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THE INVESTIGATION OF SINGLET FISSION FROM THE PERSPECTIVE OF  
HIERARCHY OF PURE STATES (HOPS)

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THE INVESTIGATION OF SINGLET FISSION FROM THE PERSPECTIVE OF  
HIERARCHY OF PURE STATES (HOPS)

A Dissertation Presented to the Graduate Faculty of the  
Dedman College

Southern Methodist University

in

Partial Fulfillment of the Requirements

for the degree of

Master of Science

with a

Major in Theoretical and Computational Chemistry

by

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July 31, 2023

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The Investigation of Singlet Fission From the Perspective of  
Hierarchy of Pure states (HOPS)

Advisor: Dr. Doran I. G. B. Raccah

Master of Science degree conferred July 31, 2023

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This thesis provides a preliminary investigation of singlet fission from the perspective of Hierarchy of pure states (HOPS), which provides a numerical exact solution for the investigation of a series of open quantum systems. Since the inception of the concept of singlet fission about half a century ago, this photo-physical process has attracted the attention of a multitude of researchers and has been extensively studied theoretically and experimentally. However, these previous methods for the investigation of singlet fission focus more or less on tackling the underlying mechanisms of singlet fission from the perspective of perturbation. So far, the HOPS method has been the first trial for the investigation of this photo-physical process. This thesis is organized as follows. The Chapter 1 will introduce the basics of singlet fission and the brief history of the investigation of this phenomenon over the last half century. Chapter 2 will focus on the introduction of the method of HOPS and its applications to various open quantum systems. The investigation of singlet fission from the perspective of HOPS will be introduced in Chapter 3. The focus of Chapter 4 will be on the discussion of the current research. Chapter 5 will conclude the thesis and present some outlooks on the future research.

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This thesis is dedicated to my parents, who have supported me physically and  
psychologically.

## CHAPTER 1

### Introduction

Singlet fission refers to a photo-physical process associated with certain organic compounds where a singlet excited state evolves into two triplet excited states with the conservation of the overall spin. The investigation of the process of singlet fission began in 1965 [1]. However, interest toward this process has grown rapidly in the last few years. Therefore, the recent years have witnessed a soaring trend in terms of the number of publications focusing on the exploitation of singlet fission from the perspective of theoretical analysis, modeling, and experimental analysis. Among these studies, theoretical and computational investigations have played a pivotal role in deepening the scientific community’s understanding of this peculiar photo-physical phenomenon. In particular, computational investigations play a decisive role in understanding the most relevant factors for singlet fission efficiency, the properties of electronic states associated with singlet fission, the potential mechanisms of singlet fission, the key parameters describing fission rates, and the most significant characteristics regarding the dynamics of singlet fission [2,3]. In spite of multiple studies characterizing these factors, there is still much work to do to fully comprehend the mechanisms and applications of singlet fission.

In this chapter, we will illustrate a brief history of the investigation of singlet fission. After that, we will focus on the experimental investigation of singlet fission before delving into the applications of singlet fission. In addition, we will also discuss the electronic states involved in singlet fission. In addition, we will also discuss the electronic states involved in singlet fission, and then compare the differences between these states when they undergo singlet fission.

### 1.1. A brief history of the investigation of singlet fission

The inception of the exploration of singlet fission can be traced back to the year 1963, when Singh and Stoicheff discovered a dark intermediate state in single crystals of anthracene, capable of absorbing two photons, that is not present in the free anthracene molecule [4]. In 1965, this intermediate state was characterized as a high-energy state, formed by two coupled triplet excited states, which can either disassociate or relax to the lowest excited singlet state [1]. The year 1968 saw the proposition of biomolecular decay, which is described by a rate model, of a singlet excited state into a pair of triplet excited states in tetracene crystals by Swenberg and Stacy [5] in order to explain the phenomenon of extremely low fluorescence quantum yield [6]. In 1969, two experimental papers presented relevant evidence of singlet fission process in crystalline tetracene [7,8] to verify the predictions made by Swenberg and Stacy. A 1970 work hypothesized the existence of an intermolecular correlated triplet-pair state as an intermediate for the triplet-triplet annihilation process in anthracene crystals [9]. The singlet fission kinetic models in these theoretical works relied mostly on singlet fission and triplet-triplet annihilation model developed by Johnson and Merrifield [9,10], which were improved by Suna that included the effects of triplet exciton diffusion in the model [11]. These theories were successful in advancing the investigation of singlet fission, despite the inability to describe the electronic states involved in the singlet fission mechanism due to the limit of quantum chemistry electronic structure calculations at that time.

Due to the limit of the power of quantum chemistry electronic structure calculations, the research community paid less and less attention to the detailed investigation of singlet fission in the following decades [12-14]. It was not until in 2006 that the investigation of singlet fission was revitalized, when Hanna and Nozik proposed multiple exciton generation (MEG) in organic materials via singlet fission as a path to overcome the Shockley-Queisser limit [15,16], which opens the door to a series of potential applications of singlet fission to the improvement of conversion efficiency between solar energy and electricity.

### **1.2. Experimental investigations of singlet fission**

In addition to the theoretical and computational efforts devoted to the exploration of singlet fission, singlet fission has also been detected and measured in a variety of experiments, such as delayed fluorescence via magnetic variations of spectroscopic characteristics, or that using photo-induced transient absorption techniques. The timescale of fluorescent emission is much longer than that of delayed fluorescence, which indicates the recombination of two triplet excited states [17-23]. In addition to these experimental methods, some other approaches have also been applied to the exploration of singlet fission to detect the triplet excited states, e.g., transient absorption, or time-resolved two-photon photo-emission spectroscopies. Transient absorption can be used to determine the radiation transmission variation of a material in response to photo-excitation. The emergence of laser pulses on the femtosecond timescale provides an opportunity for researchers to explore the time evolution of electronic states of singlet fission, and the laser pulses are one of the main experimental methods to detect singlet fission, which serves as the basis of the exploration of the dynamics of singlet fission. The theoretical investigation of excited state absorption measurements applied to the study of singlet fission in solid pentacene has been realized by Khan and Mazumdar [24].

### **1.3. Application of singlet fission to solar cells**

Since the work of Hanna and Nozik [15], researchers have tried their utmost use singlet fission to improve solar cells by converting the solar photons into electricity in photovoltaic devices or producing solar fuels. By combining singlet fission materials with solar cell architectures, it may be possible to alleviate losses caused by conversion of the excess kinetic energy of hot carriers to heat by generating a second exciton for solar photons with energies at least twice the band gap of the semiconductor [25].

The Shockley-Queisser limit is an important quantity proposed to describe the previous understanding of the maximum efficiency of solar cells. In order to exceed this limit, two or more light harvesting components are required in the solar cells associated with singlet fission, i.e., a singlet fission material which is able to absorb high-energy photons and a chromophore that converts lower energy solar radiation into a single electron-hole pair per solar photon [15,26]. Theoretical results show that singlet fission in solar cells is capable of doubling the photocurrent for short wavelength photons with the voltage of a single junction cell. This can be explained by a potential loss mechanism that is the electron transfer channel from the singlet excited state before the multi-exciton formation, and this mechanism is used in singlet fission solar cells. Therefore, singlet fission needs to be fast to produce two charge carriers for each absorbed photon. To date, by incorporating the phenomenon of singlet fission, the external and internal quantum efficiencies of solar cells have reached 126% and 200%, respectively [27,28].

Solar cells can be integrated with singlet fission materials consisting of a singlet fission donor and acceptor via charge separation of triplet excitons. The ionization of triplet excited states at the donor-acceptor interface has been demonstrated in pentacene and  $C_{60}$ , serving as singlet fission donor and electron acceptor materials, respectively [29]. In addition, singlet fission compounds can also be used as sensitizers coupled to semiconductor solar cells such as crystalline or amorphous silicon [30] or perovskites [31]. The efficiency of one such singlet fission sensitized parallel tandem solar cell was predicted to be approximately 45% [30]. Compared to the fast charge transport of inorganic semiconductors, the poor charge transport properties associated with organic semiconductors have hindered their applications to photovoltaics. The combination of singlet fission molecular sensitizers with dye-sensitized solar cells (DSSCs) has been proposed as a means of overcoming this gap [32], which has been explored in a 2006 paper [33]. After discussing the potential applications of singlet fission, we will focus on the basics and electronic states associated with singlet fission.

## 1.4. The overview of singlet fission

### 1.4.1. The basics of singlet fission

Singlet fission, which can also be referred to as singlet exciton fission, is a photo-physical reaction in which a spin singlet excited state is converted to two spin triplet excitons, as described by the following equation:



Despite bridging the gap between singlet excited states and triplet excited states, singlet fission is a spin-allowed process as the triplet states involved in this process are coupled as an overall singlet state.

Singlet fission is a down-conversion process of high-frequency photons into low-energy excitons, which, initially, was considered as the reverse process of the triplet-triplet annihilation process [1,8]. Singlet fission can also be regarded as the molecular counterpart of multiple exciton generation (MEG) in organic semiconductors, such as quantum dots [34], and quantum cutting in lanthanide ions [35-37]. Singlet fission leads to two triplet excitons located in two monomers, as opposed to MEG, in which the excitons are produced in a single nano-crystal or quantum dot. One advantage associated with singlet fission is that the lifespan of triplet excited states in organic materials is in the microsecond realm, whereas triplet excitons tend to decay via Auger recombination in just a few tens of picoseconds in inorganic nano-structures [38].

Singlet fission can be seen as the result of two successive steps in which an initial excited state is the lowest excited singlet of a monomeric chromophore, which can be described by the following equation [39],

$$S_1 \rightleftharpoons {}^1TT \rightleftharpoons T_1 + T_2 \quad (1.2)$$

As singlet fission, a photo-physical reaction, starts from an excited singlet state, it needs the initial activation energy as the driving force to trigger the singlet fission. The required activation energy is usually provided by photo-absorption and initial electronic promotion of the system to an optically active state, even if singlet fission could occur due to some other activation sources [40]. Photoexcitation of the system triggers the (coherent or incoherent) formation of an intermediate state, the singlet fission precursor  ${}^1TT$ , with a very particular electronic structure containing the seed for the formation of two triplet states. Once the intermediate state is formed it can, in principle, dissociate into two independent triplets via the Dexter energy transfer mechanism [41]. Electronic coupling between the two triplet excitons is lost upon spatial separation, but the two triplets might remain entangled as an overall spin singlet (quantum or spin coherence) [42,43]. Experimentally, it has been shown that spin coherence can be preserved for a relatively long time, typically in the order of nanoseconds [44,45]. Theoretical investigations in singlet fission have focused on addressing static and dynamic aspects of the photo-physical reaction up to the formation of two (electronically) independent triplets, while other important and closely related processes, such as singlet and triplet state diffusion in singlet fission materials and, in particular, the loss of spin coherence between the fission triplets as they diffuse through the electronic material, remain largely unexplored.

#### 1.4.2. Requirements for singlet fission

Despite a large number of research efforts devoted to the investigation of singlet fission, the kinds of organic materials that exhibit singlet fission are limited by restrictions originating



from the requirements for such a phenomenon. The requirements for singlet fission have been intensively explored by Michl et al. [33,46]. Here, we will elaborate on these requirements.

**Thermodynamic requirement** In order for spontaneous singlet fission to occur, the energy of the initial excited state  $S_1$  must be equal or greater than twice the energy of the lowest-energy triplet state:  $E(S_1) \geq 2E(T_1)$ . Due to that the singlet fission rate is slower than the rate of vibration relaxation and that there are tremendous differences in terms of the geometry relaxation of the lowest singlet and triplet states, it may be pivotal in order to predict the right energetics and/or trends for a given system [33]. In order to deduce thorough thermodynamic conditions, enthalpy and entropy contributions to the Gibbs free energy originating from the nuclear degrees of freedom also must be taken into account. In addition, to investigate the case without energy loss from the initial photo-excitation, the vertical energy associated with the bright state at the Franck-Condon geometry must be computed and applied.

**Kinetic requirement** As an overly exoergic process tends to slow down the photo-physical reaction rate, such a process can prevent singlet fission and lead to energy loss due to the heating of the system. Therefore, systems in which the energy of the  $S_1$  state is slightly greater than twice the energy of the  $T_1$  state are optimal for singlet fission. One example in this respect is pentacene.

**Deactivation channel requirement** Some additional energy requirements should be satisfied so that singlet fission outcompetes alternative decay paths for the sake of efficient singlet fission. One of the potential channels associated with singlet fission is the recombination of the triplet states into higher spin states, which is described by the following triplet and quintet states in Eq. (1.3) and Eq. (1.4), respectively. The triplet and quintet states tend to prevent the generation of two electron-hole pairs.

$$T_1 + T_1 \rightarrow T_2 \tag{1.3}$$

$$T_1 + T_1 \rightarrow Q_1 \tag{1.4}$$

Triplet-triplet fusion to the triplet manifold is energetically forbidden if the energy of the second triplet state is higher than the two lowest triplet states, i.e.,  $E(T_2) > 2E(T_1)$ , introducing another singlet fission condition. The energy of the lowest quintet state associated with organic molecules is typically very high, and the condition that  $E(Q_1) > 2E(T_1)$ , related to Eq. (1.4), can be easily achieved. Failing to meet these two conditions, which are related to the tetra-radicaloid character of the chromophore, is unfavorable for singlet fission [39].

The direct transition from the excited singlet states into the triplet manifold through intersystem crossing (ISC), which is shown in the following Eq. (1.5), is another competing pathway. As typical organic conjugated molecules associated with good singlet fission properties are characterized by weak spin-orbit couplings which result in inefficient ISC, this channel is usually not considered in the investigation of singlet fission.

$$S_1 \rightarrow T_n \tag{1.5}$$

However, ISC pathways can be facilitated by the introduction of heavy atoms [47].

Photo-excited molecules tend to decay efficiently back to the ground state via symmetrical interstate crossings, as shown in the following Eq. (1.6) [48-50]. Polyenes, such as the retinal molecule, are good examples in this respect of the internal conversion to the state  $S_0$  via molecular relaxation along the  $S_1$  potential energy surface (PES) [51-54].

$$S_1 \rightarrow S_0 \tag{1.6}$$

The generation of multiple spatially close singlet excitons, which can coexist simultaneously in large exciton densities, favors the channel of singlet-singlet annihilation, which reduces the number of fission events [55].

$$S_1 + S_1 \rightarrow S_n \tag{1.7}$$

Some other unintended deactivation paths competing against singlet fission are the recombination to the singlet-exciton manifold, which stays away from long triplet-pair lifetimes to allow for the separation of triplet states, the formation of charge-separated states, or the decay to dark singlet states [56].

In addition to the above mentioned conditions, some other conditions should also be taken into consideration. First, good light-harvesting properties, that is, the chromophore should have a large absorption coefficient molecules with large absorption coefficients, are needed in the  $\pi$ -conjugated rigid chromophores. Second, molecules which are involved in singlet fission must be chemically stable over long periods of time. Chemical instability is one of the major problems for the application of long linear polyacenes as a result of their soaring diradical character with respect to their molecular length. One example of inconvenient chemical instability is the tendency of acenes to react with fullerenes via the Diels-Alder reaction [57,58], which renders acene-fullerene solar cells associated with singlet fission based on donor-acceptor heterojunctions nonviable. Another limiting factor of the acene-fullerene system is the existence of high acceptor levels in  $C_{60}$ , which may allow for the transfer of a single electron from the donor and prohibits the two-electron injections in each

harvested photon [59]. Therefore, acene-fullerene systems have had their acceptors replaced with a number of substitutes [60-65].

So far, we have covered the following electronic states are associated with singlet fission: the lowest spin-singlet with mono-excitonic character ( $S_1$ ), the two independent triplet states ( $T_1$ ), and the multiexcitonic states ( $^1TT$ ). Some other electronic states may also be involved in singlet fission processes, such as the charge transfer ( $CT$ ) states and charge resonant ( $CR$ ) states [39]. In the following sections, we will discuss all of these electronic states.

#### 1.4.3. Singlet exciton

Singlet fission systems can be promoted to an optical spin single state corresponding to a single electron transition due to the initial photo-excitation. When it comes to weakly interaction chromophores, the optical excitation is associated with a molecular bright state in the limit of singlet fission in dilute solution [66]. In singlet fission, a common assumption is that the singlet fission system will quickly decay to the lowest excited singlet state ( $S_1$ ) before it undergoes singlet fission [67], even if there exists the possibility of singlet fission from upper vibrational states of  $S_1$  [68] or from a higher excited singlet state  $S_n$  [69].

The lowest singlet-electron excited singlet state of the overall system is usually denoted  $S_1$ , which can be used to label the lowest excited state in the molecule or monomer. Furthermore, the singlet-electron excited state of the entire system can also be labeled as local exciton (LE), Frenkel exciton (FE), or exciton state (EX) from the perspective of condensed matter physics [39].

According to Equation 1.1, which defines singlet fission in the sense of general photo-physics reaction, the mechanism of singlet fission is relevant to the energy repackaging of a singlet exciton located in one molecule into two triplet states on two different chromophores. Although these pictures were applied in previous research [2,3], this model does not reflect

the physical nature of the excitonic state ( $S_1$ ) of extended systems, e.g., organic molecular crystals or aggregates, as singlet excited states are inclined to delocalize over multiple chromophores [70-73]. Exciton delocalization can be investigated with a variety of computational methods, such as the Green’s function (GW) method and the Bethe–Salpeter equation (BSE) method [74-82]. For example, a computational study on 5,12-diphenyltetracene and rubrene shows that at least 7 molecules are involved in the photo-excited states, which indicates that more than 10 molecules are involved in exciton delocalization [83], which can be seen in Figure 1.1 below. Due to the rapid formation of triplet-pair states, exciton delocalization improves the efficiency of singlet fission in nanocrystals of pentacene derivatives [84]. Furthermore, delocalization of the  $S_1$  state permits the emergence of ultrafast singlet fission as a result of vibrational coherent transfer between a photoexcited singlet and singlet fission triplets in TIPS–pentacene [85]. Based on the discussion of singlet excited state, we can continue to discuss triplet states involved in singlet fission.

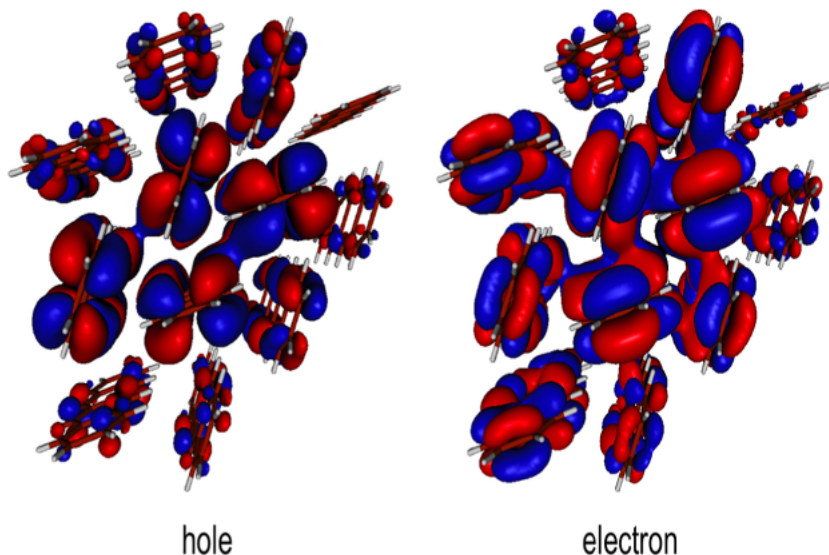


Figure 1.1: (Adapted From Ref. [39]) The exciton delocalization is represented by natural transition orbitals [82] for  $S_1$  state in tetracene. Hole (left) and electron (right) isodensities are obtained with the calculations from for a cluster of 12 tetracene molecules in the crystal structure.

#### 1.4.4. Triplet state

The final product of singlet fission (i.e., the independent triplet state) has a strong molecular character and corresponds to the single-electron occupation of the HOMO and LUMO associated with the chromophore to a first approximation. Many organic conjugated molecules are characterized by large exchange interactions, which leads to an energy separation between singlet and triplet states on the order of 1eV [72]. For a two-electron model, the singlet-triplet energy gap is approximately twice the exchange integral between HOMO and LUMO ( $K_{hl}$ ).

$$E(S_1) - E(T_1) \approx 2K_{hl} \quad (1.8)$$

The ability of organic materials to exhibit singlet fission can be ascribed to the energy difference between the lowest excited singlet and triplet states, whereas inorganic materials (e.g., quantum dots) cannot exhibit singlet fission as a result of the degeneration of singlet and triplet states and a different mechanism followed by multi-exciton generation and singlet and triplet degeneration [87].

Triplet excited states tend to have greater binding energy and be more localized than singlet excited states as a result of a lack of electron-hole exchange interaction [88], which is similar to the vertical transition energy of  $T_1$  states in the solid, solution and gas phases [89]. Some exceptions exist: for example, the triplet excited states in perylenediimide (PDI) are particularly stable in the solid state (the triplet excitation energy is about 0.14 eV with a redshift of 0.26 eV in the  $S_1$  state) [90].

#### 1.4.5. Triplet-pair state

Singlet fission is a process which takes place from the lowest singlet excited state ( $S_1$ ) to two independent triplet excited states ( $T_1$ ) via an intermediate state characterized by multiple excited states corresponding to a triplet-pair coherently coupled state as an overall

spin singlet state. This can be described as a strong spin correction from the perspective of the valence bond theory [91]. Triplet-pair states serve as the cornerstone of the singlet fission mechanism, as triplet-pair states provide a spin-allowed pathway between singlet excited states and triplet excited states. Triplet-pair states are usually labeled  ${}^1TT$  or  ${}^1T_1T_1$  [39]. In order to investigate the triplet-pair states  ${}^1TT$ , one must focus on their electronic structure, which is a great theoretical and computational challenge. From the perspective of experimental detection and characterization, it is more difficult to detect  ${}^1TT$  states than to detect  $S_1$ ,  $T_1$ , or  $CT$  states [92,93]. In the basis of molecular orbitals, the complete form of triplet-pair states associated with spins within the dimer model is a linear combination of couplings between two monomeric triplet states characterized by the sum of two local spin quantum numbers being zero, i.e.,

$$|{}^1TT\rangle = \frac{1}{\sqrt{3}}(|T_+T_-\rangle + |T_-T_+\rangle - |T_0T_0\rangle) \quad (1.9)$$

In Eq. (1.9),  $T_+$ ,  $T_-$  and  $T_0$  are three triplet micro-states of the monomer corresponding to three different quantum numbers  $m_s$ . Eq. (1.9) can be seen as a combination of 6 double-excited configurations if it is expanded on the basis of the direct product (see Fig. 2)

$$|{}^1TT\rangle = \frac{1}{\sqrt{3}} \left( \begin{array}{c} \uparrow \downarrow \\ \uparrow \downarrow \end{array} \right) + \begin{array}{c} \downarrow \uparrow \\ \downarrow \uparrow \end{array} + \frac{1}{2} \left( \begin{array}{c} \downarrow \uparrow + \uparrow \downarrow - \downarrow \downarrow - \uparrow \uparrow \\ \uparrow \downarrow + \downarrow \uparrow - \uparrow \uparrow - \downarrow \downarrow \end{array} \right)$$

$|T_+T_-\rangle$ 
 $|T_-T_+\rangle$ 
 $|T_0T_0\rangle$

Figure 1.2: (Adapted From Ref. [39]) Electronic configurations for the  ${}^1TT$  state derived from HOMO and LUMO (bottom and top) for two monomers (left and right) in a dimer model.

In Ref. [94], the  ${}^1TT$  state can be regarded as a combination of zero-field triplet spin states  $|x\rangle$ ,  $|y\rangle$ , and  $|z\rangle$ , i.e.,

$$|^1TT\rangle = \frac{1}{\sqrt{3}}(|xx\rangle + |yy\rangle + |zz\rangle) \quad (1.10)$$

The two triplet states can form an overall triplet or quintet state via being coupled to each other. The expressions for triplet and quintet triplet-pair states have been investigated in previous research [39], with the super-indices symbolizing spin multiplicity and  $m_s$  values, respectively.

$$|^{3,0}TT\rangle = \frac{1}{\sqrt{2}}(|T_+T_-\rangle - |T_-T_+\rangle) \quad (1.11)$$

$$\begin{aligned} |^{3,+1}TT\rangle &= \frac{1}{\sqrt{2}}(|T_+T_0\rangle - |T_0T_+\rangle) \\ |^{3,-1}TT\rangle &= \frac{1}{\sqrt{2}}(|T_-T_0\rangle - |T_0T_-\rangle) \end{aligned} \quad (1.12)$$

$$|^{5,0}TT\rangle = \frac{1}{\sqrt{6}}(|T_+T_-\rangle + |T_-T_+\rangle + 2|T_0T_0\rangle) \quad (1.13)$$

$$\begin{aligned} |^{5,+1}TT\rangle &= \frac{1}{\sqrt{2}}(|T_+T_0\rangle + |T_0T_+\rangle) \\ |^{5,-1}TT\rangle &= \frac{1}{\sqrt{2}}(|T_-T_0\rangle + |T_0T_-\rangle) \end{aligned} \quad (1.14)$$

$$|^{5,+2}TT\rangle = |T_+T_+\rangle; |^{5,-2}TT\rangle = |T_-T_-\rangle. \quad (1.15)$$



The electronic interaction between two  $^1TT$  triplet states at short distance in the singlet state, derived from the required energy to dissociate the two  $^1TT$  triplet states, is stronger than that for the  $^3TT$  and  $^5TT$  states [95]. Configuration interaction with other singlet configurations can be used to stabilize the singlet triplet-pair state, but the quintet state is characterized by a much larger diabatic character. The mixing of the  $^5TT$  with some other quintet states is limited due to their high energy [96]. Therefore, the binding energy of the triplet states can be expressed as follows,

$$E_b \approx E(^5TT) - E(^1TT). \quad (1.16)$$

As an intermediate state in singlet fission, the role of  $^5TT$  has been investigated via the spin Hamiltonian of the triplet states interacting with each other [97,98]. A triplet-pair state can be formed from the spin pure state  $^1TT$  due to the spin dipole-dipole interactions between the two triplets [99], allowing the mixing of the singlet state and the quintet  $TT$  state (i.e.,  $m_s = 0$ ) in symmetrical systems, i.e., homo-fission. The triplet-pair quintet states have been observed to form in tetracene films [100] and pentacene dimers [101].

The large separation in space gives rise to the disappearance of the electronic coupling associated with two triplet states and the degeneracy of  $TT$  states with different spin multiplicities. In this situation, the pure character of  $^1TT$  can be obtained via the wave function of the multi-exciton singlet state, without mixing with other configurations. The two triplet states are not independent of one another, even though they are decoupled electronically, as spin entanglement exists and decoherence is necessary to generate independent triplet states [94]. Spin coherence is stable in organic materials, but will ultimately be lost due to finite temperature effects, energetic disorder, and dynamic disorder (i.e., exciton-phonon coupling) [98,102]. The loss of spin coherence through interaction with the environment plays a pivotal role in understanding the fate of the generated triplets. Due to the quantum decoherence,

the spins of the two triplet states are decoupled and their overall spin state is equal to a statistical average of  $^1(T \cdots T)$ ,  $^3(T \cdots T)$ , and  $^5(T \cdots T)$  states.

As the  $^1TT$  state is involved in the concomitant excitation of two electrons (two electron-hole pairs), calculations concerning the  $^1TT$  state electronic structure models must account for doubly excited configurations. Hence, calculations of electronic transitions associated with the  $^1TT$  state cannot be achieved through standard linear response single reference approaches. In order to make it feasible to calculate the  $^1TT$  state, researchers have developed a series of computational methods, such as the complete active space self-consistent field (CASSCF) method [103-105] and the multi-reference Møller-Plesset perturbation theory (MRMP) method [106-108], to investigate singlet fission in a dimer model. One outstanding method is the restricted active space spin-flip (RAS-SF) approach, which can be used to investigate the  $^1TT$  state in different systems with singlet fission [109]. In addition, the construction of a spin-Heisenberg-Dirac-Van Vleck Hamiltonian can be used to investigate the wave function associated with the  $^1TT$  state with very low computational cost [110].

#### 1.4.6. Charge transfer/resonance states

When it comes to the adiabatic electronic states of chromophore dimers, aggregates, or molecular solids, the localized singlet excited states and multi-exciton states, such as the  $^1TT$  states, are inclined to mix with the charge transfer (CT) states and /or charge resonance (CR) states. CT states refer to a net charge displacement to some extent, but CR states, which are associated with symmetric arrangements of chromophoric units, refer to charged configurations concerning the ionic nature of the electronic wave function, but do not imply a permanent charge separation (see Figure 3) [111].

Singlet fission associated with CT and CR states is a central topic for scientific community [112-116], and CT and CR states play a pivotal role in distinguishing between different

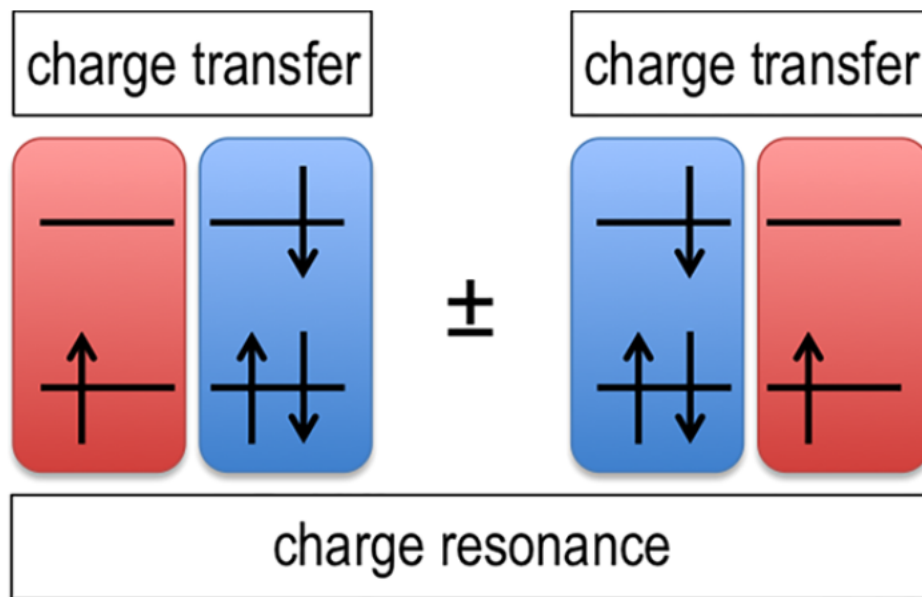


Figure 1.3: (Adapted From Ref. [39]) A schematic view of charge transfer (CT) and charge resonance (CR) configurations for a pair of chromophores.

potential electronic fission mechanisms in the formation of  $^1TT$  state (see Figure 1.4): these mechanisms include 1) direct internal conversion from the  $S_1$  state to the  $^1TT$  state, where CT states are not involved, 2) singlet fission mediated by CT states, where CT states serves as the assisting virtual states in forming the  $^1TT$  state via a super-exchange mechanism, and 3) two one-electron transfer steps in order with CT state as a real intermediate effectively populated prior to the generation of the triplet-pair states.

The low-lying singlet excitons in covalent dimers, aggregates or molecular solids possess some CT/CR character. The weight of the CT configurations in the adiabatic wave function of an  $S_1$  state depends strongly on the relative energy of CT state with respect to FE states and the inter-chromophoric couplings. One previous investigation has shown that the CT state have been suggested the lowest singlet excited state in some cases [117]. On other other hand, molecular crystals with high-lying CT states exhibit FE/CT state mixing and great localization of the  $S_1$  excited state [118]. The mixing of CT configurations with the  $^1TT$  state is much lower than with the  $S_1$  state and higher singlet states (i.e., the  $S_n$  state), and

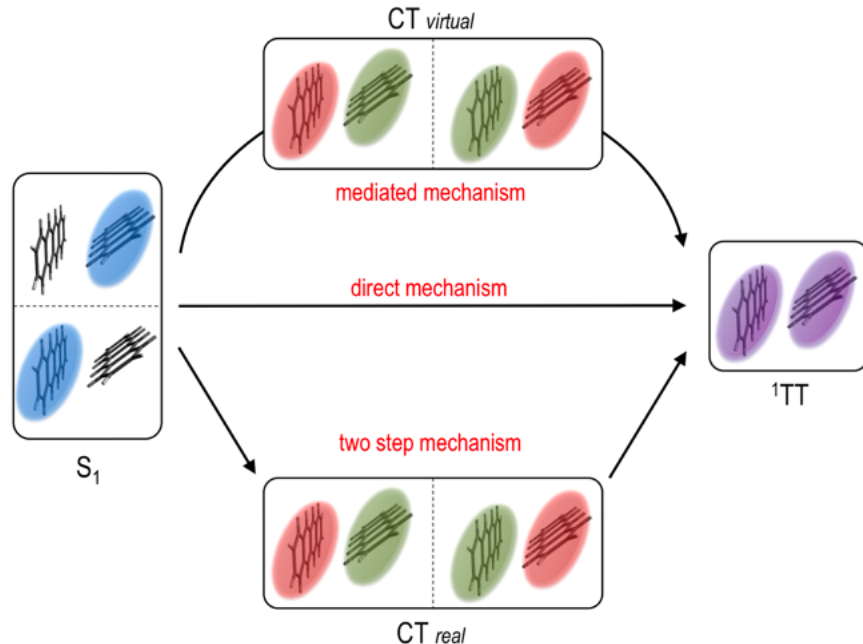


Figure 1.4: (Adapted From Ref. [39]) Possible mechanisms for the formation of  $^1TT$  state with regards to the involvement of CT states.

has a much weaker effect on its energy and electronic properties. Therefore, the differing abilities of the  $S_1$  and  $^1TT$  states to mix with CT configurations has been related to the much larger spatial extension of the  $S_1$  and  $^1TT$  states and the magnitude of the binding energy of the two triplets (see Eq. (25) in Ref. [39]). In previous research, the coupling of CT configurations with  $S_1$  and  $^1TT$  states has been considered with the singlet fission mediated mechanism, which is the most accepted path for singlet fission in extended systems, e.g., crystal tetracene and pentacene [116,119]. On the other hand, in weakly coupled covalent dimers of pentacene, the CT states in weakly coupled covalent dimers of pentacene have been calculated at rather high relative energies, which indicates that CT configurations play a minor role and supports a mechanism of direct transition from the  $S_1$  state to the  $^1TT$  state for intra-molecular singlet fission in these dimers [120].

In order to investigate the role played by CT states in singlet fission, diabatic energies and wave functions must be calculated directly. The energy of CT or CR configurations associated with the dimer model can be approximated as the interaction of oxidized and

reduced chromophores:

$$E(CT) \approx IP - EA + C \tag{1.17}$$

where  $IP$  and  $EA$  are the molecule’s ionization potential and electron affinity, respectively, and  $C$  is inversely proportional to the charge separation distance. In order to use Eq. (1.17), one should keep in mind that this equation only takes into account the Coulomb interaction between charges and ignores orbital contribution terms. If one needs to calculate the CT states in a more refined way, one can resort to the constrained DFT (C-DFT) method [121], where constraints on the charge localization are applied during the self-consistent field calculation to force negatively and positively charged densities on individual chromophores. This method has been used to evaluate the relative energy of CT states in several singlet fission systems [122,123] and explore how CT states in crystal pentacene are largely stabilized through electrostatic screening and the formation of electronic bands [124].

#### 1.4.7. Organization of this thesis

In this Chapter, we have introduced some basic concepts of singlet fission and previous investigations of singlet fission. This thesis will be organized as follows: Chapter 2 will focus on previous methods and our counterparts for the investigation of singlet fission. Some comparisons between these methods and our own method, the Hierarchy of Pure States (HOPS), will be made. Chapter 3 will concentrate on the results of HOPS simulations of singlet fission. Chapter 4 will focus on discussion of the results from Chapter 3. Chapter 5 will conclude the thesis and discuss the outlook of current and further research.

## CHAPTER 2

### The Comparisons between Different Quantum Dynamics Methods

So far, the majority of theoretical and computational investigations of singlet fission dynamics in early days of the singlet fission exploration have been devoted to understanding the characteristics of the electronic states involved in this photo-physical process, the exploration of appropriate chromophores with optimal energetics, the investigation of electronic couplings, and the determination of possible singlet fission mechanisms. These investigations were based on calculations and computations without explicit dependence on time and provided good platforms for estimating singlet fission rates through different kinetic models associated with experimental and/or computational energy and couplings [39]. Another method used to investigate singlet fission is time-resolved spectroscopic measurements, which include delayed fluorescence [128-130], transient absorption [131-135], and time-resolved two-photon emission [95,136]. Time-resolved spectroscopic measurements have promoted the experimental explorations of singlet fission and resulted in comprehensive understanding of the possible mechanisms of singlet fission, the time scales concerning this photo-physical process, and some pivotal parameters associated with the efficiency of singlet fission (e.g., chemical composition and topology) in a multitude of organic materials.

Theoretical and modeling investigations of singlet fission have attracted researchers' attention in addition to experimental studies. Since the inception of simulations of time evolution of singlet fission in 2010, a multitude of computational methods for investigating electron and energy transfer processes have been applied to the exploration of singlet fission, which has sparked further experimental measurements and electronic structure calculations and helped researchers gain deep understanding of this photo-physical process. Singlet fission

dynamics have previously been explored via quantum dynamics methods which are capable of simulating exciton energy transfer (EET) processes. Generally speaking, these phenomena can be regarded as an out-of-equilibrium multilevel systems coupled to thermal baths, i.e., the environmental degrees of freedom interacting with the system. For the example of singlet fission, the bath refers to relaxation after photo-excitation resulting in the creation of two independent triplet states. In this Chapter, we would like to introduce some quantum dynamics methods which can be used to model dynamic processes in singlet fission, and then to compare these methods.

### 2.1. Wave function approach

The wave function approach is the first method we will explore for theoretical investigation and modeling of singlet fission. This approach solves the time-dependent Schrödinger equation numerically via a series of approximations, e.g., the multiconfigurational time-dependent Hartree (MCTDH) method [137], the density matrix renormalization group (DMRG) method [138], or path-integral techniques [139-143].

The MCTDH method refers to the propagation of the wave packet of the nuclei on one or more electronic states with explicit (discretized) bath modes, which are limited to a small number of degrees of freedom. By taking into account the the propagation of selected vibrational modes on the PESs of the lowest electronic states of the system, this treatment can be successfully applied to the investigation of singlet fission [144,145]. With the combination of the MCTDH method, DFT geometry optimization and frequency analysis, and multireference second-order perturbation theory calculations, Tamura and collaborators [146] solved the problem of singlet fission dynamics in TIPS-pentacene and rubrene. These calculations can not only be applied to the dimer model, but also to up to three chromophores from the crystal structure. In addition, the authors reached the conclusion that TIPS-pentacene-based singlet fission takes place through an avoided crossing and that resonances between the  $S_1$  state and the  $^1TT$  state are mediated by intramolecular vibrations, and that vibronic

coherence is transferred through the mixings with CT states (i.e., super-exchange). On the other hand, rubrene-based thermally-activated singlet fission occurs near a conical intersection controlled by the strength of two-electron coupling (without super-exchange). Another example of the wave function approach is a combination of the MCTDH method and time-resolved photo-emission and transient absorption spectroscopies showing the coexistence of the quantum coherent and incoherent mechanisms for the formation of the triplet-pair state in crystalline hexacene [147].

The dynamics of open quantum systems can be solved from the standpoint of a stochastic process in Hilbert space. Within this framework, stochastic Schrödinger equations (SSE) have been derived to describe time evolution in quantum mechanics. A particular case of SSE is the time-dependent wavepacket diffusion (TDWPD) method [148,149], which is a stochastic method where the effect of electron-phonon interactions is incorporated as random fluctuations in site energies and electronic couplings between sites, obtained from spectral density functions. The TDWPD method can be used to simulate the singlet fission dynamics in organic aggregates within the framework of 1-dimensional models [150] and to investigate the effects of exciton migration through the aggregates. Results from such simulations indicate that the rates of singlet fission increase with the length of aggregation, even though singlet fission kinetics experiences a downward trend due to the electronic couplings between  $^1TT$  states [151]. These results also stress the significance of CT mediated mechanisms.

## 2.2. Generalized quantum master equation approach

Methods that calculate the degrees of freedom associated with the environment quantum dynamically are based on different approximations to the Liouville-von Neumann quantum master equation, i.e.,

$$\frac{d\rho(t)}{dt} = -\frac{i}{\hbar} [H, \rho(t)] \quad (2.1)$$



where  $\rho(t)$  is the total time-dependent density matrix and  $H$  is the system-bath Hamiltonian. Exact solutions to Eq. (2.1) can be used to describe the time evolution of the electronic section of the system via reduced density matrices (RDMs), e.g., the Nakajima-Zwanzig equation [152,153] or the hierarchical equations of motion (HEOM) [154,155]. Exact solutions to Eq. (2.1) are very computationally expensive, and different kinds of approximations are needed. Approximations to Eq. (2.1) are perturbative in nature. On the one hand, some methods (NIBA-like approaches) deal with the coupling between electronic and bath degrees of freedom in an accurate way, whereas electronic couplings are regarded as a perturbation. On the other hand, in Redfield theories and related methods, electronic couplings are treated accurately, and the system-bath couplings are considered as a perturbation.

Generally speaking, methods related to the Liouville-von Neumann quantum master equation can either take non-equilibrium phonons (non-Markovian dynamics) into consideration or assert that the bath modes remain in equilibrium (Markov approximation) [156,157]. Generally, Markovian dynamics are accurate if the time scale of the investigated process is longer than the relaxation time of the bath. On the other hand, the system dynamics may be impacted by the memory effects if the time scale of the system dynamics is comparable to that of the bath. If this is the case, non-Markovian dynamics should be applied.

The combination of dynamic models and the quantum master equation has generated numerous results concerning the investigation of singlet fission, which reinforces some conclusions reached from previous theoretical calculations, but also sheds new light on the investigation of singlet fission mechanisms. These methods have been applied to explore many different parameter regimes related to the energies and interstate couplings between  $S_1$ ,  $^1TT$ , and  $CT$  states to explore exciton dynamics in specific systems and other aspects of singlet fission. Therefore, these methods allow researchers to extract and highlight the approximations introduced by the quantum dynamics models (e.g., three vs. five state models, Markovian vs. non-Markovian approaches, etc.).

The singlet fission dynamics in molecular coupled pairs were explored through a density matrix theory in the limit of fast coherent transfer [116], and a similar approach was employed to explore the singlet fission coherent dynamics in crystal tetracene [158]. The study in Ref. [116] confirmed the hypothesis that the energetics of electronic states exerts greater influence on the singlet fission efficiencies than the electronic couplings, in turn justifying the idea that molecular chromophores with optimal singlet-triplet energetics are good candidates for singlet fission materials. These authors conclude that high singlet fission yields can be achieved for small free-energy differences between the single exciton  $S_1$  and the  $^1TT$  state within the coherent regime. It is also crucial for the formation of the triplet-pair that the CT state is not too high-energy with respect to  $S_1$  and  $^1TT$ . In a later study, the  $S_1/{}^1TT$  near-degeneracy rule was reinforced by Teichen and Eaves [117], based on results from a method similar to NIBA that accurately treated the bath to propagate the reduced density matrix of a three state model coupled to environment vibrations. These results provided some evidence that low-frequency solvent modes exert great influence on the singlet fission yields by either facilitating or hindering the formation of the  $^1TT$  state.

As a result of the magnitude of the electronic couplings with respect to the reorganization energies in typical singlet fission systems, the appropriateness of NIBA-like methods for investigating singlet fission has been questioned by researchers [159]. Furthermore, treating the electronic degrees of freedom perturbatively seems insufficient, as doing so fails to appropriately describe CT-mediated singlet fission path. In order to overcome these challenges, a quantum dynamics model based on the Redfield approximation to the Liouville-von Neumann expression was proposed to explore the exciton dynamics in dimers, clusters, and molecular crystals in a series of papers dedicated to singlet fission [118,160]. The validity of this model was tested against the Hierarchical Equation of Motion, or HEOM, an exact method for calculating the excited-state dynamics of open quantum systems, and used to explore memory effects by comparing the results of Markovian (time-local) and non-Markovian forms of the model. The role of CT states in singlet fission in pentacene dimers (in terms of

the superexchange concept in the diabatic realm) has been investigated via Redfield theory when it comes to the study of singlet fission, providing insight into the way that singlet fission is mediated by high energy CT states [118]. In a later study on the singlet fission dynamics of pentacene dimers, the authors reached the conclusion that the combination of CT states with the  $S_1$  and  $^1TT$  states is robust to the fluctuations to the energy of CT states [160]. In addition, the Redfield model can be extended by considering multi-phonon relaxation processes in order to investigate singlet fission in crystalline hexacene in combination with transient absorption measurements [161].

With the exception of the extension of Redfield theory mentioned above, Redfield theory can also be expressed in the Markovian form to explore the role of CT and quantum interference in molecular dimers and aggregates [162], with previous results showing how different electronic couplings depend on displacements along the stacking disposition of molecular dimers of PDI, pentacene, and 1,3-diphenylisobenzofuran and how the singlet fission dynamics change in response to promote the fission of  $^1TT$  state. In addition, the role of intra-molecular and inter-molecular vibrations in the singlet fission dynamics of PDI crystals was investigated with a non-Markovian quantum jump technique within Redfield theory [163].

### 2.3. Quantum-classical nonadiabatic dynamics

Singlet fission is a process involved in excited energy transfer, the dynamics of which can be investigated through mixed quantum-classical approaches [164-166], in which electrons are regarded as quantum mechanical particles and the fluctuations of the atomistic structure are dealt with classically. The trajectory-based solutions of the nuclear dynamics based on different can be coupled to electronic structure calculations beyond the limit of the atomic motions of a rather small number of relevant degrees of freedom. Furthermore, quantum-classical hybrid approaches are able to treat fast bath dynamics and describe the system dynamics atomistically. Most of these investigations rely on the idea of trajectories hopping

between different electronic potential energy surfaces [167-174] and are based on the original trajectory surface hopping (TSH) method [175,176]. Singlet fission has been investigated with the combination of nonadiabatic quantum molecular dynamics (NAQMD) and kinetic Monte Carlo (KMC) simulations [177,178] to confirm experimental results [134].

## 2.4. Quasi-classical dynamics

Non-adiabatic dynamics can be approximated by using quasi-classical (QC) models in conjunction with classical molecular dynamics simulations. Several versions of QC models originated from the initial quasi-classical model have emerged, the most standard of which applies window functions to recover quantum state information from classical models [179]. One of the QC methods is the symmetrical quasi-classical (SQC) nonadiabatic molecular dynamics method, which is used to explore singlet fission in a general sense [180,181]. The SQC method has been used to determine the impact of electronic energies, electronic couplings, and electronic-phonon interactions, as well as bath modeling in singlet fission [181], showing the pivotal role of reorganization energy and supporting the conclusion that while singlet fission dynamics do not depend on temperature for high-energy photons, the dynamics stemming from low-frequency photons still depend on temperature.

## 2.5. Hierarchy of pure states (HOPS) method

We have shown several different classes of methods used to tackle the problem of singlet fission above. However, these methods, aiming for the investigation of excited-state processes such as singlet fission, tackle the problem from the perspective of perturbation to some extent. Therefore, they are not guaranteed to obtain accurate results. In order to investigate singlet fission with high accuracy and without relying on perturbation approximations, a group of researchers have developed the hierarchy of pure states (HOPS) method to investigate the non-Markovian dynamics of excited-state processes such as singlet fission. This method solves the dynamics of a system linearly coupled to a bath of harmonic oscillators, with the

Hamiltonian of the system expressed as follows,

$$H_{tot} = H + H_B + H_{int} \quad (2.2)$$

where  $H$  is the system Hamiltonian and  $H_B$  and  $H_{int}$  are the bath Hamiltonian and the interaction Hamiltonian, respectively. The expressions of  $H_B$  and  $H_{int}$  are as follows,

$$H_B = \sum_{\lambda} \omega_{\lambda} a_{\lambda}^{\dagger} a_{\lambda} \quad (2.3)$$

$$H_{int} = \sum_{\lambda} (g_{\lambda}^* L \otimes a_{\lambda}^{\dagger} + g_{\lambda} L^{\dagger} \otimes a_{\lambda}). \quad (2.4)$$

Here,  $L$  is a system-bath coupling operator in the Hilbert space of the system.  $a_{\lambda}^{\dagger}$  and  $a_{\lambda}$  are the creation and annihilation operators of bath mode  $\lambda$ . The strength of interaction between the system and the bath mode  $\lambda$  is described by the complex-value parameter  $g_{\lambda}$ . In many important cases,  $L = L^{\dagger}$ . The frequency depends on the strength of interaction in the form of  $J(\omega) = \sum_j |g_j|^2 \delta(\omega - \omega_j)$ , which is related to the bath-correlation function  $\alpha(\tau)$  by the following equation [178],

$$\alpha(\tau) = \int_0^{\infty} J(\omega) [\coth(\frac{\omega}{2T}) \cos(\omega\tau) - i \sin(\omega\tau)] d\omega \quad (2.5)$$

where  $T$  is the temperature and  $\alpha(-\tau) = \alpha^*(\tau)$ .

By using the method in Ref. [182], the authors have derived the following equation, which is the basis of the hierarchy of pure states (HOPS) method,

$$\frac{\partial \psi_t^{(k)}}{\partial t} = (-iH - kw + Lz_t^*) \psi_t^{(k)} + k\alpha(0) L \psi_t^{(k-1)} - L^{\dagger} \psi_t^{(k+1)} \quad (2.6)$$

with  $\psi_{(t=0)}^{(0)} = \psi_0$  and  $\psi_{(t=0)}^{(k)} = 0$  for  $k > 0$ .

Eq. (2.6) consists of the auxiliary pure state  $\psi_t^{(1)}$  with the following form

$$\psi_t^{(1)} = \int_0^t \alpha(t-s) \frac{\delta \psi_t}{\delta z_s^*} ds \quad (2.7)$$

According to Ref. [174], Eq. (2.7) can be written as  $\psi_t^{(1)} = D_t \psi_t$ , where the expression of  $D_t$  is

$$D_t = \int_0^t \alpha(t-s) \frac{\delta}{\delta z_s^*} ds \quad (2.8)$$

Furthermore, one can obtain the derivatives of Eq. (2.7) and Eq. (2.8) as follows

$$\begin{aligned} \dot{\psi}_t^{(1)} &= \frac{\partial(D_t \psi_t)}{\partial t} = \dot{D}_t \psi_t + D_t \dot{\psi}_t \\ \dot{D}_t \psi_t &= \int_0^t \alpha(t-s) \frac{\delta \dot{\psi}_t}{\delta z_s^*} ds \end{aligned} \quad (2.9)$$

Similarly, we have  $\psi_t^{(k)} = D_t^k \psi_t$ . In addition,  $\alpha(\tau)$  is the bath-correlation function of the following form,

$$\alpha(\tau) = g e^{-w\tau} (\tau \geq 0); \alpha(\tau) = \alpha^*(-\tau) (\tau < 0) \quad (2.10)$$

where  $w = \gamma + i\Omega$ .

As Eq. (2.6) can be used to solve the singlet fission problem associated with the infinite system, researchers need to transform this equation into a practical form for the investigation of finite systems. One of the methods in this respect can be shown as follows based on Ref. [182].

The total Hamiltonian for singlet fission materials takes the same form as Eq. (2.2). The system Hamiltonian  $H$ , the bath Hamiltonian  $H_B$ , and the interaction Hamiltonian  $H_{int}$

take the following forms [183],

$$\begin{aligned}
H &= E_g |g\rangle\langle g| + \sum_{n=1}^N E_n |n\rangle\langle n| + \sum_{n=1}^N \sum_{m \neq n}^N V_{nm} |n\rangle\langle m| \\
H_B &= \sum_{n=1}^N \sum_q \hbar \omega_{nq} b_{nq}^\dagger b_{nq} \\
H_{int} &= - \sum_{n=1}^N L_n \sum_q g_{nq} (b_{nq}^\dagger + b_{nq})
\end{aligned} \tag{2.11}$$

In Eq. (2.11), the system Hamiltonian  $H$  consists of a shared ground electronic state, electronic excited states with vertical excitation energy ( $E_n$ ), and an electronic coupling between pigments  $V_{nm}$ . The electronic states of each pigment are linearly coupled to an independent harmonic reservoir  $H_B$  through the interaction Hamiltonian  $H_{int}$  with a system-bath coupling operator  $L_n = |n\rangle\langle n|$ . The following bath-correlation function is used to describe the effects of the vibrational modes on the dynamics of the electronic system,

$$\alpha_n(\tau) = \int_0^\infty J_n(\omega) [\coth(\frac{\beta \hbar \omega}{2}) \cos(\omega \tau) - i \sin(\omega \tau)] d\omega \tag{2.12}$$

which includes the following spectral density  $J_n(\omega)$  and the inverse temperature  $\beta$ ,

$$\begin{aligned}
J_n(\omega) &= \sum_q |g_{nq}|^2 \delta(\omega - \omega_{nq}) \\
\beta &= \frac{1}{k_B T}
\end{aligned} \tag{2.13}$$

In addition, the bath-correlation function, Eq. (2.12), can also be decomposed into a sum of exponentials with a series of indexes  $j_n$  as follows,

$$\alpha_n(t) = \sum_{j_n} g_{j_n} e^{-\gamma_{j_n} t / \hbar} \tag{2.14}$$

where  $g_{j_n}$  and  $\gamma_{j_n}$  are complex valued in general.

## CHAPTER 3

### The results derived from the HOPS method

In this Chapter, we will present some results of simulations of singlet fission with the HOPS method. At first, we will use the HOPS method to reproduce the previous results generated from the Hierarchical Equations of Motion (HEOM) method [159] to confirm the applicability of the HOPS method. After that, we will discuss some the simulation of systems with differing system-environment coupling structures with the application of the HOPS method.

#### 3.1. The reproduction of HEOM results with the HOPS method

To begin with, we consider simulations of a two-state system in the realm of singlet fission [159] with different methods: the HEOM method and the HOPS method. HEOM is a method developed to investigate describe the time evolution of the density matrix  $\rho(t)$  of an open quantum system. This method is a non-perturbative and non-Markovian approach used to investigate the propagation of a quantum state over time. However, the computational cost of this method is prohibitive in large systems [184]. Thus, one may use the HOPS method to investigate this problem with reduced computational cost. This system possesses two electronic states: the photo-excited initial singlet state  $S_1$  and the multi-exciton state  $TT$ . This system can be described by the following total Hamiltonian,

$$H_{total} = H_{el} + H_{el-ph} + H_{ph} \quad (3.1)$$



where  $H_{el}$ ,  $H_{el-ph}$ , and  $H_{ph}$  are electronic Hamiltonian, the system–bath interaction Hamiltonian, and the bath Hamiltonian, respectively. Their expressions are as follows,

$$\begin{aligned}
H_{el} &= \sum_{i=S_1, TT} |i\rangle E_i \langle i| + \sum_{i=S_1, TT} |i\rangle V_{ij} \langle j| \\
H_{el-ph} &= \sum_{i=S_1, TT} \sum_{i=k, i} |i\rangle c_{k,i} \hat{q}_{k,i} \langle i| \\
H_{ph} &= \sum_{i=k} \left[ \frac{\hat{p}_k^2}{2} + \frac{1}{2} \omega_k^2 \hat{q}_k^2 \right]
\end{aligned} \tag{3.2}$$

In Eq. (3.2),  $i$  and  $j$  are the indexes of diabatic electronic basis states, and the  $k$  indexes are the inter-molecular and intra-molecular (ground-state) normal modes of the system. The system-bath coupling is a linear, diagonal coupling to uncorrelated bath degrees of freedom. The baths are described by identical Ohmic spectral densities with a Lorentzian cutoff, giving rise to an over-damped oscillator model  $J_{ii}(\omega) = 2\lambda\Omega\omega/(\omega^2 + \Omega^2)$ .

The parameters of the two-state singlet fission system are as follows. The energy gap between the two states is  $E_{S_1} - E_{TT} = 75$  meV. The bath cutoff frequency  $\hbar\Omega$  and the temperature  $T$  are  $\hbar\Omega = 150$  meV and  $T = 300$  K ( $k_B T \approx 26$  meV), respectively. The electronic coupling is fixed at  $V = 50$  meV. The reorganization energy  $\lambda$  varies, with values 25 meV, 50 meV, 100 meV and 200 meV in the simulations shown in Figure 3.1. In Ref. [159], the authors used the HEOM method to investigate the singlet fission of the two-state system and then compared the results derived from the HEOM method with the ones derived from the time-local (TL) Redfield equation, the secular and Markovian (SM) Redfield equation, and the non-interacting blip approximation.

The HEOM method is not appropriate to tackle the singlet fission systems with the size greater than a two-state system due to the increase of computational complexity [181]. In order to simulate singlet fission systems with great accuracy, we can apply the HOPS method, which was proposed in Ref. [183], to singlet fission. With the same Hamiltonian described

above, we have used the following parameter values, i.e., the number of trajectories used in the HOPS simulation  $N_{traj} = 1000$ , the timestep  $dt = 0.01\text{fs}$ , the number of Matubara modes  $N_m = 1000$ , and the depth of hierarchy  $D_h = 4$ . In addition, the system–bath coupling operators used in the simulations are  $\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$  and  $\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$ . With these parameters, we can reproduce the results in Fig. 1 of Ref. [159] via the HOPS method, as shown in Figure 3.1.

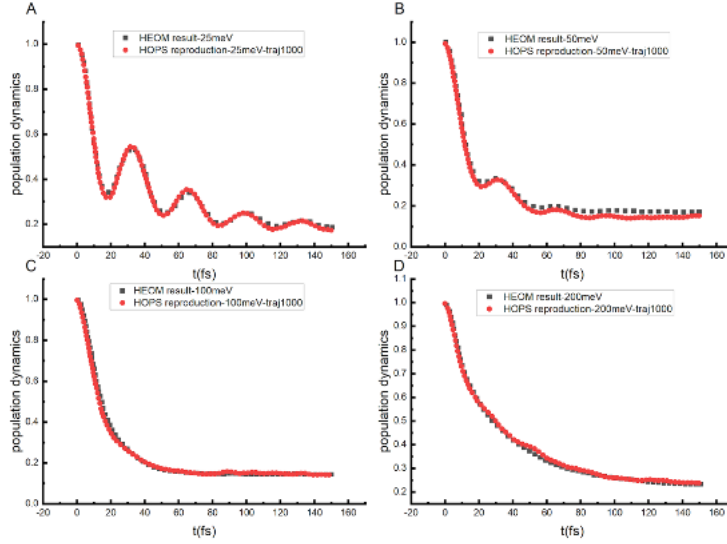


Figure 3.1: The reproduction via HOPS of the singlet fission results derived from the HEOM method in Ref. [155]. In this series of simulations, the number of trajectories is 1000, the depth of hierarchy is 4, and the reorganization energy is 25 meV, 50 meV, 100 meV, and 200 meV

### 3.2. The investigation of the connection between singlet and triplet states

After the reproduction of singlet fission results from Ref. [159], we can continue to investigate the connection between the singlet excited states and the triplet-triplet states via the charge transfer states that mix these electronic configurations. Our investigation in this part is based on Ref. [188]. This paper assumes that each electronic state is coupled to an independent vibrational environment. As an extension of the results in this paper, we will investigate the connection between the singlet excited states and triplet excited states

with the assumption that the vibrations of the charge states could be correlated with the ones of the triplet excited states because both types of states reside on the same molecule as the singlet excited states. In order to understand the role of bath correlation, we need to investigate the two extreme cases, that is, the case in which all types of states interact with completely independent environment and the case in which they interact with perfectly correlated environments, respectively. It is important to note that neither of the two extreme cases are likely to be a good representation of the physics of realistic materials. Therefore, we need to consider the use of partially correlated environments. These environments can be represented by independent, correlated and partially correlated system–bath coupling operators, respectively. In this part, we will discuss the two extreme cases as follows. The Hamiltonian of the system-bath model can be represented as follows,

$$H = H_{el} + H_{el-ph} + H_{ph} \quad (3.3)$$

The electronic part of the Hamiltonian  $H_e$  includes the energies of the diabatic states and the electronic couplings between them, which can be shown as follows,

$$H_{el} = \sum_i |i\rangle E \langle i| + \sum_{i \neq j} |i\rangle V_{ij} \langle j| \quad (3.4)$$

As for the current system-bath model, we consider the five diabatic states  $|i\rangle$ , which consist of singlet FE states  $|S_1 S_0\rangle$  and  $|S_0 S_1\rangle$ , CT states  $|CA\rangle$  and  $|AC\rangle$ , and triplet-triplet pair state  $|TT\rangle$ . With these diabatic states, the electronic Hamiltonian  $H_e$  can be expressed

as the following matrix form, i.e.,

$$\begin{bmatrix} E_{S_1S_0} & 0 & t_{LL} & -t_{HH} & 0 \\ 0 & E_{S_0S_1} & -t_{HH} & t_{LL} & 0 \\ t_{LL} & -t_{HH} & E_{CA} & 0 & \sqrt{\frac{3}{2}}t_{LH} \\ -t_{HH} & t_{LL} & 0 & E_{AC} & \sqrt{\frac{3}{2}}t_{HL} \\ 0 & 0 & \sqrt{\frac{3}{2}}t_{LH} & \sqrt{\frac{3}{2}}t_{HL} & E_{TT} \end{bmatrix} \quad (3.5)$$

Here, the electronic couplings between different states are described by one-electron integrals based on the HOMO-LUMO active space formalism,  $V_{CA,S_1S_0} = \langle CA|\hat{H}_e|S_0S_1\rangle = t_{LL}$ ,  $V_{AC,S_1S_0} = \langle AC|\hat{H}_e|S_0S_1\rangle = -t_{HH}$ ,  $V_{CA,TT} = \langle CA|\hat{H}_e|TT\rangle = \sqrt{\frac{3}{2}}t_{LH}$ , and  $V_{AC,TT} = \langle AC|\hat{H}_e|TT\rangle = \sqrt{\frac{3}{2}}t_{HL}$  [151]. These one-electron integrals describe the couplings between LUMO or HOMO on individual pentacene molecules [155]. In particular, the direct coupling between singlet and triplet state  $\langle S_1S_0|\hat{H}_e|TT\rangle$ , which is related to two-electron integrals, is assumed to be zero in this model. To be exact, we use the following Hamiltonian in our simulation, i.e.,

$$\begin{bmatrix} 250 & 0 & 116 & 145 & 0 \\ 0 & 250 & 145 & 116 & 0 \\ 116 & 145 & 500 & 0 & -152 \\ 145 & 116 & 0 & 500 & 133 \\ 0 & 0 & -152 & 133 & 0 \end{bmatrix} \quad (3.6)$$

with units of meV.

As the first step, we would like to show the population dynamics associated with the case that singlet excited states, charge transfer states and triplet states are coupled to independent vibrational environment, to test the influence of purely independent vibrational environments. When it comes to the case associated with independent vibrational environments, the characteristic frequency  $\Omega = 72\text{meV}$ , the depth of hierarchy  $D_h = 4$ , and the timestep

$dt = 0.01\text{fs}$ . The system-bath coupling operators are

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}, \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix},$$

$$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}, \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix}, \text{ and } \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}.$$

As for the case associated with the perfectly correlated vibrational environment, the characteristic frequency  $\Omega = 72\text{meV}$ , the depth of hierarchy  $D_h = 4$ , and the timestep  $dt = 0.01\text{fs}$ . The system-bath coupling op-

erators are

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}, \text{ and } \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}.$$

bath coupling operators, as well as the system Hamiltonian shown Eq. (36) and Eq. (37), we used HOPS to generate the simulation results presented in Figures 3.2 and 3.3.

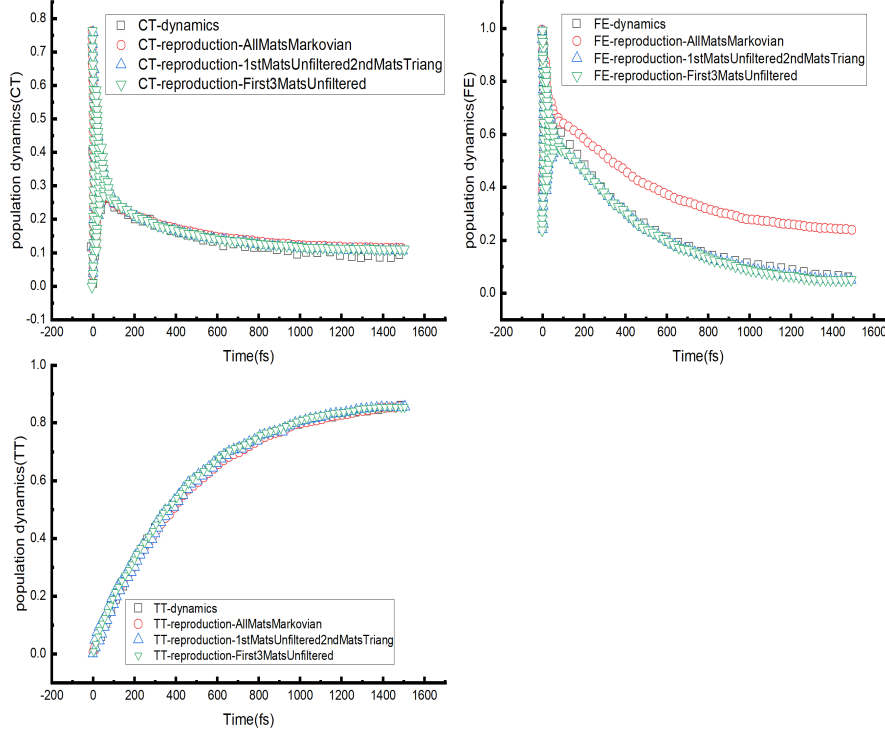


Figure 3.2: The reproduction of Fig. 2A in Ref. [186] with the HOPS method with the characteristic frequency  $\Omega = 72\text{meV}$ , the depth of hierarchy  $D_h = 4$ , the timestep  $dt = 0.01\text{fs}$ , and the above five independent system-bath coupling operators representing independent vibrational environments. In these simulations, we consider the comparisons between the original paper results with the simulation results generated from different conditions.

In the above simulations, we truncate the Matsubara terms in the hierarchy with various filters to ensure convergence. From these simulation results, one can see that the population dynamics generated from the condition that the singlet state, the charge transfer states and the triplet states are coupled to perfectly correlated vibrational environment (2 perfectly correlated system-bath coupling operators) reaches equilibration much faster (from approximately 200 fs) than the dynamics generated from the condition that the singlet state, the

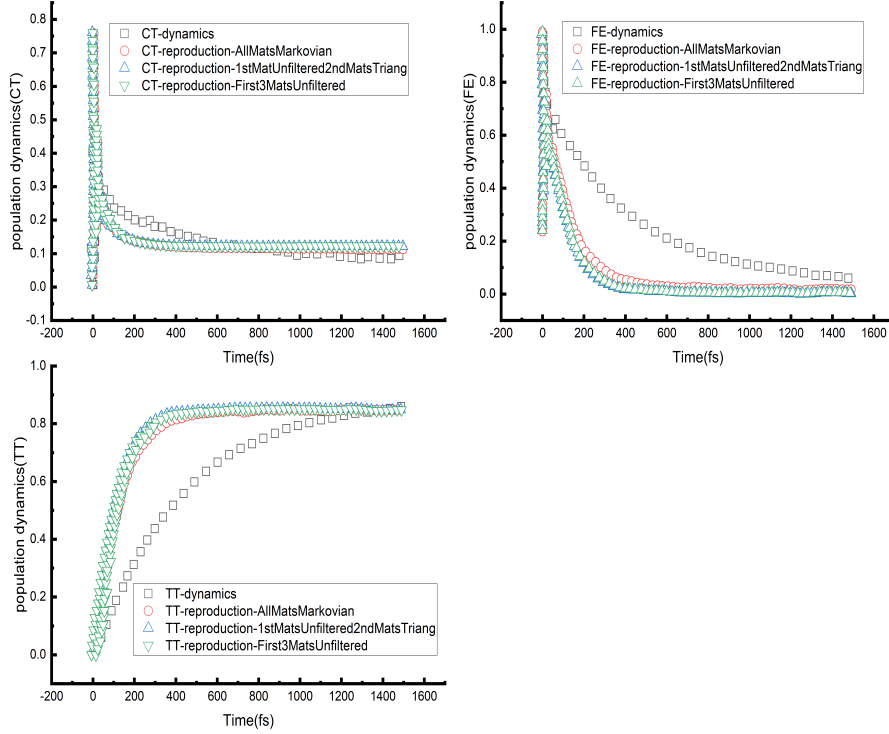


Figure 3.3: The reproduction of Fig. 2B in Ref. [186] with the HOPS method with the characteristic frequency  $\Omega = 72\text{meV}$ , the depth of hierarchy  $D_h = 4$ , the timestep  $dt = 0.01\text{fs}$ , and the above two perfectly correlated system-bath coupling operators representing correlated vibrational environments of various electronic states. In these simulations, we consider the comparisons between the original paper results with the simulation results generated from different conditions.

charge transfer states and the triplet states are coupled to independent vibrational environment (5 independent system-bath coupling operators).



## CHAPTER 4

### Discussions on the population dynamics simulations based on HOPS method

#### 4.1. Existing problems associated with the above results

Even if the conclusion can be reached that the population dynamics generated from the condition that the singlet state, the charge transfer states and the triplet states are coupled to perfectly correlated vibrational environment (2 perfectly correlated system–bath coupling operators) equilibrate much faster (by approximately 200 fs) than the dynamics generated from the condition that the singlet state, the charge transfer states and the triplet states are coupled to independent vibrational environment (5 independent system–bath coupling operators), one can see that the simulation results based on the perfectly correlated vibrational environment still deviate conspicuously from the previous paper’s results [182]. In addition, the population dynamics simulations associated with the electronic states based on independent vibrational environment also deviate from the previous paper’s results [182]. From these results, one can conclude that the two extreme cases are not appropriate to describe population dynamics of our system-bath model, and one needs to consider the partial correlation between the electronic states and the environment associated with the model in order to tackle singlet fission in our system-bath model. In order to carry out further simulations on the population dynamics of this system-bath model, one needs to use the Hamiltonian described in Eq. (3.3), Eq. (3.4) and Eq. (3.5), and the following system-bath coupling operators associated with the partial vibrational environment, which are denoted as  $L_{A,pv}$ ,

$L_{B,pv}$ ,  $L_{A,pmixed}$ , and  $L_{B,pmixed}$ , respectively, in the following forms

$$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (4.1)$$

$$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (4.2)$$

$$\begin{bmatrix} f_{FE} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & f_{CS} & 0 & 0 \\ 0 & 0 & 0 & -f_{CS} & 0 \\ 0 & 0 & 0 & 0 & f_{TT} \end{bmatrix} \quad (4.3)$$

$$\begin{bmatrix}
0 & 0 & 0 & 0 & 0 \\
0 & f_{FE} & 0 & 0 & 0 \\
0 & 0 & -f_{CS} & 0 & 0 \\
0 & 0 & 0 & f_{CS} & 0 \\
0 & 0 & 0 & 0 & f_{TT}
\end{bmatrix} \tag{4.4}$$

In Eq. (4.3) and Eq. (4.4),  $f_{FE}$ ,  $f_{CS}$ , and  $f_{TT}$  are characteristic frequencies associated with the singlet excited state, charge transfer states, and triplet excited states. Here, we have assumed that

$$f_{CS} > f_{FE} > f_{TT}. \tag{4.5}$$

We assume that

$$\begin{aligned}
f_{CS} &= 1 \\
f_{FE} &= \lambda_{FE}/\lambda_{CS}^{mixed} \approx 0.1 \\
f_{TT} &= \lambda_{TT}/\lambda_{CS}^{mixed} \approx 0.05
\end{aligned} \tag{4.6}$$

One can see that Eq. (4.5) and Eq. (4.6) are assumptions based on Ref. [186], and we have not obtained the real values of these characteristic frequencies from previous literature to the best of our knowledge. However, these assumed values can be considered as the first series of parameter values for initial simulations.

## CHAPTER 5

### Conclusion

The present thesis has investigated singlet fission, a photo-physical process which converts a high-energy singlet state into two low-energy excited triplet states, in a general sense from the perspective of the HOPS method, rather than from the perspective of methods consisting of perturbation, such as the wave-function method and different Redfield equation approaches [185]. The HOPS method is a numerically exact method which has great potential for tackling the dynamics of open quantum systems. Therefore, we will discuss some possible problems for future investigations. For example, in order to carry out the simulation of spectroscopy of molecular aggregates with strong and structured coupling of electronic excitation to vibrational degrees of freedom, the HOPS method has been applied to provide a formally exact solution to this problem based on local stochastic trajectories. Normalized trajectories are needed to simulate the absorption spectra of large molecular aggregates by means of localization of the HOPS method [187]. By extending the HOPS method to the adaptive HOPS (adHOPS) method and further to dyadic adaptive HOPS (DadHOPS), the HOPS method can be used to investigate the linear absorption spectra of mesoscale molecular aggregates [179]. Therefore, by extending exact simulations of singlet fission to larger systems, adHOPS will allow for a more thorough understanding of this fascinating phenomenon.

#### 5.1. Future research

Singlet fission has been investigated with a multitude of methods as described in the above Chapters, including the HOPS method, which has been shown above. Singlet fission can be investigated on several different scales. In addition to the investigation of singlet fission in a

general sense, singlet fission can also be investigated on the dimer and crystal scales [188,189]. In these papers, singlet fission is investigated with perturbative methods. The HOPS method will be applied to investigate singlet fission on the dimer and crystal scales in future, which will provide an opportunity for researchers to explore the discrepancies originating from the use of different methods. In particular, the computational cost can be greatly reduced and the speed of numerical calculations increased for singlet fission for combined excitonic and vibrational systems [190] with the application of the HOPS method. The HOPS method could also be a powerful tool for the exploration of singlet fission in large systems in the condensed phase environment [191] and organic crystals [192].

In addition to the investigation of singlet fission, the investigation of triplet fusion is another direction of the application of the HOPS method. Singlet fission and triplet fusion are reversed processes. Triplet fusion, which refers to the process that converts low-energy triplet excited states into a high-energy singlet excited state, has attracted far less attention from researchers than singlet fission. One study published in 2021 [193] investigated the process of triplet fusion or triplet-triplet annihilation up-conversion by exploring the spin statistical factor  $\eta$ , which is the probability that a singlet excited state is formed from a pair of annihilating triplet excited states from the perspective of rate equations, which is also a perturbative method. As triplet-triplet annihilation up-conversion was explored from the perspective of rate equations (a perturbation method), exact solutions to this problem have not yet been obtained. As the HOPS method is a numerically exact method, numerically exact solutions to the problem of triplet fusion based on the Hamiltonian in this paper may be explored and obtained. Therefore, comparative studies can be made between the results derived from perturbation-based methods and the ones derived from the HOPS method in the future.

## BIBLIOGRAPHY

- [1] S. Singh et al., *Laser generation of excitons and fluorescence in anthracene crystals*, *J. Chem. Phys.* **42** (1965) 330–342.
- [2] M. B. Smith and J. Michl, *Singlet fission*, *Chem. Rev.* **110** (2010) 6891–6936.
- [3] M. B. Smith and J. Michl, *Recent advances in singlet fission*, *Annu. Rev. Phys. Chem.* **64** (2013) 361–386.
- [4] S. Singh and B. P. Stoicheff, *Double-photon excitation of fluorescence in anthracene single crystals*, *J. Chem. Phys.* **38** (1963) 2032–2033.
- [5] C. E. Swenberg and W. T. Stacy, *Bimolecular radiationless transitions in crystalline tetracene*, *Chem. Phys. Lett* **2** (1968) 327–328.
- [6] A. A. Kazzaz; and A. B. Zahlan, *Temperature dependence of crystalline tetracene fluorescence*, *Chem. Phys. Lett* **48** (1968) 1242–1245.
- [7] N. Geacintov et al., *Effect of magnetic field on the fluorescence of tetracene crystals: Exciton fission*, *Phys. Rev. Lett.* **22** (1969) 593–596.
- [8] R. E. Merrifield et al., *Fission of singlet excitons into pairs of triplet excitons in tetracene crystals*, *Chem. Phys. Lett* **2** (1969) 386–388.
- [9] R. C. Johnson and R. E. Merrifield, *Effects of magnetic fields on the mutual annihilation of triplet excitons in anthracene crystals*, *Phys. Rev. B* **1** (1970) 896–902.
- [10] R. E. Merrifield, *Theory of magnetic field effects on the mutual annihilation of triplet excitons*, *J. Chem. Phys.* **48** (1968) 4318–4319.
- [11] A. Suna, *Kinematics of exciton-exciton annihilation in molecular crystals*, *Phys. Rev. B* **1** (1970) 1716–1739.
- [12] H. Rademaker et al., *Carotenoid triplet yields in normal and deuterated rhodospirillum rubrum*, *Biochim. Biophys. Acta, Bioenerg.* **592** (1980) 240–257.
- [13] R. H. Austin et al., *Magnetic field effects on triplet exciton fission and fusion in a polydiacetylene*, *J. Chem. Phys.* **90** (1989) 6642–6646.
- [14] M. Wohlgenannt et al., *Singlet fission in luminescent and nonluminescent pi-conjugated polymers*, *Synth. Met.* **101** (1999) 297–298.

- [15] M. C. Hanna and A. J. Nozik, *Solar conversion efficiency of photovoltaic and photoelectrolysis cells with carrier multiplication absorbers*, *J. Appl. Phys.* **100** (2006) 074510.
- [16] W. Shockley and H. J. Queisser, *Detailed balance limit of efficiency of p-n junction solar cells*, *J. Appl. Phys.* **32** (1961) 510–519.
- [17] J. B. Birks, *Photophysics of aromatic molecules*, *Wiley Interscience* (1970) .
- [18] V. Ern et al., *Effects of exciton interactions on the fluorescence yield of crystalline tetracene*, *Chem. Phys. Lett* **10** (1971) 287–290.
- [19] S. Arnold et al., *Triplet exciton caging in two dimensions*, *J. Chem. Phys.* **64** (1976) 5104–5114.
- [20] G. Klein, *Kinematics of triplet pairs in anthracene and tetracene crystals*, *Chem. Phys. Lett* **57** (1978) 202–206.
- [21] S. Arnold and W. B. Whitten, *Temperature dependence of the triplet exciton yield in fission and fusion in tetracene*, *J. Chem. Phys.* **75** (1981) 1166–1169.
- [22] A. M. Müller et al., *Evidence for exciton fission and fusion in a covalently linked tetracene dimer*, *Chem. Phys. Lett* **421** (2006) 518–522.
- [23] A. M. Müller et al., *Exciton fission and fusion in bis(tetracene) molecules with different covalent linker structures*, *J. Am. Chem. Soc.* **129** (2007) 14240–14250.
- [24] S. Khan and S. Mazumdar, *Theory of transient excited state absorptions in solid pentacene with implications for singlet fission*, *J. Phys. Chem. Lett.* **8** (2017) 5943–5948.
- [25] P. Würfel and U. Würfel, *Physics of solar cells: From basic principles to advanced concepts*, *3rd ed.; Wiley-VCH: Weinheim, Germany* (2016) .
- [26] J. Lee et al., *Singlet exciton fission photovoltaics*, *Acc. Chem. Res.* **46** (2013) 1300–1311.
- [27] D. N. Congreve et al., *Quantum efficiency above 100% in a singlet-exciton-fission-based organic photovoltaic cell*, *Science* **340** (2013) 334.
- [28] N. J. Thompson et al., *Slow light enhanced singlet exciton fission solar cells with a 126% yield of electrons per photon*, *Appl. Phys. Lett.* **103** (2013) 263302.
- [29] A. Rao et al., *Exciton fission and charge generation via triplet excitons in pentacene/c60 bilayers*, *J. Am. Chem. Soc.* **132** (2010) 12698–12703.
- [30] B. Ehrler et al., *Hybrid pentacene/a-silicon solar cells utilizing multiple carrier generation via singlet exciton fission*, *Appl. Phys. Lett.* **101** (2012) 153507.
- [31] S. Lee et al., *Electron transfer from triplet state of tips-pentacene generated by singlet fission processes to ch<sub>3</sub>nh<sub>3</sub>pbi<sub>3</sub> perovskite*, *J. Phys. Chem. Lett.* **8** (2017) 884–888.
- [32] B. O'Regan and M. Gratzel, *A low-cost, high-efficiency solar cell based on dye-sensitized colloidal tio<sub>2</sub> films*, *Nature* **353** (1991) 737–740.
- [33] I. Paci et al., *Singlet fission for dye-sensitized solar cells: Can a suitable sensitizer be found?*, *J. Am. Chem. Soc.* **128** (2006) 16546–16553.

- [34] A. J. Nozik et al., *Semiconductor quantum dots and quantum dot arrays and applications of multiple exciton generation to third-generation photovoltaic solar cells.*, *Chem. Rev.* **110** (2010) 6873–6890.
- [35] D. L. Dexter, *Possibility of luminescent quantum yields greater than unity*, *Phys. Rev.* **108** (1957) 630–633.
- [36] R. T. Wegh et al., *Visible quantum cutting in “ligdf4:eu3+” through downconversion*, *Science* **283** (1999) 663.
- [37] Q. Y. Zhang and X. Y. Huang, *Recent progress in quantum cutting phosphors*, *Prog. Mater. Sci.* **55** (2010) 353–427.
- [38] V. I. Klimov, *Mechanisms for photogeneration and recombination of multiexcitons in semiconductor nanocrystals: Implications for lasing and solar energy conversion*, *J. Phys. Chem. B* **110** (2006) 16827–16845.
- [39] D. Casanova, *Theoretical modeling of singlet fission*, *Chem. Rev.* **118** (2018) 7164–7207.
- [40] H. E. Zimmerman and G. E. Keck, *Photochemical rearrangement without light. 95. dioxetane effected photochemistry by direct intramolecular excitation*, *J. Am. Chem. Soc.* **97** (1975) 3527–3528.
- [41] D. L. Dexter, *A theory of sensitized luminescence in solids*, *J. Chem. Phys.* **21** (1953) 836–850.
- [42] G. D. Scholes, *Correlated pair states formed by singlet fission and exciton-exciton annihilation*, *J. Phys. Chem. A* **119** (2015) 12699–12705.
- [43] R. D. Pensack et al., *Observation of two triplet-pair intermediates in singlet exciton fission*, *J. Phys. Chem. A* **7** (2016) 2370–2375.
- [44] J. M. Lupton et al., *Coherent spin manipulation in molecular semiconductors: Getting a handle on organic spintronics*, *ChemPhysChem* **11** (2010) 3040–3058.
- [45] J. J. Burdett and C. J. Bardeen, *Quantum beats in crystalline tetracene delayed fluorescence due to triplet pair coherences produced by direct singlet fission*, *J. Am. Chem. Soc.* **134** (2012) 8597–8607.
- [46] J. Michl et al., *Toward singlet fission for excitonic solar cells*, *Proc. SPIE* **6656** (2007) 66560E.
- [47] J. W. Verhoeven, *Glossary of terms used in photochemistry (iupac recommendations 1996)*, *Pure Appl. Chem.* **68** (1996) 2223.
- [48] M. Klessinger, *Conical intersections and the mechanism of singlet photoreactions*, *Angew. Chem., Int. Ed. Engl.* **34** (1995) 549–551.
- [49] D. R. Yarkony, *Diabolical conical intersections*, *Rev. Mod. Phys.* **68** (1996) 985–1013.
- [50] D. R. Yarkony, *Conical intersections: Diabolical and often misunderstood*, *Acc. Chem. Res.* **31** (1998) 511–518.
- [51] M. Garavelli et al., *The c5h6nh2+ protonated Schiff base: An ab initio minimal model for retinal photoisomerization*, *J. Am. Chem. Soc.* **119** (1997) 6891–6901.



- [52] B. G. Levine and T. J. Martínez, *Isomerization through conical intersections*, *Annu. Rev. Phys. Chem.* **58** (2007) 613–634.
- [53] S. Gozem et al., *Electron correlation effects on the ground state potential energy surface of a retinal chromophore model*, *J. Chem. Theory Comput.* **8** (2012) 4069–4080.
- [54] S. Gozem et al., *Conical intersection and potential energy surface features of a model retinal chromophore: Comparison of eom-cc and multireference methods*, *J. Chem. Theory Comput.* **9** (2013) 284–292.
- [55] A. K. Le et al., *Slow singlet fission observed in a polycrystalline perylenediimide thin film*, *J. Phys. Chem. Lett.* **7** (2016) 4922–4928.
- [56] E. Busby et al., *Fast singlet exciton decay in pushpull molecules containing oxidized thiophenes*, *J. Phys. Chem. B* **119** (2015) 7644–7650.
- [57] J. Mack and G. P. Miller, *Synthesis and characterization of a c60–pentacene monoadduct*, *Fullerene Sci. Technol.* **5** (1997) 607–614.
- [58] Y. Cao et al., *Why bistetracenes are much less reactive than pentacenes in dielsalder reactions with fullerenes*, *J. Am. Chem. Soc.* **136** (2014) 10743–10751.
- [59] S. R. Yost et al., *A transferable model for singlet–fission kinetics*, *Nat. Chem.* **6** (2014) 492–497.
- [60] D. Meng et al., *High–performance solution–processed non–fullerene organic solar cells based on selenophene–containing perylene bisimide acceptor*, *J. Am. Chem. Soc.* **138** (2016) 375–380.
- [61] Y. Zhong et al., *Molecular helices as electron acceptors in high–performance bulk hetero–junction solar cells*, *Nat. Commun.* **6** (2015) 8242.
- [62] Y. Zhong et al., *Efficient organic solar cells with helical perylene diimide electron acceptors*, *J. Am. Chem. Soc.* **136** (2014) 15215–15221.
- [63] Y. Lin et al., *An electron acceptor challenging fullerenes for efficient polymer solar cells*, *Adv. Mater.* **27** (2015) 1170–1174.
- [64] Y. Liu et al., *Tetraphenylethylene core–based 3d structure small molecular acceptor enabling efficient non–fullerene organic solar cells*, *Adv. Mater.* **27** (2015) 1015–1020.
- [65] D. Sun et al., *Non–fullerene–acceptor–based bulk–heterojunction organic solar cells with efficiency over 7%*, *J. Am. Chem. Soc.* **137** (2015) 11156–11162.
- [66] B. J. Walker et al., *Singlet exciton fission in solution*, *Nat. Chem.* **5** (2013) 1019–1024.
- [67] M. Kasha, *Characterization of electronic transitions in complex molecules*, *Discuss. Faraday Soc.* **9** (1950) 14–19.
- [68] L. Ma et al., *Two–photon–induced singlet fission in rubrene single crystal*, *J. Chem. Phys.* **138** (2013) 184508.
- [69] A. J. Musser et al., *Activated singlet exciton fission in a semiconducting polymer*, *J. Am. Chem. Soc.* **135** (2013) 12747–12754.

- [70] N. Monahan and X. Y. Zhu, *Charge transfer-mediated singlet fission*, *Annu. Rev. Phys. Chem.* **66** (2015) 601–618.
- [71] G. D. Scholes, *Insights into excitons confined to nanoscale systems: Electron-hole interaction, binding energy, and photo-dissociation*, *ACS Nano* **2** (2008) 523–537.
- [72] C. J. Bardeen, *The structure and dynamics of molecular excitons*, *Annu. Rev. Phys. Chem.* **65** (2014) 127–148.
- [73] G. D. Scholes and G. Rumbles, *Excitons in nanoscale systems*, *Nat. Mater.* **5** (2006) 683–696.
- [74] L. Hedin, *New method for calculating the one-particle green’s function with application to the electron-gas problem*, *Phys. Rev.* **139** (1965) A796–A823.
- [75] G. Strinati et al., *Dynamical correlation effects on the quasiparticle bloch states of a covalent crystal*, *Phys. Rev. Lett.* **45** (1980) 290–294.
- [76] G. Strinati et al., *Dynamical aspects of correlation corrections in a covalent crystal*, *Phys. Rev. B: Condens. Matter Mater. Phys.* **25** (1982) 2867–2888.
- [77] M. S. Hybertsen and S. G. Louie, *Electron correlation in semiconductors and insulators: Band gaps and quasiparticle energies*, *Phys. Rev. B: Condens. Matter Mater. Phys.* **34** (1986) 5390–5413.
- [78] G. Strinati, *Effects of dynamical screening on resonances at inner-shell thresholds in semiconductors*, *Phys. Rev. B: Condens. Matter Mater. Phys.* **29** (1984) 5718–5726.
- [79] G. Onida et al., *Ab initio calculations of the quasiparticle and absorption spectra of clusters: The sodium tetramer*, *Phys. Rev. Lett.* **75** (1995) 818–821.
- [80] M. Rohlfing and S. G. Louie, *Electron-hole excitations in semiconductors and insulators*, *Phys. Rev. Lett.* **81** (1998) 2312–2315.
- [81] M. Rohlfing and S. G. Louie, *Electron-hole excitations and optical spectra from first principles*, *Phys. Rev. B: Condens. Matter Mater. Phys.* **62** (2000) 4927–4944.
- [82] G. Onida et al., *Electronic excitations: Density-functional versus many-body green’s-function approaches*, *Rev. Mod. Phys.* **74** (2002) 601–659.
- [83] S.-H. Lim et al., *Exciton delocalization and superradiance in tetracene thin films and nanoaggregates*, *Phys. Rev. Lett.* **92** (2004) 107402.
- [84] R. D. Pensack et al., *Exciton delocalization drives rapid singlet fission in nanoparticles of acene derivatives*, *J. Am. Chem. Soc.* **137** (2015) 6790–6803.
- [85] A. J. Musser et al., *Evidence for conical intersection dynamics mediating ultrafast singlet exciton fission*, *Nat. Phys.* **11** (2015) 352–357.
- [86] R. L. Martin, *Natural transition orbitals*, *J. Chem. Phys.* **118** (2003) 4775–4777.
- [87] A. Szabo and N. S. Ostlund, *Modern quantum chemistry: Introduction to advanced electronic structure theory*, *Dover Publications* (1989) .

- [88] M. C. Beard, *Multiple exciton generation in semiconductor quantum dots*, *J. Phys. Chem. Lett.* **2** (2011) 1282–1288.
- [89] M. C. Beard et al., *Third generation photovoltaics based on multiple exciton generation in quantum confined semiconductors*, *Acc. Chem. Res.* **46** (2013) 1252–1260.
- [90] H. M. Jaeger et al., *Exciton multiplication from first principles*, *Acc. Chem. Res.* **46** (2013) 1280–1289.
- [91] P. Cudazzo et al., *Exciton dispersion in molecular solids*, *J. Phys.: Condens. Matter* **27** (2015) 113204.
- [92] H. Suzuki, *Electronic absorption spectra and geometry of organic molecules*, *Academic Press: New York* (1967) .
- [93] S. W. Eaton et al., *Singlet exciton fission in polycrystalline thin films of a slip-stacked perylenediimide*, *J. Am. Chem. Soc.* **135** (2013) 14701–14712.
- [94] D. W. Small and M. Head-Gordon, *Post-modern valence bond theory for strongly correlated electron spins*, *Phys. Chem. Chem. Phys.* **13** (2011) 19285–19297.
- [95] W.-L. Chan et al., *Observing the multiexciton state in singlet fission and ensuing ultrafast multielectron transfer*, *Science* **334** (2011) 1541.
- [96] H. L. Stern et al., *Identification of a triplet pair intermediate in singlet exciton fission in solution*, *Proc. Natl. Acad. Sci. U. S. A.* **112** (2015) 7656–7661.
- [97] G. B. Piland et al., *Singlet fission: From coherences to kinetics*, *J. Phys. Chem. Lett.* **5** (2014) 2312–2319.
- [98] A. B. Kolomeisky et al., *A simple kinetic model for singlet fission: A role of electronic and entropic contributions to macroscopic rates*, *J. Phys. Chem. C* **118** (2014) 5188–5195.
- [99] J. N. Schrauben et al., *Excitation localization/delocalization isomerism in a strongly coupled covalent dimer of 1,3-diphenylisobenzofuran*, *J. Phys. Chem. A* **120** (2016) 3473–3483.
- [100] A. Bencini and D. Gatteschi, *Electron paramagnetic resonance of exchange coupled systems*, *Springer-Verlag* (1990) .
- [101] H. Benk and H. Sixl, *Theory of two coupled triplet states*, *Mol. Phys.* **42** (1981) 779–801.
- [102] L. R. Weiss and other others, *Strongly exchange-coupled triplet pairs in an organic semi-conductor*, *Nat. Phys.* **13** (2017) 176.
- [103] M. J. Y. Tayebjee and other others, *Quintet multiexciton dynamics in singlet fission*, *Nat. Phys.* **13** (2017) 182–188.
- [104] B. S. Basel and other others, *Unified model for singlet fission within a non-conjugated covalent pentacene dimer*, *Nat. Commun.* **8** (2017) 15171.
- [105] A. Troisi and G. Orlandi, *Charge-transport regime of crystalline organic semiconductors: Diffusion limited by thermal off-diagonal electronic disorder*, *Phys. Rev. Lett.* **96** (2006) 086601.

- [106] P. Siegbahn et al., *A comparison of the super-ci and the newton-raphson scheme in the complete active space scf method*, *Phys. Scr.* **21** (1980) 323.
- [107] B. O. Roos et al., *A complete active space scf method (casscf) using a density matrix formulated super-ci approach*, *Chem. Phys.* **48** (1980) 157–173.
- [108] P. E. M. Siegbahn et al., *The complete active space scf (casscf) method in a newton-raphson formulation with application to the hno molecule*, *J. Chem. Phys.* **74** (1981) 2384–2396.
- [109] K. Hirao, *Multireference mller-plesset perturbation treatment of potential energy curve of n<sub>2</sub>*, *Int. J. Quantum Chem.* **44** (1992) 517–526.
- [110] K. Hirao, *Multireference mller-plesset method*, *Chem. Phys. Lett.* **190** (1992) 374–380.
- [111] K. Hirao, *Multireference mller-plesset perturbation theory for high-spin open-shell systems*, *Chem. Phys. Lett.* **196** (1992) 397–403.
- [112] M. Casanova, D.; Head-Gordon, *Restricted active space spin-flip configuration interaction approach: Theory, implementation and examples*, *Phys. Chem. Chem. Phys.* **11** (2009) 9779–9790.
- [113] N. J. Mayhall, *From model hamiltonians to ab initio hamiltonians and back again: Using single excitation quantum chemistry methods to find multiexciton states in singlet fission materials*, *J. Chem. Theory Comput.* **12** (2016) 4263–4273.
- [114] A. V. Luzanov and V. F. Pedash, *Interpretation of excited states using charge-transfer numbers*, *Theor. Exp. Chem.* **15** (1980) 338–341.
- [115] T. S. Kuhlman et al., *Interpretation of the ultrafast photoinduced processes in pentacene thin films*, *J. Am. Chem. Soc.* **132** (2010) 3431–3439.
- [116] E. C. Greyson et al., *Maximizing singlet fission in organic dimers: Theoretical investigation of triplet yield in the regime of localized excitation and fast coherent electron transfer*, *J. Phys. Chem. B* **114** (2010) 14168–14177.
- [117] P. E. Teichen and J. D. Eaves, *A microscopic model of singlet fission*, *J. Phys. Chem. B* **116** (2012) 11473–11481.
- [118] T. C. Berkelbach et al., *Microscopic theory of singlet exciton fission. ii. application to pentacene dimers and the role of superexchange*, *J. Chem. Phys.* **138** (2013) 114103.
- [119] D. Beljonne et al., *Charge-transfer excitations steer the davydov splitting and mediate singlet exciton fission in pentacene*, *Phys. Rev. Lett.* **110** (2013) 226402.
- [120] P. B. Coto et al., *Low-lying electronic excited states of pentacene oligomers: A comparative electronic structure study in the context of singlet fission*, *Phys. Rev. Lett.* **11** (2015) 147–156.
- [121] P. Cudazzo et al., *Exciton dispersion in molecular solids*, *J. Phys.: Condens. Matter* **27** (2015) 113204.
- [122] T. Zeng et al., *The low-lying electronic states of pentacene and their roles in singlet fission*, *J. Am. Chem. Soc.* **136** (2014) 5755–5764.

- [123] E. G. Fuemmeler et al., *A direct mechanism of ultrafast intramolecular singlet fission in pentacene dimers*, *ACS Cent. Sci.* **2** (2016) 316–324.
- [124] Q. Wu and T. Van-Voorhis, *Direct optimization method to study constrained systems within density–functional theory*, *Phys. Rev. A: At., Mol., Opt. Phys.* **72** (2005) 024502.
- [125] D. Casanova, *Bright fission: Singlet fission into a pair of emitting states*, *J. Chem. Theory Comput.* **11** (2015) 2642–2650.
- [126] V. Laszlo and T. Kowalczyk, *Acene–linked covalent organic frameworks as candidate materials for singlet fission*, *J. Mater. Chem. A* **4** (2016) 10500–10507.
- [127] D. H. P. Turban et al., *Supercell convergence of charge-transfer energies in pentacene molecular crystals from constrained dft*, *Phys. Rev. B: Condens. Matter Mater. Phys* **93** (2016) 165102.
- [128] M. Chabr et al., *Quantum beats of prompt fluorescence in tetracene crystals*, *Chem. Phys.* **57** (1981) 425–430.
- [129] J. Fuenfschilling et al., *Quantum beats in the fluorescence decay of tetracene crystals*, *Helv. Phys. Acta* **58** (1985) 347–354.
- [130] J. C. Johnson et al., *The role of chromophore coupling in singlet fission*, *Acc. Chem. Res.* **46** (2013) 1290–1299.
- [131] J. J. Burdett et al., *Excited state dynamics in solid and monomeric tetracene: The roles of superradiance and exciton fission*, *J. Chem. Phys.* **133** (2010) 144506.
- [132] E. M. Grumstrup et al., *Enhanced triplet formation in polycrystalline tetracene films by femtosecond optical-pulse shaping*, *Phys. Rev. Lett.* **105** (2010) 257403.
- [133] C. Wang et al., *Triplet excitons of carotenoids formed by singlet fission in a membrane*, *ChemPhysChem* **12** (2011) 2891–2894.
- [134] S. T. Roberts et al., *Efficient singlet fission discovered in a disordered acene film*, *J. Am. Chem. Soc.* **134** (2012) 6388–6400.
- [135] C. Ramanan et al., *Competition between singlet fission and charge separation in solution–processed blend films of 6,13–bis–(triisopropylsilylethynyl)pentacene with sterically–encumbered perylene–3,4:9,10–bis(dicarboximide)s*, *J. Am. Chem. Soc.* **134** (2012) 386–397.
- [136] W.-L. Chan et al., *The energy barrier in singlet fission can be overcome through coherent coupling and entropic gain*, *Nat. Chem.* **4** (2012) 840–845.
- [137] H. D. Meyer et al., *The multiconfigurational time–dependent hartree approach*, *Chem. Phys. Lett.* **165** (1990) 73–78.
- [138] A. E. Feiguin and S. R. White, *Time–step targeting methods for real–time dynamics using the density matrix renormalization group*, *Phys. Rev. B: Condens. Matter Mater. Phys.* **72** (2005) 020404.
- [139] R. P. Feynman and A. R. Hibbs, *Quantum mechanics and path integrals*, *McGraw–Hill* (1965) .



- [140] C. H. Mak and D. Chandler, *Solving the sign problem in quantum monte carlo dynamics*, *Phys. Rev. A: At., Mol., Opt. Phys.* **41** (1990) 5709–5712.
- [141] N. Makri, *Improved feynman propagators on a grid and non-adiabatic corrections within the path integral framework*, *Chem. Phys. Lett.* **193** (1992) 435–445.
- [142] D. E. Makarov and N. Makri, *Path integrals for dissipative systems by tensor multiplication. condensed phase quantum dynamics for arbitrarily long time*, *Chem. Phys. Lett.* **221** (1994) 482–491.
- [143] R. Egger et al., *Rate concept and retarded master equations for dissipative tight-binding models*, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **50** (1994) R655–R658.
- [144] J. Zheng et al., *Ultrafast nonadiabatic dynamics of singlet fission: Quantum dynamics with the multilayer multiconfigurational time-dependent hartree (ml-mctdh) method*, *J. Phys. Chem. C* **120** (2016) 1375–1389.
- [145] T. Zeng, *Through-linker intramolecular singlet fission: General mechanism and designing small chromophores*, *J. Phys. Chem. Lett.* **7** (2016) 4405–4412.
- [146] H. Tamura et al., *First-principles quantum dynamics of singlet fission: Coherent versus thermally activated mechanisms governed by molecular pi stacking*, *Phys. Rev. Lett.* **115** (2015) 107401.
- [147] N. R. Monahan et al., *Dynamics of the triplet-pair state reveals the likely coexistence of coherent and incoherent singlet fission in crystalline hexacene*, *Nat. Chem.* **9** (2017) 341–346.
- [148] X. Zhong and Y. Zhao, *Charge carrier dynamics in phonon-induced fluctuation systems from time-dependent wavepacket diffusion approach*, *J. Chem. Phys.* **135** (2011) 134110.
- [149] X. Zhong and Y. Zhao, *Non-markovian stochastic schrödinger equation at finite temperatures for charge carrier dynamics in organic crystals*, *J. Chem. Phys.* **138** (2013) 034111.
- [150] H. Zang et al., *Effects of charge transfer state and exciton migration on singlet fission dynamics in organic aggregates*, *J. Phys. Chem. C* **120** (2016) 13351–13359.
- [151] S. Nakajima, *On quantum theory of transport phenomenon-asteady diffusion*, *Prog. Theor. Phys.* **20** (1958) 948–959.
- [152] R. Zwanzig, *Approximate eigenfunctions of the liouville operator in classical many-body systems*, *Phys. Rev.* **144** (1966) 170–177.
- [153] Y. Tanimura and R. Kubo, *Time evolution of a quantum system in contact with a nearly gaussian-markoffian noise bath*, *J. Phys. Soc. Jpn.* **58** (1989) 101–114.
- [154] H. Zang et al., *Effects of charge transfer state and exciton migration on singlet fission dynamics in organic aggregates*, *J. Phys. Chem. C* **120** (2016) 13351–13359.
- [155] A. Ishizaki and G. R. Fleming, *Unified treatment of quantum coherent and incoherent hopping dynamics in electronic energy transfer: Reduced hierarchy equation approach*, *J. Chem. Phys.* **130** (2009) 234111.

- [156] C. H. Fleming and B. L. Hu, *Non-markovian dynamics of open quantum systems: Stochastic equations and their perturbative solutions*, *Ann. Phys.* **327** (2012) 1238–1276.
- [157] H.-P. Breuer et al., *Non-markovian dynamics in open quantum systems*, *Rev. Mod. Phys.* **88** (2016) 021002.
- [158] W.-L. Chan et al., *The energy barrier in singlet fission can be overcome through coherent coupling and entropic gain*, *Nat. Chem.* **4** (2012) 840–845.
- [159] T. C. Berkelbach et al., *Microscopic theory of singlet exciton fission. i. general formulation*, *J. Chem. Phys.* **138** (2013) 114102.
- [160] Y. Fujihashi and A. Ishizaki, *Fluctuations in electronic energy affecting singlet fission dynamics and mixing with charge-transfer state: Quantum dynamics study*, *J. Phys. Chem. Lett.* **7** (2016) 363–369.
- [161] E. Usby et al., *Multiphonon relaxation slows singlet fission in crystalline hexacene*, *J. Am. Chem. Soc.* **136** (2014) 10654–10660.
- [162] F. Mirjani et al., *Theoretical investigation of singlet fission in molecular dimers: The role of charge transfer states and quantum interference*, *J. Phys. Chem. C* **118** (2014) 14192–14199.
- [163] N. Renaud and F. C. Grozema, *Intermolecular vibrational modes speed up singlet fission in perylenediimide crystals*, *J. Phys. Chem. Lett.* **6** (2015) 360–365.
- [164] K. Drukker, *Basics of surface hopping in mixed quantum/classical simulations*, *J. Comput. Phys.* **153** (1999) 225–272.
- [165] I. Tavernelli, *Nonadiabatic molecular dynamics simulations: Synergies between theory and experiments*, *Acc. Chem. Res.* **48** (2015) 792–800.
- [166] L. Wang et al., *Time-domain ab initio modeling of photoinduced dynamics at nanoscale interfaces*, *Annu. Rev. Phys. Chem.* **66** (2015) 549–579.
- [167] J.-Y. Fang and S. Hammes-Schiffer, *Improvement of the internal consistency in trajectory surface hopping*, *J. Phys. Chem. A* **103** (1999) 9399–9407.
- [168] C. F. Craig et al., *Trajectory surface hopping in the time-dependent kohn-sham approach for electron-nuclear dynamics*, *Phys. Rev. Lett.* **95** (2005) 163001.
- [169] E. Tapavicza et al., *Trajectory surface hopping within linear response time-dependent density-functional theory*, *Phys. Rev. Lett.* **98** (2007) 023001.
- [170] B. F. E. Curchod et al., *Trajectory-based nonadiabatic dynamics with time-dependent density functional theory*, *ChemPhysChem* **14** (2013) 1314–1340.
- [171] L. Wang and O. V. Prezhdo, *A simple solution to the trivial crossing problem in surface hopping*, *J. Phys. Chem. Lett.* **5** (2014) 713–719.
- [172] L. Wang et al., *Global flux surface hopping approach for mixed quantum-classical dynamics*, *J. Chem. Theory Comput.* **10** (2014) 3598–3605.

- [173] M. Persico and G. Granucci, *An overview of nonadiabatic dynamics simulations methods, with focus on the direct approach versus the fitting of potential energy surfaces*, *Theor. Chem. Acc.* **133** (2014) 1526.
- [174] A. Jain et al., *An efficient, augmented surface hopping algorithm that includes decoherence for use in large-scale simulations*, *J. Chem. Theory Comput.* **12** (2016) 5256–5268.
- [175] J. C. Tully, *Molecular dynamics with electronic transitions*, *J. Chem. Phys.* **93** (1990) 1061–1071.
- [176] D. S. Sholl and J. C. Tully, *A generalized surface hopping method*, *J. Chem. Phys.* **109** (1998) 7702–7710.
- [177] R. Kapral, *Progress in the theory of mixed quantum–classical dynamics*, *Annu. Rev. Phys. Chem.* **57** (2006) 129–157.
- [178] K. A. Fichthorn and W. H. Weinberg, *Theoretical foundations of dynamical monte carlo simulations*, *J. Chem. Phys.* **95** (1991) 1090–1096.
- [179] L. Bonnet and J. C. Rayez, *Quasiclassical trajectory method for molecular scattering processes: Necessity of a weighted binning approach*, *Chem. Phys. Lett.* **277** (1997) 183–190.
- [180] G. Tao, *Electronically nonadiabatic dynamics in singlet fission: A quasi–classical trajectory simulation*, *J. Phys. Chem. C* **118** (2014) 17299–17305.
- [181] G. Tao, *Understanding electronically non–adiabatic relaxation dynamics in singlet fission*, *J. Chem. Theory Comput.* **11** (2015) 28–36.
- [182] D. Suess et al., *Hierarchy of stochastic pure states for open quantum system dynamics*, *Phys. Rev. Lett.* **113** (2014) 150403.
- [183] T. Gera et al., *Simulating optical linear absorption for mesoscale molecular aggregates: an adaptive hierarchy of pure states approach*, *J. Chem. Phys.* **158** (2023) 174103.
- [184] M. Noack et al., *A portable and scalable solver-framework for the hierarchical equations of motion*, *IEEE International Parallel and Distributed Processing Symposium Workshops (IPDPSW)* **17974931** (2018) 17974931.
- [185] Y. Tanimura, *Numerically “exact” approach to open quantum dynamics: The hierarchical equations of motion (heom)*, *J. Chem. Phys.* **153** (2020) 020901.
- [186] M. Castellanos and P. Huo, *Enhancing singlet–fission dynamics by suppressing destructive interference between charge–transfer pathways*, *J. Phys. Chem. Lett.* **8** (2017) 2480–2488.
- [187] L. Varvelo et al., *Formally exact simulations of mesoscale exciton diffusion in a photosynthetic aggregate*, *J. Phys. Chem. Lett.* **14** (2023) 3077–3083.
- [188] T. C. Berkelbach et al., *Microscopic theory of singlet exciton fission. ii. application to pentacene dimers and the role of superexchange*, *J. Chem. Phys.* **138** (2013) 114103.
- [189] T. C. Berkelbach et al., *Microscopic theory of singlet exciton fission. iii. crystalline pentacene*, *J. Chem. Phys.* **141** (2014) 074705.



- [190] S. Mardazad et al., *Quantum dynamics simulation of intramolecular singlet fission in covalently linked tetracene dimer*, *J. Chem. Phys.* **155** (2021) 194101.
- [191] Y. Xu et al., *Hierarchical mapping for efficient simulation of strong system-environment interactions*, *J. Chem. Theory Comput.* **19** (2023) 426–435.
- [192] S. Ito et al., *Molecular design for efficient singlet fission*, *J. Photo. Photo. C: Photo. Rev* **34** (2018) 85–120.
- [193] D. G. Bossanyi et al., *Spin statistics for triplet—triplet annihilation upconversion: Exchange coupling, intermolecular orientation, and reverse intersystem crossing.*, *JACS Au* **1** (2021) 2188—2201.