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„Computational study of the temporal evolution of the
excited state character in the photoexcited adenine
oligonucleotide“

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ABSTRACT

The goal of this work is to investigate the nature of the long-lived excited states observed experimentally in single stranded DNA, specifically poly-adenosine phosphate ((dA)₂₀, in the following also called polyadenine), after UV irradiation. Since there was some controversy about whether these long-lived states are charge-transfer states or excitons, non-adiabatic surface hopping dynamics have been employed in combination with an on the fly wavefunction analysis to characterise involved the long-lived excited states.

After several methodical investigations, it was found that the absorption spectrum is well described with four adenines treated at the TD-CAM-B₃LYP/def2-SV(P) level of theory, while the other parts of the single strand as well as the surrounding water are described with molecular mechanics. The non-adiabatic surface hopping dynamics were simulated for 500 fs. It was observed that initially excitons and monomer-like states are formed. Excitons decayed completely within the first 100 fs either to monomer-like states (80 %) or forming exciplexes (20 %). 75 % of the monomer-like states formed exciplexes through an intermediate excimeric state, while the other 25 % of the monomers are expected to decay to the ground state. The overall time constant for the formation of exciplexes equals around 700 fs, which is higher than the experimentally observed value (~400 fs) but still in the same order of magnitude. The decay to the ground state was simulated to occur with a time constant of around 3 ps which agrees with the experimental result of ~2 ps.

The separation between the nucleobases was observed to decrease during the formation of exciplexes which indicates that base stacking is an important factor for the dynamical behaviour of (dA)₂₀.

This study provides the first computational evidence that long-lived charge transfer states are formed in (dA)₂₀ through excited state dynamics simulations.

ABSTRACT

Das Ziel dieser Arbeit besteht darin, die langlebigen Zustände zu identifizieren, welche experimentell spezifisch in einsträngiger DNS mit einer Sequenz von 20 Adeninbasen, $(dA)_{20}$, beobachtet worden sind. Da es äußerst umstritten ist, ob diese langlebigen Zustände durch starken Ladungstransfer verursacht oder als Exzitone klassifizierbar sind, wurde nicht adiabatische Potentialflächensprungdynamik kombiniert mit gleichzeitiger Wellenfunktionsanalyse angewandt, um diese langlebigen Zustände charakterisieren zu können.

Durch vielfältige methodische Untersuchungen ist festgestellt worden, dass das Absorptionsspektrum ausreichend gut reproduziert werden kann, wenn vier Adeninbasen quantenmechanisch mit TD-CAM-B₃LYP/def2-SV(P) behandelt werden, während der Rest des Systems klassisch mit molekularer Mechanik beschrieben wird. Die nicht adiabatische Potentialflächensprungdynamik wurde 500 fs lang simuliert. Dabei wurde beobachtet, dass durch die ursprüngliche Anregung Exzitone und monomerartige Zustände gebildet werden. Die Exzitone wurden innerhalb der ersten 100 fs vollständig zu monomerartigen Zuständen (80 %) oder Exziplezen (20 %) umgewandelt. Drei Viertel der Monomere bildeten Exzipleze, wobei sie übergangsweise Exzimerzustand annahmen, während das übrige Viertel der Monomere in den Grundzustand übergingen. Die gesamte Zeitkonstante für die Entstehung von Exziplezen wurde mit circa 700 fs bestimmt, was höher liegt als der experimentell gemessene Wert (~ 400 fs), allerdings noch immer in derselben Größenordnung. Für den Übergang zum Grundzustand wurde eine Zeitkonstante von circa 3 ps simuliert, was ausreichend gut mit dem Experiment (~ 2 ps) übereinstimmt.

Der Abstand der Nucleobasen verringerte sich während der Bildung von Exziplezen, was darauf hindeutet, dass Basenstapelung eine wichtige Rolle im dynamischen Verhalten von $(dA)_{20}$ spielt.

Diese Studie bietet mittels angeregter Zustandsdynamik die ersten computergetützten Anzeichen, dass langlebige Ladungsübertragungszustände (Exzipleze) in $(dA)_{20}$ gebildet werden.

ACRONYMS

AIMD	ab initio molecular dynamics
BOA	Born-Oppenheimer approximation
COSX	chain of sphere integration for exchange integrals
COH	coherence length
CT	charge transfer
CT_{nt}	net charge transfer
DFT	density functional theory
DL	delocalisation length
DNA	deoxyribonucleic acid
FWHM	full width at half maximum
MD	molecular dynamics
MM	molecular mechanics
MO	molecular orbital
NAC	non-adiabatic coupling
PES	potential energy surface
POS_F	final/electron position
POS_I	initial/hole position
PR	participation ratio (arithmetic mean delocalisation)
QM	quantum mechanics
RI	resolution of the identity
SCF	self consistent field
SHARC	surface hopping including arbitrary couplings
TDDFT	time-dependent density functional theory
TDSE	time-dependent Schrödinger equation
TISE	time-independent Schrödinger equation
UVR	ultra violet radiation

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INTRODUCTION

Deoxyribonucleic acid (DNA) is one of the most important macromolecules inherent in all lifeforms on earth, as it can be considered the molecular repository of genetic information.¹ In the early 1940s it was found that DNA decodes the information necessary for the formation of proteins and is stored within genes in the cell nucleus. The nucleotides making up DNA consist of three components: a nitrogenous base, a pentose (β -D-deoxyribofuranose) and a phosphate, as shown in figure 1.1.

The base, called nucleobase, is covalently bonded to the 1' carbon of the pentose and the phosphate is esterified to the 5' carbon. In DNA, the four nucleobases decoding all the information, are the two purine bases adenine (A) and guanine (G) and the two pyrimidine bases cytosine (C) and thymine (T), whose structures are shown in figure 1.2. In 1953, James Watson and Francis Crick unravelled the mystery of the molecular structure of DNA.² Based on X-ray diagrams they were able to suggest a radically different structure for DNA than what was postulated before. Their structure consists of two helical chains coiled around the same axis. The two chains are joined together through single bases from the one strand being hydrogen-bonded to single bases of the other chain. Adsorption chromatography of nucleic acids extracted from different microorganisms found adenine occurring as often as thymine while the amount of guanine equals the one of cytosine.³ Hence, it was concluded that the base pairing can only occur between adenine-thymine and guanine-cytosine nucleotides. As the hydrogen-bonding happens between the two different strands, the nucleobase sequence of the one strand is necessarily determined by the sequence of the other strand, hence the strands are complementary.

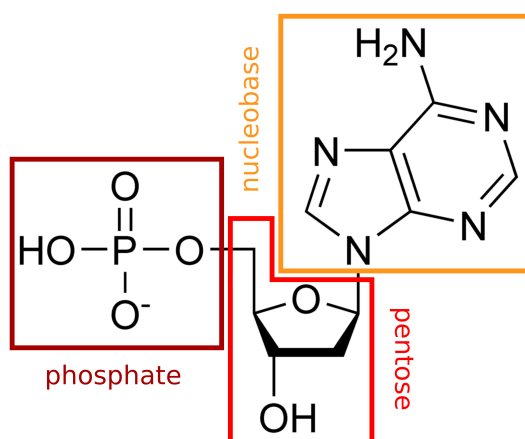


Figure 1.1: Two dimensional molecular structure of a nucleotide consisting of a phosphate, pentose (β -D-deoxyribofuranose) and nucleobase, in this case adenine is depicted as an example for the nucleobase.

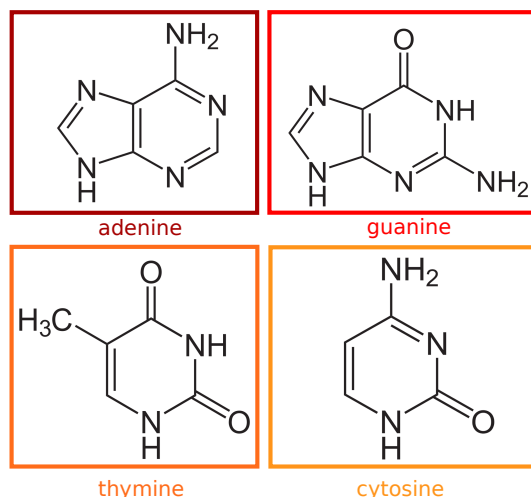


Figure 1.2: Structures of the four nucleobases of DNA.

Thanks to the complementarity of the two strands, transcription and replication of DNA is easily possible.⁴ In the case of transcription, one of the two strands is used as a template and for replication, the two preexisting strands each serve as a template for biosynthesis of a complementary “daughter” strand. Replication is necessary to copy and transfer the whole genetic information to daughter cells, while transcription is used to convert parts of the genes into ribonucleic acid chains (RNA) which will then code for a specific sequence of amino acids, the building blocks of proteins. Hence, as the nucleobase sequence of DNA determines the sequence of amino acids in the biosynthesis of proteins, the preservation of the genetic code is fundamental for the correct functionality of any organism. Despite several control and regulation mechanisms, harmful modifications (mutations) of DNA cannot be avoided completely. One threat that can cause pathological modifications to DNA is ultra violet radiation (UVR) in sunlight.⁵ If photolesions are not recognised and repaired, replication and transcription of DNA can be blocked or mutations of the genetic code may occur. Cell death of bacteria due to absorption of UVR was already observed very early, and the absorbing substances were later identified as DNA.^{6,7} UVR consists of light with shorter wavelengths than visible and can be classified as UVC (200 – 280 nm), UVB (280 – 315 nm) and UVA (320 – 400 nm).⁸ The sunlight reaching the surface of earth only contains small but still very harmful amounts of UV light (6%), where UVA is 10 to 100 times more abundant than UVB. There are two major classes of mutagenic DNA lesions resulting from UVR, cyclobutane pyrimidine dimers and 6-4 photoproducts, which are pyrimidine adducts.⁹

In order to understand the mechanisms of DNA-photodamage, it is essential to face the challenge of characterising the electronically excited states involved in the photoinduced events and investigating their time-evolution. For more than 50 years, researchers have studied UV absorption spectra of single and double stranded DNA in detail using experimental as well as computational means in order to answer the question to what extent the initial absorption involves monomer-like excitations or collective excitations.^{10–18} These studies overall showed the importance of stacking interactions between the nucleobases for the collective ex-

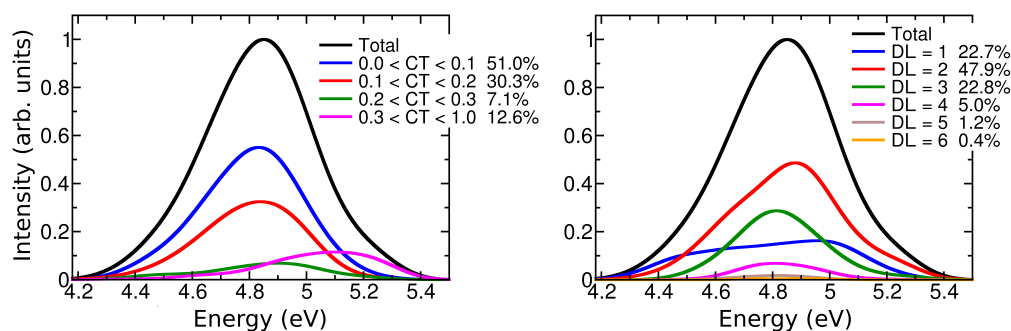


Figure 1.3: Decomposition of the lowest-energy absorption band for (dA)₂₀, including 8 adenines in the QM region, into different charge-transfer contributions (left) and delocalisation lengths (right) obtained by Nogueira et al.¹⁸ The percentages denote the intensity contribution to the total spectrum.

cited state behaviour of DNA. Therefore, large differences between the excited state behaviour of nucleobase stacks in contrast to isolated nucleobases and mononucleotides were observed.¹⁷ These stacking interactions cause the formation of delocalised exciton states upon UV absorption.¹⁵ A very detailed study of the lowest-energy UV absorption band of single stranded polyadenine (dA)₂₀ was recently provided by Nogueira et al.¹⁸ In their computational work, they treat eight nucleobases on a quantum mechanical level, employing time-dependent density functional theory (TDDFT) and account for conformational sampling and environmental effects. Their thorough wavefunction analysis provided insight into the charge transfer character and delocalisation of the electronic excitations. Figure 1.3 shows their absorption spectrum decomposed with respect to charge transfer character and delocalisation length. They found that exciton states delocalised over two nucleobases contribute about half of the spectral intensity of the absorption band, with the remaining intensity being distributed between monomer-like excitations and excitons delocalised over three nucleobases. Furthermore, they found charge transfer states only as a minor contribution to the spectral intensity located at the high energy part of the spectrum. Although it can be concluded from their work that direct population of charge transfer states to be unlikely, they could only attribute about 50 % of the spectrum to pure Frenkel excitons and local excitations.

Generally, five different kinds of excited-states were discussed as contributions to the complete excited state behavior of poly adenine: monomer-like excitations, delocalised Frenkel excitons, charge transfer states (exciplexes), charge resonance states and excited dimers (excimers). Figure 1.4 depicts these excitations schematically. Monomer-like excitations (1.4a) are localised and occur on only one nucleobase. Frenkel excitons also only involve excitations where the hole and electron are located on the same nucleobase but they can occur on several nucleobases simultaneously. In the case of charge transfer states or so-called exciplexes the hole and electron are found on different nucleobases but charge transfer only occurs from one nucleobase to another. In contrast charge resonance states not only include charge transfer from one nucleobase to the other but additionally vice versa. In the so-called excited dimer states (abbreviated to excimer) the excitation is shared

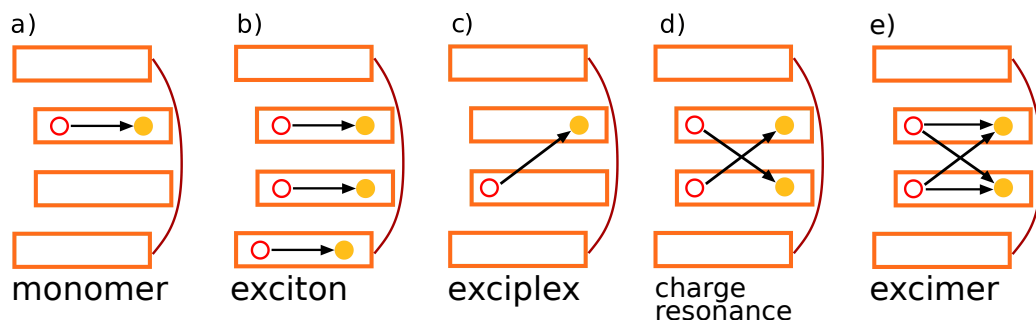


Figure 1.4: Excitation schemes for the different type of states occurring in poly adenine. An empty circle represents the hole orbital, a filled circle the final orbital, the orange rectangles and dark red curves depict nucleobases and sugar-phosphate backbone, respectively.

between between charge transfer from one nucleobase to another and vice versa and also localised excitations on each of the two involved nucleobases.

In order to understand the photoreactions of DNA induced by UV light it is also necessary to investigate the time evolution of the excited states upon UV light absorption. Transient absorption spectroscopy showed very similar spectra for single and double stranded DNA polynucleotides, which leads to the conclusion of the relative unimportance of the second strand.¹³ For the excited states dynamics large differences were observed between single nucleobases and nucleobase assemblies.^{13;19–21} Single nucleobases and mononucleotides were observed to decay to the ground state mainly by undergoing ultrafast internal conversion within a time scale of several hundred femtoseconds. Experiments employing femtosecond transient absorption spectroscopy revealed that the lifetimes of the excited states are drastically increased in polynucleotides.^{13;22–24} The schematic deactivation pathways of the adenine monomer adenosine as well as polyadenine (dA)₂₀ as observed by Kwok et al.²³ are shown in figure 1.5.

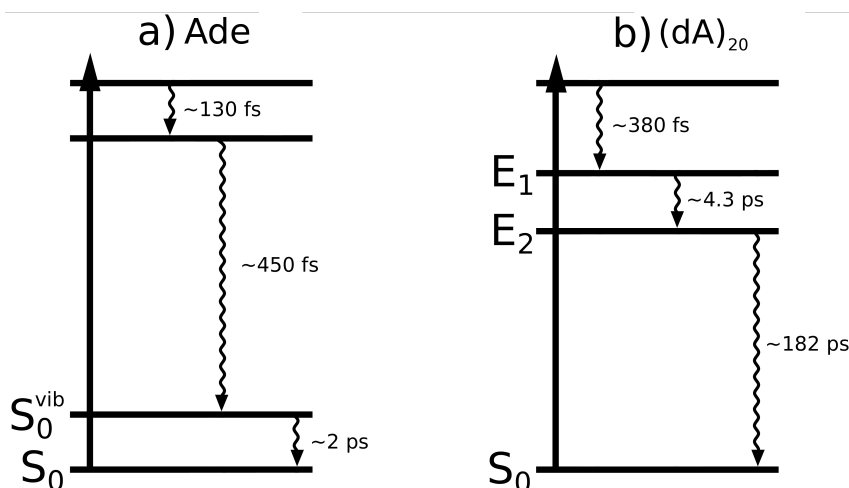


Figure 1.5: Schematic relaxation pathways with time constants as measured by Kwok et al.²³ upon excitation at 267 nm for a) adenosine and b) (dA)₂₀ in an aqueous solution. E_1 and E_2 are the long-lived excited states, as explained in the text.

For the adenosine monomer they observed ultrafast internal conversion between two excited states within 130 fs, as well as from the lowest excited state to the ground state within 450 fs. However, for polyadenine they first observed ultrafast internal conversion to a long-lived excited state (E_1) within 380 fs which then was further stabilised to E_2 with a ~ 4.3 ps time constant. In all transient absorption spectroscopy experiments mentioned before, there is consensus on the general behaviour that polyadenine transforms to a long-lived excited state within around 400 fs.

However, the nature of the long-lived excited state has been the subject of some controversy over the course of the last years. Several fs transient absorption studies performed mainly by Kohler and co-workers suggest the formation of exciplexes and excimeric states, where the excitation is shared between two closely spaced molecules.^{13;19–29} π -stacking of planar aromatic molecules, which can occur in DNA, generally facilitates the formation of excimeric states. The assignment as excimeric states is further supported by the low radiative transition rates measured and by the red-shifted emission observed from nucleobase multimers in room-temperature solution.^{30;31} Several computational studies also support the suggestion of the excimer.^{32;33} Olasso-González et al.³² performed static scans over several reaction coordinates for a system consisting of two adenine molecules at the ab initio CASPT2 level of theory in gas phase and included water as a solvent. They found an energetically minimal dimer conformation. Santoro et al.³³ used a polarizable continuum model (PCM) with TDDFT. By analysing their excited state potential energy surfaces, they found that the lowest lying excited state is a dark excimeric state due to intermonomer charge transfer between two stacked bases and the bright state can easily decay to the excimeric state. In contrast to this assignment, Markovitsi and co-workers suggest Frenkel excitons delocalised over several nucleobases as the long-lived excited states.^{14;31;34} They support their assignment with the findings from fluorescence up-conversion experiments as well as calculations performed within the framework of exciton theory, where they observe a very complex decay behaviour which they interpret in terms of a large number of excited states. Bucharov et al.¹⁵ assume an electronically relaxed exciton to determine the long lifetime of polyadenine. The computational studies of Garavelli and co-workers found this long-lived excited state to be a localised excitation on a single nucleobase.^{35;36} They suggest a deactivation mechanism including a direct intra-monomer relaxation along a barrier-controlled path to a conical intersection with the ground state.

Although polyadenine has been extensively studied in the past, excited state dynamics simulations describing more than two adenines³⁷ at the quantum mechanical level have not yet been performed. Hence, the goal of this work is to simulate the excited state dynamics of (dA)₂₀ with describing as many adenines as feasible at the quantum mechanical level with TDDFT while describing the remaining parts of the adenine strand as well as a surrounding box of water with a classical force field. For this to be possible, an interface to the quantum chemistry program ORCA³⁸ had to be implemented in the surface hopping dynamics program SHARC^{39;40}.

The rest of the thesis will be organised as follows. First, the theoretical formalism behind all the methods used for the computations will be given. In the second part, the influence of the computational method on the decomposition of the absorption spectrum will be investigated. Differently sized QM regions, different TDDFT formulations and different basis sets will be compared, in order to find a suitable method to carry out the excited state dynamics simulations. Then, surface hopping dynamics will be carried out for 500 fs with wavefunction analysis performed in each time step. With the wavefunction analysis it will be possible to differentiate between excimeric, exciton and charge transfer states and it will allow an assignment of the long-lived excited state whose occupation was observed experimentally.

THEORETICAL BACKGROUND

2.1 THE SCHRÖDINGER EQUATION

The complete time evolution of any quantum mechanical system relative to its surroundings is described by the time-dependent Schrödinger equation (TDSE), that has been formulated by Erwin Schrödinger in 1926.^{41;42} It reads

$$\hat{H}(\mathbf{R}, \mathbf{r}, t) |\Psi(\mathbf{R}, \mathbf{r}, t)\rangle = i\hbar \frac{\partial}{\partial t} |\Psi(\mathbf{R}, \mathbf{r}, t)\rangle \quad (2.1.1)$$

where $\hat{H}(\mathbf{R}, \mathbf{r}, t)$ denotes the time-dependent quantum mechanical Hamiltonian of the system, which represents all internal and external interactions of the system and $|\Psi(\mathbf{R}, \mathbf{r}, t)\rangle$ denotes the wavefunction that contains the complete information of the system. Therefore both, wavefunction and Hamiltonian, depend on the coordinates of the nuclei $\mathbf{R}$, the electrons $\mathbf{r}$ and the time t .

In the case of the system being in an eigenstate of a time-independent Hamiltonian, it is possible to split the TDSE into a spatial and temporal part. The temporal part can be solved analytically as a complex phase factor for the wavefunction of e^{-iEt} . The time-independent, spatial part yields the time-independent Schrödinger equation (TISE)

$$\hat{H}(\mathbf{R}, \mathbf{r}) |\Psi(\mathbf{R}, \mathbf{r})\rangle = E_{\text{total}} |\Psi(\mathbf{R}, \mathbf{r})\rangle. \quad (2.1.2)$$

Now, the wavefunction $|\Psi(\mathbf{R}, \mathbf{r})\rangle$ represents stationary states and E_{total} denotes the total energy of the respective state. $\hat{H}(\mathbf{R}, \mathbf{r})$ is the time-independent Hamiltonian, that, for a molecule, is composed of the terms

$$\hat{H}(\mathbf{R}, \mathbf{r}) = \hat{T}_e(\mathbf{r}) + \hat{T}_N(\mathbf{R}) + \hat{V}_{ee}(\mathbf{r}) + \hat{V}_{Ne}(\mathbf{R}, \mathbf{r}) + \hat{V}_{NN}(\mathbf{R}). \quad (2.1.3)$$

$\hat{T}_e(\mathbf{r})$ and $\hat{T}_N(\mathbf{R})$ account for the electronic and nuclear kinetic energies and the potential energy is separated into the electron and nuclear Coulomb repulsion, described by $\hat{V}_{ee}(\mathbf{r})$ and $\hat{V}_{NN}(\mathbf{R})$, respectively, and the interaction between electrons and nuclei, described by $\hat{V}_{Ne}(\mathbf{R}, \mathbf{r})$.

Considering a molecule with n electrons and N nuclei, the kinetic energy contributions to the total energy can be expressed in atomic units (i.e., electron mass m_e , charge e , the reduced Planck's constant $\hbar$ and the permittivity of the vacuum $\frac{1}{4\pi\epsilon_0}$ are set to 1) as

$$\hat{T}_e(\mathbf{r}) = - \sum_{i=1}^n \frac{1}{2} \nabla_i^2 \quad (2.1.4)$$

$$\hat{T}_N(\mathbf{R}) = - \sum_{A=1}^N \frac{1}{2M_A} \nabla_A^2 \quad (2.1.5)$$

with i and A running over all electrons and nuclei, respectively. The potential energy terms then read

$$\hat{V}_{ee}(\mathbf{r}) = \sum_{i=1}^n \sum_{j>i}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (2.1.6)$$

$$\hat{V}_{NN}(\mathbf{R}) = \sum_{A=1}^N \sum_{B>A}^N \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}, \quad (2.1.7)$$

$$\hat{V}_{Ne}(\mathbf{R}, \mathbf{r}) = - \sum_{A=1}^N \sum_{i=1}^n \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}_i|}. \quad (2.1.8)$$

However, since solving the full TISE (equation 2.1.1) constitutes a $(N+n)$ -body problem, no analytical solution exists for any system with $(N+n) > 2$.

2.2 THE BORN-OPPENHEIMER APPROXIMATION

To overcome the insurmountable obstacle of solving the full TISE, an approximation was introduced by Born and Oppenheimer in 1927.⁴³

The Born-Oppenheimer approximation (BOA) is premised on the fact that electrons move much faster than the nuclei, due to their mass being much less than that of the nuclei. In the BOA this large difference in mass allows to decouple the motion of electrons and nuclei and $\hat{H}$ is separated into an electronic and a nuclear contribution. Then, the total wavefunction $|\Psi(\mathbf{r}, \mathbf{R})\rangle$ can equally be split into the corresponding electronic $|\Psi_e(\mathbf{r}; \mathbf{R})\rangle$ and nuclear wavefunctions $|\Psi_N(\mathbf{R})\rangle$

$$\hat{H}(\mathbf{r}, \mathbf{R}) = \hat{H}_e(\mathbf{r}; \mathbf{R}) + \hat{T}_N(\mathbf{R}), \quad (2.2.1)$$

$$|\Psi(\mathbf{R}, \mathbf{r})\rangle = |\Psi_N(\mathbf{R})\rangle |\Psi_e(\mathbf{r}; \mathbf{R})\rangle. \quad (2.2.2)$$

Now, there is only a parametric dependence of the electronic wavefunction $|\Psi_e(\mathbf{r}; \mathbf{R})\rangle$ on the nuclear coordinates $\mathbf{R}$ and we can define the electronic TISE

$$\hat{H}_e(\mathbf{r}; \mathbf{R}) |\Psi_e(\mathbf{r}; \mathbf{R})\rangle = E_e(\mathbf{R}) |\Psi_e(\mathbf{r}; \mathbf{R})\rangle, \quad (2.2.3)$$

with $\hat{H}_e(\mathbf{r}; \mathbf{R})$ being the electronic Hamiltonian

$$\hat{H}_e(\mathbf{r}; \mathbf{R}) = \hat{T}_e(\mathbf{r}) + \hat{V}_{ee}(\mathbf{r}) + \hat{V}_{Ne}(\mathbf{r}; \mathbf{R}) + \hat{V}_{NN}(\mathbf{R}). \quad (2.2.4)$$

By assuming the nuclei to be static, $\hat{T}_N(\mathbf{R})$ is rendered zero and $\hat{V}_{NN}(\mathbf{R})$ constant. The electronic Hamiltonian $\hat{H}_e(\mathbf{r}; \mathbf{R})$ only depends directly on the electron coordinates $\mathbf{r}_i$, whereas the nuclear coordinates are treated parametrically. Each set of nuclear coordinates $\mathbf{R}$ represents one molecular geometry. The energy of the system obtained with the electronic Hamiltonian from eq. 2.2.4 contains the electronic energy as well as and the nuclei repulsion and is thus summarised as the potential energy of the system, $E(\mathbf{R})$

In order to obtain the nuclear Schrödinger equation, we insert equations 2.2.2 and 2.2.3 into the TISE (2.1.2) and arrive at

$$[\hat{T}_N(\mathbf{R}) + E(\mathbf{R})] |\Psi_e(\mathbf{r}; \mathbf{R})\rangle |\Psi_N(\mathbf{R})\rangle = E_{\text{total}} |\Psi_e(\mathbf{r}; \mathbf{R})\rangle |\Psi_N(\mathbf{R})\rangle, \quad (2.2.5)$$

with $\hat{T}_N$ still acting on the whole wavefunction. We can thus write

$$\begin{aligned}
 \hat{T}_N(\mathbf{R}) |\Psi_e(\mathbf{r}; \mathbf{R})\rangle |\Psi_N(\mathbf{R})\rangle &= - \sum_{A=1}^N \frac{1}{2M_A} \nabla_A^2 |\Psi_e(\mathbf{r}; \mathbf{R})\rangle |\Psi_N(\mathbf{R})\rangle \\
 &= - \sum_{A=1}^N \frac{1}{2M_A} \left(\nabla_A^2 |\Psi_e(\mathbf{r}; \mathbf{R})\rangle + 2 \nabla_A |\Psi_e(\mathbf{r}; \mathbf{R})\rangle \nabla_A + |\Psi_e(\mathbf{r}; \mathbf{R})\rangle \nabla_A^2 \right) |\Psi_N(\mathbf{R})\rangle \\
 &= - \sum_{A=1}^N \frac{1}{2M_A} \left(T_2 + 2T_1 \nabla_A + |\Psi_e(\mathbf{r}; \mathbf{R})\rangle \nabla_A^2 \right) |\Psi_N(\mathbf{R})\rangle, \tag{2.2.6}
 \end{aligned}$$

where T_1 and T_2 denote the first and second order derivatives, respectively, of the electronic wavefunction with respect to the nuclear coordinates. They are known as the nonadiabatic couplings (NACs) and describe the couplings between adiabatic states. The NACs give information about how much the electronic wavefunction changes with respect to the nuclear coordinates. Within the framework of the BOA the assumption is made that these changes of the electronic wavefunction are small. Hence, the NACs are neglected and the BOA is called an adiabatic approximation and, analogously, the resulting PES is called adiabatic. However, in the case of two electronic states coming close in energy, this assumption breaks down, as T_1 and T_2 can no longer be expected to vanish. In these cases, the approximation is no longer valid and couplings between different states have to be accounted for.

Despite this, the BOA is fundamental for quantum chemistry and serves as a starting point for almost all electronic structure calculations. Even though the separation of the electronic and nuclear wavefunctions greatly simplifies the Schrödinger equation, we are still facing a n -body problem (eq. 2.2.3) and a N -body problem (eq. 2.2) which cannot be solved analytically in most cases. Therefore, further approximations need to be introduced. For the electronic Schrödinger equation, in this work density functional theory is used and will be presented below. The time evolution of the nuclear Schrödinger equation will be simulated with the surface hopping framework which will be presented in section 2.7.2.

2.3 DENSITY FUNCTIONAL THEORY

The use of the electronic wavefunction has several drawbacks, one of which is the lack of a direct physical interpretation, and another being its dependence on $3n$ spatial as well as n spin coordinates, which results in it containing more information than necessary. Thus, an alternative function with fewer variables that is based on a physical observable was sought. According to equation 2.2.4, the electronic Hamiltonian depends only on the total number of electrons, nuclear coordinates and atomic numbers. Therefore, the electron probability density $\rho(\mathbf{r})$ presents a suitable observable.⁴⁴ $\rho(\mathbf{r})$ is a function of three spatial variables and for a given $\rho(\mathbf{r})$, the energy and other properties of the electronic state associated with this density can be derived. Density functional theory (DFT) provides the necessary formalism to solve the Schrödinger equation with respect to $\rho(\mathbf{r})$.

2.3.1 Formal Foundations

2.3.1.1 Hohenberg-Kohn Theorems

Hohenberg and Kohn provided a rigorous foundation for DFT in 1964 with their Hohenberg-Kohn theorems.⁴⁴ The most fundamental basis of DFT is the Hohenberg-Kohn existence theorem, as it proves that the ground-state electron density determines the Hamiltonian and therefore determines completely the ground-state electronic energy. The proof is as follows: The Hamiltonian for a system of electrons enclosed in a box that are interacting with each other and an external potential can be expressed as

$$\hat{H} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{\text{ext}}, \quad (2.3.1)$$

with $\hat{T}_e$ denoting the kinetic energy of the electrons, $\hat{V}_{ee}$ the interaction between two different electrons and $\hat{V}_{\text{ext}}$ the interaction with the external potential. They are defined as

$$\hat{T}_e = \frac{1}{2} \sum_i \int \nabla \overline{\psi_i(\mathbf{r})} \nabla \psi_i(\mathbf{r}) d\mathbf{r}, \quad (2.3.2)$$

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i,j} \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \overline{\psi_i(\mathbf{r})} \overline{\psi_j(\mathbf{r}')} \psi_j(\mathbf{r}') \psi_i(\mathbf{r}) d\mathbf{r} d\mathbf{r}', \quad (2.3.3)$$

$$\hat{V}_{\text{ext}} = \sum_i \int v(\mathbf{r}) \overline{\psi_i(\mathbf{r})} \psi_i(\mathbf{r}) d\mathbf{r}. \quad (2.3.4)$$

Here, ψ_i denotes a one-electron wavefunction and v the external potential. Complex conjugation is denoted by the overbar. Now we assume two different potentials (v and v') give rise to the same non-degenerate ground-state density ρ . The two corresponding Hamiltonians $\hat{H}$ and $\hat{H}'$ would only differ in $\hat{V}_{\text{ext}}$ and $\hat{V}'_{\text{ext}}$ and possess different ground-state wavefunctions Ψ and Ψ' with energies E and E' . According to the variational principle, as stated below, the energy of any approximate wavefunction will always be higher than the exact energy and thus

$$\begin{aligned} E &= \langle \Psi | \hat{H} | \Psi \rangle < \langle \Psi' | \hat{H} | \Psi' \rangle = \langle \Psi' | \hat{H}' + \hat{V}_{\text{ext}} - \hat{V}'_{\text{ext}} | \Psi' \rangle, \\ E' &= \langle \Psi' | \hat{H}' | \Psi' \rangle < \langle \Psi | \hat{H}' | \Psi \rangle = \langle \Psi | \hat{H} + \hat{V}'_{\text{ext}} - \hat{V}_{\text{ext}} | \Psi \rangle. \end{aligned} \quad (2.3.5)$$

By denoting the ground-state electron density as

$$\rho(\mathbf{r}) = \langle \Psi | \sum_i \overline{\psi_i(\mathbf{r})} \psi_i(\mathbf{r}) | \Psi \rangle = \langle \Psi' | \sum_i \overline{\psi_i(\mathbf{r})} \psi_i(\mathbf{r}) | \Psi' \rangle, \quad (2.3.6)$$

we can rewrite equation 2.3.5 as

$$\begin{aligned} E &< E' + \int (v(\mathbf{r}) - v'(\mathbf{r})) \rho(\mathbf{r}) d\mathbf{r}, \\ E' &< E + \int (v'(\mathbf{r}) - v(\mathbf{r})) \rho(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (2.3.7)$$

By combining these two equations the following inconsistency is obtained:

$$E + E' < E' + E. \quad (2.3.8)$$

Thus, it is shown that since two different external potentials, $v(\mathbf{r})$ and $v'(\mathbf{r})$, cannot give rise to the same ground-state electron density $\rho(\mathbf{r})$, $v(\mathbf{r})$ is necessarily a unique functional of the electron density $\rho(\mathbf{r})$ and therefore the ground-state energy must be a unique functional, too.

Following the existence theorem, Hohenberg and Kohn provided in a second theorem a way to determine the ground-state electron density by showing that the electron density obeys a variational principle. Hence, the energy for every trial electron density $\tilde{\rho}(\mathbf{r})$ will be higher than the exact ground-state energy and equal it in case of $\tilde{\rho}(\mathbf{r})$ being the exact ground-state electron density.

$$E_0 \leq E[\tilde{\rho}(\mathbf{r})] = T_e[\tilde{\rho}(\mathbf{r})] + E_{ee}[\tilde{\rho}(\mathbf{r})] + E_{Ne}[\tilde{\rho}(\mathbf{r})] \quad (2.3.9)$$

This implies that minimising the energy will lead to the exact ground-state electron density. Unfortunately the Hohenberg-Kohn variational principle only holds in case of the exact functional $E[\rho(\mathbf{r})]$, which is a drawback of DFT that will be discussed later.

2.3.1.2 Kohn-Sham Methodology

In spite of the importance of the Hohenberg-Kohn theorems, they do not provide any information about how to derive the density without knowledge of the wavefunction or how to compute the ground-state energy E_0 . Therefore, Kohn and Sham introduced their methodology in 1965 which is an important foundation for the practical application of DFT.⁴⁵

Their approach is based on the simplest form of the Schrödinger equation: the assumption of a fictitious system of non-interacting electrons with the same ground-state electron density as the real system of interacting electrons. Therefore, the Kohn-Sham wavefunction is only a single Slater determinant and the energy functional can be split

$$E[\rho(\mathbf{r})] = T_{ni}[\rho(\mathbf{r})] + V_{Ne}[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] + \Delta T[\rho(\mathbf{r})] + \Delta V_{ee}[\rho(\mathbf{r})], \quad (2.3.10)$$

with $T_{ni}[\rho(\mathbf{r})]$ being the kinetic energy of the non-interacting electrons and $\Delta T[\rho(\mathbf{r})]$ and $\Delta V_{ee}[\rho(\mathbf{r})]$ being corrections for the kinetic energy and electron interaction potential, respectively, arising from the interacting nature of electrons. Expressing the density in terms of Kohn-Sham orbitals χ_i^{KS} ,

$$\rho(\mathbf{r}) = \sum_{i=1}^n |\langle \chi_i^{KS} | \chi_i^{KS} \rangle|^2, \quad (2.3.11)$$

allows to rewrite equation 2.3.10 for a system consisting of n electrons and N nuclei as

$$E[\rho(\mathbf{r})] = -\frac{1}{2} \sum_{i=1}^n \langle \chi_i^{KS} | \nabla_i^2 | \chi_i^{KS} \rangle - \sum_{i=1}^n \sum_{A=1}^N \langle \chi_i^{KS} | \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}_i|} | \chi_i^{KS} \rangle + \frac{1}{2} \sum_{i=1}^n \langle \chi_i^{KS} | \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}_i - \mathbf{r}'|} d\mathbf{r}' | \chi_i^{KS} \rangle + E_{xc}[\rho(\mathbf{r})]. \quad (2.3.12)$$

Here, the two correction terms from equation 2.3.10 have been summarised in the exchange-correlation functional $E_{\text{xc}}[\rho(\mathbf{r})]$. In order to compute this energy, it is necessary to find the Kohn-Sham orbitals by solving the pseudo-eigenvalue equations, which are similar to the Hartree-Fock equations,

$$\hat{h}_i^{\text{KS}} |\chi_i^{\text{KS}}\rangle = \epsilon_i^{\text{KS}} |\chi_i^{\text{KS}}\rangle, \quad (2.3.13)$$

with the one-electron Kohn-Sham operator being

$$\hat{h}_i^{\text{KS}} = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^N \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}_i|} + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}_i - \mathbf{r}'|} d\mathbf{r}' + \frac{\partial E_{\text{xc}}[\rho(\mathbf{r})]}{\partial \rho(\mathbf{r})}. \quad (2.3.14)$$

Solving equation 2.3.13 will result in a set of orbitals, which can be used for the computation of the total energy. As the Kohn-Sham one-electron operator (2.3.14) depends on its own eigenfunctions, an iterative procedure using the variational principle is used to determine these orbitals, which is called self-consistent field (SCF) method.

Since KS theory does not involve any approximations, using the correct exchange-correlation functional should yield exact ground-state energies. However, the exact form of this correction is unknown and thus, a lot of work has been invested to find functions that allow reasonable approximations of $E_{\text{xc}}[\rho(\mathbf{r})]$. These approximated functionals may depend solely on the electron density, as local-density approximation (LDA) functionals⁴⁶, or on additional quantities like the gradient or Laplacian of the density, for generalised-gradient approximation (GGA) functionals⁴⁷ or meta-GGA functionals⁴⁸, respectively.

A further step towards an accurate description of $E_{\text{xc}}[\rho(\mathbf{r})]$ is partially including exact, nonlocal exchange, computed by the Hartree-Fock method.⁴⁹ These functionals can be generally expressed by

$$E_{\text{xc}} = (1 - a)E_{\text{xc}}^{\text{DFT}} + aE_{\text{x}}^{\text{HF}}, \quad (2.3.15)$$

where a is an empirically determined constant controlling the addition of Hartree-Fock-exchange. In the case of range-separated functionals (like CAM-B3LYP⁵⁰, which will be used throughout this work), the same form of hybrid functionals is used but a dependence of $\mathbf{r}$ is introduced into the parameter a .

2.3.2 Dispersion Correction

Even though DFT yields a good description for a lot of systems, there are some areas where standard DFT tends to fail.⁵¹ One of these challenges is the description of long-range electron correlation and thus, the description of dispersive van-der-Waals forces. For this particular problem, Grimme⁵¹ proposed an empirical dispersion correction that is added to the total Kohn-Sham energy E_{KS} after the convergence of the SCF iterations.

$$E_{\text{DFT-D}} = E_{\text{KS}} + \Delta E_{\text{disp}} \quad (2.3.16)$$

Now, $E_{\text{DFT-D}}$ is the total energy that includes the empirical dispersion correction ΔE_{disp} . For the DFT-D3 energy⁵², ΔE_{disp} is a sum of two- and three-body terms,

$$\Delta E_{\text{disp}} = E^{(2)} + E^{(3)}, \quad (2.3.17)$$

with the most important two-body term given by

$$E^{(2)} = \sum_{A,B} \sum_o s_o \frac{C_o^{AB}}{R_{AB}^o} f_{d,o}(R_{AB}) \quad (2.3.18)$$

where the first sum runs over all atom pairs in the system and o over the order of the dispersion coefficients C_o^{AB} ($o = 6, 8, 10 \dots$). R_{AB} is the internuclear distance, s_o are global scaling factors (adjusted only for $o > 6$) and $f_{d,o}$ describes a damping function to determine the range of the dispersion correction.

2.3.3 Resolution of the Identity Approximation

The computational cost of the iteration process for computing the Kohn-Sham energy is dominated by the interelectronic repulsion term.⁵³ As stated in equation 2.3.12 the Coulombic repulsion, in the following denoted as $J[\rho(\mathbf{r})]$, is given as

$$J[\rho(\mathbf{r})] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 = \frac{1}{2} \langle \rho(\mathbf{r}) | \rho(\mathbf{r}) \rangle. \quad (2.3.19)$$

Expanding the electron density into atomic orbitals ϕ and collecting the expansion coefficients in the density matrix P , allows us to express the Coulombic repulsion within the atomic orbital basis as the following:

$$\begin{aligned} J_{cd}[\rho(\mathbf{r})] &= \sum_{a=1}^m \sum_{b=1}^m P_{ab} \int \int \frac{\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_1)\phi_c(\mathbf{r}_2)\phi_d(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \sum_{a=1}^m \sum_{b=1}^m P_{ab} \langle ac | bd \rangle. \end{aligned} \quad (2.3.20)$$

with a, b running over the basis functions. As equation 2.3.20 involves a four-centre two-electron integral, it is computationally costly. Thus, Almlöf et al.⁵⁴ introduced an approximated method to solve this integral, which was later refined by Ahlrichs and coworkers⁵³, by representing $\rho(\mathbf{r})$ in terms of a linear combination of $\tilde{m}$ atom-centred auxiliary basis functions α .

$$\rho(\mathbf{r}) \approx \sum_{\alpha=1}^{\tilde{m}} c_{\alpha} \alpha(\mathbf{r}) = \tilde{\rho}(\mathbf{r}) \quad (2.3.21)$$

Minimisation of the Coulombic repulsion and a transformation similar to the resolution of the identity in Hilbert space results in the following approximation of the Coulombic repulsion operator:

$$\tilde{J}[\rho(\mathbf{r})] = \frac{1}{2} \langle \tilde{\rho}(\mathbf{r}) | \rho(\mathbf{r}) \rangle = \frac{1}{2} \sum_{\alpha=1}^{\tilde{m}} \sum_{a,b=1}^m c_{\alpha} \langle a\alpha | b \rangle P_{ab}. \quad (2.3.22)$$

This approximation reduced the four-centre two-electron to a three-centre two-electron integral, which leads to almost a 10-fold saving in computational time, while introducing only minor errors caused by the finite auxiliary basis set.

A similar problem is posed by the integration of the Hartree-Fock exchange term. Thus, in the ORCA program package^{38;55} additionally the so-called RIJCOSX approximation is implemented, which includes the aforementioned resolution of the identity approximation (RI-J) for Coulomb integrals and numerical chain-of-sphere integration for the HF Exchange integrals (COSX⁵⁵).

2.3.4 Time-Dependent DFT

So far, we limited DFT to the description of time-independent systems, i.e. the ground state. In order to describe excited states, a time-dependent formalism becomes necessary, which has been developed as time-dependent DFT (TDDFT). In analogy to DFT, TDDFT is based on three foundations:⁵⁶

1. *The Runge-Gross theorem*: An existence theorem, which establishes a relation between the time-dependent electron density and the wavefunction.
2. *The action integral*: A variational principle, which presents a way to compute the exact time-dependent electron density
3. *The time-dependent Kohn-Sham equations*: a method to compute the orbitals

These foundations will be briefly explained in the following.

2.3.4.1 Formal Foundations

RUNGE-GROSS THEOREM

In analogy to the Hohenberg-Kohn existence theorem for the time-independent case, the Runge-Gross theorem states that the time-dependent wavefunction $|\Psi(\mathbf{r}, t)\rangle$ is determined by the time-dependent electron density $\rho(\mathbf{r}, t)$.⁵⁷

Runge and Gross' proof can be outlined as follows: First, they proved that current densities corresponding to different potentials have to be different. Subsequently, via reductio ad absurdum, it was shown that different current densities give rise to different electron densities. Finally, they proved that different time-dependent external potentials at a given time t_0 result in different time-dependent electron densities infinitesimally later than t_0 and thus, through induction it was proven that at any time t the electron density $\rho(\mathbf{r}, t)$ gives rise to a unique wavefunction $|\Psi[\rho(\mathbf{r}, t)]\rangle$.

ACTION INTEGRAL

In TDDFT the variational principle is based on the quantum mechanical action integral $A[\rho(\mathbf{r}, t)]$. The wavefunction $|\Psi(\mathbf{r}, t)\rangle$ as a solution of the time-dependent Schrödinger equation (2.1.1) corresponds to a stationary point of the quantum mechanical action integral.^{56;57}

$$A[\rho(\mathbf{r}, t)] = \int_{t_0}^{t_1} dt \langle \Psi[\rho(\mathbf{r}, t)] | i \frac{\partial}{\partial t} - \hat{H}(\mathbf{r}, t) | \Psi[\rho(\mathbf{r}, t)] \rangle \quad (2.3.23)$$

From this, with the application of appropriate boundary conditions, the exact electron density $\rho(\mathbf{r}, t)$ can be obtained.

$$\frac{\partial A[\rho(\mathbf{r}, t)]}{\partial \rho(\mathbf{r}, t)} = 0 \quad (2.3.24)$$

Analogously to the Hamiltonian, the action integral can be separated into a universal part $B[\rho(\mathbf{r}, t)]$ and a part dependent on the applied potential $v(\mathbf{r}, t)$.

$$B[\rho(\mathbf{r}, t)] = \int_{t_0}^{t_1} dt \langle \Psi[\rho(\mathbf{r}, t)] | i \frac{\partial}{\partial t} - \hat{T}_e(\mathbf{r}) - \hat{V}_{ee}(\mathbf{r}) | \Psi[\rho(\mathbf{r}, t)] \rangle \quad (2.3.25)$$

$$v(\mathbf{r}) = V_{Ne}(\mathbf{r}) + V(\mathbf{r}, t) \quad (2.3.26)$$

$$A[\rho(\mathbf{r}, t)] = B[\rho(\mathbf{r}, t)] - \int_{t_0}^{t_1} d\mathbf{r} \rho(\mathbf{r}, t) v(\mathbf{r}, t) \quad (2.3.27)$$

Thus, variation of the action integral with respect to the time-dependent electron density according to equation 2.3.24 leads to the exact density.

TIME-DEPENDENT KOHN-SHAM EQUATIONS

Analogously to the time-independent case, we assume a fictitious system of non-interacting particles with the same electron density $\rho_s(\mathbf{r}, t)$, as the real system, which can be expressed in terms of single electron orbitals $\phi_i(\mathbf{r}, t)$,⁵⁶

$$\rho_s(\mathbf{r}, t) = \sum_{i=1}^n |\phi_i(\mathbf{r}, t)|^2, \quad (2.3.28)$$

where the single electron orbitals solve the time-dependent one-particle Schrödinger equation

$$i \frac{\partial}{\partial t} \phi_i(\mathbf{r}, t) = \left(-\frac{1}{2} \nabla_i^2 + v_s(\mathbf{r}, t) \right) \phi_i(\mathbf{r}, t), \quad (2.3.29)$$

with the external one-particle potential $v_s(\mathbf{r}, t)$. The action integral of the non-interacting system can be written analogously to the action integral of the interacting system (cf. eq. 2.3.23 and 2.3.25) without the electron-electron interaction term.

After applying the stationary action principle and inserting the resulting equation for the single particle time-dependent potential into the corresponding Schrödinger equation, the time-dependent Kohn-Sham equations are obtained

$$i \frac{\partial}{\partial t} \phi_i(\mathbf{r}, t) = \left(-\frac{1}{2} \nabla_i^2 + v(\mathbf{r}, t) + \int d\mathbf{r}' \frac{\rho(\mathbf{r}, t)}{|\mathbf{r} - \mathbf{r}'|} + \frac{\partial A_{xc}[\rho(\mathbf{r}, t)]}{\partial \rho(\mathbf{r}, t)} \right) \phi_i(\mathbf{r}, t), \quad (2.3.30)$$

with $A_{xc}[\rho(\mathbf{r}, t)]$ denoting the exchange-correlation part of the action integral.

2.3.4.2 Linear Response TDDFT

To find excitation energies, one needs to compute for which frequency ω of a periodic external potential the density undergoes a resonant response. In principle, TDDFT calculations can be carried out by propagation of the time-dependent

Kohn-Sham orbitals using the time-dependent Kohn-Sham equation (2.3.30).^{58–60} However, a more common approach is to consider the response of the density to a time-dependent perturbation, including only the linear term for simplicity's sake. For an excited state with excitation energy $\omega_I = E_I - E_0$, the linear response problem can be written as a matrix pseudo-eigenvalue problem

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{pmatrix} \mathbf{X}_I \\ \mathbf{Y}_I \end{pmatrix} = \omega_I \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{pmatrix} \mathbf{X}_I \\ \mathbf{Y}_I \end{pmatrix}, \quad (2.3.31)$$

with the matrix elements of $\mathbf{A}$ and $\mathbf{B}$ being given as

$$A_{iajb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + \langle ij|ab \rangle + \langle ij|f_{xc}|ab \rangle, \quad (2.3.32)$$

$$B_{iajb} = \langle ib|aj \rangle + \langle ib|f_{xc}|aj \rangle. \quad (2.3.33)$$

Here $\mathbf{X}_I$ and $\mathbf{Y}_I$ describe the particle-hole and hole-particle excitations, respectively. f_{xc} denotes the exchange-correlation kernel, that includes all non-trivial many body effects. Within the framework of the adiabatic approximation, it is defined as

$$\langle ij|f_{xc}|ab \rangle = \langle \phi_i(\mathbf{r})\phi_j(\mathbf{r}') | \frac{\delta^2 E_{xc}}{\delta \rho(\mathbf{r})\delta \rho(\mathbf{r}')} | \phi_a(\mathbf{r})\phi_b(\mathbf{r}') \rangle. \quad (2.3.34)$$

TAMM-DANCOFF APPROXIMATION

Within the framework of the Tamm-Dancoff Approximation (TDA) the matrix describing the perturbation densities is reduced by neglecting hole-particle excitations, i.e. setting $\mathbf{Y}_I = 0$, and only taking particle-hole excitations into account. Thus, the dimension of eq. 2.3.31 is reduced by half,

$$\mathbf{A}\mathbf{X} = \omega\mathbf{X}, \quad (2.3.35)$$

where the matrix entries of $\mathbf{A}$ are defined by eq. 2.3.32.

Since correlation is often already included in the exchange-correlation functionals in the ground state, TDA/TDDFT usually is a very good approximation of TDDFT.

2.4 WAVEFUNCTION ANALYSIS

Throughout this work, excited state analysis was performed with the TheoDORÉ package.^{61;62} There, the one-electron transition matrix elements $D_{\mu\nu}$ in the basis of atomic orbitals μ and ν will be derived from the excitation vector X_{ia} , which is a matrix element of $\mathbf{X}$ in equations 2.3.31 and 2.3.35, between two molecular orbitals i and a utilising the elements of the respective MO coefficients (C):

$$D_{\mu\nu} = \sum_{i,a} C_{\mu i} X_{ia} C_{\nu a} \quad (2.4.1)$$

In order to further analyse the system it is necessary to divide the system into appropriate fragments, which has to be done on an intuitive basis, but recently advances have been made to automatise this choice.⁶³ Then, with respect to these

fragments, excitations can be termed local if both orbitals μ and ν of the aforementioned matrix element $D_{\mu\nu}$ are located on the same fragment A . The weight of local excitations on A is the respective matrix element Ω_{AA} of the charge transfer number matrix. Consequently, in the case of the orbitals being assigned to different fragments A and B , the excitation has charge transfer character and the charge transfer number Ω_{AB} weighs the charge transfer character between the fragments A and B . The charge transfer numbers are the result of a two-dimensional population analysis (e.g. Mulliken or Löwdin) of the transition density matrix. They divide each excitation into n_{frag}^2 (the number of fragments squared) contributions for excitations from orbitals on A to orbitals on B . The charge transfer matrix for two fragments A and B is defined as:

$$\Omega_{AB} = \sum_{\mu \in A, \nu \in B} (\tilde{D}_{\mu\nu})^2 \quad (2.4.2)$$

where $\tilde{\mathbf{D}}$ is the transition density matrix on which a Löwdin orthogonalisation is applied

$$\tilde{\mathbf{D}} = \mathbf{S}^{1/2} \mathbf{D} \mathbf{S}^{1/2} = (\mathbf{P} \mathbf{Q}^T) \mathbf{D} (\mathbf{P} \mathbf{Q}^T)^T \quad (2.4.3)$$

where $\mathbf{S}$ denotes the overlap matrix and $\mathbf{P}$ and $\mathbf{Q}$ are the matrices that contain the left and right singular vectors of the MO-coefficient matrix $\mathbf{C}$.

Ω_{AB} can be used to compute a variety of descriptors that hold meaningful information. Since the aim of this work is to distinguish between Frenkel exciton, charge transfer states and excited dimers, the relevant information are the delocalisation of the excitation as well as the charge transfer character of the state. The charge transfer character CT is obtained by summation over the off-diagonal elements of Ω_{AB} normalised by the factor $\Omega^{61;62}$

$$\text{CT} = \Omega^{-1} \sum_{A, B \neq A} \Omega_{AB} \quad (2.4.4)$$

$$\Omega = \sum_{A, B} \Omega_{AB} \quad (2.4.5)$$

CT can range from 0 (in the case of local excitations and Frenkel excitons) to 1 (for pure charge transfer states).

A measure for the extent of the delocalisation is the participation ratio PR. For the general case of a nonsymmetric Ω matrix, the definition of the participation ratio consists of two parts for the hole and electron, respectively. The participation ratios for the initial (PR_I) and final orbitals (PR_F) are defined analogously as

$$\text{PR}_I = \frac{\Omega^2}{\sum_B (\sum_A \Omega_{AB})^2} \quad (2.4.6)$$

$$\text{PR}_F = \frac{\Omega^2}{\sum_A (\sum_B \Omega_{AB})^2} \quad (2.4.7)$$

which measure over how many fragments the hole and electron are delocalised, respectively. The number of fragments involved in the excited states is then represented by the average of these two participation ratios

$$\text{PR} = \frac{1}{2} (\text{PR}_I + \text{PR}_F). \quad (2.4.8)$$

Table 2.1: Values of different descriptors for the discussed types of excited states.

	State	CT	DL	PR	CT _{nt}	COH
	a) monomer	0	1	1	0	1
	b) exciton	0	3	3	0	1
	c) exciplex	1	2	1	1	1
	d) charge res.	1	2	2	0	1
	e) excimer	0.5	2	2	0	2

A closely to PR related descriptor is the delocalisation length, DL. It can be calculated utilising Ω_{AB} as an inverse participation ratio and yields the number of fragments involved in the excitation of the state of interest.

$$DL = \frac{\Omega^2}{\sum_B (\sum_A \frac{(\Omega_{AB} + \Omega_{BA})^2}{2})^2} \quad (2.4.9)$$

The delocalisation of the hole as well as of the electron is taken into consideration. DL can range from 1 to the number of fragments included.

Additionally, the coherence length is also related to the average hole-electron separation and can be defined as

$$COH = \frac{1}{PR} \frac{\Omega^2}{\sum_A \sum_B \Omega_{AB}^2} \quad (2.4.10)$$

A valuable additional information is to not only know how many but also which nucleobases are involved in a transition. A possible quantity for analysis with respect to this are the positions of the hole orbital, POS_I , and the position, where the electron will be located, POS_F .^{61,62}

$$POS_I = \Omega^{-1} \sum_A A (\sum_B \Omega_{AB}) \quad (2.4.11)$$

$$POS_F = \Omega^{-1} \sum_B B (\sum_A \Omega_{AB}) \quad (2.4.12)$$

The difference between the centers of charge of the electron and hole is the so-called signed net charge transfer length (CT_{nt})

$$CT_{nt} = POS_F - POS_I. \quad (2.4.13)$$

To illustrate the possibilities and limitations of these descriptors, figure 1.4 shows five possible excited states. The corresponding descriptors are listed in table 2.1.

In the case of a local excitation on one adenine (1.4a) the DL and PR will be 1 and as both hole and electron are located on the same fragment, CT will be 0.^{18,64} Analogously, for Frenkel excitons (1.4b) the CT will remain 0, but if the exciton state is

delocalised over three nucleobases, the DL will yield 3 and since electron as well as hole is delocalised over three nucleobases PR will be 3 as well. For pure Frenkel excitons, where only diagonal elements of Ω are nonzero, the COH = 1. The situations of a charge transfer state (exciplex) and a charge resonance state (1.4c and 1.4d) cannot be distinguished only based on the DL and CT. For the charge transfer state the CT will obviously be 1, as all excitation is transferred to the second nucleobase. In the case of the charge resonance state, half of the excitation is transferred from fragment 2 to 3 and the other half vice versa. Thus, in the charge transfer matrix Ω_{AB} two symmetric off-diagonal elements will equal 0.5. Consequently, since according to eq. 2.4.4, CT is calculated as the sum of the off-diagonal elements of Ω_{AB} , this case will equally yield a CT of 1. The exciplex as well as the charge resonance state are both localised over two nucleobases and therefore yield a DL of 2. However, the PR differs in the two cases, since for the exciplex the hole and electron are each located on only one nucleobase and thus, PR = 1, while in a charge resonance state hole and electron are both delocalised over two bases and therefore, PR = 2. Furthermore, the exciplex is the only state where the hole and electron are located on different fragments resulting in a $CT_{nt} = 1$. The excited dimer (excimer, 1.4e) includes charge transfer excitations as well as local excitations on two fragments. It differs from the charge resonance in its CT of 0.5. The coherence length relates to the intrinsic structure of the excitation. It is largest when locally excited and charge transfer configurations are contributing equal amounts to the excitation. Hence, the coherence length will be largest for excimeric states.

With these values for the electron and hole positions, a differentiation between charge transfer states and excimers becomes possible. In the example of a charge transfer state like in figure 1.4c, the hole is located at fragment 3 and thus, $POS_I = 3$ while the electron is located at fragment 2 and $POS_F = 2$. Hence, the CT_{nt} is 1. In contrast in the case of an excimer as shown in figure 1.4d, the hole and electron are equally located at fragments 2 and 3, thus POS_F and POS_I are both 2.5 and the $CT_{nt} = 0$

2.5 MOLECULAR MECHANICS

As mentioned in previous sections, calculating the electronic energy for a system consisting of a large number of atoms poses a seemingly insurmountable obstacle in computational chemistry.⁶⁵ In molecular mechanics (MM) this hurdle is overcome by expressing the electronic energy in terms of a parametric function of the nuclear coordinates and fitting the parameters with respect to experimental or quantum mechanical results for smaller molecules or fragments. Electrons are not considered as individual particles in MM and also the quantum aspects of the nuclear motion are neglected. Hence, in contrast to all methodology discussed until now, MM is a classical approach for the calculation of the energy of a molecule. Usually, the energy is split into bonded and non-bonded interactions and simply adding the single contributions of bonded and non-bonded terms will yield the total potential of the molecule.⁶⁶ A set of functions in combination with the appropriate set of parameters is called a force field. A great variety of force fields has

been developed for simulations of different systems with varying accuracy. The most commonly used approach of functions is the following:⁶⁷

$$E_{tot} = \sum_{\text{bonds}} k_b (R - R_{eq})^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_{eq})^2 + \sum_{\text{dihedrals}} \frac{V_p}{2} [1 + \cos(p\phi - \gamma)] + \sum_{i < j} \left[\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^6} + \frac{q_i q_j}{\epsilon r_{ij}} \right] \quad (2.5.1)$$

The potential energy function expressed above is also used in the force field employed in this work. The first three terms of eq. 2.5.1 represent the bonded interactions. They account for bond stretching (first term) and angles (second term) according to harmonic expressions with force constants, k_b and k_θ , and equilibrium distance, R_{eq} , and angle, θ_{eq} , respectively. The third bonded interaction included is torsion, represented by the third term of eq. 2.5.1 with torsion barrier V_n , phase γ and periodicity p . The last term of eq. 2.5.1 describes non-bonded van-der-Waals and electrostatic interactions. The former are represented by a 6-12 Lennard-Jones potential with the attraction and repulsion parameters A_{ij} and B_{ij} , respectively and the distance R_{ij} between two atoms i and j ; the latter are modeled by a Coulombic interaction of atom-centered point-charges (q_i and q_j on atoms i and j , respectively).

2.6 QUANTUM MECHANICS/MOLECULAR MECHANICS

The size and complexity of biochemical systems very often necessitates the use of molecular mechanics (MM).⁶⁸ However, especially for excited states, there is a lack of chemical accuracy involved with the usage of force fields. At the same time, the use of any quantum mechanical (QM) method for the description of biochemical systems usually is beyond any computational resources. To overcome the limitations of full quantum mechanics as well as of a fully classical description, methods have been developed where a small, feasible part of the system is treated at the QM level, while for the larger rest of the system MM is employed. This approach was originally presented by Warshel and Levitt in 1976.⁶⁹ The usage of the QM/MM approach can be justified by the fact that most processes of interest occur locally.⁶⁸ In these cases, the QM region would include all parts of the total system that are involved in the simulated process, for example in this work, nucleobases involved in photoabsorption. Hence, the MM region contains all atoms that are hardly affected by the process but may have some influence via long-range interactions, like for example additional nucleobases, the sugar-phosphate backbone and the water environment in this work.

The energy obtained through this hybrid QM/MM approach contains three types of interactions: interactions within the QM region as well as within the MM region and interactions between the QM and MM region. Describing the interactions within the QM and MM region is relatively straightforward, as this is done at the respective level. However, the description of the interactions between the two subsystems is more complex and two main approaches have been proposed to do so: subtractive and additive coupling schemes. In the subtractive scheme, first, the energy of the whole system (i.e. containing QM and MM region) is computed at

the MM level, then the QM energy of the isolated QM subsystem is added and finally, the MM energy of the QM subsystem is subtracted.

$$E^{\text{QM/MM}} = E^{\text{MM}}(\text{MM} + \text{QM}) + E^{\text{QM}}(\text{QM}) - E^{\text{MM}}(\text{QM}) \quad (2.6.1)$$

The superscripts indicate the level of theory at which the energies are computed, QM and MM denote the atoms in the QM and MM subsystems, respectively. The implementation of the subtractive scheme is relatively straightforward, since the quantum chemistry and molecular mechanics routines can work independently.

The alternative to the subtractive scheme is the additive scheme. There, the QM system is embedded within the MM system and the total energy is obtained as the sum of QM energy, MM energy and QM/MM coupling terms.

$$E^{\text{QM/MM}} = E^{\text{QM}}(\text{QM}) + E^{\text{MM}}(\text{MM}) + E^{\text{QM-MM}}(\text{QM} + \text{MM}) \quad (2.6.2)$$

Here, the interactions between the two subsystems are computed explicitly as $E^{\text{QM-MM}}(\text{QM} + \text{MM})$. The simplest way to treat this interaction is the mechanical embedding. There all interactions between the subsystems are evaluated with the force field, hence the charges of the outer region will have no influence on the QM charge density. A more elaborate approach than mechanical embedding is electrostatic embedding, where polarisation effects are considered. This is achieved by including the MM point charges as one-electron operators in the QM Hamiltonian, thus the QM computation is carried out in the presence of MM charges

$$\hat{h}_i^{\text{QM-MM}} = \hat{h}_i^{\text{QM}} - \sum_{J=1}^M \frac{Q_J}{|\mathbf{r}_i - \mathbf{R}_J|}, \quad (2.6.3)$$

with the positions of electron and MM atom, $\mathbf{r}_i$ and $\mathbf{R}_J$, respectively, $\hat{h}_i^{\text{QM}}$ denotes the original one-electron Hamiltonian for electron i , M the number of MM atoms with partial charge Q_J . Thus, electrostatic embedding allows polarisation of the QM density by changes in the charge distribution of the outer system. This idea is furthered by the polarisation embedding where both regions can mutually polarise each other, meaning that the QM region can also induce polarisation in the MM region, just as well as vice versa. For that it is necessary to compute the MM polarisations during each step of the iteration of the QM wavefunction and therefore, the polarisation embedding is computationally very expensive.

2.6.1 Link Atoms

If chemical bonds connect the QM and MM regions, like in the case of the bonds between adenine and the pentose, problems with the evaluation of the QM wavefunction may occur, since simply breaking the bond would result in one or more unpaired electrons, which would lead to an erroneous treatment of the system. Therefore, the most straightforward way is to introduce a monovalent link atom along the bond vector between the QM and MM atom. The most commonly used link atom type is hydrogen but in principle there is no restriction to the type of link atom. The introduced link atoms are only considered in the QM computation and

are invisible to the MM region. In practice, the link atoms are placed at appropriate fixed positions along the bond, so there are no additional degrees of freedom introduced by the link atoms. In each step the force acting on the link atoms will be distributed over the QM and MM atoms of the bond.

2.7 MOLECULAR DYNAMICS

The chapters above all discussed the possible treatment of electronic states by solving the electronic Schrödinger equation. However, if we are interested in the time-dependent behaviour of a molecular system, it is necessary to solve the nuclear Schrödinger equation (2.2.5).^{70,71} While this may be a reasonable approach for small systems, it is not feasible for large molecules. The dimensionality of the PES increases linearly with the size of the system, whereas the necessary number of grid points of the PES grows exponentially. In order to circumvent the obstacle of having to know the whole PES in advance, on-the-fly methods like semi-classical *ab initio* molecular dynamics (AIMD) have become a widely used alternative.

The main principle of AIMD is to treat the electrons quantum mechanically by solving the electronic Schrödinger equation while the nuclei are treated classically.³⁹ By doing this, the problem of solving the nuclear Schrödinger equation is evaded, since the propagation of the nuclei only depends on the energies, gradients and NACs of the electronic states of each time step. This leads to a large reduction of computational effort which enables the simulation of the excited-state dynamics of larger systems. However, the classical approximation leads to the loss of quantum effects like tunneling and coherence, which the classical propagation cannot account for.

2.7.1 *Newton's Equations of Motion*

Over 300 years ago, Sir Isaac Newton first postulated the classical laws of motion, which describe the motion of any macroscopic body. Using Newton's second law, stating that the force acting on a body equals the time derivative of the momentum, one can derive Newton's equation of motion⁷²

$$M_A \frac{d^2}{dt^2} \mathbf{R}_A(t) = -\nabla_A E_i(\mathbf{R}(t)), \quad (2.7.1)$$

where the molecule is assumed to be in an electronic state with energy $E_i(\mathbf{R}(t))$ which depends on all nuclear coordinates. Integration of eq. 2.7.1 would yield the complete trajectory of the molecule for any given initial condition, however this is not possible analytically. Thus, numerical methods, where the time is discretised to intervals and propagated from time step t to time step $t + \Delta t$, are necessary. The most prominent numerical method for this problem is the Velocity-Verlet al-

gorithm, where the atomic coordinates $\mathbf{R}(t + \Delta t)$, the velocity $\mathbf{v}(t + \Delta t)$ and acceleration $\mathbf{a}(t + \Delta t)$ are calculated according to the following equations:⁷³

$$\mathbf{R}(t + \Delta t) = \mathbf{R}(t) + \mathbf{v}(t)\Delta t + \mathbf{a}(t)\frac{\Delta t^2}{2}, \quad (2.7.2)$$

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \frac{\Delta t}{2} (\mathbf{a}(t) + \mathbf{a}(t + \Delta t)), \quad (2.7.3)$$

$$\mathbf{a}(t + \Delta t) = -\frac{1}{m} \nabla E(\mathbf{R})|_{\mathbf{R}=\mathbf{R}(t+\Delta t)}. \quad (2.7.4)$$

The advantage of the Velocity-Verlet algorithm over simpler methods is that the new velocity can be calculated simultaneously to the new coordinates. Additionally, the global error of the Velocity-Verlet algorithm is of order $\mathcal{O}(\Delta t^2)$, compared to an error of $\mathcal{O}(\Delta t)$ in the case of Euler's algorithm.

2.7.2 Surface Hopping

Following Newton's equation of motion the nuclei of the system would always propagate on the potential of one state. In order to transfer between different states the so-called surface hopping method has been developed.^{74,75} There, between every step, the system occupying the electronic state $|\Psi_i\rangle$ can "hop" to another electronic state $|\Psi_j\rangle$ in a probabilistic manner.* Assuming the total electronic wavefunction $|\Psi\rangle$ to be a linear combination of electronic states $|\Psi_i\rangle$ one can account for the time-dependence in the expansion coefficients and obtain

$$|\Psi(t)\rangle = \sum_i c_i(t) |\Psi_i\rangle. \quad (2.7.5)$$

The probability of finding a trajectory in the electronic state i depends on the state coefficient c_i , given by $c_i \bar{c}_i = |c_i|^2$. In order to satisfy the completeness relation, these coefficients need to be normalised so that

$$\sum_i |c_i|^2 = 1. \quad (2.7.6)$$

In Tully's Fewest Switches algorithm⁷⁵, it is assured that the actual population of the states is consistent with the states coefficients, as hops are only allowed out of states with decreasing coefficient and into states if the coefficients increase. Thereby, the number of hops is minimised. In an ensemble of N_T trajectories of which $N_j(t_n)$ occupy state j at time t_n , with the coefficients c_j determining the population of the state j , we obtain

$$\frac{N_j(t_n)}{N_T} = |c_j(t_n)|^2. \quad (2.7.7)$$

If the population decreases by ΔN within the time interval $[t_n; t_{n+1}]$ and we only consider hops out of j into another state, due to the Fewest Switches criterion, we obtain the probability to hop out of j

$$h_{j \rightarrow \dots} = \frac{\Delta N}{N_j(t_n)} = \frac{N_j(t_n) - N_j(t_{n+1})}{N_j(t_n)} = \frac{|c_j(t_n)|^2 - |c_j(t_{n+1})|^2}{|c_j(t_n)|^2}. \quad (2.7.8)$$

*For simplicity, the dependencies of the electronic wavefunction will not be stated explicitly in the following section.

For an infinitesimally small time step, the difference of the squares of the coefficients becomes the time derivative of the square of the coefficient, which can be expressed as

$$\begin{aligned}\frac{\partial}{\partial t}|c_j|^2 &= \frac{\partial}{\partial t}c_j\bar{c}_j = \left(\frac{\partial}{\partial t}\bar{c}_j\right)c_j + \bar{c}_j\left(\frac{\partial}{\partial t}c_j\right) \\ &= \left(\overline{\bar{c}_j\frac{\partial}{\partial t}c_j}\right) + \bar{c}_j\frac{\partial}{\partial t}c_j = 2\operatorname{Re}\left(\bar{c}_j\frac{\partial}{\partial t}c_j\right)\end{aligned}\quad (2.7.9)$$

Then, we arrive at the hopping probabilities in terms of the coefficients and their time derivatives

$$h_{j\rightarrow\ldots} = -\frac{2\Delta t}{\bar{c}_j c_j} \operatorname{Re}\left(\bar{c}_j \frac{\partial}{\partial t} c_j\right). \quad (2.7.10)$$

For the calculation of the time derivatives of the state coefficients, we insert the expansion of the electronic wavefunction as a linear combination of electronic states (eq. 2.7.5) into the TDSE and after projection on $\langle\Psi_j|$ we obtain for the time-evolution of the coefficients

$$\frac{dc_j(t)}{dt} = -\sum_i \left(\underbrace{i\langle\Psi_j|\hat{H}_e|\Psi_i\rangle}_{H_{ji}} + \underbrace{\langle\Psi_j|\frac{d}{dt}|\Psi_i\rangle}_{K_{ji}} \right) c_i(t). \quad (2.7.11)$$

The first term, H_{ji} denotes an element of the electronic Hamiltonian matrix $\mathbf{H}^e$; the nonadiabatic coupling term K_{ji} can be computed with the nonadiabatic coupling vector between the electronic states and the velocity of the nuclei

$$K_{ji} = \langle\Psi_j|\nabla_R|\Psi_i\rangle \cdot \mathbf{v}_R. \quad (2.7.12)$$

Consequently, the surface hopping probability $h_{j\rightarrow i}$ from state j to state i can be calculated as

$$h_{j\rightarrow i} = \frac{2\Delta t}{\bar{c}_j c_j} \operatorname{Re}\left(\bar{c}_j c_i [iH_{ji} + K_{ji}]\right). \quad (2.7.13)$$

The above presented surface hopping formalism is valid in the adiabatic picture of the BOA, where $\mathbf{H}^e$ is diagonal as in the simulation presented in this work. However, it requires the integration over the NAC term $\mathbf{K}$, which is computationally challenging, as very small time steps need to be used for the numerical integration. Thus, alternative propagation methods for surface hopping dynamics have been developed. The surface hopping scheme used throughout this work, called SHARC (Surface hopping including arbitrary couplings)^{39,40}, propagates the coefficients according to

$$\mathbf{c}(t + \Delta t) = \mathbf{P}(t + \Delta t)\mathbf{c}(t), \quad (2.7.14)$$

where $\mathbf{P}$ denotes the propagator matrix in the local diabatisation approach.⁷⁶ The propagator has the following form

$$\mathbf{P} = \mathbf{S}^\dagger(t + \Delta t, t) \hat{T} \exp\left[-\int_t^{t+\Delta t} i\mathbf{S}(t, \tau) \mathbf{H}^e(\tau) \mathbf{S}(\tau, t) d\tau\right] \quad (2.7.15)$$

$$S_{ij} = \langle\Psi_i(t)|\Psi_j(t + \Delta t)\rangle, \quad (2.7.16)$$

where $\mathbf{S}(t + \Delta t, t)$ is the wavefunction overlap between the time steps and $\hat{T}$ denotes the time ordering operator. With this approach, the hopping probabilities can be calculated as

$$h_{j \rightarrow i} = \left(1 - \frac{|c_j(t + \Delta t)|^2}{|c_j(t)|^2} \right) \frac{\text{Re}(c_i(t + \Delta t) \overline{P_{ij} c_j(t)})}{|c_j(t)|^2 - \text{Re}(c_j(t + \Delta t) \overline{P_{jj} c_j(t)})}. \quad (2.7.17)$$

By considering of the hopping probabilities with the propagation of the trajectories, all the requirements for surface hopping are met in this scheme, while integration of $\mathbf{K}$ is avoided.

STATIC CALCULATIONS

This chapter contains a detailed investigation of the description of the absorption spectrum of polyadenine. Several methodical aspects will be discussed and compared in detail, namely the influence of the size of the QM region (6 or 4 nucleobases), the DFT formulation (using TDA or standard TDDFT), inclusion of the nucleobases on the edge of the QM region in the wavefunction analysis and the influence of the basis set size. This information is critically important to perform subsequently feasible and accurate dynamics simulations.

The results obtained by Nogueira et al.¹⁸ are used as a reference for these analyses. They computed the absorption spectrum of polyadenine (dA)₂₀ and included 8 adenine bases in the QM region. For an ensemble of 100 geometries, the first 60 excited states were computed employing the CAM-B3LYP density functional and the Ahlrichs def2-SV(P) basis set. The absorption spectra resolved with respect to the charge transfer character and delocalisation lengths are shown in figure 3.1. Their absorption spectra are red shifted by 0.7 eV to match the absorption maximum of the experimental spectrum. Among the main findings of their study was that exciton states delocalised over two nucleobases contribute about half of the lowest UV absorption band, since half of the spectrum consists of pure Frenkel excitons with CT smaller than 0.1 and half of the excitations occur delocalised over two nucleobases. They also observed a significant fraction of states with non-negligible CT admixture, where states with CT higher than 0.3 only occur at the blue side of the spectrum.

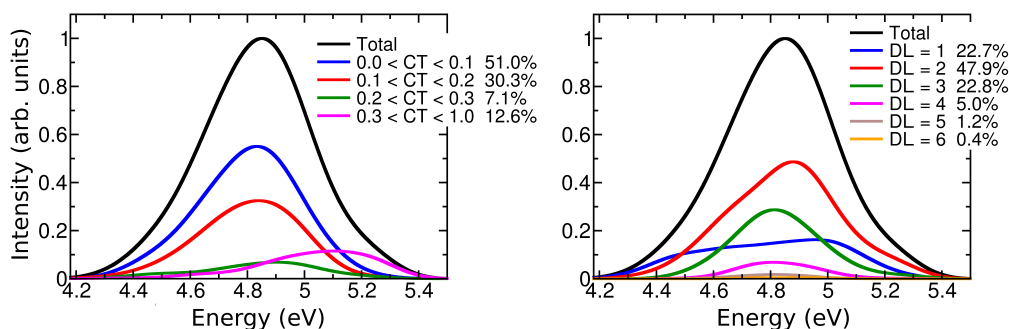


Figure 3.1: Decomposition of the lowest-energy absorption band for (dA)₂₀, including eight adenines in the QM region, into different charge-transfer (CT) contributions (left) and delocalisation lengths (DL) (right). The percentages denote the intensity contribution to the total spectrum.

3.1 COMPUTATIONAL DETAILS

In order to sample the Franck-Condon region in the electronic ground state classical molecular dynamics simulations of solvated (dA)₂₀ were performed with the Amber14⁷⁷ using the Amber ff99 force field. The system was first minimized and heated at 300 K in the canonical ensemble. Afterwards, it was equilibrated for 600 ps where the restraints applied during the heating were gradually removed and for the last 200 fs it was changed to the isothermal-isobaric ensemble. Then, a production run of 60 ns was evolved in the isothermal-isobaric ensemble. Two ensembles of 100 and 300 equidistant snapshots from the last 35 ns of the dynamics were selected for the system.

The following closer investigation of the absorption spectrum was performed on the ensemble consisting of 100 snapshots. For each snapshot the electronic excitations of the lowest 30 or 20 singlet states, depending of the number of nucleobases included in the QM region, were computed employing an electrostatic embedding QM/MM scheme. Two differently sized QM regions were investigated: including either six or four adenines in the middle of the (dA)₂₀ strand. The atoms in the QM region are described by time-dependent density functional theory (TDDFT) employing the CAM-B3LYP functional⁵⁰ and the Ahlrichs def2-SV(P) basis set⁷⁸ as well as Grimme's D3 dispersion correction.⁵¹ For comparison the calculations were performed with and without usage of the Tamm-Dancoff approximation (TDA).⁷⁹ The quantum mechanical computations were carried out with the ORCA program package.³⁸ Due to the large system size, the resolution of the identity approximation, implemented as RIJ-COSX^{55;80} in ORCA, was used in combination with the def2/j auxiliary basis set. During the SCF iterations the angular integration grid Lebedev194 with a radial grid with IntAcc=4.34 was chosen whereas for the final energy evaluation after SCF convergence a larger grid (Lebedev434, IntAcc=5.01) was used, the keywords GRID3 and FINALGRID5 were set in ORCA. For the COSX grid a sequence of three grids with IntAcc=3.34, 4.01, 4.67 was used, controlled by the GRIDX4 keyword and additionally the GRIDXC was set to 5. The energy difference criteria for SCF convergence was set to 10^{-8} au. The influence of the MM region was simulated by inclusion of point charges obtained with the molecular mechanics program Tinker 8⁸¹ and bonds between the QM and MM region were treated according to the hydrogen link atom approach.⁸²

The obtained excitation energies were convoluted with a Gaussian function of FWHM = 0.2 eV. All computed spectra were decomposed into the charge transfer character and delocalisation length of their excitations, classified according to the rules explained below. The values for these properties were obtained using the TheoDORÉ wavefunction analysis package.^{64;83}

3.2 SIZE OF QM REGION AND DFT FORMULATION

In a first step, QM regions including six and four adenines in the center of the (dA)₂₀ strand were compared. Any excitations where either the hole or final orbital were mainly located on the edge nucleobases were removed from this analysis in order to avoid artifacts arising from the proximity of MM nucleobases. This was

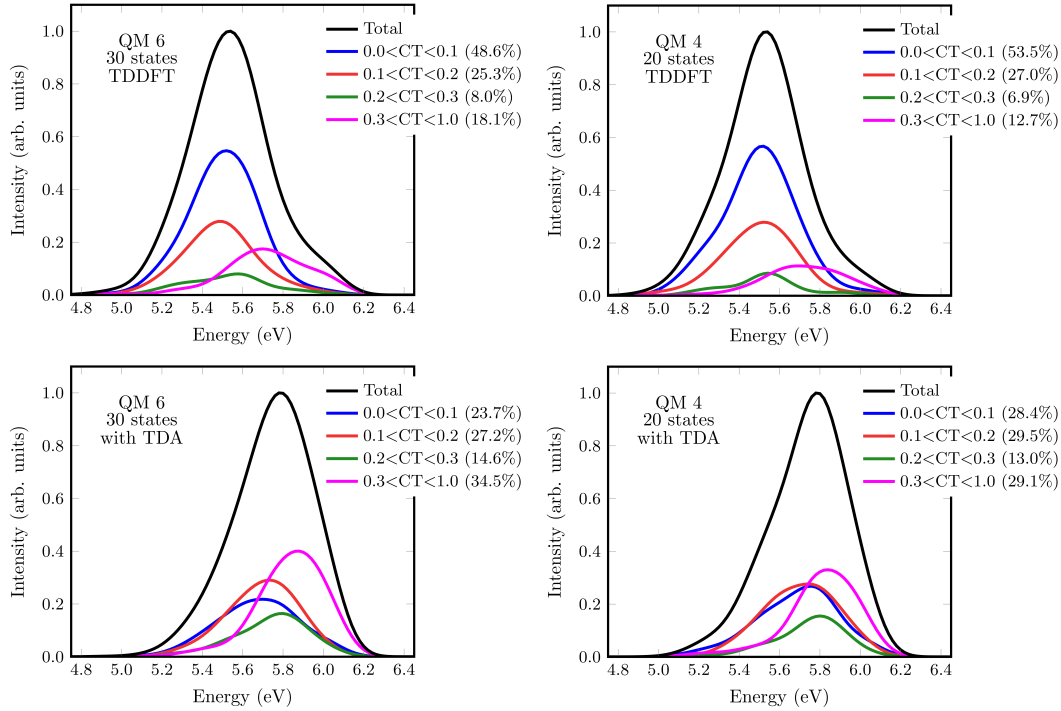


Figure 3.2: Decomposition of the lowest-energy absorption band for (dA)₂₀, including six (left plots) and four (right plots) adenines in the QM region, into different charge-transfer contributions. The top plots are obtained with the standard formulation of TDDFT, in the bottom plots TDA was employed. The numbers in parentheses denote the intensity contribution to the total spectrum.

done by excluding all excitations whose POS_I or POS_F value was smaller than 1.5 or larger than 5.5 or 3.5 for the QM regions with six or four adenines, respectively. This influence will be discussed later on. The lowest band of the absorption spectra was calculated from an ensemble of 100 geometries using the standard TDDFT formulation first and also with employing the Tamm-Dancoff approximation (TDA).

3.2.1 Charge Transfer States

The decomposition of the lowest-energy band of the UV absorption spectrum of (dA)₂₀ computed with TDDFT with respect to the charge transfer character of the states is shown in the top plots of figure 3.2 for the QM regions including six and four nucleobases. The comparison between the two differently sized QM regions shows no significant differences. In both cases, around half of the spectral intensity derives of states with less than 0.1 CT (48.6 % for QM 6 and 53.6 % for QM 4), which can be termed pure Frenkel excitons or pure local excitations.¹⁸ The remaining half of the spectral intensity comes from states with non-negligible CT admixture, the states with high CT character (more than 0.3) are located at the higher energy region of the absorption band. These observations are true for both sizes of QM regions and are also in close agreement with the results obtained by Nogueira et al. for a QM region including eight nucleobases.

Table 3.1: Computed arithmetic (arith. av.) and oscillator strength weighted averages (osc. str. av.) of the CT character of the states contributing to the lowest energy absorption band.

QM size	method	arith. av.	osc. str. av.
6	TDDFT	0.2669	0.1922
6	TDA	0.2794	0.2863
4	TDDFT	0.2198	0.1594
4	TDA	0.2479	0.2503

Subsequently, it was investigated how the use of TDA influences the absorption band. These plots for both QM regions (six and four nucleobases) are shown in the bottom plots in figure 3.2.

It can be observed that TDA significantly overestimates the excitation energies by almost 0.3 eV. For both differently sized QM regions, the lowest energy absorption band is centered around 5.5 eV for TDDFT and shifted to 5.8 eV under the usage of TDA. Previous studies comparing TDA and TDDFT showed either an underestimation of excitation energies of long range charge transfer states when employing TDA⁸⁴, an overestimation of only the energies of the valence states⁸⁵ or only negligible effects^{79;86}.

Furthermore, the CT character of the absorption band changes drastically with the use of TDA. The fraction of pure local excitations of the spectral intensity decreases from 48.6 % to 23.7 % when using TDA with six nucleobases in the QM region and from 53.5 % to 28.4 % for the QM region including four nucleobases. Analogously, the contribution of CT states (states with CT 0.3 and higher) almost doubles when using TDA, from 18.1 % to 34.5 % and from 12.7 % to 29.1 % for QM 6 and QM 4, respectively. These observations from the spectra were quantified by calculating the arithmetic average of the CT character of the whole spectrum. In addition to the arithmetic average, the average weighted with respect to the oscillator strength was calculated as well. Table 3.1 shows the calculated averages for both QM regions with TDA and TDDFT. The arithmetic average of the CT character over the whole absorption band does not change significantly when using TDA. However the average weighted with respect to the oscillator strength, i.e. counting only the states contributing to the spectrum, does increase drastically, by 0.08 and 0.14 for QM 6 and QM 4, respectively. This shows that TDA largely overestimates the contribution of CT states to the absorption band.

Additionally, the average energies for states with CT character within intervals of 0.05 were computed, again as an arithmetic average as well as weighted with the oscillator strength. This is plotted in figure 3.3. For the arithmetic average, both TDA and TDDFT show a very similar trend, with increasing CT character corresponding to higher energies. TDA seems to slightly overestimate the energies especially for states with very low CT character. When looking at the oscillator strength weighted averages, one can observe an overestimation of the states with CT of 0.7 and lower when TDA is employed. The energies of states with CT up to 0.3 are between 0.2 and 0.3 eV higher with TDA than with TDDFT. Comparison

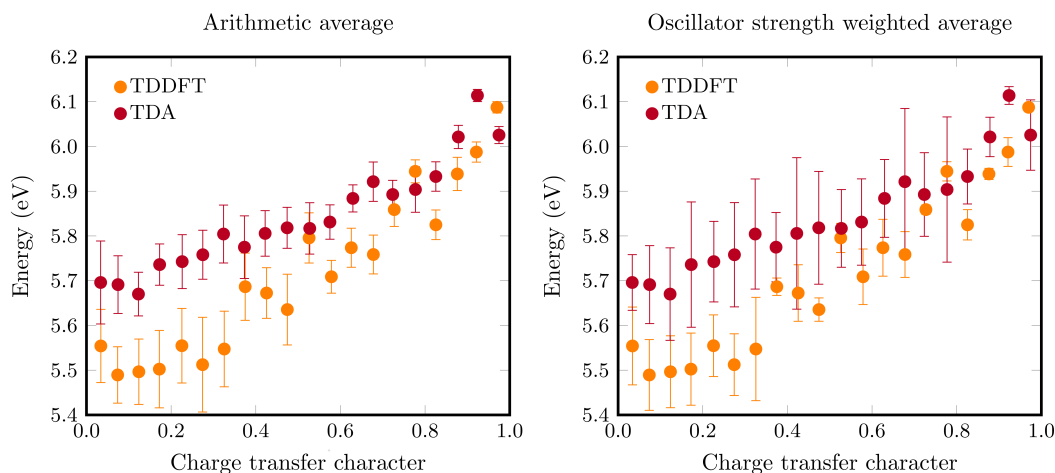


Figure 3.3: Average energies of states with corresponding CT character, split in intervals of 0.05. The energies are averaged arithmetically (left) and weighted by the oscillator strength.

of the two different averaged plots shows that bright states are influenced significantly stronger by TDA than dark states. It was shown before that low CT states dominate the spectral intensity of the lower absorption band and since the energy of low CT states with a high oscillator strength is overestimated by TDA, this lead to the overall overestimation of the energy of the absorption band.

3.2.2 Delocalisation Length

Subsequently, the lower absorption band of polyadenine was also decomposed with respect to the delocalisation length. The two upper plots in figure 3.4 show the absorption spectra for both QM regions (including 6 and 4 nucleobases) calculated with standard TDDFT, resolved in terms of the delocalisation of the excitations. For these plots, the DL of each state has been rounded to the closest integer value. The spectra of both QM regions show very similar features. Around half of the excitations, 44.9 % for QM 6 and 53.9 % for QM 4, are delocalised over two nucleobases, the other half consists mainly of excitations over one or three nucleobases (24.4 % and 24.6 % as well as 26.8 % and 17.9 % for QM 6 and QM 4, respectively). Further delocalised excitations contribute only little in both cases. These observations are in close agreement with the findings of Nogueira et al.¹⁸, who also found around half of the electronic transitions to be localised over two nucleobases (47.9 %) and the other main contributions to be delocalised over three nucleobases (22.8 %) and monomer-like excitations (22.7 %). Although for the smaller QM region localised excitations contribute higher than for the larger QM region this effect is negligible, since the overall averaged DL are similar for both cases; the arithmetically averaged DL are 2.06 and 1.78 for QM 6 and 4, respectively, and when weighted with respect to the oscillator strength they only change slightly to 2.16 and 1.83. Hence, there is also no significant difference in the DL of bright and dark states.

Employing TDA does not have any significant impact on the DL. As shown in the bottom plots of figure 3.4, half of the spectral intensity can be attributed

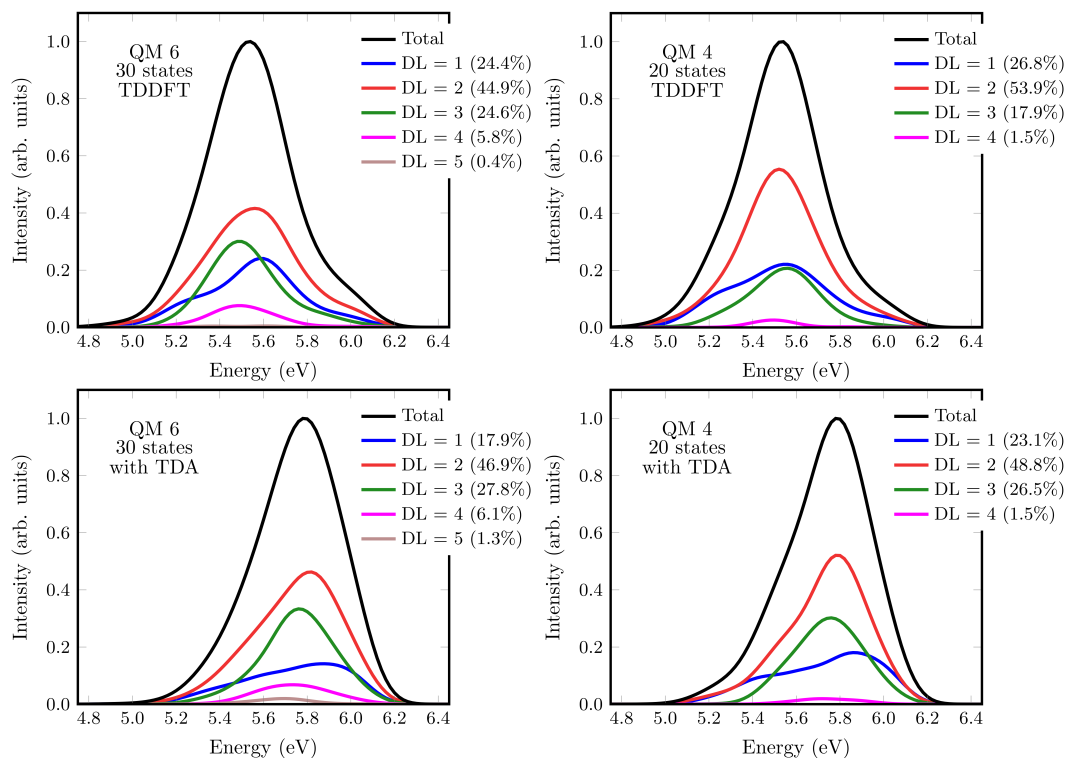


Figure 3.4: Decomposition of the lowest-energy absorption band for (dA)₂₀, including six (left plots) and four (right plots) adenines in the QM region, into contributions of different delocalisation lengths. The top plots are obtained with the standard formulation of TDDFT, in the bottom plots TDA was employed. The numbers in parentheses denote the intensity contribution to the total spectrum.

to states with DL 2, 46.9 % and 48.8 % for QM 6 and 4, respectively, and the other main contributions are localised states as well as states delocalised over three nucleobases. Also, a comparison of the averaged DL for all four spectra, as can be seen in table 3.2, does not show large differences. Neither the arithmetic average nor the oscillator strength weighted average computed for the spectra employing TDA differ significantly from those obtained with TDDFT, for both QM regions.

Thus, one can conclude that TDA fails to correctly describe CT states, however it does not pose any problems for the description of delocalised excitations. Also, increasing the size of the QM region from including four to including six nucleobases does not result in significant changes of the absorption spectrum, and the overall obtained results are in very good agreement with the findings of Nogueira et al.¹⁸ for a QM region including eight adenines.

3.3 INFLUENCE OF THE EDGE NUCLEOBASES

In the previously discussed analyses, electronic states with primary contributions on nucleobases located at the edge of the QM region were not included in order to avoid artifacts arising from the close proximity of the MM nucleobases.¹⁸ The location of the hole and electron positions were evaluated with the calculated POS_i

Table 3.2: Computed arithmetic (arith. av.) and oscillator strength weighted averages (osc. str. av.) of the DL of the states contributing to the lowest energy absorption band.

QM size	method	arith. av.	osc. str. av.
6	TDDFT	2.0763	2.1637
6	TDA	2.2466	2.2984
4	TDDFT	1.8871	1.8827
4	TDA	2.0911	2.1164

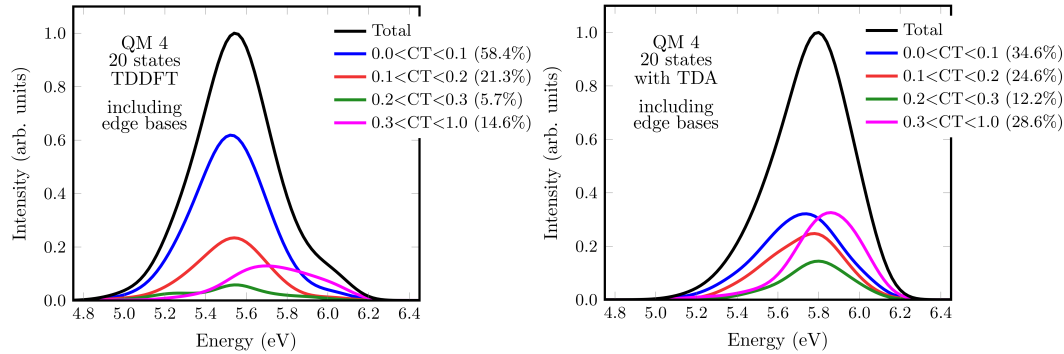


Figure 3.5: Decomposition of the lowest-energy band into different CT states, including all nucleobases in the analysis. The numbers in parentheses denote the intensity contribution to the total spectrum.

and POS_F values, where states with either value below 1.5 and above 3.5, for the QM region including four nucleobases, and above 5.5 for the QM region including six nucleobases, were discarded. In this section, the influence of these excitations located at the edge nucleobases will be discussed.

3.3.1 Charge Transfer States

The spectra for QM 4, where all states (including the ones with primary contributions on the edge nucleobases) were included, are shown, resolved with respect to the CT states, in figure 3.5. It can be observed, that inclusion of all nucleobases does not have any significant impact on the distribution of CT states. In the case of standard TDDFT, more than half of the spectral intensity (58.4 %) arises from local excitations and almost 80 % of the spectrum consists of states with CT character below 0.2. But also states with CT character higher than 0.3 contribute relevantly to the spectrum (14.6 %) and are located at the blue tail of the spectrum. When TDA is employed the same deviations from the TDDFT spectrum as observed when only including the middle nucleobases are obtained for the spectrum with all nucleobases. The overall CT increases and especially states with high CT character almost double in intensity which leads to an overall blue shift of the spectrum. The contribution of states with negligible CT character is reduced largely. Thus, for the QM region with four nucleobases, inclusion of the edge nucleobases does not influence the CT distribution of the states. In table 3.3 the arithmetic and oscillator strength

Table 3.3: Comparison of the arithmetic (arith. av.) and oscillator strength weighted averages (osc. str. av.) of the CT character of the states contributing to the lowest energy absorption band, including all nucleobases in the analysis (with edge) and discarding states with primary contributions on nucleobases at the edge of the QM region (middle).

QM size	method		arith. av.	osc. str. av.
6	TDDFT	with edge	0.2699	0.1860
		middle	0.2669	0.1922
6	TDA	with edge	0.2754	0.2800
		middle	0.2794	0.2863
4	TDDFT	with edge	0.2461	0.1780
		middle	0.2198	0.1594
4	TDA	with edge	0.2516	0.2505
		middle	0.2479	0.2503

weighted averages of the CT character of the spectrum with and without including the edge nucleobases are listed for both QM regions, including four and six nucleobases. For the smaller QM region consisting of four nucleobases, the conclusions from the plotted spectra are supported that it does not have a large influence whether or not edge nucleobases are considered in the analysis. Also for the larger QM region with six nucleobases the averaged CT values do not differ significantly with and without including the edge nucleobases. Hence, it can be concluded that the nucleobases on the edge of the QM region show a similar behavior with respect to CT to those centered in the QM region.

3.3.2 Delocalisation Length

Additionally, the change of the contributions of differently delocalised states to the absorption spectrum with and without including the nucleobases on the edge of the QM region has been investigated. The spectra for QM 4 including all nucleobases resolved with respect to the DL for both standard TDDFT and TDA are shown in figure 3.6. When comparing with the results obtained only considering excitations on bases in the center of the strand (figure 3.4), it is evident that including the edge nucleobases leads to a higher localisation of the excitation. For standard TDDFT the contribution of locally excited states to the spectral intensity is increased from 26.8 % to 43.2 %. In total, almost 90 % of the spectrum arise from states delocalised over maximal two nucleobases. When TDA is employed, a similar behavior can be observed, albeit to a lesser degree than for standard TDDFT.

For better quantification of these observations, table 3.4 once more shows the computed arithmetic and oscillator strength weighted averages for both QM regions and formulations of TDDFT. The oscillator strength weighted averages of the delocalisation length are found to be between 0.17 and 0.23 lower when all nucleobases are considered. A comparable underestimation of the delocalisation

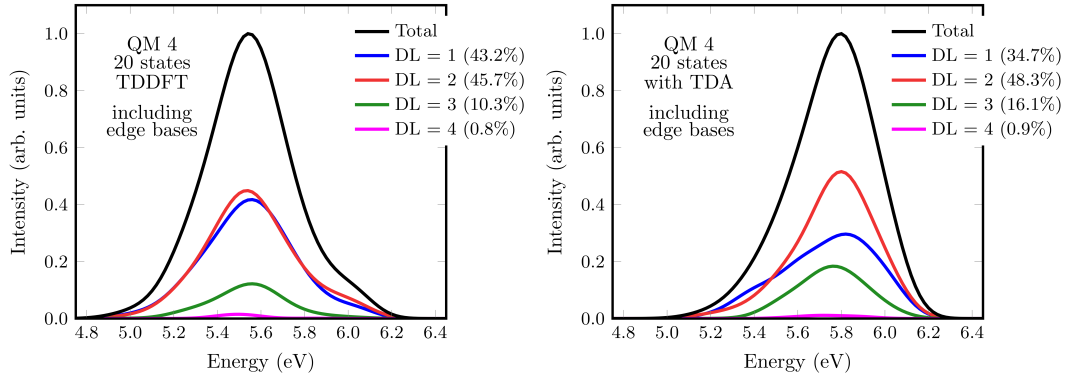


Figure 3.6: Decomposition of the lowest-energy band into different DL contributions, including all nucleobases in the analysis. The numbers in parentheses denote the intensity contribution to the total spectrum.

Table 3.4: Comparison of the arithmetic (arith. av.) and oscillator strength weighted averages (osc. str. av.) of the delocalisation of the states contributing to the lowest energy absorption band, including all nucleobases in the analysis (with edge) and discarding states with primary contributions on nucleobases at the edge of the QM region (middle).

QM size	method		arith. av.	osc. str. av.
6	TDDFT	with edge	1.9317	1.9718
		middle	2.0763	2.1637
6	TDA	with edge	2.0742	2.1153
		middle	2.2466	2.2984
4	TDDFT	with edge	1.7205	1.7114
		middle	1.8871	1.8827
4	TDA	with edge	1.8713	1.8867
		middle	2.0911	2.1164

including the edge nucleobases is observed for the arithmetic average of the delocalisation length. The errors are also similar for both differently large QM regions and both TDDFT formulations. Thus, it can be concluded that inclusion of the two edge nucleobases induces an increase of the contribution of monomer-like excitations and a decrease of the contribution of delocalised excited states. These findings are expected because excited states involving nucleobases at the end of the QM region can only be delocalised towards the neighboring QM nucleobases but not towards the MM nucleobases, which leads to an underestimation of their delocalisation length. This is an indication that realistic results can only be obtained for QM/MM calculations including a minimum of four nucleobases in the QM region, since in the case of two nucleobases both are located at the edge of the QM region. Nogueira et al.¹⁸ found the exact same behavior in their study including eight nucleobases in the QM region.

3.4 SIZE OF THE BASIS SET

In order to validate the usage of the small Ahlrichs def2-SV(P) basis set, the absorption spectrum for the QM region consisting of four nucleobases was computed with the standard TDDFT formulation employing the larger Ahlrichs def2-TZVP basis set. The spectra resolved with respect to the CT and DL are shown in figure 3.7.

First, a decrease of excitation energies with increasing the size of the basis set can be observed. The maximum of the absorption band with the smaller basis set was located around 5.5 eV and decreased to 5.3 eV with the larger basis set. This can be explained by the fact that electrons in excited states are loosely bound to the nuclei compared to electrons in the ground state.⁸⁷ Hence, an increase of the basis set leads to a larger stabilisation of the excited states than the ground state and therefore a decrease of the excitation energy. This shift of the absorption band to lower energies was also observed in the work of Nogueira et al.¹⁸

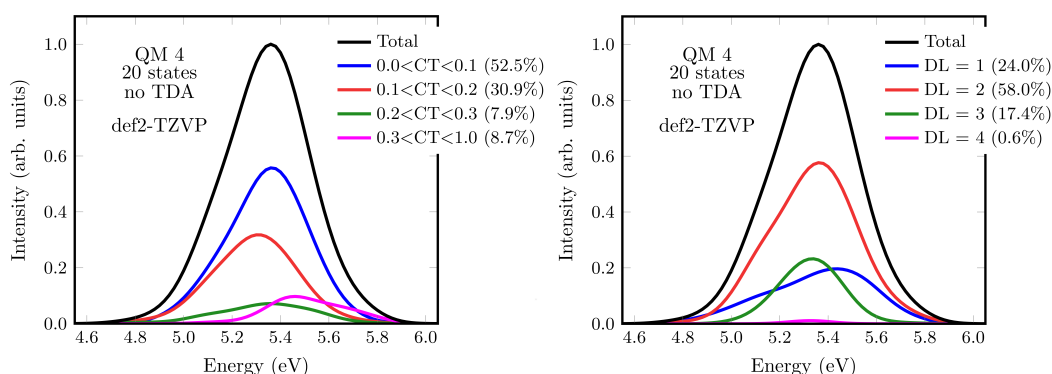


Figure 3.7: Decomposition of the absorption band of $(dA)_{20}$ with respect to charge-transfer (left) and delocalisation length (right) computed using Ahlrichs def2-TZVP basis set.

However, it is also important to investigate whether the usage of a larger basis set also results in significant modifications of the electronic wavefunction and thus changes of the electronic properties. Therefore, the absorption band was decomposed into different CT and DL contributions. The decomposition into different CT contributions was very similar for both basis sets. Locally excited states dominate the band with more than half of the spectral intensity, and states with small, non-negligible CT character (between 0.1 and 0.2) also contribute significantly. High CT states (above 0.3) are located at the blue side of the spectrum. These findings are comparable for both basis sets. However, overall a slight increase of the CT character can be observed. The overall CT character of the absorption band, weighted with respect to the oscillator strength is 0.1692, employing the def2-TZVP basis set and 0.1594 for the def2-SV(P) basis set. The arithmetic average of the CT character increases from 0.2479 to 0.2723 when increasing the basis set. The CT character increases slightly because the more extended orbitals of the larger basis set result in stronger orbital interactions which can favor charge transfer.

Looking at the different DL contributions to the spectrum, both basis sets yield very similar results. The contribution of locally excited states decreases slightly from 26.8 % to 24.0 % with the larger basis set, and excitations delocalised over two nucleobases increase from 53.9 % to 28.0 %. However, the contribution of states delocalised over all four nucleobases is also decreased slightly from 1.5 % to 0.9 %. The averaged DL of the whole band, weighted with respect to the oscillator strength is almost the same for both bases (1.8827 for def2-SV(P) and 1.8215 for def2-TZVP) and analogously the arithmetic averages do not differ significantly (1.8871 for def2-SV(P) and 1.8148 for def2-TZVP). Thus, although a lower contribution of local excitations can be observed, the overall delocalisation is described sufficiently well also with the smaller basis set.

DYNAMICS SIMULATION

In this chapter the simulation of surface hopping dynamics of polyadenine will be discussed. A detailed wavefunction analysis will be performed in order to be able to characterise the excited states formed throughout the dynamics.

4.1 COMPUTATIONAL DETAILS

The previous static calculations showed that, for an accurate description of polyadenine, including four adenines in the QM region is sufficient but it is necessary to use the standard formulation of TDDFT and not apply the Tamm Dancoff approximation. Furthermore, the nucleobases at the edge of the QM region have to be excluded in the wavefunction analysis due to artifacts arising from the proximity of the MM environment. Concerning the choice of basis set, def2-SV(P) yields a sufficiently good description and the much larger def2-TZVP basis set does not notably improve it. Hence, within this framework the simulation of the excited-state dynamics have been carried out.

An exemplary DNA strand is shown in figure 4.1. The four nucleobases treated at the quantum mechanical level are located in the center of the strand and are highlighted by bold bonds.

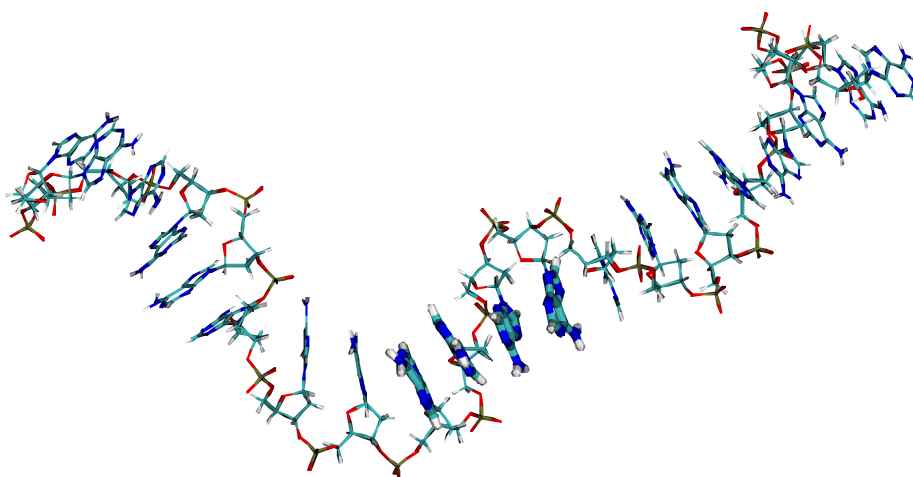


Figure 4.1: Single strand of $(dA)_{20}$ with the four central adenines, which are included in the QM region, marked with bold lines.

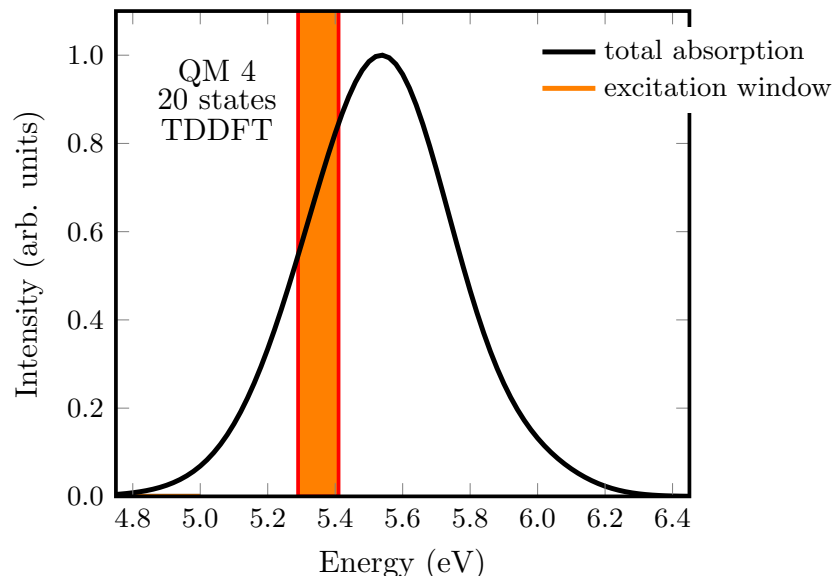


Figure 4.2: Absorption spectrum of $(dA)_{20}$ computed from 300 initial conditions with the energy window from where the initial conditions will be taken shown as the orange box.

4.1.1 Choice of Initial Conditions

First, the complete spectrum with all 300 initial conditions chosen as equidistant snapshots from the molecular dynamics simulation is computed at the level of theory as stated above with the identical settings as for the static calculations, described in section 3.1. Using this spectrum, 120 initial conditions are selected within the excitation window between 5.29 and 5.41 eV. Since the computed absorption spectrum is blue shifted by 0.7 eV with respect to the experimental spectrum, this excitation window corresponds to the photoexcitation at 4.65 eV in the different time-resolved experiments.^{13;24;88} The selection is based stochastically on the oscillator strength and thus, on the brightness of the state.⁸⁹ The computed absorption spectrum with the used excitation window is shown in figure 4.2.

The 120 initial conditions were excited to the 8 energetically lowest excited singlet states. Based on these 120 initial conditions, 120 trajectories were propagated. However, 20 of these initial conditions could not complete at least 790 of the 1000 time steps due to technical problems that lead to incomplete restart files. Thus, in the analysis of the dynamics 100 trajectories were considered. The distribution of the amount of trajectories that were started in each of the 8 singlet states, including as well as excluding the trajectories that did not run long enough, is shown in table 4.1. It shows that the trajectories failing due to technical reasons are quite equally distributed over all initial states and hence, fortunately no initial state is underrepresented.

Table 4.1: Numbers of trajectories started in the 8 lowest excited states, a total of 120 trajectories started and 100 that completed more than 790 times steps were analysed.

initial state	started	% started	analysed
S_1	13	10.8 %	10
S_2	27	22.5 %	21
S_3	27	22.5 %	22
S_4	17	14.2 %	13
S_5	21	17.5 %	20
S_6	9	7.5 %	9
S_7	4	3.3 %	4
S_8	2	1.7 %	1
Σ	120	100 %	100

4.1.2 Electronic Calculations

For the electronic calculation at each time step, the above described level of theory was used. The simulation of the QM region was carried out with the ORCA program³⁸ with the identical settings as described in section 3.1 and the MM region was modeled with Tinker⁸¹. For the dynamics, only the lowest ten excited states were computed in order to reduce the computational cost assuming that the higher states do not have a significant impact on the dynamical behaviour.

4.1.3 Nuclear Dynamics

The trajectories are propagated according to the surface hopping approach with a development version of the molecular dynamics program SHARC 2.0.^{39/40} In order to carry out the simulations of this work, it was necessary to create an interface between SHARC 2.0 and ORCA since this was not yet implemented in the currently released version of SHARC 2.0. The dynamics are simulated for 500 fs with a time step of 0.5 fs for the nuclear dynamics and 0.02 fs for the electronic wavefunction. The electronic wavefunction is propagated in the local diabatisation approach⁶⁴ using wavefunction overlap couplings computed from truncated wavefunction, using 99 % of the wavefunction norm.⁹⁰ During hops the full velocity vector of the QM region without the hydrogen link atoms is rescaled. The decoherence is corrected according to a energy based scheme⁹¹, where instead of the full kinetic energy of the system, only the kinetic energy of the QM region is taken into account.

4.1.4 SHARC-ORCA Interface

In order to perform the dynamics simulation, we implemented an interface between SHARC and ORCA. Since the goal was to carry out QM/MM computations, the

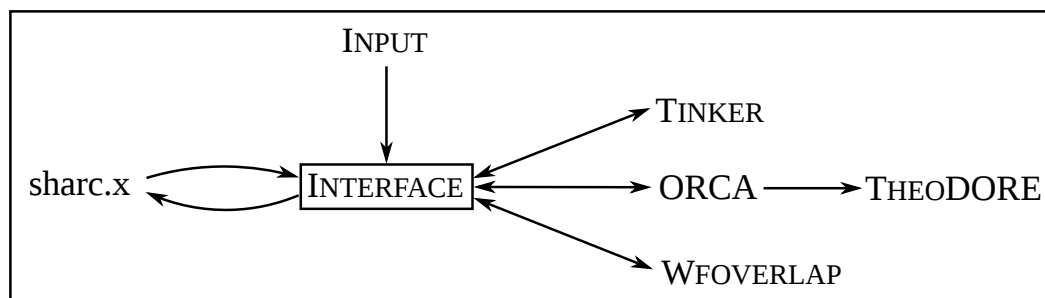


Figure 4.3: Overview over the work flow of the SHARC-ORCA interface showing the programs that are being called.

interface had to include not only ORCA, but also Tinker for the MM calculations and some algorithm to take care of any link atoms. The general work flow of the processes involved in the interface will be shortly described here and figure 4.3 illustrates this process.

1. **Input:** The xyz coordinates as well as the connectivities of all atoms, the assignment as QM or MM atom and the atom type for the used force field are read from input files. For the specifications of the intended simulation the quantum chemistry template and resource file needed to be created.
2. **Call Tinker:** The *energy* and *gradients* of the MM region ($E^{\text{MM}}(\text{MM})$, $\nabla E^{\text{MM}}(\text{MM})$) as well as the Van-der-Waals interaction between the QM and MM regions ($E_{\text{vdW}}^{\text{MM}}(\text{QM} + \text{MM})$, $\nabla E_{\text{vdW}}^{\text{MM}}(\text{QM} + \text{MM})$) are computed with Tinker as described in section 2.5. It returns these energy contributions as well as the *point charges* for all MM atoms.
3. **Link atoms:** As explained in section 2.6.1, each bond between the QM and MM region has to be broken and hydrogen atoms are added as caps to the QM region. They are placed at a specified length (0.7 times the QM-MM bond length) between the two atoms. The point charge of the MM atom involved in the bond is redistributed to all neighboring MM atoms and set to zero on the bonded MM atom.
4. **Call ORCA:** The *energy* and *gradient* of the QM region ($E^{\text{QM}}(\text{QM})$, $\nabla E^{\text{QM}}(\text{QM})$) as well as the electrostatic interaction with the point charges of the MM region ($E_{\text{el}}^{\text{QM}}(\text{QM} + \text{MM})$, $\nabla E_{\text{el}}^{\text{QM}}(\text{QM} + \text{MM})$) are computed with ORCA. ORCA returns the ".log" file that contains the energies and gradients and a molden file is generated from the ".gbw" file which contains the *MO coefficients* as well as the *basis set information*. The *CI coefficients* are obtained from the ".cis" file.
5. **Calculating the wavefunction overlap:** The basis set information read from the molden file used with the geometry information to compute the *mixed AO overlaps*, meaning the overlap between basis functions of the geometry of the current time step and of the previous time step. This is carried out with the PyQuante⁹² code. Since ORCA works in spherical coordinates while PyQuante uses Cartesian coordinates, we transferred the MO coefficients to

Cartesian coordinates. With the AO overlaps, the MO coefficients and the CI coefficients, the *wavefunction overlaps* can be computed with the wfoverlap code.

6. **Call TheoDORE:** If a wavefunction analysis is required on-the-fly, the TheoDORE program is called and uses the “.log” and “.cis” output files from ORCA and returns the specified analysis.
7. **Propagation with SHARC:** The surface hopping dynamics step is carried out with the SHARC program, that uses the energy, gradient and wavefunction overlaps and computes hopping probabilities as described in section 2.7.2 and propagates the nuclei according to section 2.7.1 to the next time step. Then, SHARC writes a new input for the interface and the workflow returns to step 1.

4.2 ADIABATIC POPULATION ANALYSIS

Of the 100 trajectories 90 % were excited to states energetically higher than the S_1 . The population of the ground state and ten excited states during the 500 fs of propagation in the dynamics as well as an exponential fit are shown in figure 4.4.

For the kinetic fit all excited states higher than the S_1 are treated together to simplify the kinetic model because they show a very similar decay behaviour. It can be observed that all these excited states above the S_1 decay to the S_1 state within the first 100 fs with a decay rate constant of 28 ± 3 fs obtained from the exponential fit. In the model a fictious, vibrationally cold S_1^{cold} state was included, which represents the long lived excited states as observed experimentally. The actual population of the S_1 was assumed to be the sum of the population of the normal and cold S_1 state and population transfer from the normal S_1 to the vibrationally cold S_1^{cold} state was allowed.

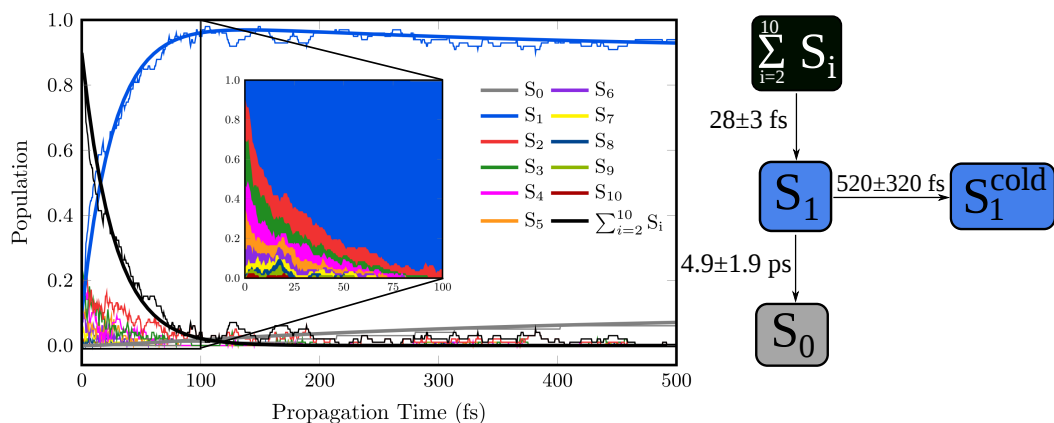


Figure 4.4: The time evolution of the population of the ten lowest excited states as well as the ground state including an exponential fit of the ground state (S_0), first excited state (S_1) and the sum of the higher lying excited states ($\sum_{i=2}^{10} S_i$). The right plots shows the schematic kinetic model of the decay to the ground state and cold S_1 states, including time constants obtained from the exponential fit.

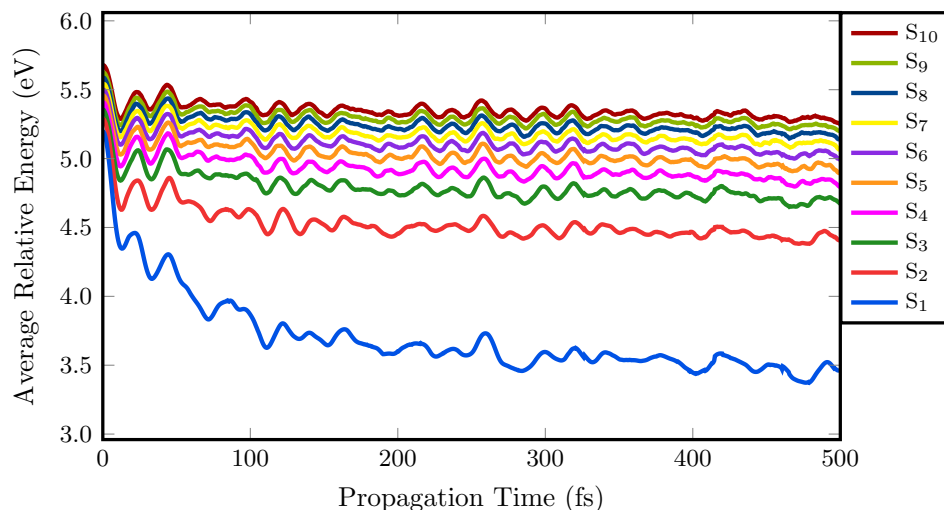


Figure 4.5: Time evolution of the average energy of the lowest ten excited states, relative to the energy of the ground state.

However, with the data obtained from the adiabatic population of the dynamics simulation, it is not possible to differentiate between the S_1 and the fictitious S_1^{cold} . Thus, the time constant of 520 ± 320 fs can only be estimated with this large error. From the fast decay to the S_1 state, it can be concluded that the S_1 state is energetically stabilised during the dynamics. This can also be observed by plotting the time evolution of the average relative energies of the first ten excited states as depicted in figure 4.5.

It can be seen, that all ten excited states initially are very close in energy. However, the relative energy of the S_1 states decreases rapidly and after 100 fs it is already 0.8 eV lower than the S_2 state. After around 280 fs the separation between the two lowest excited states is 1 eV and stays constant around this value throughout all the further time steps.

4.2.1 Decay to the Ground State

In total six trajectories were observed to have an energy gap between the S_1 and S_0 states smaller than 0.1 eV and thus assumed to deactivate to the ground state. In the experiment by Kohler and coworkers¹³ the time constant for the decay to the ground state was found to be around 2 ps. The kinetic model obtained in this work suggests a time constant of 4.6 ± 1.9 ps. This large error is due to the fact that only six trajectories were observed decaying to the ground state and therefore it is not possible to extract a more definite time constant from it. Although the exact value of the experimental findings are not reproduced, the same order of magnitude of the time constant is obtained and thus, qualitatively the model agrees very well with the experiment.

Analysing the structure of the six trajectories around the time of the decay to the ground state showed for all of them that one of the nucleobases undergoes an out-of-plane distortion of the C_2 atom on the six ring. An exemplary structure that was observed in one of the six trajectories is shown in plot 4.6. This structure is

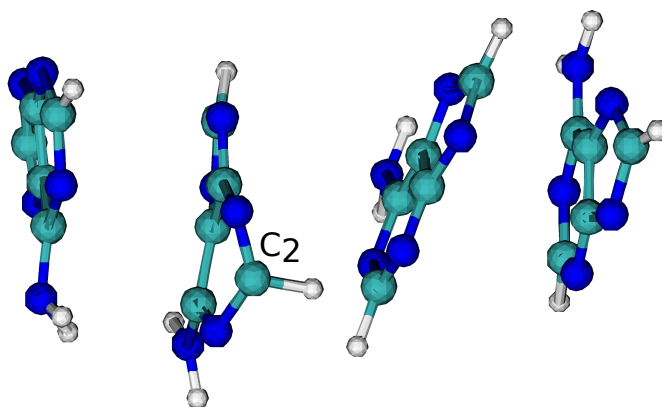


Figure 4.6: Exemplary geometry of the 4 adenines of the QM region from one trajectory of the dynamics simulation, showing a C₂ puckered conical intersection⁹³ between the S₁ and S₀ states.

in perfect agreement with the computational findings for the S₁/S₀ conical intersection for isolated adenine by Barbatti et al.⁹³ Therefore, it can be assumed that a deactivation to the ground state occurs in the case of the excitation being monomer-like localised on a single nucleobase, that does not interact with the neighboring bases. This proposition will be further investigated in the following wavefunction analysis.

4.3 CHARACTERISATION OF THE EXCITED STATES

Since the main goal of this work is to follow the evolution of the excited states during the dynamics of polyadenine, a thorough wavefunction analysis for all the trajectories is unavoidable. The main differentiation aimed at was between monomer-like, excitonic, excimeric, charge transfer (exciplex) and charge resonance states. These types of excited states are explained in detail in section 2.4 and visualised in figure 1.4 in the respective section. It was assumed that the descriptors for the charge transfer character CT and the participation ratio PR will be sufficient to assign the states.

The CT allows a differentiation of excitons or monomers from exciplexes or charge resonance states as well as from excimers. Excitons and monomers as well as exciplexes and charge resonance states can then be differentiated using the PR. Therefore, the coherence length (COH), which would allow a separation of excimeric states from the others and the net charge transfer (CT_{nt}), which would allow to distinguish exciplexes, were not considered to be necessary for the classification of the excited states. The intervals of the CT and PR used to assign the excited state character are shown in table 4.2. Figure 4.7 shows schematically which regions of CT and PR values can be attributed to which type of excited state. Since monomer like excitations are localised on only one nucleobase, the CT value is expected to be very low and PR found around 1 and hence the intervals were chosen as CT 0 – 0.5 and PR 1 – 1.5. Excitons are delocalised over several nucleobases but should

Table 4.2: Intervals of CT and PR used for the characterisation of the five different types of excited states.

state	CT min	CT max	PR min	PR max
monomer	0	0.35	1	1.5
exciton	0	0.35	1.5	4
	0.35	0.8	2.5	4
excimer	0.35	0.8	1	2.5
exciplex	0.8	1	1	2
charge res.	0.8	1	2	4

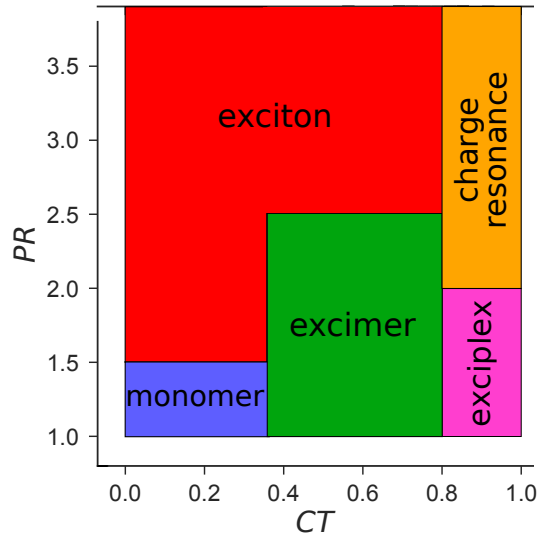


Figure 4.7: Schematic representation of the assignment of different types of excited states regarding their charge transfer character (CT) and participation ratio (PR).

not have large CT. Therefore, the interval was chosen for CT 0 – 0.35 and for PR 1.5 – 4 and additionally, all excitations with CT < 0.8 but PR > 2.5 were assigned to excitonic states. In the case of excimers, there are local excitations on the nucleobases as well as charge transfer between two nucleobases and thus, the CT was chosen between 0.35 and 0.8 and PR between 1 and 2.5. Exciplexes involve charge transfer between two nucleobases and therefore, states with CT > 0.8 and PR < 2 were characterised as exciplexes.

4.3.1 Kinetic Model and Decay Mechanism

In order to investigate the nature of the long lived excited states observed during the dynamics, the population was analysed with regard to the type of excited states. For this, the CT and PR value of each trajectory in different time intervals

throughout the dynamics are represented as scatter plots in figure 4.8. For each trajectory at each time step in the respective interval, the PR vs CT value is depicted as a point in the scatter plots. With the help of the histograms on the top and the right hand side of the diagrams the amount of population with the respective CT and PR values can be estimated. The intervals used for the classification as the different excited states are marked in all the plots. Throughout the whole 500 fs no trajectory occupies a charge resonance states ($CT > 0.8$ and $PR > 2$). Therefore, this category of excited states will be neglected in all following analysis. The first plot depicts the populations of the first 10 fs. It can be seen that mainly excitons and monomers are formed. Within the following plots for the time intervals 10 – 20 fs, 20 – 50 fs and 50 – 100 fs the population of excitonic states decreases, which can be seen clearly at the histogram showing that the population with high PR becomes very small. In all plots after 100 fs the population of states with high PR values is neglectably small. The population of monomer states increases very fast. Already the plot for the time interval 10 – 20 fs shows that the largest part of the population occupies monomer-like states, the histogram shows the largest contribution of states with low CT (< 0.35) and low PR (< 1.5). Throughout all the time intervals, the monomer like states are the most populated. The other excited state that get populated throughout the dynamics simulation is the exciplex state. It has high CT values (> 0.8) and low PR values (< 2), hence following the histogram for the CT values, it can be seen that exciplexes start being formed after 10 fs and the amount steadily increases. In the final plot depicting the final 50 fs of the dynamics, already half as many exciplexes are populated as monomers. Excimeric states seem mainly to be formed as an intermediate before population of exciplexes. For the first 100 fs the transition from excitons and monomers to exciplexes seems to follow a path from an intermediate of $CT = 0.5$ and $PR = 1.5$ to the exciplex with $CT = 1$ and $PR = 1$. However after 100 fs the intermediate changes and the transition occurs over states with higher PR values.

Initially, the population was mainly excited to excitonic states and a smaller fraction of less than 20 % to monomeric states. From the initial exciton states a smaller fraction was observed to quickly convert to exciplexes without spending a long time in the intermediate excimeric state. An exemplary trajectory undergoing this process is shown in figure 4.9. For the first 15 fs the PR of the excitation is between 1.8 and 2.3, thus the excitation is delocalised over two nucleobases, and the CT is below 0.2. After that the PR decreases very rapidly to around 1.0 while the CT increases to 1.0 and after around 25 fs an exciplex is formed. For the rest of the time the CT and PR values stay mostly constant at around 1.0. After 275 fs an unprobable hop to the S_3 state occurs, where the PR is slightly higher (1.4), however it relaxes quickly back to the exciplexic S_1 state.

The largest part of the initially formed excitons localises the excitation to form monomer-like states. From the monomer-like form, the population can evolve through the intermediate excimeric state to an exciplex. The evolution through the intermediate excimeric to the exciplex can either take place almost instantly or it stays for a long time in the excimer, where the latter observed more often. Two exemplary trajectories forming exciplexes from monomer-like states are presented in figure 4.10. In the example of figure 4.10a, the trajectory is excited to an excitonic

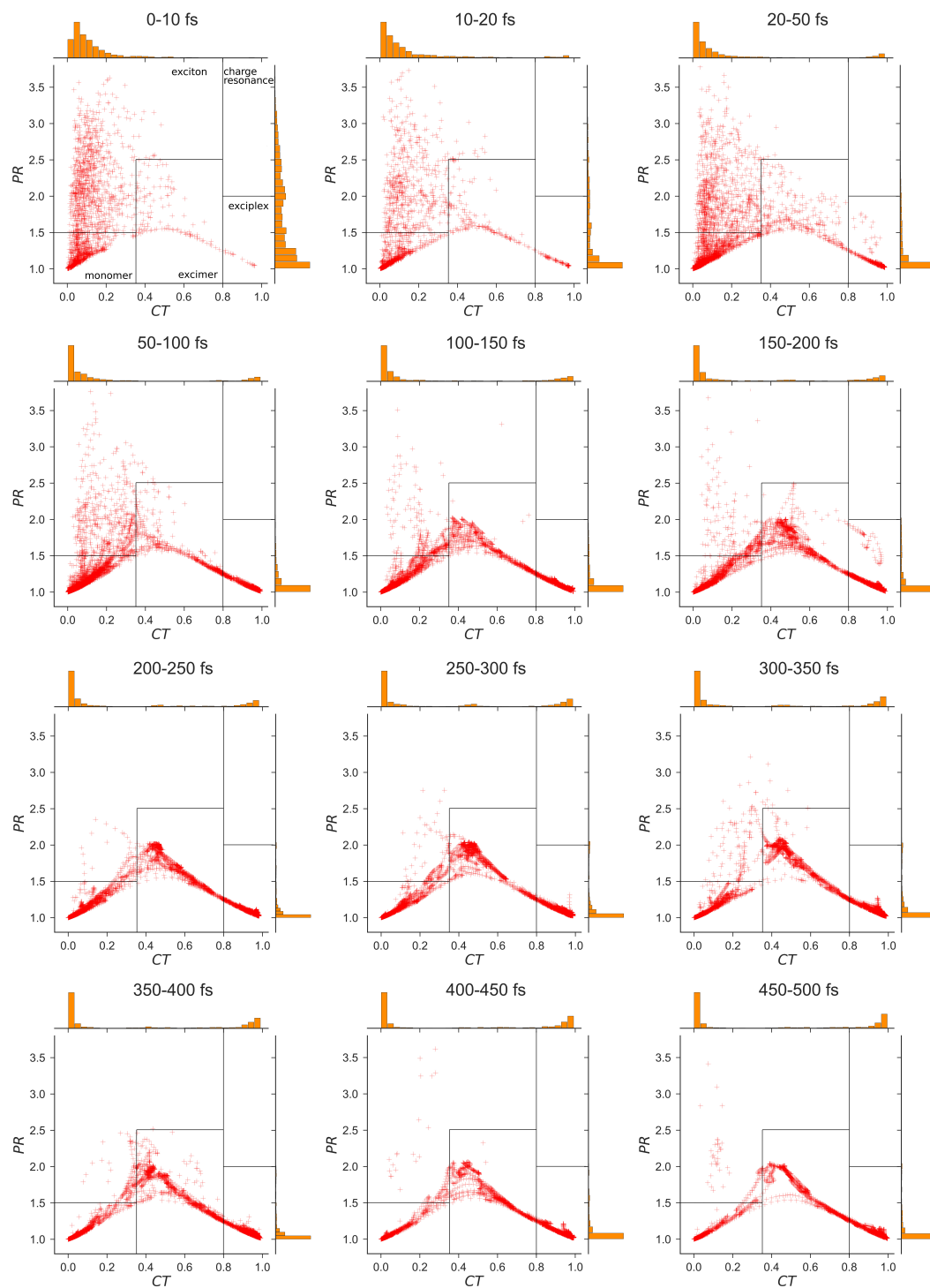


Figure 4.8: The CT vs PR values for each trajectory at each time step during several time intervals are depicted in red. On the right side of each plot, the amount of trajectories found to have the respective PR value are depicted as histograms, the same is shown for the CT on top of each plot.

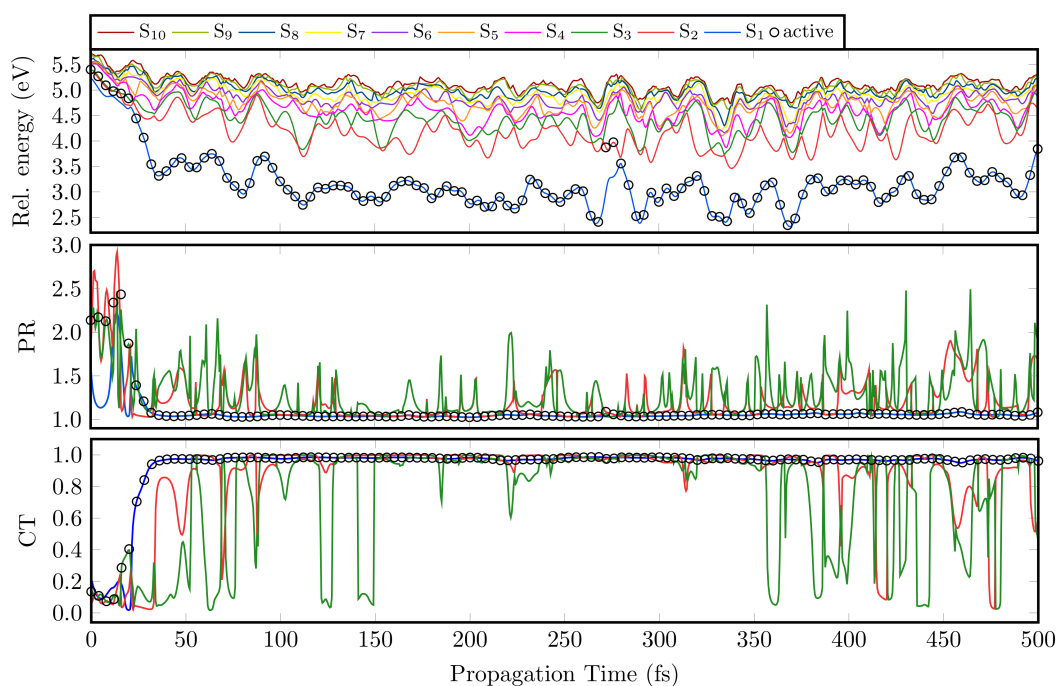


Figure 4.9: Time evolution of a exemplary trajectory forming an exciplex from an excitonic state. In all plots the active state is depicted with black circles. Top: relative energy of the lowest 10 excited states and active state with respect to the ground state; the participation ration (PR, middle plot) and the charge transfer character (CT, bottom plot) of the lowest three excited states and the active state. The active state is only depicted every 4 fs for more clarity.

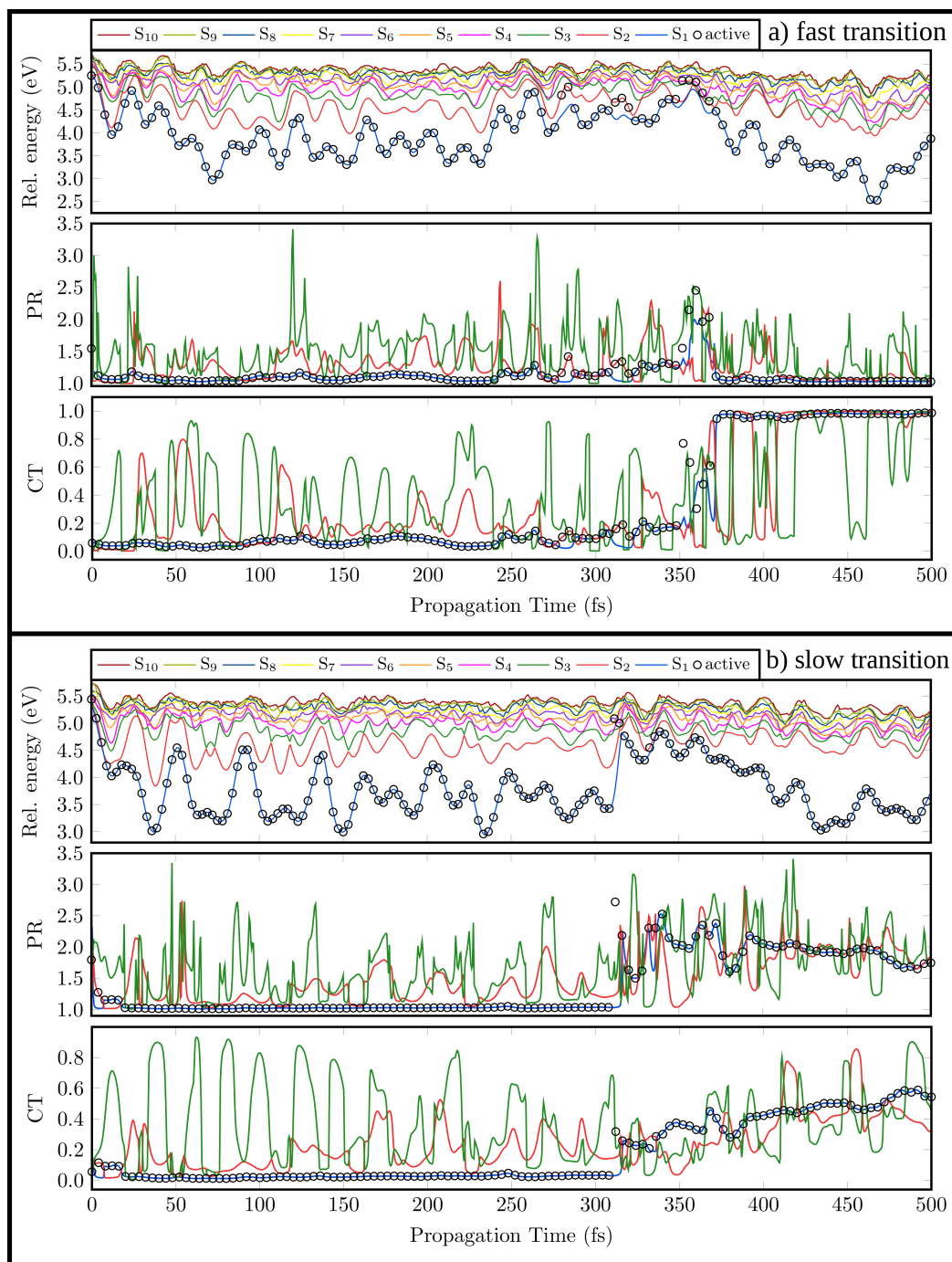


Figure 4.10: Time evolution of a exemplary trajectory forming an exciplex from a monomer-like state. In all plots the active state is depicted with black circles. a) Slow formation of the exciplex, b) fast formation of the exciplex. In both plots, top: relative energy of the lowest 10 excited states and active state with respect to the ground state; the participation ration (PR, middle plot) and the charge transfer character (CT, bottom plot) of the lowest three excited states and the active state. The active state is only depicted every 4 fs for more clarity.

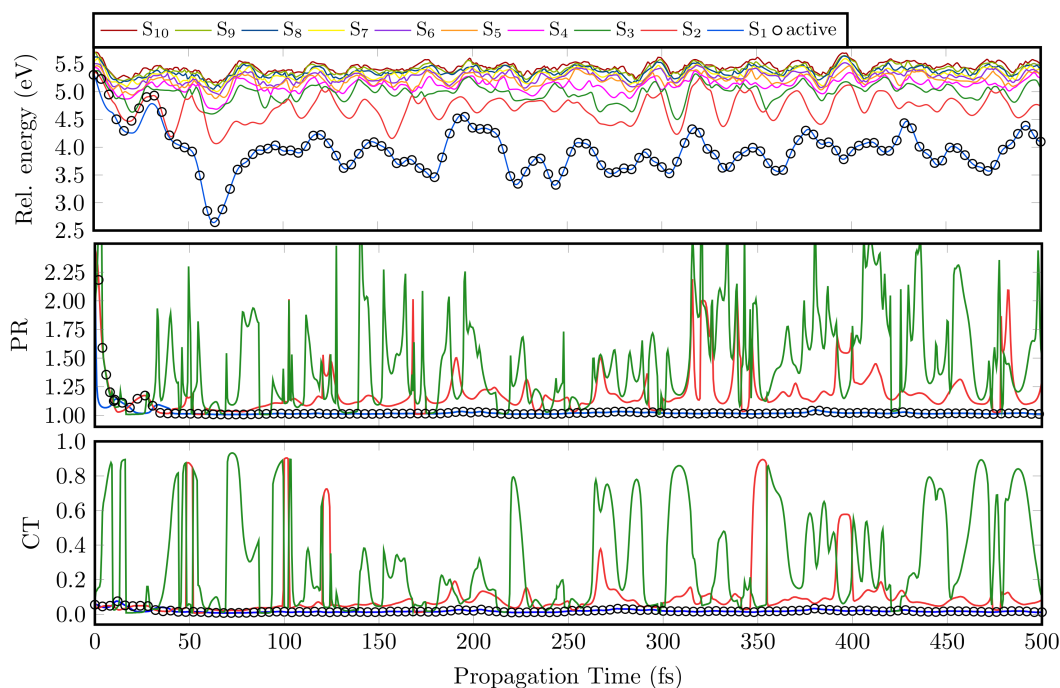


Figure 4.11: Time evolution of an exemplary trajectory transitioning from the excitonic state to a monomer within the first 30 fs. In all plots the active state is depicted with black circles. Top: relative energy of the lowest 10 excited states and active state with respect to the ground state; the participation ratio (PR, middle plot) and the charge transfer character (CT, bottom plot) of the lowest three excited states and the active state. The active state is only depicted every 4 fs for more clarity.

state. Within the first 10 fs the excitation is localised to a monomer-like state and stays for around 300 fs. Then, in the energy curves it can be observed that the trajectory is subjected to a hop to an energetically higher state but quickly converts back to the S_1 state. After that hop the PR increases to values around 2.0, which is characteristic for excimeric states and excitons but during the rest of the dynamics the PR reduces constantly. Also the CT is increased to around 0.4 after the hop and keeps increasing throughout the dynamics. Thus, it was concluded that it forms an excimer state. However, since the PR is decreasing steadily while the CT is increasing, it was concluded that the excimer state serves as an intermediate between the monomer and exciplex states, where the exciplex is not yet formed within the simulation time of 500 fs. In contrast in the example shown in figure 4.10b, the transition from monomer to exciplex occurs within 10 fs. The trajectory occupies a monomer-like state for the first 350 fs, where both PR and CT fluctuate slightly. Within 10 fs, the CT then increases from 0.1 to 1.0 while the PR shortly increases up to 2.4 and is reduced to 1.0. Hence, an excimer is still formed as intermediate but the exciplex is formed almost instantly.

However, a large fraction of the population in the monomer-like states does not undergo any transition within the first 500 fs of the dynamics. An example is shown in figure 4.11. This trajectory is initially excited to an excimeric state but

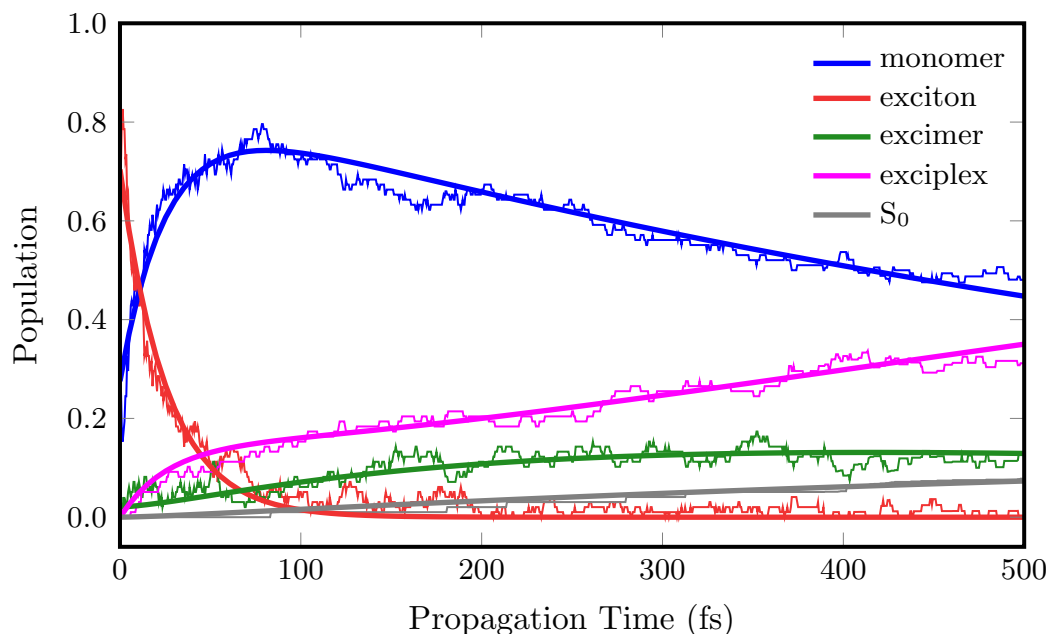


Figure 4.12: Populations of the different states (thin lines) and exponential fits for the kinetic model (bold lines).

within 30 fs a pure monomer-like state is formed. This state is stable throughout the dynamics and not subjected to any major changes.

As already mentioned in the previous part, for six trajectories, the energy gap between the S_1 and S_0 was observed to be lower than 0.1 eV and they were assumed to decay to the ground state. All six trajectories occupy monomeric states before the assumed decay.

The time evolution of the populations of the different excited states and ground state are depicted in figure 4.12. The thin lines are the actual populations and the bold lines are exponential fits of the population of the respective states. The kinetic model underlying the exponential fits is schematically represented in figure 4.13. Initially, exciton and monomer-like states are excited. The formation of exciplexes directly from excitons was only observed in few trajectories and the intermediate formation of excimers was always very short. Therefore, in the model, the transition was assumed to be directly from the exciton to the exciplex without an excimer in between. The time constant for this conversion was found to be 135 ± 64 fs. As stated above, this was only a minor pathway occurring in only around 20 % of the excitons and observed in only few trajectories, which leads to the impossibility of determining a more exact time constant. The largest part of the initial excitons localise the excitation to monomer-like states, which occurs with a time constant of 31 ± 5 fs. Hence, around 80 % of the initially formed excitons relax to monomers. From the monomer-like states, excimeric states can be formed. This process takes place on a slower time scale with a time constant of 944 ± 180 fs. The excimer is not a stable state and is only populated intermediately. It transforms to the stable exciplex form with a time constant of 227 ± 97 fs. For six trajectories occupying monomer-like states, energy gap lower than 0.1 eV was observed between

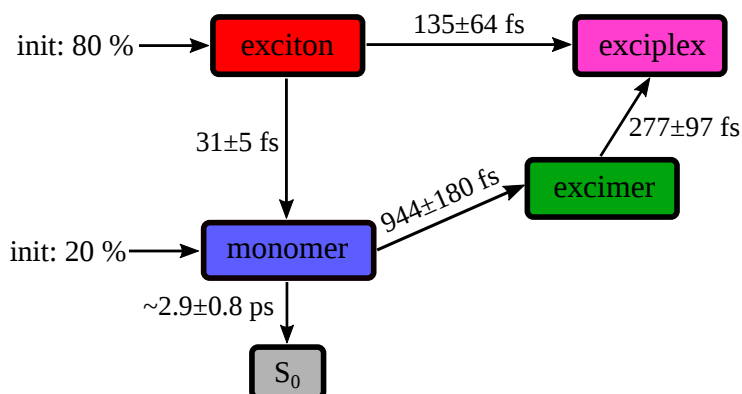


Figure 4.13: Schematic representation of the assumed kinetic model with time constants obtained from the exponential fits of the populations.

the S_1 and S_0 . These were included in the model as deactivating to the S_0 . The time constant found for the deactivation from the monomer to the ground state is 2.9 ± 0.8 ps, thus only around 1/4 of the monomer-like states decays to the ground state.

Experimentally, a time constant for the monomer-like decay channel to the S_0 of ~ 2 ps was measured^{13,24} and thus, the computational results slightly overestimate the deactivation time. Kohler and coworkers¹³ suggest that ~ 65 % of the absorbed photons generate exciplexes. Extrapolation of the kinetic model described above yields an estimation of ~ 80 % of the population occupying exciplexes after 10 ps. Hence, also the population of the excimeric states is overestimated and consequently the deactivation to the ground state is underestimated. This may be caused by the fact that TDDFT usually cannot well describe the interaction between the ground state and excited states. Furthermore, since deactivation to the ground state is not possible within the framework of TDDFT, it was assumed that in each region, where the potential energy surfaces of the S_1 and S_0 are separated by less than 0.1 eV, deactivation to the S_0 takes place. This might be a reasonable approximation but it neglects several factors such as the hopping probability.

The time constant for the population of the experimentally observed long-lived excited states was around 400 fs.^{13,23} In order to have a comparable measure, the populations of the excitonic and monomer-like states were combined to the initial states and the excimers and exciplexes were attributed to the long-lived excited states, since it is most likely that experimentally excimers and exciplexes are hardly distinguishable. Then, the time constant for the population of the long-lived excited states was found to be 687 ± 109 fs. While this differs from the experimental value, it is still in the same order of magnitude. One reason for the difference may be the differentiation of monomers and excitons from excimers where cutoff values for the PR and CT were chosen. Slight changes of these cutoff values yielded larger differences in the time constant. However, all these transient absorption experiments mentioned above assigned the long-lived excited states to exciplexes formed between two bases and highlighted the high charge transfer character of the resulting excited state. The computational results from this study fully support this assignment and although the time constants are not perfectly reproduced,

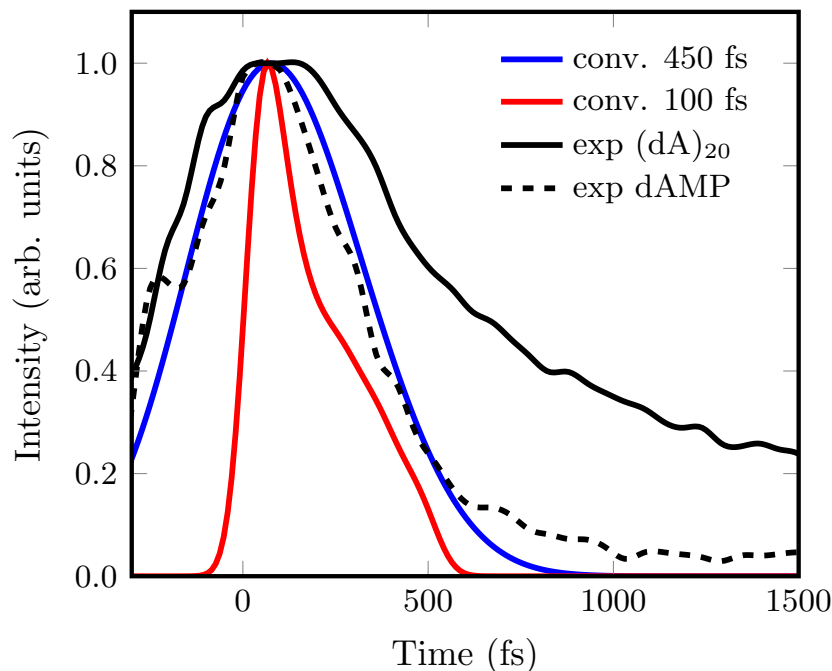


Figure 4.14: Comparison of the experimental fluorescence decays recorded at 3.76 eV for (dA)₂₀ (black, solid) and dAMP (black, dashed) with the computed fluorescence decays convoluted with Gaussians with FWHM=100 fs (red) and FWHM=450 fs (blue). The computed spectra are shifted temporally so that the maxima of all spectra are aligned.

given the methodological restraints of the computational study, the results are still in good agreement with the experiments.

4.4 TIME-RESOLVED FLUORESCENCE SPECTRUM

There are several records of experimental time-resolved fluorescence spectra for polyadenine,^{14;88;94} that lead to the interpretation of the long-lived excited states as excitons. Here, a fluorescence spectrum was simulated as a sum over Gaussians for each trajectory at each step, positioned at the energy difference between the active state and ground state with the oscillator strength assigned to the height. Then a gaussian convolution was applied on the time axis in order to mimic the time-resolution of the experiment. Gustavsson and coworkers⁸⁸ stated that their apparatus function was 450 fs full width at half maximum and judged the time-resolution to be 100 fs after deconvolution. Therefore, two convolutions with gaussian functions with a width of 450 and 100 fs were applied o the computational data. The experimental time-resolved fluorescence spectra for (dA)₂₀ and adenosine monophosphate (dAMP) are shown together with the two computational fluorescence spectra in figure 4.14. In the experiment the fluorescence decay was recorded at 3.76 eV. Since in the computational absorption spectrum a blue shift of 0.7 eV with respect to the experiment was observed, the computational fluorescence was evaluated between 4.4 and 4.5 eV. The computational spectra are shifted

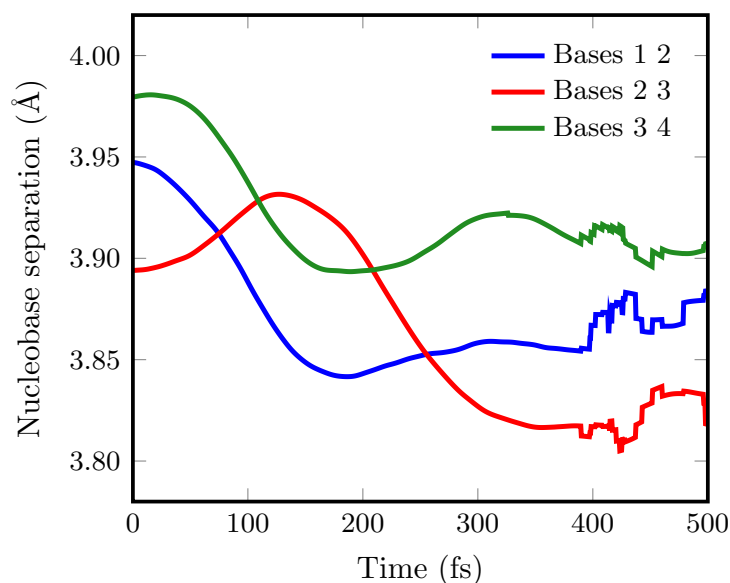


Figure 4.15: Average distance between the centers of mass of neighboring nucleobases in the QM region.

temporally so that the maxima of all the spectra are aligned in order to facilitate a comparison.

It can be seen that in the computed dynamics the fluorescence decay is a lot faster for (dA)₂₀ than in the experiment. The decay time depends largely on the applied convolution but in both cases, the computational decay is closer to the experimental result for dAMP than for (dA)₂₀.

Further in-depth analysis is necessary in order to discover the cause of the discrepancy between the computed and experimental time-resolved fluorescence spectrum.

4.5 INTER BASE SEPARATION

In addition to the analysis of the electronic wavefunction it necessary to investigate the nuclear motion and thus the geometrical changes throughout the dynamics. For polyadenine the most interesting structural feature is the inter base separation since according to several experimental and computational studies stacking of the nucleobases controls the dynamical behaviour. Therefore, the distance between the centers of mass of the four nucleobases included in the QM region was averaged for each time step. This is shown in figure 4.15. The two nucleobases on the edge of the QM region behave very similar. The distance to the respective neighboring base inside the QM region is initially high at around 3.95 and 3.98 Å but decreases very rapidly to 3.85 and 3.90 Å, respectively, after 200 fs. After that, another slight increase can be observed. The distance between the two bases in the middle of the QM region increases within the first 120 fs from 3.89 to 3.93 Å and then decreases fast to 3.82 Å after 350 fs. It can be seen that after 350 fs of the dynamics all nucleobases are closer to each other than initially.

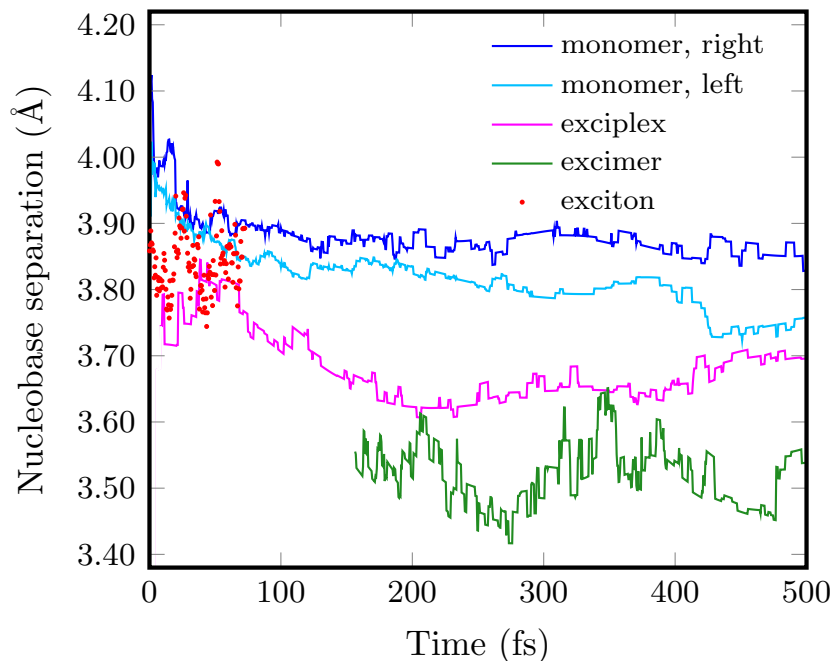


Figure 4.16: Time evolution of the spatial separation of the bases involved in the different excited states, and of the neighboring bases in the case of the monomers.

However, to interpret this with respect to the different types of excited states, it is necessary to investigate the average distances between the bases involved in the respective excitation. Thus, figure 4.16 shows the time evolution of the distance between the centers of mass of the nucleobases involved in the excitation for exciplexes, excimers and excitons. For monomer-like excitations the distances to both neighboring bases are plotted. Table 4.3 shows the average of the nucleobase distances for the different excited states, which are averaged over all time steps and all trajectories of the dynamics simulation.

Nucleobases on which monomer-like states are localised are generally the most separated. The separation to both neighboring nucleobases behaves very similar, although the left neighbors (left according to the depiction of the strand in figure 4.1) tend to be slightly closer to the excitation. The two nucleobases forming

Table 4.3: Average over all time steps of spatial separation of the nucleobases involved in the different excited states, and of the neighboring bases in the case of the monomers.

state	nucleobase separation (Å)
monomer, right	3.881
monomer, left	3.822
exciton	3.791
exciplex	3.671
excimer	3.575

an exciplex are up to 0.25 Å closer to each other than in the case of the monomer. The averages of the distance of the monomer-like excitation to neighboring bases are 3.881 and 3.822 Å, while the two nucleobases forming an exciplex are separated by 3.671 Å in average. The separation of excitonic states is only plotted for the first 50 fs, because after that point excitons were almost no more observed. Their separation seems to lay between the separation of monomer-like excitations and exciplexes with an average of 3.791 Å. The nucleobases involved in the formation of an excimer are even closer than in the exciplex, but the time evolution is only plotted after 150 fs since due to the small number of excimers formed before that, the average was oscillating heavily. The overall average separation of the two nucleobases involved in an excimeric state is the lowest with 3.575 Å.

Using these characteristics of the different excited states, the overall average distances can tentatively be interpreted. For the nucleobases on the edge it seems that at the beginning the amount of monomer-like excitations is high since the overall separation is large. After 200 fs excimers and exciplexes start being formed, with excimers as intermediates. This leads to the large decrease in the inter base separation. Since in excimers the nucleobases are even closer than in exciplexes there is a slight increase after 250 fs when more exciplexes are being formed. The two bases in the center are initially closer together which indicates a higher percentage of excitons. The average separation increases within the first 100 fs, which can be interpreted as monomers being formed. After 150 fs another decrease can be observed due to the formation of exciplexes.

Since stacked nucleobases are spatially closer to each other than unstacked bases, this analysis underlines the importance of base stacking for the formation of long-lived excited states. As mentioned in the previous sections the long-lived excited states observed in polyadenine can be characterised as exciplexes and they occur between bases with less spatial separation.

4.6 CONCLUSION

In this section the excited states dynamics of (dA)₂₀ was simulated for 500 fs, describing four adenine bases at the TD-CAM-B₃LYP/def2-SV(P) level of theory, while the other nucleobases, the backbone and explicit aqueous solution are treated classically.

Initially, around 80 % of the trajectories were excited to excitonic states and the other 20 % to monomer-like states. Of the initially formed excitons around 20 % decayed to exciplexes in a temporarily localised way. The larger part of the excitons (80 %) transformed to monomer-like states, with a time constant of 31 ± 5 fs. Within the first 100 fs nearly all of the initially formed excitons transitioned in either of the two ways.

From the monomer-like states, two deactivation channels were observed. For only 6 of the trajectories, energy gaps below 0.1 eV between the S₁ and S₀ were observed, and it was assumed that deactivation to the ground state would take place at these points. This occurred through the an out of plane distortion of the C2 group that was also observed for the S₁/S₀ conical intersection of the adenosine monomer.⁹³ However, around 75 % of the monomer-like states transitioned to the

intermediate excimeric state and ended in the exciplex state. Hence, the results of this simulation show that the long-lived excited states observed experimentally in (dA)₂₀ upon irradiation with UV light, are exciplexes. This supports the findings of several experimental groups. As mentioned before, there has been some controversy about whether states with high charge transfer character^{13;21–24} or excitons^{14;15;31;34} are formed during the dynamics. The findings of this computational study strongly indicate that excitons are only formed upon irradiation but are not stable and decay to states with high charge transfer (exciplexes). The overall time constant observed for the decay to the ground state was found to be 2.9 ± 0.8 ps, which is good agreement with the experimental value of around 2 ps. For the occupation of the long-lived excited states (exciplexes), the experiments deduced a time constant of around 400 fs. The simulated dynamics yielded the time constant to be 687 ± 109 fs, which is comparable to what was observed in the experiments.

It was also aimed to reproduce the experimental time-resolved fluorescence spectrum. However, the spectrum obtained from the simulation is very close to the experimental fluorescence spectrum of the adenosine monomer but not to (dA)₂₀. It is unclear where this difference exactly arises from, but during the dynamics simulation hardly any excitons were observed, although excitons should be the states responsible for fluorescence, and the experimentalists concluded the presence of excitons from their spectra.

A structural analysis with respect to the inter base separation between the bases of the QM region showed that the nucleobases forming exciplexes are spatially closer than the ones in monomer-like states. The separation of bases forming excitons is found to be larger than in exciplexes and smaller than in monomers. Since the structural differences between excitons and exciplexes are smaller than between monomers and exciplexes, the transition can take place more easily. This may be part of the reason why exciplexes are faster formed from excitons than from monomers who first generate a more stable intermediate excimer. The observation of the reduced separation of the nucleobases in the long-lived exciplexes is also supported by several experimental studies.^{13;24} They concluded that base stacking, which results in spatially closer nucleobases, controls the excited state dynamics of (dA)₂₀.¹³

This simulation of the excited state dynamics of (dA)₂₀ provided valuable insights on the decay channels and types of excited states formed. Several experimental findings are well reproduced and the hypothesis about the long-lived excited states being exciplexes was fully supported.

SUMMARY

In this thesis, the excited state dynamics of single stranded DNA, consisting of 20 adenines, (dA)₂₀, in aqueous solution were investigated. In the literature, several transient absorption and time-resolved fluorescence experiments are reported to have found that upon excitation with UV radiation long-lived excited states are formed in (dA)₂₀. The nature of these long-lived excited states was subject of some controversy. The transient absorption experiments suggested states with high charge transfer character such as exciplexes or excimers are formed.^{13;21–24} In contrast, the time-resolved fluorescence experiments indicated that excitons are not only formed initially but are also the observed long-lived excited states.^{14;31;34} A recent computational study¹⁸ showed that the absorption spectrum of (dA)₂₀ is determined by excitonic and monomer-like states, where states with high charge transfer character only contribute minorly. However, these computations only shed light on the states initially excited not their evolution. Therefore, the scope of this work was to simulate 500 fs of the excited state dynamics of (dA)₂₀ and performing a thorough analysis of the electronic wavefunction in order to identify the nature of the long-lived excited states.

In the first part, the influence of methodical changes on the absorption spectrum were investigated. A QM/MM scheme with the QM region being described at the TD-CAM-B₃LYP⁵⁰/def2-SV(P)⁷⁸ level of theory was used. It was found that including either four or six nucleobases at the QM level of theory did not significantly change the absorption spectrum. However, usage of the Tamm-Dancoff approximation⁷⁹ led to an even higher overestimation of the excitation energy than obtained with TDDFT and yielded too high contributions of charge transfer states. Furthermore, it was seen that while a much larger basis set, def2-TZVP, decreases the energy of the absorption spectrum, it does not notably change the composition of the spectrum with regard to charge transfer character and delocalisation of the states. Hence, four nucleobases are treated at the CAM-B₃LYP/def2-SV(P) level of theory using the standard formulation of TDDFT. The other nucleobases, the backbone of the single strand as well as the surrounding water are described at the classical level employing the Amber ff99 force field. According to the absorption spectrum, this was considered a suitable method for the simulation of (dA)₂₀ in aqueous solution.

With this method, the excited state dynamics of 100 trajectories were simulated for 500 fs. For the propagation of the semi-classical trajectories, an interface was developed for the SHARC program package^{39;40} to perform QM/MM on-the-fly electronic structure calculations with the ORCA^{38;55} and Tinker⁸¹ programs. Employing the TheoDORÉ program^{64;83} enabled performing an on the fly wavefunction analysis, which was used to differentiate monomer-like states, excitons, excimers and exciplexes.

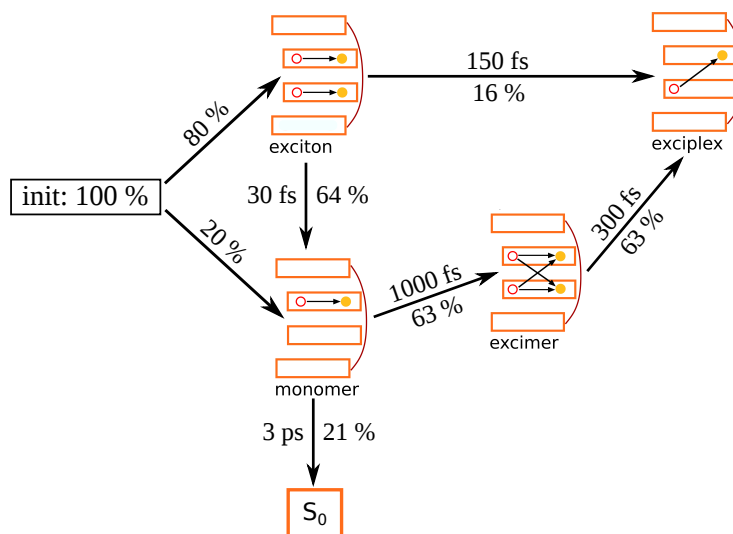


Figure 5.1: Graphical summary of the main findings of this study, the excited states formed upon photoexcitation of (dA)₂₀. The percentages are extrapolated values and all with respect to the initial population.

Figure 5.1 graphically summarises the main findings of the non-adiabatic surface hopping dynamics simulation. Initial excitation was observed to excitonic states (80 %) and monomer-like states (20 %). From the initial excitons, the larger part (64 % of the total population) transitions to monomer-like states, while the smaller part directly forms exciplexes. From the monomer-like states deactivation to the ground state is possible and in total 21 % of the initially excited population were extrapolated to deactivate. The other part of the monomer-like state (63 % of the total population) form exciplexes through an intermediate excimeric state. The findings of this computational study strongly indicate that excitons are only formed upon irradiation but are not stable and decay to states with high charge transfer (exciplexes). The overall time constant observed for the decay to the ground state was found to be 2.9 ± 0.8 ps, which is good agreement with the experimental value of around 2 ps. For the occupation of the long-lived excited states (exciplexes), the experiments deduced a time constant of around 400 fs. The simulated dynamics yielded the time constant to be 687 ± 109 fs, which is comparable to what was observed in the experiments.

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by several experimental studies.^{13;24} They concluded that base stacking, which results in spatially closer nucleobases, controls the excited state dynamics of (dA)₂₀.¹³

This simulation of the excited state dynamics of (dA)₂₀ provided valuable insights on the decay channels and types of excited states formed. Several experimental findings are well reproduced and the hypothesis about the long-lived excited states being exciplexes was fully supported. This study provides the first computational evidence of charge transfer states forming in (dA)₂₀ through excited state dynamics simulations.

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