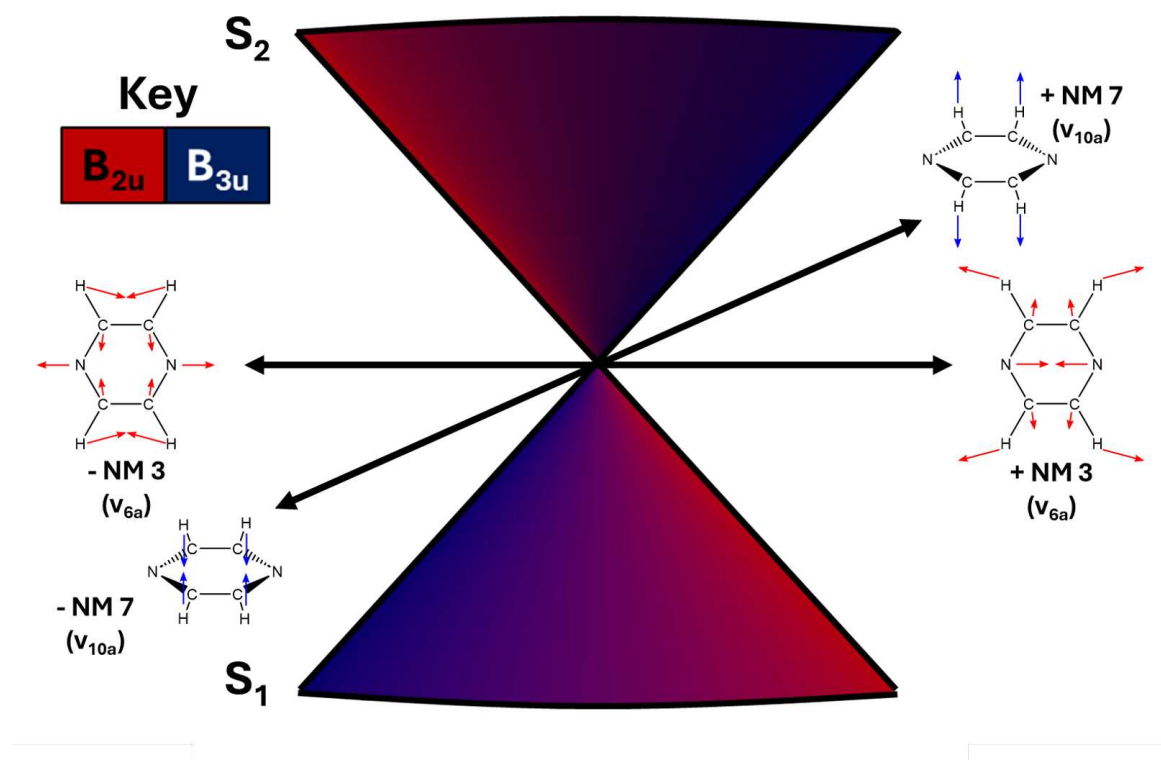


Figure 5.1: A cartoon representing two idealised potential surfaces to interpret the main results of our dynamics computations near the conical intersection (CoIn) between the two adiabatic states  $S_1$  and  $S_2$ . The two PESs labelled  $S_1$  and  $S_2$  represent the adiabatic states. The colour on the surfaces gives the diabatic components: the diabatic  ${}^1B_{2u}$  ( $\pi\pi^*$ ) state is red and the diabatic  ${}^1B_{3u}$  ( $n\pi^*$ ) state is blue. These diabatic states are the adiabatic states at time zero and the strength of red vs blue gives the diabatic composition at any position. We note that to specify the state at any point, two indices are required: i)  $S_1$  or  $S_2$  and ii) the diabatic composition. In all our discussions of the dynamics, these two quantities are plotted separately for clarity. The axes denote the branching space for the conical intersection. In the case of this study  $NM\ 7\ (\nu_{10a})$  is the derivative coupling vector and  $NM\ 3\ (\nu_{6a})$  is the (simplified) gradient difference vector.

between the  $S_1\ {}^1B_{3u}$  state and the  $S_2\ {}^1B_{2u}$  state. The colours of the potential surfaces represent the diabatic composition of the states (which we choose to be the adiabatic states at time 0). Beginning from the top left-hand side of the upper cone (the FC region), for a ball rolling along the direction derivative coupling vector,  $\nu_{10a}$ , we see that the diabatic composition is changing (from red to blue) because of the derivative coupling between the two diabatic components  ${}^1B_{3u}$  and  ${}^1B_{2u}$ . This changing of the diabatic states couples to the nuclear motion via the derivative coupling and is the origin of coherence formation. For additional information on this representation, see the work of Jenkins *et al.*<sup>159</sup> and Meisner *et al.*<sup>154</sup>

The major component of the corresponding gradient difference vector is  $NM\ \nu_{6a}$ . Moving along

the direction of the gradient difference vector, the surface does not change colour (i.e. remains red) as it passes through the CoIn, and the diabatic composition ( $^1B_{2u}$ ) remains the same. The gradient difference vector only ‘feels’ the derivative coupling by coupling with other modes.

Because  $\nu_{10a}$  is non-totally symmetric but equivalent in the plus and minus directions, we can observe the same coherences along  $\nu_{10a}$  from time zero in the plus and minus directions. Due to the Berry phase,<sup>46</sup> as one crosses the CoIn in the opposite direction, the geometric phases accumulated by going in the plus and minus directions will be opposite to each other. As we shall show, this effect cancels out the coherences approximately (i.e. except for numerical error) in our computations. This is a more general statement of the ideas discussed by Neville *et al.*<sup>24</sup>

In our computations we shall perform two different types of simulation. In one case, we begin with an Ehrenfest wavefunction corresponding to a pure adiabatic state, in this case the  $S_2$  state. In the other case, we begin with an Ehrenfest wavefunction corresponding to a superposition of the adiabatic states, in this case  $S_1$  and  $S_2$ . In the latter case, there will be a component of the initial gradient that arises from the interstate gradient<sup>200</sup> corresponding to the derivative coupling. Thus, a mixture of states ‘tips’ the dynamics more onto one side of the CoIn than the other. Therefore, the initial conditions create a mixture of states, including the optically bright and energetically close-lying  $S_1$  state. By doing so, one breaks the symmetry from time 0 in the direction of the derivative coupling, and electronic coherences can be documented. The specific idea that nonadiabatic coupling can influence the coherence of electronic state superpositions, and that different relative phases of these state mixtures can influence the subsequent nuclear dynamics, has been discussed by Arnold *et al.* using exact quantum dynamics simulations on a 2-mode 2-state model CoIn.<sup>252</sup> The present study extends on this work, discussing pyrazine as a molecular system specifically, using 2-, 4- and 9-mode and 3- and 6-state models in conjunction with the Qu-Eh method.

Although our simulations are connected to experimental findings and designed to provide theoretical insight into the dynamics of pyrazine, the aim is not to reproduce a specific experimental setup. Rather, it explores the fundamental mechanisms underlying coherence generation near CoIns and the effects of symmetry. Where appropriate, we draw comparisons with experiment,

particularly regarding the  $S_2$  decay time and the observed coherences. Finally, while in principle we could have used the MCTDH method on one of the well-known pyrazine models,<sup>203–205</sup> our objective here is to test/demonstrate the Qu-Eh method in the special situation where the initial wavefunction lies in the ‘catchment’ region of the conical intersection.

## 5.2 Theory

### 5.2.1 Electronic coherences and electron dynamics

In our results and discussion, we use two measures to study electronic coherences. The first is the coherence itself, which is defined as the off-diagonal element of the electronic state density matrix. In the Qu-Eh method, however, we cannot obtain complete coherences since Qu-Eh only has the electronic state populations at the centres of the GWPs. Thus, Qu-Eh does not give the coherences in the same manner as other wavepacket methods since the electronic populations are folded into the potentials. For a quantitative approximation for the upper bound of the coherence,  $M_{coh}$ , we use the product of the adiabatic state populations,  $P$ , which approximates the off-diagonal values of the electronic state density matrix for the DD-vMCG nuclear wavepacket, as used in the work of Vacher *et al.*:<sup>253</sup>

$$\begin{aligned} M_{coh} &\leq 2 \left| \sum_{i,j} A_j^{(S_1)}(t) A_i^{(S_2)*}(t) S_{ij}(t) \right|^2 \\ &= 2P^{(S_1)}P^{(S_2)}, \end{aligned} \tag{5.1}$$

where  $A_j^X$  are the coefficients for the GWP on state  $X^\dagger$  and  $S_{ij}(t)$  is the GWP overlap matrix. This definition of the coherence has also been used in surface hopping.<sup>254</sup>

The second measure is performed through tracking the crude diabatic state populations over time, which in the case of this study corresponds to the adiabatic states at time 0. To under-

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<sup>†</sup>As discussed in Section 2.4.7, DD-vMCG is very similar to Qu-Eh but has multi-set formalism, i.e. GWPs are sent along individual (typically diabatic) states. In Qu-Eh, there is only a single Ehrenfest potential surface, and in this case  $A_j^X$  would reduce down to  $A_j$ .

stand why these should be tracked, consider a coherent superposition of electronic states. A wavefunction corresponding to the coherent superposition of adiabatic electronic states at time 0 is not an eigenstate and thus the wavefunction will evolve in time as a solution of the TDSE. If the electronic wavefunction,  $\psi(t)$ , is expressed in the basis of crude diabatic states,  $\zeta_i$ , with complex coefficients  $z_i(t)$ , and energies  $E_i(t)$ , we have:

$$\Psi(t) = \sum_i z_i(t) \zeta_i e^{-iE_i(t)}, \quad (5.2)$$

and the time-independent probability density is then given by:

$$|\Psi(t)|^2 = \sum_i |z_i(t)|^2 |\zeta_i|^2 + \sum_i \sum_{j < i} \Re\{z_i(t) z_j(t) e^{-(E_i(t) - E_j(t))} \zeta_i \zeta_j\}. \quad (5.3)$$

The oscillatory terms of the form  $e^{-(E_i(t) - E_j(t))}$  are the quantum mechanical origin of the electron dynamics. Invoking the Planck-Einstein relation ( $E = h\nu$ ), we would then expect oscillations to occur at frequencies as a function of the energy gap between states:

$$\nu = \frac{E_i - E_j}{h}. \quad (5.4)$$

From Eqns 5.2 and 5.3 it is clear that one will see oscillations (electron dynamics) if at least two diabatic states are both populated and the larger the energy difference is, the shorter the period of the oscillations will be. We note, however, that while this effect is purely electronic and occurs when the nuclei are static, it explains the origin of the oscillatory behaviour that arises in electronic state superpositions. For comparison with other work, we will clarify the term ‘crude diabatic states’. Since we are not running dynamics on diabatic states, we can select these in any chemical way we choose and gain chemical information by following the dynamics in such states. In this study we use the initial adiabatic states, but we could have equally used a valence bond projection, for example.

In summary we are interested in the electronic part of the coherence, manifested in the electron dynamics in Eqn 5.3 or equivalently in Eqn 5.1.

### 5.2.2 Symmetry and electronic state superpositions

In this chapter symmetry is discussed in three slightly different but connected ways. In the first, it concerns the point group symmetries of the electronic states and the assertion made by Neville *et al.*,<sup>24</sup> that a coherence cannot be generated by passing through a CoIn if the two states involved at the crossing have different Abelian point group symmetries at the Franck-Condon (FC) region. In this case, pyrazine has an S<sub>1</sub>-S<sub>2</sub> CoIn where the S<sub>1</sub> state has a <sup>1</sup>B<sub>3u</sub> symmetry and the S<sub>2</sub> state has a <sup>1</sup>B<sub>2u</sub> symmetry, hence the states have different symmetries and thus via Neville *et al.*<sup>24</sup> we expect the coherences formed from a CoIn to be small/negligible.

The second is related to the NMs of pyrazine which we denote as  $Q_i^{\alpha_i}$ , where the  $i$  is the mode index and  $\alpha_i$  is its symmetry. Each NM has their own point group symmetry which is either totally (<sup>1</sup>A<sub>g</sub>) or non-totally symmetric. For a totally symmetric mode (e.g.  $\nu_{6a}$ ), motion along the positive and negative directions of these modes are not equivalent – in other words the potential surface is asymmetric with respect to  $+Q$  and  $-Q$ . For a non-totally symmetric mode (e.g.  $\nu_{10a}$ ), the potential surface is symmetric with respect to  $+Q$  and  $-Q$ , hence motion in either direction is equivalent.

The third is the point group symmetry of the interstate gradient, which requires some discussion. When dealing with a superposition of electronic states, the nuclear gradient (or force) that governs the nonadiabatic dynamics consists of two components: intrastate and interstate. If we consider a wavefunction,  $\Theta$ , consisting of a superposition of two adiabatic states,  $\phi_I$  and  $\phi_{II}$ , as shown in Eqn 2.55, the Hellmann-Feynman component<sup>101</sup> of the gradient with respect to nuclear displacement can be represented as:

$$\begin{aligned} \nabla \langle \Theta | \hat{H}_e | \Theta \rangle = & \cos^2 \left( \frac{\theta}{2} \right) \langle \phi_I | \nabla \hat{H}_e | \phi_I \rangle + \sin^2 \left( \frac{\theta}{2} \right) \langle \phi_{II} | \nabla \hat{H}_e | \phi_{II} \rangle \\ & + \sin(\theta) \cos(\epsilon) \langle \phi_I | \nabla \hat{H}_e | \phi_{II} \rangle, \end{aligned} \quad (5.5)$$

where  $\hat{H}_e$  is the electronic Hamiltonian. The first two terms in Eqn 5.5 are intrastate gradient terms for the adiabatic states  $\phi_I$  and  $\phi_{II}$ , while the final term is an interstate term between the two states. The intrastate terms are controlled by  $\theta$  and the interstate component is

determined by  $\theta$  and  $\epsilon$ . The interstate term corresponds to off-diagonal components of the gradient (derivative couplings), which for the Hellmann-Feynman component can be written as  $\langle \phi_I | \partial Q_i^{\alpha_i} \hat{H}_e | \phi_{II} \rangle$ , where  $\partial Q_i^{\alpha_i}$  is the gradient operator for a given NM  $i$  with symmetry  $\alpha_i$ . If we have a trajectory on state  $\phi_I$  moving along  $Q_i^{\alpha_i}$ , the state  $\phi_I$  will mix with  $\phi_{II}$  to form a superposition of  $\phi_I$  and  $\phi_{II}$ . Thus, motion along the derivative coupling close to a CoIn will generate a superposition. Conversely, if we create a superposition  $\phi_I$  and  $\phi_{II}$ , we will generate a gradient component along  $Q_i^{\alpha_i}$  and therefore motion along that coordinate. For the intrastate terms, the gradient is non-zero only along NMs associated with totally symmetric irreducible representations. However, for interstate terms involving the superposition of two states  $I$  and  $II$ , the presence of an off-diagonal gradient component along  $Q_i^{\alpha_i}$  depends on symmetry rules. Specifically, such a component is ‘allowed’ if the product of irreducible representations  $a^I \otimes a_i^{Q_i^{\alpha_i}} \otimes a^{II} = A_g$  (where  $A_g$ , or  $A_{1g}$ , is the totally symmetric irreducible representation in the  $D_{2h}$  point group). Here,  $\alpha$  denotes an irreducible representation label. Consequently, in the case of a coherent superposition of states, initial motion may occur along non-totally symmetric NMs. This behaviour is summarized in Table 5.1. Thus, mixing states  $S_2$   $^1B_{2u}$  ( $\pi\pi^*$ ) with  $S_1$   $^1B_{3u}$  ( $n\pi^*$ ) gives a gradient of symmetry  $^1B_{1g}$  that is the same as NM 7 ( $\nu_{10a}$ ).

## 5.3 Computational Details

### 5.3.1 Dynamics

Qu-Eh dynamics simulations were propagated for 50 fs in general, beginning from the pure  $S_2$  state at the FC geometry which has been optimised using DFT-B3LYP/6-31G\* level of theory. In the nuclear propagation, all simulations used the Adams-Bashforth-Moulton predictor-corrector integrator with an adaptive time-step, which ranged from  $10^{-4}$  to  $10^{-1}$  fs. The energy/wavefunction was evaluated every 0.4 fs. At each energy evaluation we have a quadratic representation of the potentials which is used to propagate the electronic wavepacket coefficients. Simulations were also run at 0.2, 0.6 and 1 fs energy/wavefunction timesteps, and qualitative convergence was found by 0.4 fs (as discussed in Section 3.4.2).

Table 5.1: Direct product symmetries of the pairs of electronic states  $S_0$ - $S_5$  for pyrazine and the allowed normal modes (NM) that are associated with the same irreducible representations. NMs used over the 2-, 4-, and 9-mode simulations (see Section 5.3.1 and Fig. 5.2) are indicated in **bold**.

|                               | $S_0, {}^1A_g, \text{Ground}$                                                                                                                          | $S_1, {}^1B_{3u}, n\pi^*$                                                                                                                              | $S_2, {}^1B_{2u}, \pi\pi^*$                                                                                                                            | $S_3, {}^1B_{2g}, n\pi^*$                                                                                                                              | $S_4, {}^1A_u, n\pi^*$                                                                                                                                 | $S_5, {}^1B_{1g}, n\pi^*$                                                                                              |
|-------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------|
| $S_0, {}^1A_g, \text{Ground}$ | ${}^1A_g$<br><b>NM 3</b> ( $\nu_{6a}$ )<br><b>NM 11</b> ( $\nu_1$ )<br><b>NM 15</b> ( $\nu_{9a}$ )<br><b>NM 20</b> ( $\nu_{8a}$ )<br>NM 24 ( $\nu_2$ ) | ${}^1B_{3u}$<br>NM 2 ( $\nu_{16b}$ )<br>NM 6 ( $\nu_{11}$ )                                                                                            | ${}^1B_{2u}$<br>NM 12 ( $\nu_{18b}$ )<br><b>NM 14</b> ( $\nu_{14}$ )<br>NM 17 ( $\nu_{19b}$ )<br>NM 23 ( $\nu_{20b}$ )                                 | ${}^1B_{2g}$<br><b>NM 5</b> ( $\nu_4$ )<br>NM 8 ( $\nu_5$ )                                                                                            | ${}^1A_u$<br><b>NM 1</b> ( $\nu_{16a}$ )<br>NM 9 ( $\nu_{17a}$ )                                                                                       | ${}^1B_{1g}$<br><b>NM 7</b> ( $\nu_{10a}$ )                                                                            |
| $S_1, {}^1B_{3u}, n\pi^*$     |                                                                                                                                                        | ${}^1A_g$<br><b>NM 3</b> ( $\nu_{6a}$ )<br><b>NM 11</b> ( $\nu_1$ )<br><b>NM 15</b> ( $\nu_{9a}$ )<br><b>NM 20</b> ( $\nu_{8a}$ )<br>NM 24 ( $\nu_2$ ) | ${}^1B_{1g}$<br><b>NM 7</b> ( $\nu_{10a}$ )                                                                                                            | ${}^1B_{1u}$<br>NM 10 ( $\nu_{12}$ )<br>NM 13 ( $\nu_{18a}$ )<br>NM 18 ( $\nu_{19a}$ )<br>NM 22 ( $\nu_{13}$ )                                         | ${}^1B_{3g}$<br>NM 4 ( $\nu_{6b}$ )<br>NM 16 ( $\nu_3$ )<br><b>NM 19</b> ( $\nu_{8b}$ )<br>NM 21 ( $\nu_{7b}$ )                                        | ${}^1B_{2u}$<br>NM 12 ( $\nu_{18b}$ )<br><b>NM 14</b> ( $\nu_{14}$ )<br>NM 17 ( $\nu_{19b}$ )<br>NM 23 ( $\nu_{20b}$ ) |
| $S_2, {}^1B_{2u}, \pi\pi^*$   |                                                                                                                                                        |                                                                                                                                                        | ${}^1A_g$<br><b>NM 3</b> ( $\nu_{6a}$ )<br><b>NM 11</b> ( $\nu_1$ )<br><b>NM 15</b> ( $\nu_{9a}$ )<br><b>NM 20</b> ( $\nu_{8a}$ )<br>NM 24 ( $\nu_2$ ) | ${}^1A_u$<br><b>NM 1</b> ( $\nu_{16a}$ )<br>NM 9 ( $\nu_{17a}$ )                                                                                       | ${}^1B_{2g}$<br><b>NM 5</b> ( $\nu_4$ )<br>NM 8 ( $\nu_5$ )                                                                                            | ${}^1B_{3u}$<br>NM 2 ( $\nu_{16b}$ )<br>NM 6 ( $\nu_{11}$ )                                                            |
| $S_3, {}^1B_{2g}, n\pi^*$     |                                                                                                                                                        |                                                                                                                                                        |                                                                                                                                                        | ${}^1A_g$<br><b>NM 3</b> ( $\nu_{6a}$ )<br><b>NM 11</b> ( $\nu_1$ )<br><b>NM 15</b> ( $\nu_{9a}$ )<br><b>NM 20</b> ( $\nu_{8a}$ )<br>NM 24 ( $\nu_2$ ) | ${}^1B_{2u}$<br>NM 12 ( $\nu_{18b}$ )<br><b>NM 14</b> ( $\nu_{14}$ )<br>NM 17 ( $\nu_{19b}$ )<br>NM 23 ( $\nu_{20b}$ )                                 | ${}^1B_{3g}$<br>NM 4 ( $\nu_{6b}$ )<br>NM 16 ( $\nu_3$ )<br><b>NM 19</b> ( $\nu_{8b}$ )<br>NM 21 ( $\nu_{7b}$ )        |
| $S_4, {}^1A_u, n\pi^*$        |                                                                                                                                                        |                                                                                                                                                        |                                                                                                                                                        |                                                                                                                                                        | ${}^1A_g$<br><b>NM 3</b> ( $\nu_{6a}$ )<br><b>NM 11</b> ( $\nu_1$ )<br><b>NM 15</b> ( $\nu_{9a}$ )<br><b>NM 20</b> ( $\nu_{8a}$ )<br>NM 24 ( $\nu_2$ ) | ${}^1B_{1u}$<br>NM 10 ( $\nu_{12}$ )<br>NM 13 ( $\nu_{18a}$ )<br>NM 18 ( $\nu_{19a}$ )<br>NM 22 ( $\nu_{13}$ )         |

We also ran simulations beginning from the FC region with an initial coherent superposition of the  $S_2 {}^1B_{2u} (\pi\pi^*)$  state with a small admixture of  $S_1 {}^1B_{3u} (n\pi^*)$  to simulate the experimental situation where the  $S_1$  state may be partially populated. This superposition is initiated with the form shown in Eqn 2.55, where values of  $\theta = \pm 20^\circ$  are used to give a  $S_1:S_2$  state mixture ratio of 3:97. Error accumulated over the course of all simulations led to non-quantitative results post-30 fs, therefore discussion is centred within the first 30 fs of dynamics.

The Ehrenfest wavefunction and its corresponding nuclear gradients and Hessian are computed by propagating the complete active space configuration interaction (CAS-CI) wavefunction,<sup>26</sup> using the same CASSCF 10 electron 8 orbital active space used in Chapter 4, seen in Fig. 4.1, with a 6-31G\* basis set. Both SA(6)- (for the 4- and 9-mode pure  $S_2$  runs) and SA(3)-CASSCF (for the 2- and 4-mode pure  $S_2$  runs and 2-, 4-, and 9-mode state-mixture runs) methods are used in the Qu-Eh simulations. The Qu-Eh calculations are performed with an interface between the Gaussian and QUANTICS software packages.<sup>193,201</sup>

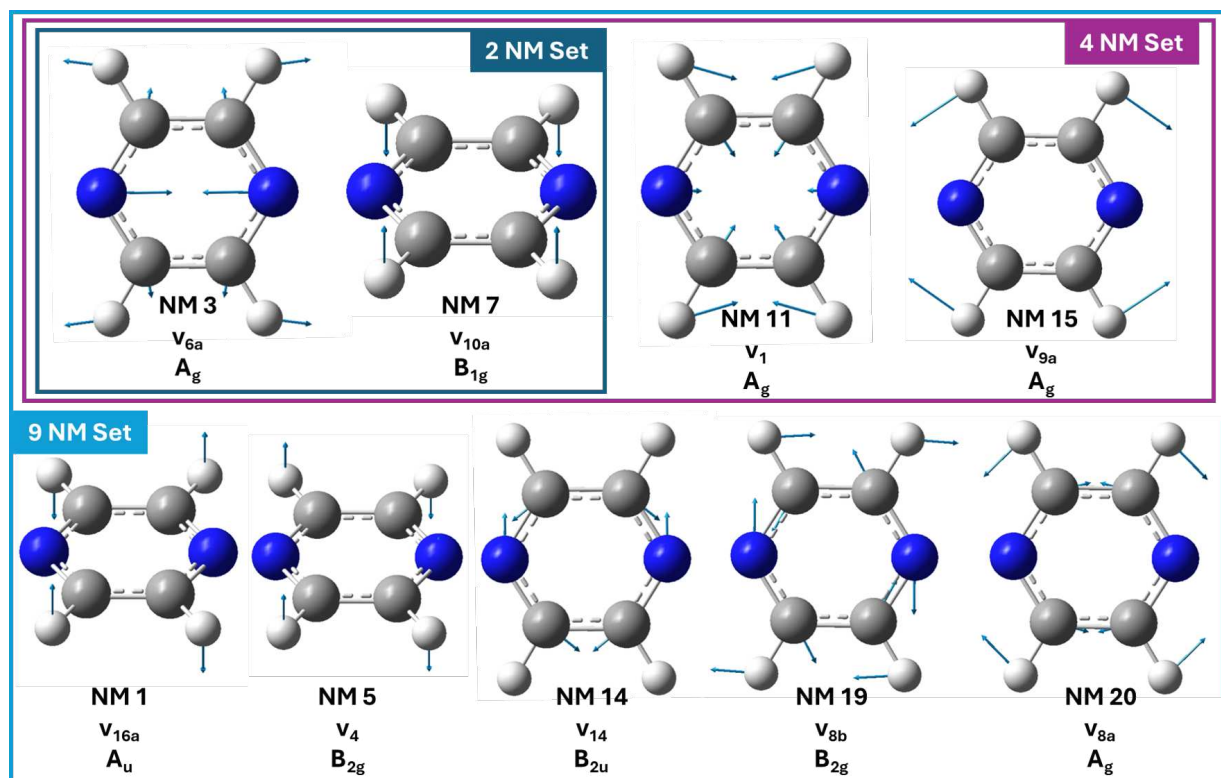


Figure 5.2: NMs which are used in Qu-Eh simulations for the excited state decay of pyrazine. The keys denote the three sets of simulations ran including 2, 4, and 9 modes, and show which NMs are used in each set, including their corresponding symmetry from the  $D_{2h}$  point group.

### 5.3.2 Nuclear basis for dynamics

For nuclear propagation Qu-Eh uses a set of GWPs each associated with its own Ehrenfest wavefunction. In practice the dynamics simulations are carried out in a reduced dimensional space. These GWP coordinates are defined in terms of mass- and frequency-scaled NM vectors obtained from a ground state FC point frequency calculation performed at the B3LYP/6-31G\* level of theory.

In our study, we ran simulations with three different sets of NMs, shown in Fig. 5.2. The first is a minimal 2 NM set including the two modes that correspond to the branching space of the  $S_2$ - $S_1$  CoIn, where  $\nu_{10a}$  corresponds to the derivative coupling and  $\nu_{6a}$  corresponds to the (approximate) gradient difference vector, as shown in Fig. 4.2. The second is a 4 NM set, where totally symmetric modes  $\nu_1$  and  $\nu_{9a}$  are added to better describe the gradient difference vector. The third is a 9 NM set, adding out-of-plane modes  $\nu_{16a}$  and  $\nu_4$  and modes  $\nu_{14}$ ,  $\nu_{8b}$ , and  $\nu_{8a}$ , the former of which connects the  $S_2$  state to the ground state by symmetry (see Table 5.1),

and the other two are stated to be involved in the 4-mode decay mechanism involving the dark  $^1A_u$  state.<sup>8</sup> In reduced dimensionality studies of pyrazine for grid-based quantum dynamics and MCTDH simulations 2-mode ( $\nu_{6a}$  and  $\nu_{10a}$ ),<sup>212</sup> 3-mode ( $\nu_{6a}$ ,  $\nu_{10a}$ , and  $\nu_1$ ),<sup>204,211,212,255</sup> and 4-mode ( $\nu_{6a}$ ,  $\nu_{10a}$ ,  $\nu_1$ , and  $\nu_{9a}$ )<sup>24,256</sup> models have been successfully used in the study of pyrazine. Higher numbers of modes such as 9 ( $\nu_{6a}$ ,  $\nu_{10a}$ ,  $\nu_1$ ,  $\nu_{9a}$ ,  $\nu_{8a}$ ,  $\nu_{8b}$ ,  $\nu_4$ ,  $\nu_5$ ,  $\nu_3$ )<sup>216</sup> or 10 ( $\nu_{6a}$ ,  $\nu_{10a}$ ,  $\nu_1$ ,  $\nu_{9a}$ ,  $\nu_{8a}$ ,  $\nu_{8b}$ ,  $\nu_4$ ,  $\nu_5$ ,  $\nu_{16a}$ , and  $\nu_{17a}$ ) have been used also,<sup>214,215</sup> noting as well that complete 24-mode simulations of the system have been studied.<sup>203,257</sup>

### 5.3.3 Interpreting the results

In the results section, we look at four primary properties of the Qu-Eh simulations to analyse the dynamics.

- (i) NM excitations for the NMs selected for GWPs to initially move along.
- (ii) Adiabatic state populations which are labelled to the states in terms of energy order i.e.  $S_0$  is ground state,  $S_1$  is first excited state, etc.
- (iii) ‘Diabatic’ state populations, usually termed the crude adiabatic basis, which we define as the projection of the adiabatic states onto the states at the FC geometry (i.e.  $t=0$ ).
- (iv) The calculated coherence value,  $M_{coh}$ , corresponding to the upper bound value approximated by the product of the adiabatic state populations according to Eqn 5.1.

The diabatic state population (iii) and coherence (iv) are plotted together, as both are connected to electron dynamics.

## 5.4 Results and Discussion

In this section, we begin with a comparison of different sets of Qu-Eh simulations with different numbers of included NMs and CASSCF state-averaging for dynamics initiated on an Ehrenfest

wavefunction corresponding to the pure  $S_2$  state. We then study in more depth a 2-mode 3-state Qu-Eh simulation to show specifically, through the derivative coupling mode  $\nu_{10a}$ , why coherences do not form in calculations initialised in the pure  $S_2$  state. The 2-mode 3-state simulation will allow for a more focused analysis of the  $\nu_{10a}$  mode, and as will be shown subsequently the simulation is qualitatively similar to the larger mode simulations. Following this, discussion will move on to 2-, 4-, and 9-mode 3-state Qu-Eh simulations initiated from a slight 3:97 mixture of  $S_1$  and  $S_2$  states. These results will show how in this scenario non-zero coherences can form, and that depending on the composition of the state mixture dynamics can be biased in different directions due to the interstate gradient.

### 5.4.1 Pure $S_2$ state initiated dynamics

#### 5.4.1.1 Comparison of 2-, 4- and 9-mode and 3- and 6-state Qu-Eh simulations

Fig. 5.3 shows the GGP-averaged results for the 2-, 4-, and 9-mode sets of simulations, with either 3- or 6-state averaging CASSCF. As discussed in Section 2.4.6.3, the GGP can produce at certain isolated points unphysical values such as negative adiabatic and diabatic state populations. For clarity and consistency, our plots constrain the population values to the range between 0 and 1.

##### 5.4.1.1.1 Normal mode (NM) excitations

For the GGP-averaged NM populations over time, the black line on Fig. 5.3(a,d,g,j) shows that the NM excitation along  $\nu_{10a}$  is near zero across all simulations, independent of the number of modes included or state-averaging used. Looking at the  $\nu_{6a}$  mode (purple line) in Fig. 5.3(a,d,g,j), which approximates the gradient difference, excitation occurs in the -ve direction, corresponding to an outward ring-breathing motion, reaching a maximum around 25 fs consistently throughout all simulations.

Comparing the 2-mode 3-state and 4-mode 3-state simulations in Fig. 5.3(a) and 5.3(d) respectively, the addition of modes  $\nu_1$  (light blue line) and  $\nu_{9a}$  (orange line) which also contribute

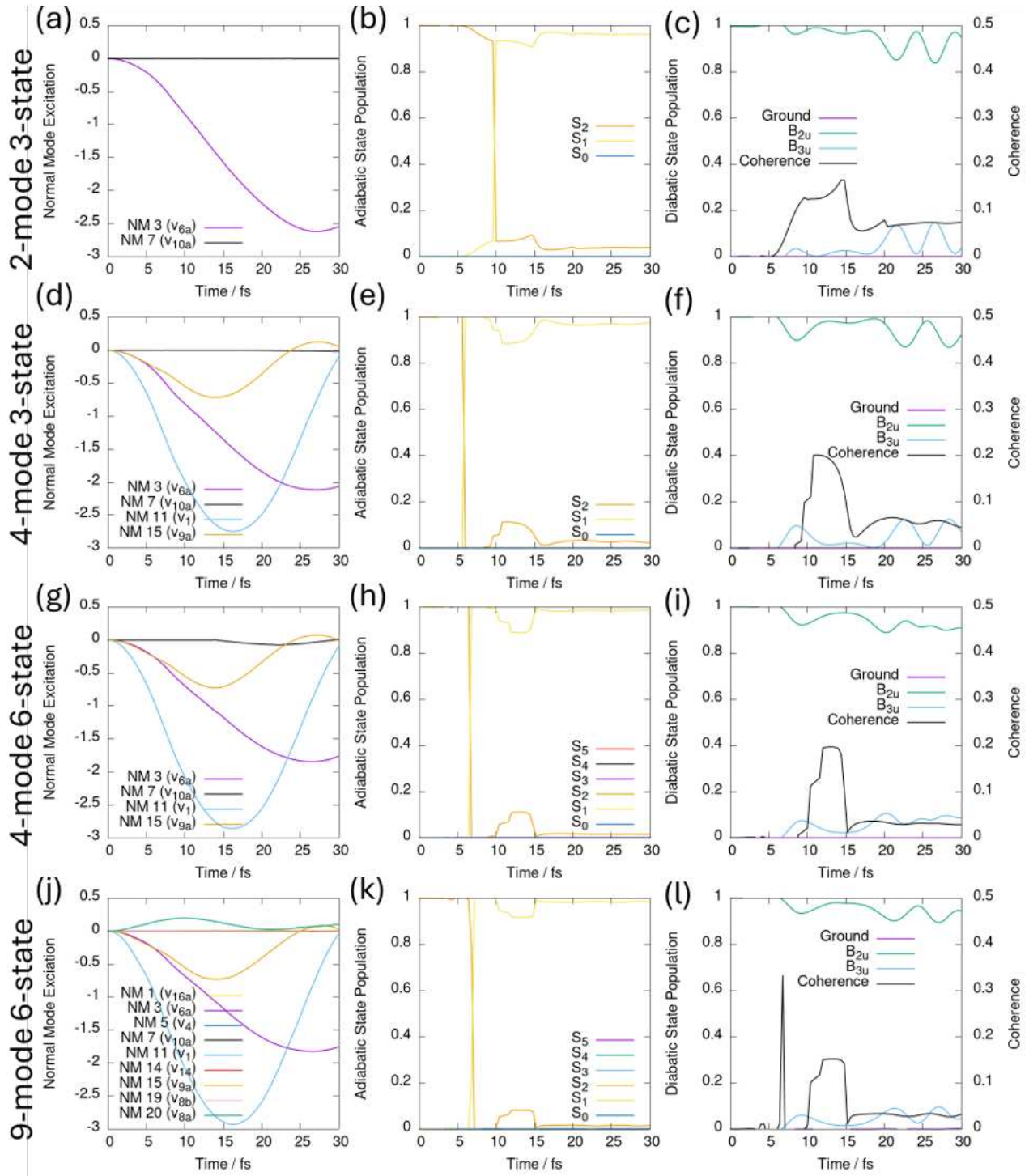


Figure 5.3: GGP-averaged results for four different Qu-Eh simulations of pyrazine beginning from the pure  $S_2$  state at the FC geometry. (a-c) denote the 2-mode set with SA(3)-CASSCF, (d-f) denote the 4-mode set with SA(3)-CASSCF, (g-i) denote the 4-mode set with SA(6)-CASSCF, and (j-k) denote the 9-mode set with SA(6)-CASSCF. Along the columns we plot the NM excitations, adiabatic state populations, diabatic state populations, and approximate coherence values over time, as discussed in Section 5.3.3.

to the gradient difference vector can be shown, where the  $\nu_1$  mode is now the most activated. Comparing the NM activation in Fig. 5.3(d) and Fig. 5.3(g), one can see that NM activation is very similar, showing that the impact of state averaging on the Ehrenfest wavefunction in dynamics is small. Looking at the additional  $\nu_1$  and  $\nu_{9a}$  modes in the 9-mode 6-state simulation in Fig. 5.3(j) show qualitative similarity, sharing the same maxima at around 14 and 15 fs respectively, and level of excitation.

The 9-mode 6-state simulation also shows the addition of the mode  $\nu_{8b}$  (pink line), another mode which adds to the description of the gradient difference,  $\nu_{14}$  (red line),  $\nu_{8a}$  (red line) and out of plane modes  $\nu_{16a}$  (yellow line) and  $\nu_4$  (dark blue line) seen in Fig. 5.3(j). All these modes, bar  $\nu_{8a}$ , are non-totally symmetric like  $\nu_{10a}$ , hence these remain around zero as expected. The  $\nu_{8a}$  mode proves to be excited less than the other modes which connect to the gradient difference vector, and as we shall discuss shortly, these additional modes do not appear to have a significant effect on the adiabatic and diabatic state decay, as the simulation is qualitatively similar to the 4-mode simulations.

In summary, in terms of NM excitation the 2-, 4-, and 9-mode simulations, regardless of state averaging, are qualitatively similar, showing a near-zero value for the derivative coupling  $\nu_{10a}$ , and similar timescales and excitations for motion along the gradient difference vectors through modes  $\nu_{6a}$ ,  $\nu_1$ , and  $\nu_{9a}$ . This favourable convergence arises because, as discussed in Chapter 4, at the FC region where dynamics begins, pyrazine is already within the catchment area of the  $S_1$ - $S_2$  conical intersection where dynamics is dominated within the branching space.

#### 5.4.1.1.2 Adiabatic state populations

Observing the decay of the adiabatic states over the course of dynamics shows that full, quasi-diabatic, ‘step-change’-like decay occurs from the  $S_2$  state (orange line) to the  $S_1$  state (yellow line) within 10 fs for the 2-mode 3-state simulation in Fig. 5.3(b), and consistently within 7 fs for the larger 4- and 9-mode simulations, shown in Fig. 5.3(e,h,k). These results compared with experimental have been discussed already in Section 4.3.3 but shall briefly note that this is in relatively close agreement with recent TD-PES experimental results,<sup>210</sup> though noting less

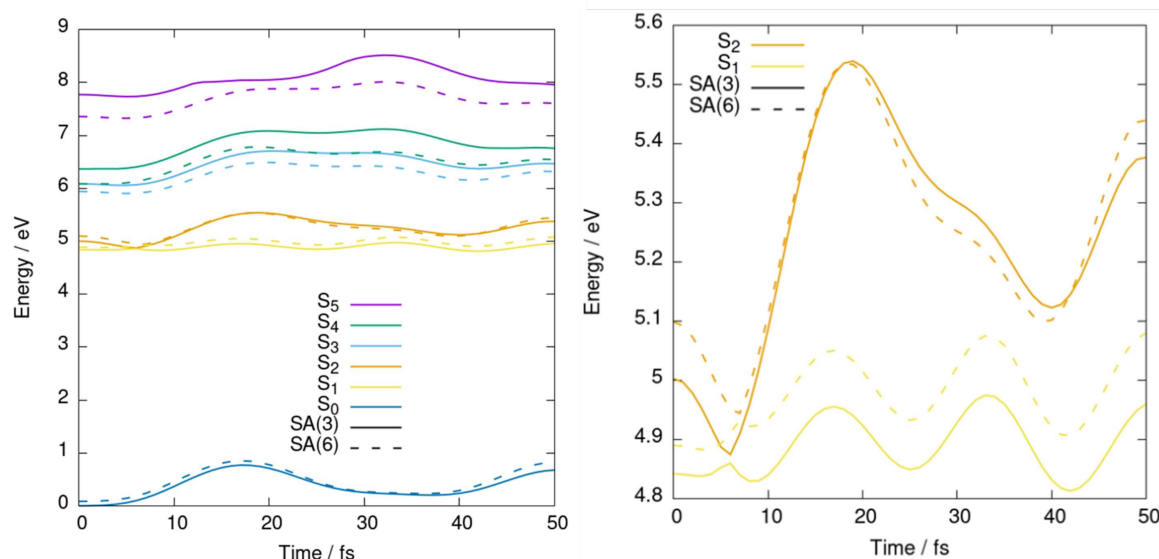


Figure 5.4: Adiabatic state energies over time for the centroid GWPs in the 4-mode simulations using SA(3)- and SA(6)-CASSCF, depicted by the solid and dashed lines respectively. The left plot shows the energies for  $S_0$ - $S_5$  states, while the RHS plot shows only the  $S_1$  and  $S_2$  states.

agreement with recent XR-TAS results.<sup>8,219</sup>

In these simulations, there is no population transfer to the higher lying  $n\pi^*$  states in our 6-state simulations, shown in Fig. 5.3(h) and 5.3(k). Though we use both SA(3)- and SA(6)-CASSCF in our simulations, as state averaging only varies the orbitals and not the CI coefficients, the orderings of the states should not significantly change if using a robust active space. Indeed, we see that when comparing the 4-mode simulations with different state averaging that dynamics is qualitatively very similar, implying that the topology of the surfaces do not change significantly. One can also compare the adiabatic state energies over the centroid GWPs of these simulations and show that the energies and state orderings are similar for the lower lying ‘active’ states in the simulation. This is shown in Fig. 5.4, where the SA(6)- energies (dashed lines) show that averaging over a wider number of states raises the  $S_1$  energy relative to the SA(3) energies (solid lines), lowers the higher lying  $S_3$ - $S_5$  states, and keeps the  $S_2$  state generally the same. In terms of topology, the adiabatic states are very similar between SA(3) and SA(6).

### 5.4.1.1.3 Coherences and diabatic state populations

As discussed in Section 5.2.1, the approximate upper bound of the coherence is calculated using the product of the  $S_1$  and  $S_2$  adiabatic state populations via Eqn 5.1. As dynamics begin on a pure state, this value is initially zero. Across all simulations the coherence, shown by the black line in Fig. 5.3(c,f,i,k), initially spikes to a maximum around 6-10 fs at the crossing point of the CoIn. After this point, near full adiabatic population transfer occurs leading to small coherence values lying generally below the value of 0.1 (where the maximum possible value is 0.5). These simulations therefore suggest that the formation of electronic coherences via the passage of the  $S_1$ - $S_2$  CoIn is small, in line with the work of Neville *et al.*,<sup>24</sup> who suggest that coherence formation when passing through a CoIn is small/negligible when the states involved have differing Abelian point group symmetries.

The reason why coherence values are not exactly zero can also be tied to why oscillations and population transfer can be seen in the diabatic state populations. As will be discussed in more detail in Section 5.4.1.2, the derivative coupling mode is responsible for the mixing of diabatic states and formation of coherences. The GWPs sent along these modes should be equal and opposite with respect to NM amplitude, as well as geometric phase, therefore should cancel out to give zero in the average. Due to numerical error, however, these GWPs are not exactly equivalent, which leads to non-zero coherence values (black line) and mixture of the  $^1B_{2u}$  and  $^1B_{3u}$  diabatic state populations (green and blue lines respectively), as can be seen in Fig. 5.3(c,f,i,l).

### 5.4.1.1.4 Summary

Overall, across NM excitations, adiabatic and diabatic state populations, and coherence values, as one increases the number of NMs and GWPs used, dynamics remains qualitatively similar. Specifically, across all simulations one sees near total population transfer from the  $S_2$  state within around 6-10 fs, the derivative coupling mode is close to zero, and that coherences formed through the passage of the conical intersection are small. Additionally, SA-CASSCF simulations show no involvement from higher lying  $n\pi^*$  states. Therefore, we can justify using the 2-mode

3-state set to further explain conceptually the main results shown in Fig. 5.3, which we will explore in the next section.

#### 5.4.1.2 Role of the $\nu_{10a}$ mode on coherence formation

Looking in more detail at the 2-mode 3-state simulation shown in Fig. 5.5(a-c), we can better understand the formation (or lack of formation) of coherences in the simulations previously discussed.

We begin by looking at the NM excitation along  $\nu_{10a}$  for the GWPs which are sent along + and - directions of the same mode, shown in Fig. 5.5(a). The GWPs sent in the + (purple line) and - (green line) directions of  $\nu_{10a}$  are excited in opposing directions, but equal magnitude. This leads to zero excitation along this mode in the GGP average (blue line).

The  $\nu_{10a}$  mode is responsible for state-mixing and formation of coherences within pyrazine in this model. Fig. 5.5(b) and 5.5(c) show the adiabatic and diabatic state populations respectively for the GWP moving in the + direction of  $\nu_{10a}$  (the GWP sent in the - direction is near identical, so left out for clarity). We can see in Fig. 5.5(b) for the adiabatic state population that the mixing of the  $S_2$  (orange line) and  $S_1$  (yellow line) states occur from time zero, and that the population transfer is slow and partial, bar for a partial crossing at 15 fs. This mixing leads to a large, sustained coherence value (black line) in Fig. 5.5(c) throughout the 30 fs timescale. There are also large and fast oscillations in the populations of the  $^1B_{3u}$  (blue line) and  $^1B_{2u}$  (green line) diabatic state populations, which are indicative of electron dynamics.

The reason why we do not see these large coherence values in the average, as shown previously in Fig. 5.3(c), is because the GWPs sent along the + and - directions of  $\nu_{10a}$  pass through the  $S_1$ - $S_2$  conical intersection in opposing directions. The trajectories these GWPs take can be drawn (conceptually) on a vibronic coupling model potential surface, as shown in Fig. 5.5(d) and 5.5(e). As these GWPs cross through the CoIn, they generate geometric phases which are opposite to one another. The phase of the  $S_1$  state for each GWP, and the absolute phase difference between the two, is shown in Fig. 5.5(f), where the absolute difference is shown to

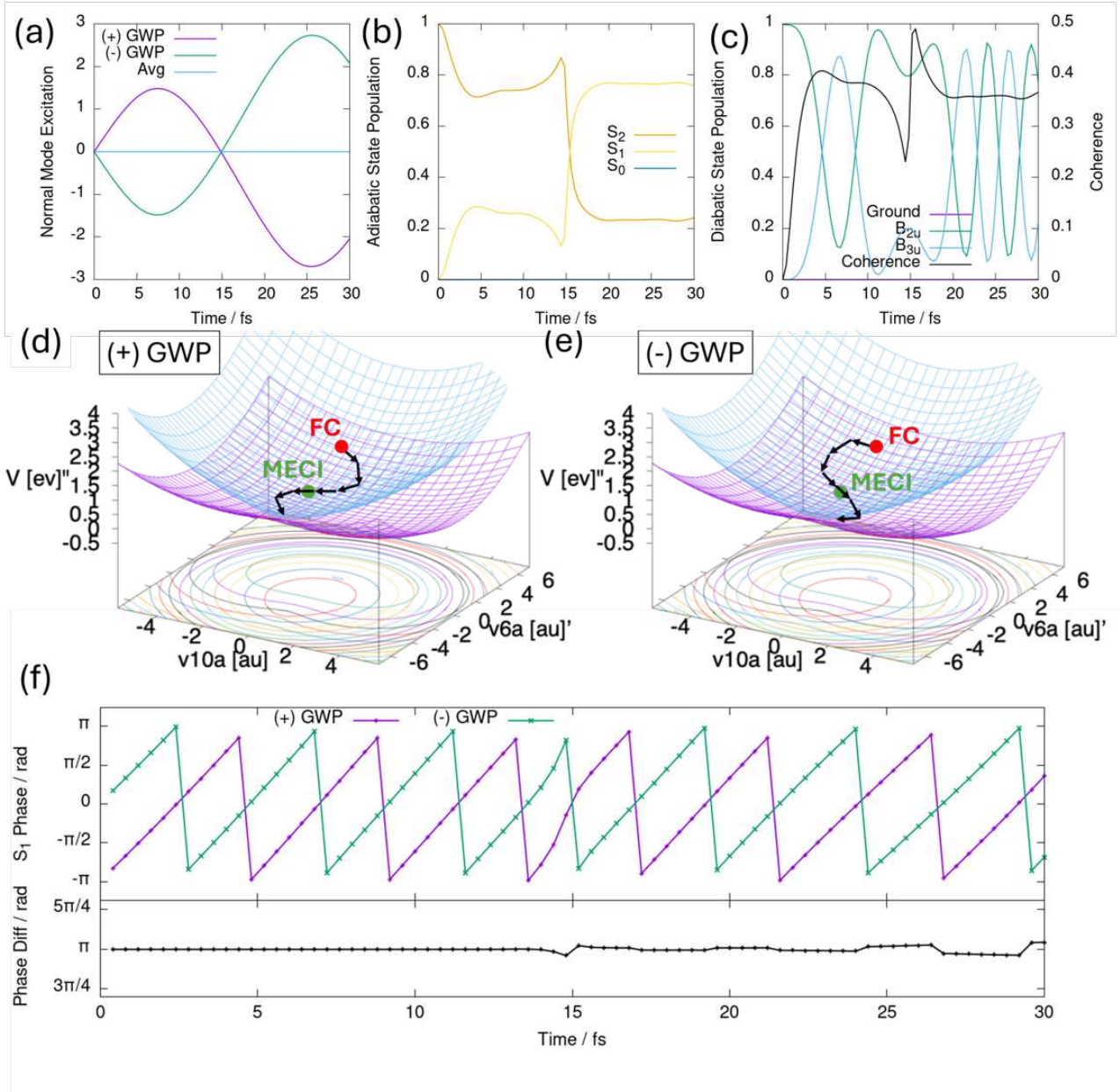


Figure 5.5: Results from the 2-mode 3-state Qu-Eh simulation starting from the pure  $S_2$  state at the FC geometry (see Fig. 5.3(a-c)). (a) Excitation of NM 7 ( $\nu_{10a}$ ) over time for GWPs sent in the + and - directions of  $\nu_{10a}$  (purple and green), and the GGP average (blue). (b,c) Adiabatic and diabatic state populations for the  $+\nu_{10a}$  GWP. (d,e) Conceptual trajectories of GWPs sent along the + and -  $\nu_{10a}$  directions on a vibronic coupling model potential surface, where the axes are the  $\nu_{10a}$  and  $\nu_{6a}$  modes. (f) Phase of the  $S_1$  state for both GWPs ( $\epsilon$  from Eqn 2.55) and their absolute phase difference over time.

be constantly close to  $\pi$ , i.e. totally out of phase. The opposing phases leads to the formed coherences in these GWPs, shown in Fig. 5.5(b), to cancel out in the average, leading to small/negligible coherences. Numerical errors in simulations can lead to less equivalence in the GWPs, creating larger coherence values and mixing of diabatic states, as discussed earlier.

### 5.4.2 $S_1:S_2$ mix initiated dynamics

We now discuss the results obtained for the simulations where the Ehrenfest wavefunction corresponds to a 3:97 ( $\theta = 20^\circ$ )  $S_1:S_2$  adiabatic state mixture according to Eqn 2.55. For each set of 2-, 4-, and 9-mode simulations, two simulations are run, where the state mixture ratio is the same, but one value of  $\theta$  is +ve and the other is -ve. This will change the sign of the Hellmann-Feynman term of the interstate gradient as seen in Eqn 5.5 and cause dynamics to show biases in opposing directions; in this case the direction is that of the derivative coupling,  $\nu_{10a}$ .

The summary information for these simulations is shown in Fig. 5.6, and discussion begins with the 2-mode 3-state simulations. Focusing on the NMs first, in the  $\theta = 20^\circ$  simulation, we see in Fig. 5.6(a) that unlike the pure state simulations shown in Fig. 5.3, the NM excitation for  $\nu_{10a}$  (black line) is non-zero and negative. This is because the interstate gradient created by the state mixture generates a bias towards the negative direction of  $\nu_{10a}$  determined by  $\theta$  in Eqn 5.5, meaning that now the GWPs moving along  $\nu_{10a}$  are no longer equal and opposite, and therefore don't cancel each other out. This allows the  $\nu_{10a}$  mode to have a non-zero large component in the average. As discussed in Section 5.4.1.2, motion along the derivative coupling mode causes population transfer in the diabatic state populations, as well as the 'slow' transfer of population (unlike the 'step-change' like population transfer seen in Fig. 5.3(b,e,h,k) from the  $S_2$  state (orange line) to the  $S_1$  state (yellow line) beginning from time zero, which is now seen in Fig. 5.6(b), akin to the population transfer seen in Fig. 5.5(b). This gives rise to large and sustained coherence values (black line) for at least 20 fs in Fig. 5.6(c).

Looking at the simulation where  $\theta = -20^\circ$  in the second row of Fig. 5.6, the GGP average NM excitation for  $\nu_{10a}$  shown by the black line in Fig. 5.6(d) is also non-zero, but positive, and

mirrors the magnitude and motion along  $\nu_{10a}$  in the  $\theta = 20^\circ$  simulation up to around 25 fs, as well as similar excitation along the  $\nu_{6a}$  mode. This is because now the  $\theta$  value is negative, the interstate gradient creates a bias in an equal but opposite direction to that of the  $\theta = 20^\circ$  simulation. We see that up to 20 fs these simulations have qualitatively the same effect on the mixing of states and generation of coherences, where differences between the simulations are likely due to numerical error accumulated over time.

We now focus on the 4-mode 3-state simulations in the third and fourth rows of Fig. 5.6, which show the effect of the inclusion of the  $\nu_1$  and  $\nu_{9a}$  modes in dynamics. Starting with the NM excitations in Fig. 5.6(g) and Fig. 5.6(j) for the  $\theta = 20^\circ$  and  $\theta = -20^\circ$  simulations respectively, the mode  $\nu_{10a}$  (black line) is non-zero and negative for the former and equivalently non-zero and positive for the latter, demonstrating the same effect shown in the 2-mode 3-state simulations. In contrast, however, the oscillations of the  $\nu_{10a}$  mode in these simulations are slower than those in the 2-mode 3-state, possibly arising from the coupling of additional  $\nu_1$  and  $\nu_{9a}$  modes.

The adiabatic state populations of the 4-mode simulations, shown in Fig. 5.6(h) and Fig. 5.6(k) show a more complete, though still partial, decay. The decay in the  $\theta = 20^\circ$  and  $\theta = -20^\circ$  simulations also look much more similar compared to the 2-mode simulations. This decay leads to similarly long-sustained, though slightly weaker, coherences (black line) shown in Fig. 5.6(i) and Fig. 5.6(l), staying around a value of 0.3 compared to the 2-mode simulations staying around 0.45. This may be because additionally added totally symmetric modes which dominate the motion of the molecule, such as  $\nu_1$  (blue line) as shown in Fig. 5.6(g), have more weight in the GGP average. These modes do not generate coherences, therefore the coherence value in the average will be lower, acting as a damping effect. This could also be interpreted as the additional modes moving the nuclear wavepacket further away from the CoIn after crossing, leading to further decoherence.

Furthermore, when we turn to the 9-mode 3-state simulation results shown in Fig. 5.7, we see very similar results to that of the 4-mode 3-state simulations in Fig. 5.6(g-l). The black lines in Fig. 5.7(a) and 5.7(b) show that  $\nu_{10a}$  mode is again non-zero and negative for  $\theta = 20^\circ$  and positive for  $\theta = -20^\circ$  respectively, in a similar period of oscillation and magnitude as the

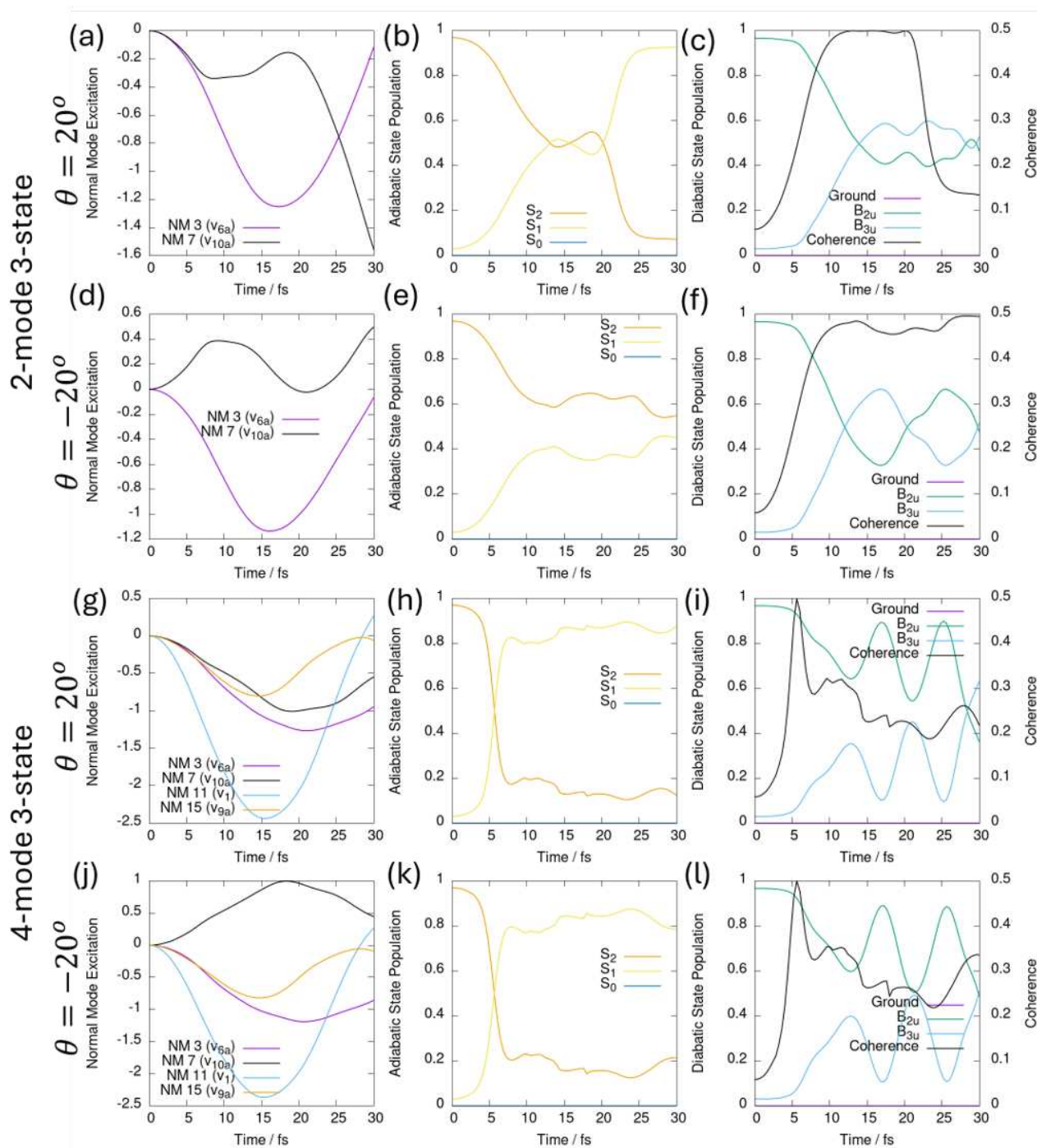


Figure 5.6: GGP-averaged results for four different Qu-Eh simulations of pyrazine beginning with a 3:97  $S_1:S_2$  state mixture ( $\theta = \pm 20^\circ$  according to Eqn 2.55) at the FC geometry using SA(3)-CASSCF(10,8). The first (a-c) and second (d-f) rows denote the 2-mode 3-state sets with  $\theta = 20^\circ$  and  $\theta = -20^\circ$  respectively. The third (g-i) and fourth (j-l) rows denote the 4-mode 3-state sets with  $\theta = 20^\circ$  and  $\theta = -20^\circ$  respectively. For further information on plotted data see Section 5.3.3

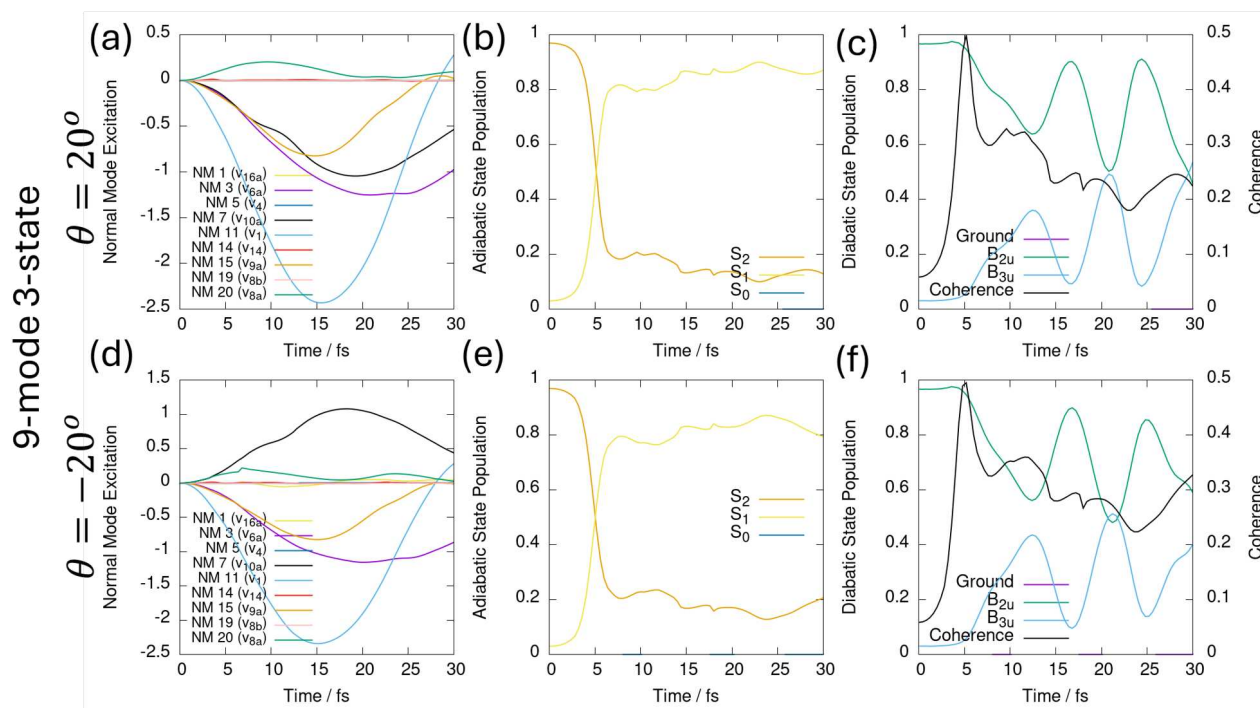


Figure 5.7: GGP-averaged results for two 9-mode 3-state Qu-Eh simulations of pyrazine beginning with a 3:97  $S_1$ : $S_2$  state mixture ( $\theta = \pm 20^\circ$  according to Eqn 2.55) at the FC geometry using SA(3)-CASSCF(10,8). The first (a-c) and second (d-f) rows denote each simulation with  $\theta = 20^\circ$  and  $\theta = -20^\circ$  respectively. For further information on plotted data see Section 5.3.3.

4-mode results shown in Fig. 5.6(g) and Fig. 5.6(j). The  $\nu_1$  (light blue line) and  $\nu_{9a}$  (orange line) modes are also excited similarly to the 4-mode simulation, with some activation in the totally symmetric  $\nu_{8a}$  (green line) mode, but not to the same extent as the  $\nu_{6a}$ ,  $\nu_{10a}$ ,  $\nu_1$ , and  $\nu_{9a}$  modes involved in the 4-mode sets. Adiabatic state decay shown in Fig. 5.7(b) and 5.7(d) are also similar to that of the 4-mode case in Fig. 5.6(h) and Fig. 5.6(k), where there is more complete (though still partial) decay than the 2-mode case in Fig. 5.6(b) and Fig. 5.6(d). As a result, the calculated coherence values are also similar for the 4- and 9-mode simulations shown in Fig. 5.6(i) & 5.6(j) and Fig. 5.7(c) & 5.7(f) respectively, with a note that in the 9-mode simulation there is a faint mixing of the  $S_2$  state into the ground state due to the  $\nu_{14}$  mode (see Table 5.1).

In summary, these sets of 2-, 4-, and 9-mode Qu-Eh simulations show that even with a small mixture of the states involved in a CoIn, in this case a 3:97  $S_1$ : $S_2$  ratio, large and sustained coherences can form. Furthermore, depending on the specific mixture of states created, one can bias the dynamics in one direction or another, shown by changing the sign of the  $\theta$  value in

dynamics, which dictates which direction the symmetry of the  $\nu_{10a}$  mode is broken in. We also note that moving from the 2-mode model to the 4- and 9-mode models that there is a slight decrease in the calculated coherence value, which could suggest a damping effect. Studying quantum dynamics simulations with additional NMs on this effect in future would help better understand and highlight this.

## 5.5 Conclusion

In this chapter, we have examined the excited state ultrafast decay of pyrazine which occurs via a CoIn from the  $S_2$   $^1B_{2u}$   $\pi\pi^*$  state to the  $S_1$   $^1B_{3u}$   $n\pi^*$  state, using the Qu-Eh method. Dynamics were explored primarily with a minimal 2-mode model consisting of NMs  $\nu_{6a}$  and  $\nu_{10a}$  which span the  $S_2$ - $S_1$  CoIn branching space. These simulations were compared with simulations with larger 4 and 9 NM spaces, which showed qualitatively similar dynamics. This arises because dynamics begins in the catchment region of the CoIn, so motion is dominated within the branching space. The simulations consistently show the population on the  $S_2$  state decaying rapidly to the  $S_1$  state within 6-10 fs, in relatively close agreement with recent TD-PES experimental results,<sup>210</sup> though noting less agreement with recent XR-TAS results.<sup>8,219</sup>

Coherences and state mixing occur due to the motion along the non-totally symmetric derivative coupling mode  $\nu_{10a}$ . Qu-Eh simulations initiated from the pure  $S_2$  state found that GWPs sent along the + and - directions of the  $\nu_{10a}$  mode are equal in magnitude but accumulate opposite geometric phases when passing through the  $S_2$ - $S_1$  CoIn, and hence coherences cancel out in the gross Gaussian population (GGP) average. This result is consistent with the theoretical predictions of Neville *et al.*,<sup>24</sup> who state that CoIns with states with differing Abelian point group symmetries (at the FC point) will form negligible coherences.

However, when initial conditions include a small admixture of the  $S_1$  state in with the  $S_2$  state, the interstate gradient creates a bias towards one direction of the derivative coupling, GWPs sent along the + and - directions no longer cancel out, and we circumvent this condition. The relative phase of the superposition determines which direction this bias occurs in. In

these simulations, we observe large, sustained coherences. Going from the 2-mode to the 4- and 9-mode simulations, one observes slightly smaller coherence values, which may be caused by damping effects of the additional NMs added in the dynamics. Further simulations with additional NMs could be performed to better understand this effect. Though analysis is based on the three-state decay model of pyrazine using SA-CASSCF, rather than the four-state decay model where the dark  $^1A_u n\pi^*$  state is also involved in the decay,<sup>8,209,213,214,217–219</sup> the underlying principles of coherence formation and symmetry explored in this work remain valid regardless of the assumed state ordering. While our simulations are informed by experimental observations and aim to offer theoretical insight into pyrazine’s excited-state dynamics, they are not intended to reproduce any specific experimental setup. Instead, this work focuses on uncovering the fundamental principles governing coherence generation near CoIns.

# Chapter 6

## Conclusion

This thesis aimed to better understand electron-nuclear coupled dynamics of medium-sized molecular systems, focusing on two primary questions: i) how electronic coherences form when passing through conical intersections (CoIns), and ii) how the choice of theoretical methods used, both electronic structure and nonadiabatic dynamics, alongside methodological choices within those methods, influences the resulting dynamics. These questions have been explored using pyrazine as the principal system of interest, employing the semi-classical second order Ehrenfest (2OE) and fully quantum mechanical Quantum Ehrenfest (Qu-Eh) nonadiabatic dynamics methods, which are both intertwined with the complete active space self-consistent field (CASSCF) electronic structure method. This has involved shedding light on how theoretical methods capture pyrazine’s well-known non-radiative decay from the (historical)  $S_2$  state to the  $S_1$  state, as well as how electronic coherences form as the nuclear wavefunction passes through the  $S_1$ - $S_2$  CoIn.

We began this study in Chapter 3 by outlining the key numerical and methodological challenges associated with using the 2OE and Qu-Eh methods, and providing solutions and work-arounds for these issues. Then, in the first study of pyrazine, in Chapter 4, the radiationless decay of pyrazine was examined both from a static perspective, using CASSCF and various electronic structure methods, and a dynamic perspective, using the 2OE and Qu-Eh methods. Analysis from looking at various electronic structure methods, both calculated and from the literature,

showed that the ordering of the low-lying excited singlet states of pyrazine are highly sensitive to the level of detail applied to the electron correlation within the electronic wavefunction, particularly around the  $n\pi^*$  states. We demonstrated that the state orderings could be explained through the splittings of two pairs of  $n\pi^*$  states. Variational methods such as CASSCF and MRCI produced smaller splittings of these state pairs ( $^1B_{3u}$ - $^1B_{2g}$  and  $^1A_u$ - $^1B_{1g}$ ) than that of the restricted active space self-consistent field (RASSCF) method, and perturbative methods such as CASPT2 and ADC(2) produced even larger splittings, which lead to different state orderings. Comparison of the CASSCF and RASSCF results along an effective minimum energy pathway (MEP) showed that both methods generally preserve the same state ordering over the course of dynamics, which suggests that CASSCF can be considered qualitatively faithful to the RASSCF method which restored a majority of the dynamic correlation that CASSCF misses.

2OE and Qu-Eh simulations beginning from the pure  $S_2$  state at the Franck-Condon (FC) geometry showed that full decay to the  $S_1$  state occurred within  $\sim 7$  fs, showing no involvement of the higher lying dark  $^1A_u$  or  $^1B_{2g}$   $n\pi^*$  states. This timescale is much shorter than predicted by well-known multiconfigurational time-dependent Hartree (MCTDH) models<sup>203–205</sup> and recent X-ray transient absorption spectroscopy (XR-TAS) studies<sup>8,219</sup> and their supporting ADC(2) TSH simulations,<sup>243–246</sup> but does align more with the most recent time-resolved photoelectron spectroscopy (TR-PES) experiments.<sup>210</sup> This suggests that when using the CASSCF method, pyrazine lies within the catchment region of the CoIn once excited to the  $S_2$  state, allowing for near-instant nonadiabatic decay. It is worth noting while the strongest evidence for the involvement of these higher lying dark  $n\pi^*$  states lies in these XR-TAS studies and their corresponding theoretical calculations, these discrepancies suggest that both further experimental and theoretical work is required to underpin the precise mechanism of the non-radiative decay of the  $^1B_{2u}$  state of pyrazine. Despite the difference in accuracy between the 2OE, a classical nuclei method, and Qu-Eh, a quantum nuclei method, both simulations produced similar dynamics. This is mainly due to the fact that dynamics is governed through the normal modes (NM) which correspond to the gradient difference vector ( $\nu_{6a}$  and  $\nu_1$ ), as the nuclear wavepacket lies very close to the CoIn.

In the second study of pyrazine, in Chapter 5, we utilised the Qu-Eh method to explore how coherence formation arises in pyrazine after passing through the aforementioned CoIn. Dynamics was studied using a 2-mode, 4-mode, and 9-mode model systems, chosen to best describe the branching space of the  $S_1$ - $S_2$  CoIn, out-of plane motion, and couplings between the involved excited states. The resulting dynamics were found to be qualitatively similar across all models, again owing to the fact that dynamics is mediated through the branching space of the CoIn as the nuclear wavepacket lies in the catchment region of the CoIn. This also partially explains why pyrazine is so well described in reduced dimensionality in other models.

Analysis of the coherence formation found that when dynamics was initiated on the pure  $S_2$  state, GWPs moving along the  $\nu_{10a}$  mode, which is similar to the derivative coupling vector and responsible for the mixing of the  $S_1$  and  $S_2$  states and therefore coherence formation, accumulate opposite geometric phases. As the  $\nu_{10a}$  mode is non-totally symmetric, the motion in either direction is equal but opposite, and this leads to the cancellation of the formation of electronic coherence in the average, leading to small/negligible coherences. This is consistent with theoretical predictions by Neville *et al.*,<sup>24</sup> who suggest that coherence formation when passing through a CoIn is small/negligible if the states involved have differing Abelian point group symmetry. However, if dynamics are initiated using a small mixture (a 3:97  $S_1$ : $S_2$  mix) of the states included in the CoIn, then the interstate gradient can create a bias towards one direction of the derivative coupling, which means that the GWPs sent along the  $\nu_{10a}$  mode no longer cancel out and large coherences can then be observed. By changing the relative phase of this mixture one can change the direction of this bias. Comparing the 2-, 4-, and 9-mode simulations with these initial conditions show the 4- and 9-mode simulations have slightly smaller coherence values, which suggest that a damping effect could arise from the additional normal modes added into the dynamics. As discussed in the first study, these results are based on the CASSCF model of pyrazine, where no dark  $n\pi^*$  states are involved, but regardless of the state ordering, the fundamental principles of coherence formation and symmetry should still apply.

In further work with pyrazine, with the Qu-Eh and CASSCF method it would be useful to run simulations in larger dimensionality in order to further study the dampening effect on

coherence formation as more normal modes are included. It would be informative to compare other dynamics methods, such as MCTDH, ideally with potential surfaces constructed from the CASSCF method, which also correctly describe the nonadiabatic dynamics of the system, to see if results are in accordance. In terms of using Qu-Eh to study the role of coherence formation, it would be useful in the next version of implementation to make it feasible to access the off-diagonal values of the reduced density matrix to calculate the explicit coherence values, rather than relying on upper bounds created from the product of the adiabatic state populations. The pyrazine study used a specific 3:97  $S_1:S_2$  excited state mixture. It would be interesting to span out the parameter space of different sized mixtures to see how this effect varies given the composition of the state mixture, and the effect that this has on the dynamics. Given this, it would also be informative to see how pyrazine behaves under an external field such as a laser pulse, and see how the mixing of states impacts dynamics in this sense. Theoretical studies have already taken place for pyrazine by utilising the dynamic Stark effect, for example, in accelerating or decelerating the rate of decay from the  $S_2$  state.<sup>258</sup>

In the same vein, as discussed in Chapter 4, the choice of electronic structure method for pyrazine can change the state ordering and therefore the decay mechanism. One caveat of the 2OE and Qu-Eh methods is that the CASSCF wavefunction is embedded within them. It would be useful in future to be able to extend 2OE and Qu-Eh out to other electronic structure methods (CASPT2 would be a natural extension, for example), so that these studies of coherence could be compared and confirmed using a different electronic structure method and state ordering. Unfortunately, in these methods the Ehrenfest gradient and Hessian would need to be determined analytically, as is the case for the CASSCF method currently. There would be considerable difficulty in then deriving and developing for other methods. This level of effort appears to be the rate-determining step for advancing the 2OE and Qu-Eh methods in this direction.

The many-state analogue of Qu-Eh, direct-dynamics variational multiconfigurational Gaussian (DD-vMCG) method, is able to work with different electronic structure methods and their corresponding quantum chemistry software packages. The additional benefit of database formation as dynamics progresses is also favourable, and is a useful and accessible alternative if

trying to study similarly sized systems with a different electronic structure method.

This speaks in a more broad sense to more frequently compare electronic structure methods and dynamics methods in these scenarios, and make the software which facilitate their use more accessible. As of writing this thesis, more studies, such as the work of Tran *et al.*,<sup>147</sup> and the work of the COSMOS project,<sup>251</sup> which aims to develop a universal software and methodology for quantum dynamics simulations, are pursuing this direction of research.

As discussed in Chapter 3, there are numerical challenges associated with the current versions of the 2OE and Qu-Eh code. For 2OE, workarounds are highlighted for issues with step size and active space loss, but genuine development would be useful in developing a more robust laser pulse implementation. Ideally, this implementation would allow a pulse interaction which did not disturb the active space so greatly in simulation, as well as be practically usable with the Hase and Schlegel predictor-corrector scheme. A laser pulse implementation that incorporates the second-order field interaction (i.e. the polarizability of the pulse is included) would allow for more accurate pulse interactions, such as the dynamic Stark effect.<sup>259</sup> This would open up the ability to study competing mechanisms in pulse control, such as the effect of the pulse exciting and creating an electronic state mixture, and the effect of the electric field on the system itself.

In Qu-Eh, solving the issue of linear dependence would greatly progress the feasibility of using this method, allowing for the modelling of systems in higher dimensionality, given these additional dimensions do not cause the loss of the active space. While this thesis also looks into the challenge of which integrator type to use as well as the corresponding step size, a detailed study of different integrators and step sizes for a model system would be beneficial and informative to current and future Qu-Eh users.

With these fixes in mind, this opens up the possibility of studying the electron-nuclear coupled dynamics of larger molecular systems, and better understanding how phenomena such as coherence formation arise in them.

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# Appendix A

## Integration Methods

In Section 3.4, we discuss different integration methods which are used for the Qu-Eh method, notably the Runge Kutta and Adams-Bashforth-Moulton methods. In the following sections these are discussed in more detail.

### A.1 Runge Kutta Methods

Runge Kutta methods provide a numerical approach to solve a general ODE:

$$\frac{dy}{dt} = f(y, t), \tag{A.1}$$

subject to  $y(t_i) = y_0$ , for an unknown function,  $y$ . Here,  $f$ ,  $t_0$  and  $y_0$  are assumed to be known. By denoting  $y_i$  as the solution at the value  $t_i$ , i.e.  $y_i = y(t_i)$ , the Runge Kutta method approximates the value of  $y_{i+1}$  from  $y_i$  via:

$$y_{i+1} = y_i + s \sum_{m=1}^{m_{\max}} b_m k_m, \tag{A.2}$$

where  $s$  is a chosen time step,  $m_{\max}$  is a chosen order,  $c_1 = 0$ ,  $a_{11} = 0$  and

$$k_m = f \left( y_i + s \sum_{n=1}^{m-1} a_{mn} k_n, t_i + c_i s \right). \quad (\text{A.3})$$

The order of the method is determined by the choice of  $m_{\max}$ . The values of  $b_m$ ,  $c_i$ , and  $a_{11}$  depend on  $m_{\max}$ , and are determined through comparison of the Taylor expansion of the Runge-Kutta method, and the Taylor expansion of  $\frac{dy}{dt} = f(y, t)$ . These values can conveniently be represented in a Butcher tableau.<sup>260</sup>

## A.2 Adams-Bashforth-Moulton Predictor-Corrector Scheme

The Adams-Bashforth-Moulton predictor-corrector scheme is a combination of two linear multistep methods for solving ODEs. For multistep methods, the solution at the value of  $t_{i+n}$  for general  $n$ , i.e.  $y_{i+n}$ , is determined from information from prior steps. This gives the general overall form:

$$\alpha_0 y_i + \alpha_1 y_{i+1} + \cdots + y_{i+n} = s(\beta_0 f(y_i, t_i) + \beta_{i+1} f(y_{i+1}, t_{i+1}) + \cdots + \beta_n f(y_{i+n}, t_{i+n})), \quad (\text{A.4})$$

which can be more compactly expressed as:

$$\sum_{j=0}^n \alpha_j y_{i+j} = s \sum_{j=0}^n \beta_j f(y_{i+j}, t_{i+j}), \quad (\text{A.5})$$

where  $s$  is the determined step size and  $\alpha_n = 1$ . The values of  $\alpha$  and  $\beta$  determine the method.

The Adams-Bashforth method is an explicit method (i.e.  $\beta_n = 0$ ) where  $\alpha_{n-1} = -1$  and  $\alpha_j = 0$  for  $j < n - 1$ . This gives the general form:

$$y_{i+n} = y_{i+n-1} + s \sum_{j=1}^n \beta_j f_{i+n-j}, \quad (\text{A.6})$$

where  $f_i = f(y_i, t_i)$ , and the values of  $\beta_j$  are chosen in a similar fashion to Runge-Kutta such that the method has an error of order  $n$ .

The Adams-Moulton method follows a similar approach but is implicit (i.e.  $\beta_n \neq 0$  in Eqn A.6). While this can allow the method to reach order  $n + 1$ , the implicit nature of the equation makes each step more involved.

This issue can be circumvented; the Adams-Bashforth-Moulton predictor corrector combines both methods, where the Adams-Bashforth method is used to produce a predictor step, which by definition has a higher order of error, and the Adams-Moulton method acts as a more accurate corrector step. The Adams-Bashforth step provides the  $y_{i+n}$  for the Adams-Moulton step, overcoming the implicit nature of the method.

## Appendix B

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|-------------------|---------------------------------------------------------------------------------------|------------------|-----------------------------------------------------------------------------------------------------------------|
| Publication Title | Annual review of physical chemistry                                                   | Publication Type | e-Journal                                                                                                       |
| Article Title     | The diabatic picture of electron transfer, reaction barriers, and molecular dynamics. | Start Page       | 149                                                                                                             |
|                   |                                                                                       | End Page         | 170                                                                                                             |
|                   |                                                                                       | Issue            | 1                                                                                                               |
|                   |                                                                                       | Volume           | 61                                                                                                              |
| Date              | 01/01/1950                                                                            | URL              | <a href="http://arjournals.annualreviews.org/loi/physchem">http://arjournals.annualreviews.org/loi/physchem</a> |
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|-----------------|------------------------------------------------------------------------------|----------------------------|-------------------------|
| Title           | Understanding and Controlling Electron-Nuclear Coupled Dynamics in Molecules | Institution Name           | Imperial College London |
|                 |                                                                              | Expected Presentation Date | 2026-03-01              |
| Instructor Name | Luke Moore                                                                   |                            |                         |

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| Title, Description or Numeric Reference of the Portion(s) | Figure 1                                                                                      | Title of the Article / Chapter the Portion Is From | The diabatic picture of electron transfer, reaction barriers, and molecular dynamics.         |
| Editor of Portion(s)                                      | Van Voorhis, Troy; Kowalczyk, Tim; Kaduk, Benjamin; Wang, Lee-Ping; Cheng, Chiao-Lun; Wu, Qin | Author of Portion(s)                               | Van Voorhis, Troy; Kowalczyk, Tim; Kaduk, Benjamin; Wang, Lee-Ping; Cheng, Chiao-Lun; Wu, Qin |
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| Page or Page Range of Portion                             | 150                                                                                           | Issue, if Republishing an Article From a Serial    | 1                                                                                             |
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Figure B.1: Proof of permission to use Fig. 2.1 from T. Van Voorhis *et al.*<sup>39</sup>