Theoretical investigation of optical and transport properties of organic semiconductors

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**THEORETICAL INVESTIGATION OF
OPTICAL AND TRANSPORT PROPERTIES OF
ORGANIC SEMICONDUCTORS**

YE JUN

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2012

**THEORETICAL INVESTIGATION OF
OPTICAL AND TRANSPORT PROPERTIES OF
ORGANIC SEMICONDUCTORS**

YE JUN

School of Materials Science and Engineering

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in partial fulfillment of the requirement for the degree of
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Dedicated to my families and the memories of my grandfather Ye Lifan...

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List of Abbreviations

TFT	Thin Film Transistor
LED(s)	Light Emitting Diode(s)
OLED(s)	Organic Light Emitting Diode(s)
EL	Electroluminescence
OTFT(s)	Organic Thin Film Transistor(s)
TTF-TCNQ	Tetrathiafulvalene-Tetracyanoquinodimethane
NDIs	Naphthalene Diimide(s)
PDI	Perylene Diimide(s)
FET	Field Effect Transistor
HPC	High Performance Computing
AM1	Austin Model 1
DFT	Density Functional Theory
B3LYP	Becke, three-parameter, Lee-Yang-Parr hybrid functional
LDA	Local Density Approximation
IMDHO	Independent Mode Displaced-Harmonic Oscillator Model
TD-DFT	Time-Dependent Density Functional Theory
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Un-occupied Molecular Orbital
INDO	Intermediate Neglect of Differential Overlap
SDCI	Singles and Doubles Configuration Interaction
LRC	Long-range-corrected
PBE	Perdue Burke Ernzerhof functional
MD	Molecular Dynamics
ED	Exact Diagonalization

QMC	Quantum Monte Carlo
DMRG	Density Matrix Renormalization Group
VED	Variational Exact Diagonalization
MBO	Multi-mode Brownian Oscillator model
IMDHO-T	Independent Mode Displaced Harmonic Oscillator Model with Temperature effect
HF-SCF	Hatree-Fock Self-Consistent Field
GGA	Grand Gradient Approximation
MNDO	Modified Neglect of Diatomic Overlap
DOS	Density of State
BO	Born-Oppenheimer
HF	Hatree-Fock
LCAO	Linear Combination of Atomic Orbitals
ZDO	Zero Differential Overlap
CNDO	Complete Neglect of Differential Overlap
ZINDO	Zerner's Intermediate Neglect of Differential Overlap
XC	Exchange-Correlation
L(S)DA	Local (Spin-) Density Approximation
ZPL	Zero Phonon Line
LO	Longitude Optical
FC	Franck-Condon
GL	Global-Local
DNP	Double Numerical plus Polarization
PDOS	Partial Density of States
TDB3LYP	Time Dependent Density Functional theory with B3LYP type of hybrid exchange-correlation functional
DIIS	Direct Inversion in the Iterative Subspace
ES	Excited State
TZVP	Triple Zeta Valence Plus Polarization
BHandHLYP	Becke-Half-and-Half- Lee-Yang-Parr hybrid functional
DHO	Displaced Harmonic Oscillator model
PL	Photoluminescence
DCPA	Dynamical Coherent Potential Approximation
DMFT	Dynamical Mean Field Theory
LH2	Light-Harvesting System II
GPU	Graphic Processing Unit

Abstract

Application of organic semiconductors in electronic devices has inspired and revived many academic and technological research fields. Academically, there are many unanswered questions. For example, understanding of two fundamental physical processes in organic semiconductors, *i.e.*, the optical and charge carrier transport processes is crucial to improve the performance of materials and devices. These two processes depend on the behavior of a quasi-particle named polaron. Polaron formation occurs in organic semiconductors in which various physical processes are determined by electrons, holes or excitons coupled diagonally or off-diagonally to phonon coordinates. In this thesis, a theoretical framework which combines molecular and crystal/aggregate structures, optical spectroscopy, and charge carrier transport has been established. By applying this theoretical framework to organic semiconductors such as rubrene, optical spectra (photoluminescence and absorption) obtained from quantum-chemical calculations and corresponding measurements can be utilized to extract important material parameters. These parameters can be subsequently fed to a microscopic polaron transport model to find intrinsic transport properties. The material parameters obtained in this work are in good agreement with many well established references. More importantly, the calculated optical and transport properties, *i.e.*, absorption spectra, photoluminescence spectra, and mobility versus temperature for molecular and single crystal rubrene agree well with the experimental results. These results reflect the success of the proposed theoretical scheme in obtaining material parameters and related properties for rubrene. Finally, future research works on improving current framework have been proposed.

Chapter 1: Introduction

1.1 Background

Organic electronic devices such as thin film transistors (TFT) [1-3] and light emitting diodes (LEDs) [4, 5] are primarily based on conjugated materials such as oligoacenes and their derivatives [6-8], oligothiophene [9], and poly(phenylenevinylene) [4]. Worldwide, organic electronics has been studied intensively for a few decades. Advantages offered by the organic semiconductors in terms of low processing temperature, flexibility and availability of low cost and large-area printing devices have stoked interests and intensive research activities in the semiconductor industry.

The discovery of halogen-doped perylene charge-transfer complexes [10] in 1954 and decades of study that followed opened the door of semiconducting organic compounds. Following this work, Weiss *et al.* [11-15] discovered the doped polymers with semiconducting properties in 1963 and 1965. Theoretical explanations came about in the works of McGinness *et al.* [16, 17] in the following years. The development of iodine-doped polyacetylene [18] in 1977 finally lead to a Nobel Prize in Chemistry in 2000.

These prototypical organic semiconductors do not belong to the general category of materials that are used in many applications of organic electronics today. The semiconducting properties of these materials are achieved only by extensive doping, otherwise intrinsic conductivities of un-doped materials are often very low owing to extremely low carrier concentration in most aromatic organic materials (usually the value

is about 1cm^{-3} compared to density of states at $\sim 10^{19}\text{cm}^{-3}$). Such a low carrier concentration in most potential organic semiconductors makes them fall into the regime of insulators. In contrast to the low carrier concentration, mobility of these organic materials can be substantial high, with values of $10^{-7}\text{cm}^2/\text{V}\cdot\text{s}$ to $10\text{cm}^2/\text{V}\cdot\text{s}$ or even higher [19, 20]. These materials are often considered for charge transport purposes, and traditional semiconducting concepts may not be appropriate in describing transport behavior.

As early as in the 1980s, the organic semiconductors were first applied to the xerography [21] field thanks to the detailed work of Martin Pope and his colleagues [22-24] on ground/excited electronic structures and charge transport properties of many acene crystals such as naphthalene and anthracene. Utilization of the photoreceptor organic materials to photocopier and laser-printer drums helped to solve the problem of generating and transporting charges. These prototype materials are usually composed of solid mixtures of molecular semiconductors and inert polymer matrices. Other early applications include organic electroluminescence [25], organic photovoltaic cells and so on, and Martin Pope and his colleagues laid the foundation of the development of this family of materials. Thanks to these pioneer work, organic light emitting diode (OLED) [26] displays based on both polymers and small acene molecules have offered a low-cost and high-performance choice, and have been deployed commercially nowadays.

Despite relatively low mobilities and intrinsic carrier densities in organic semiconductors comparing to their inorganic counterparts, these materials are still quite attractive owing to a wide range of properties such as high solubility in organic solvent and tunable color

of light emission via chemical synthesis. Therefore specific requirements raised by customers can be met by molecular designing and engineering. Another attractive factor is the processibility of these materials, as they can be easily deposited or printed onto large areas of variety of substrates at low temperatures, even onto flexible substrates such as a polymer film *etc.*, while keeping the cost of fabrication low. These attractive properties make it possible to fabricate displays containing pixelated OLEDs using these materials [27].

However, problems such as the low charge carrier mobility of the organic semiconductors at room temperature, and low stability in an environment with air, water or ultraviolet light [28] are yet to be solved. Furthermore, it is also difficult to make reliable contacts. Such drawbacks limit the application range of these materials, thus even until very recently, organic electronics devices are still far away from the replacements of their inorganic counterparts. They are more likely to be used to complement inorganic electronic devices [27]. Therefore fundamental understandings of important processes such as optical and charge carrier transport processes are still highly important and largely needed.

1.2 Literature Review

1.2.1 General Reviews of Organic Semiconductors

Work on organic semiconductors pioneered by Martin Pope and colleagues [29] has brought an immense impact on the fields of physics, chemistry, materials science, electronic engineering *etc.* The interplay between geometry and dominant electronic

structure of π electrons has opened up novel materials with almost infinite possibilities due to the variability of organic materials, which lead to enormous theoretical and experimental studies. Strong interests from both academic and industrial sectors lead to such a huge amount of publications that a thorough review is difficult to be accommodated within the scope of the current thesis. Thus, we will only focus on some well-cited and landmark works as well as some latest works of the major material of interest in this thesis, namely, rubrene [20, 30]. Rubrene is one of the organic materials with the highest hole mobility, for which exponentially growing number of publications can be found in recent years. However, relatively less theoretical works have been carried out on rubrene, mainly due to the computational difficulties involved owing to large number of atoms in a rubrene crystal unit cell, as a result, is chosen as the test bed for this thesis. The subsequent discovery of electroluminescence [31, 32] in organic molecular crystals opened the possibility of OLED. Demonstration of organic electroluminescence (EL) diodes [5, 33] and organic thin film transistors (OTFTs) [34-36] fabricated from either small molecules [2, 5] or polymers [1, 3, 4] has attracted intensive interest from industry, where possibilities of applying organics semiconductors to replace their inorganic counterparts have been initiated ever since. However, owing to high operating voltage as well as low lighting efficiency and many other deficiencies of these early materials, development of this field has suffered serious challenges.

Much needed breakthroughs in this field were provided by the discoveries of TTF-TCNQ complexes and conducting polymers in 1973 and 1977, respectively. High conductivity at room temperature with inverse temperature dependence was found in TTF-TCNQ which suggested possibility of having molecular solids consisting of carbon *etc.*, with behavior

similar to typical inorganic extended metallic materials. Soon the research efforts on this family of materials led to the discovery of their superconductivity. Naturally all other possible condensed matter phenomena (such as quantum phase transition, charge transport, spin transport, optical excitation and so on) can be established for these materials. In these materials, transport was possible due to the formation of narrow bandwidth originated from the overlapping of π -molecular orbital in an end-to-end fashion. However unfavorable nature of some of their physical properties, especially mechanical strength, chemical stability and crystal size hindered the industrial application despite the establishment of potentially ground-breaking work on transport properties.

Decades of efforts have been dedicated to the research of organic semiconducting materials, leading to significant progress in design and fabrication of devices. The impressive range of devices includes: high performance OLEDs [37, 38] that are commercially available, organic transistors [39, 40] with performance comparable to amorphous Si transistors, organic photovoltaic cells [41, 42] with efficiency as high as 5%, as well as memory devices [43].

Similar to the traditionally inorganic semiconductors, organic materials can also be categorized into n-type and p-type. In n-type materials, the charge carriers are electrons while in p-type materials, holes are the charge carriers. It is interesting to note that most of the research work to date concerns p-type materials such as some well known benchmark materials like pentacene [44], anthracene [45] and rubrene [30]. Rubrene in particular, was reported to have hole mobility as high as $43\text{cm}^2/\text{V}\cdot\text{s}$, which is known so far as one of the highest among all organic semiconductors. However n-type materials

have received much less attention owing to their lower mobility compared to the p-type ones. To date, there are only a handful of n-type organic semiconducting materials, which include well studied tris(8-hydroxyquinolino)aluminum (Alq₃) [46] in OLED applications, such as 1,1-bis(pentafluorophenyl)-2,3,4,5-tetraphenylsiloles [47], rylene diimides such as well used naphthalene diimides (NDIs) [48] and perylene diimides (PDIs) [49], acene derivatives [50] and fullerene based acceptors [51].

1.2.2 Rubrene

A comprehensive review of all the organic semiconductors is an extremely challenging task. Diversity and rapid development of this field as well as almost unlimited possibilities that reside in organic synthesis have led to an enormous number of materials. Broadly though, it is still possible to categorize these materials with respect to at least organic molecular crystals and polymers. As pointed out earlier, it is preferable to choose some of representative materials as the test beds to verify the validity of the theoretical framework in this thesis, thus only rubrene will be reviewed in detail in this section.

The high hole mobility of single crystal rubrene and extremely high photoluminescent yield have brought great interests to the research works of the organic semiconductors in recent years. When fabricated into a field effect transistor (FET) structure, it has been shown that the hole mobility in single crystalline rubrene can reach as high as 30 cm²/V·s at low temperature (~200K) [20] or even more interestingly, 20 cm²/V·s at room temperature [52]. Recent developments indicate that the maximum mobility can reach as high as 43 cm²/V·s at room temperature [53] for the charge carriers deep in the crystal. Despite the mobility anisotropy [20] in rubrene and many other materials alike, this high

value of mobility is essentially very attractive, which has exceeded some well-known inorganic semiconducting materials such as amorphous silicon.

Despite exciting findings from experiments, theoretical work on rubrene is still rare. Due to large number of atoms for a rubrene molecule (70) and rubrene crystal unit cell (980), it is hard to have a direct evaluation of its electronic structure and various properties related such as band structures and phonon dispersions. With the development of high-performance computing (HPC) techniques, a full evaluation of electronic structures of organic crystals is becoming increasingly feasible. A natural choice lies in the form of semi-empirical methods to study the properties of a molecule as big as rubrene. Austin Model 1 (AM1) [54] method has been applied to study the electronic properties of rubrene and its peroxide isomer [55], where stable endothermic non-planar structures of these molecules have been revealed. A twisted conformation of rubrene adsorbed on copper surfaces has been revealed with the DFT method at LDA level [56], where good agreement between theoretical calculation and scanning tunneling microscopy images on absorption geometry has also been obtained. Further joint experimental and theoretical (DFT at B3LYP level) investigation suggested [57] non-planar structure of rubrene in solution and thin film. Experimental spectra of rubrene in amorphous thin film and solution have been analyzed with independent mode displaced-harmonic oscillator model (IMDHO), and with results further supported by the TD-DFT (B3LYP) calculations [58], the two forms of rubrene isomers, *i.e.*, planar and twisted, were found distinctively from optical spectra.

With the aid of quantum chemical method, insightful work on the transport properties of

rubrene has been carried out by Bredas and coworkers in Ref. [59] at the level of DFT-B3LYP/6-31G(d,p). The co-facial π -interactions such as the one found along a -direction of a rubrene single crystal is found to be responsible for the effective electronic couplings, suggesting a desirable direction in increasing charge carrier mobility in organic semiconductors based on oligomers. Attempts of seeking computationally affordable methods to understand the inter- and intra-molecular charge-transfer parameters have been carried out in Ref. [60]. More importantly, the reorganization energy has been examined for a handful of well known organic semiconducting materials including rubrene in this work. This detailed investigation in comparison with multiple other methods provided a useful guide, suggesting that the hybrid DFT methods were reliable and capable of providing realistic parameters. However it was also suggested that care must be taken owing to the overestimation of HOMO-LUMO gaps and large value of reorganization energy, where the stacking of oligoacenes became important. Efforts have been made to simplify the calculation of external reorganization energy using a polarizable force field [61], where the values of energy for various polyacenes including rubrene have been tested with the methodology. Results suggested the method was robust and also revealed much smaller value of external reorganization energy compared to its internal counterpart. However it was also found that even this small energy can be effective in determining the absolute mobility through its influence on the hopping mechanism.

The UV-vis spectra and two-photon absorption cross sections as well as third-order nonlinear optical properties have been investigated using INDO/SDCI [62]. It was suggested that extension of π -conjugation critically determines the magnitude of

two-photon absorption cross section. It was also found that the existence of charge transfer from phenyl groups to the tetracene backbone had direct correspondence to the two-photon absorption. Such symmetrical charge transfer was found to effectively increase the transition dipole moments of the molecule which leads to the enhancement of two-photon absorption cross section. Using a combination of the DFT-GGA level calculations, GW-Bether-Salpeter equation and quantum Monte Carlo calculations, the optical and electronic properties of crystalline rubrene have been inspected from the many body effects point of view [63]. Results suggested that such effect dominate the optical spectrum and quasi-particle gap of the crystal. From this work, the origin of yellow-green photoluminescence in rubrene has been revealed as a result of formation of intermolecular, charge-transfer, spin-singlet excitons, in which the exchange energy plays an essential role in raising the energy of intra-molecular excitons. Time-dependent DFT (TD-DFT) method has been employed at the level of B3LYP and long-range-corrected (LRC) PBE to investigate the role of molecular aggregation in determining the temperature related optical properties that are closely related to the crystal spectra of rubrene [64]. As referred in Ref. [64], rubrene crystal was found to be composed of both H- and J aggregates, where the interactions along the *a*-axis exhibit a prominent role in determining spectral characteristics of crystalline rubrene. A very detailed joint experimental and theoretical study on dissolved rubrene molecules in analyzing their optical spectra (absorption and emission) can be found in Ref. [65]. In this study, normal coordinate analysis and frequency calculations using DFT in conjunction with the linear response TDDFT have been applied to unveil the physical origin of the excited state difference between rubrene and tetracene. Results suggested that the destabilization of HOMO of rubrene due to the

addition of phenyl groups was the key to such difference, and also that found the spectra of rubrene were strongly affected by the temperature.

A computational protocol [66] has been proposed to predict absolute charge carrier mobility using rubrene as the example material. Such protocol incorporates numerical evaluation of a model Hamiltonian describing electronic and electron-phonon couplings, where the system-dependent model parameters were obtained with a combination of classical molecular dynamics (MD) simulation and INDO/S level semi-empirical calculation. Coupling of the first-principles DFT calculations and random-walk simulations allowed evaluation of temperature-dependence of the 3D averaged hole mobility of rubrene and tetracene [67]. In this work, nuclear tunneling effects were found to be important to the understanding of charge carrier transport and the survival of the band-like behaviors for a wide range of temperature was also noted. Molecular structure, morphology, percolation network and charge carrier mobility for rubrene and three other molecules have been investigated within the framework of high-temperature non-adiabatic Marcus theory or semi-classical dynamics [68]. This systematic work suggested that the upper limit of mobilities can be reached for various molecular crystals and revealed some design rules to achieve high mobilities. It was found that the close packing and cofacially alignment are preferable to achieve high mobilities, however it was also important to introduce higher dimension transport channel other than 1D to reduce the influence of defects as demonstrated in rubrene.

Impurity effects on transport properties have been investigated using DFT at the LDA level, which helped to determine the role of both oxygen and hydrogen impurities [69].

For oxygen impurities, distinct peaks in electronic density of states were induced, and energy band gaps, shape as well as the width were therefore changed. However for hydrogen impurities, the roles were two-sided, showing the capability of forming and annihilating carrier traps due to these impurities. The following work on impurities in rubrene crystal by the same group of people also using DFT at the LDA level has revealed possibilities of modulating electronic properties of rubrene crystal using defects such as water and oxygen [70]. The water molecules were found to have easy access to the system and ketone or hydroxyl groups can induce deep impurity levels in the energy band gap of crystalline rubrene.

1.2.3 Optical Spectroscopy

The optical spectroscopy is an important method of probing the structural and dynamical processes taking place in matter interacting nonlinearly with laser fields. Other tools such as nuclear magnetic resonance, microwave, infrared, ultraviolet and X-ray spectroscopy are also important in obtaining important microscopic material information. With the continual development of optical spectroscopy, it has become possible to probe the dynamics of vibrational motions, photo-dissociation and so on for molecules in the gas phase, clusters, matrix and restricted geometries. The ability to control nonlinear optical properties is also vital in exploring new optical materials and devices. Optical spectroscopy also helps to explore the physical properties such as electron-phonon coupling, relaxation and so on for the organic semiconducting materials, providing valuable information for interpreting the charge carrier transport in these materials.

Many nonlinear optical spectroscopy [34] techniques have been developed to characterize

the rich photophysics of the semiconducting organic materials. The basis of understanding these nonlinear optical spectroscopic techniques is the formation of nonlinear response, which requires the evaluation of the density operator [35] that represents the state of matter in Liouville space [71, 72]. Some of the most representative techniques include absorption, photoluminescence, fluorescence, spontaneous-Raman, coherent-Raman, photon echoes, resonant gratings, pump-probe, hole-burning, off-resonance Raman and polarization spectroscopy.

Optical spectroscopy techniques are important for investigating the electronic states and photophysics in semiconductors with particular relevance to the organic semiconductor due to the strong anisotropy exhibited in their electronic and optical properties. The fundamental electronic properties of the organic semiconductors and the operational characteristics of optoelectronic devices are also strongly dependent on the spatial arrangements of the organic molecules, as the interactions between bulk molecules as well as those at the interfaces become crucial in determining the device performance. To date, techniques such as broadband time-domain THz spectroscopy [73], luminescence [36] and photo current spectroscopy [74] have been used in studying the rubrene single crystal. The dominant excitonic effects in the optical response [75] of the rubrene single crystal have been revealed. However, the spectral interpretations lag behind due to the complications arising from the environmental factors such as surface oxidation [76]. To have a general view on the optical processes in molecular crystals, one can also explore the conjugated polymers, since both types of materials share similar characteristics of the π -conjugation. Many theories [34] on optical processes in general and those specific to organic and inorganic materials have been developed in recent decades. Recent interest in

conjugated polymers is focused on the optical properties of the light emitting phenyl-based systems [77], in which, luminescence arises mainly due to fact that the dipole connection of the lowest-lying singlet excited states to the ground state occurs via electron-phonon interactions. Nonlinear optical devices including optical switches [33], frequency multipliers [29] and so on fabricated using conjugated polymers open other fields of potential applications. Simply classified, the linear processes provide information about the energy of dipole allowed states, while nonlinear processes are more related to the transition between dipole-forbidden states. The probing of the transition of dipole allowed states helps to understand the intrinsic electron-phonon interactions in the materials, whereas spectroscopy techniques such as transient absorption [78], ultrafast spectroscopy [79] and photoelectron spectroscopy [80] can be used to probe the charge transport processes and determine the mobility of the organic semiconducting materials.

1.2.4 Polaron Dynamics

The central point of this thesis is a quasiparticle named polaron which is formed due to the electron/hole/exciton–phonon interactions. As a starting point, it is usually preferable to use a single particle picture to study the underlying physics of systems interested. It is usually also true that the relatively low carrier density (as low as 1cm^{-3} in many organic semiconductors) allows one to deal with the essential physics of the system using one-particle picture. One of the most well known models for treating polaron problem is the Holstein molecular crystal Hamiltonian [81, 82] established in the 1950s in the seminal work by Holstein.

To treat the Holstein Hamiltonian more accurately, various numerical approaches have

been developed in the past decades, such as exact diagonalization (ED) [83], quantum Monte Carlo (QMC) method [84], trial wave function variational methods [85-92], density matrix renormalization group (DMRG) method [93, 94], and variational exact diagonalization (VED) [95, 96]. It is worth noting that most of these approaches were designated to investigate the ground and low-lying excited states properties of polaron. Despite the fact that higher excited state properties can be obtained by ED, in practice finite computer memory restricts the method to small-sized lattices (typically, below 20 sites). QMC is capable of treating large systems with hundreds of sites, but it suffers from the well-known sign problem. DMRG has been proved to be an extremely accurate method in solving for the ground and low-lying excited states properties of 1D system and the method is also capable of dealing with systems of large sizes. However, its availability for the higher excited states has not been proved to be accurate enough, and so far there is no DMRG algorithm efficient enough to tackle non-trivial problems in two or higher dimensions.

The advent of femtosecond laser spectroscopy [97, 98] made it possible to probe quasi-particle dynamics such as relaxation dynamics at the time scale equivalent to the periods of optical phonons in molecular crystals, which is close to the relaxation time scales in condensed matter. In cases such as a system with strong exciton-phonon interaction, the oscillation of coherent phonon wave packet along an adiabatic potential surface can now be observed experimentally [98]. The research of ultrafast relaxation dynamics occurring on femtosecond to picosecond time scales is a strategic domain from both fundamental and technological points of view. With the aid of ultrafast optical experiments, the detailed information on temporal evolution on femtosecond scale can be

revealed. The obtained information then provides insights into the fundamental processes governing the dynamics. State of art technologies based on ultrafast laser physics can now be successfully used for studying non-equilibrium carrier/exciton dynamics that was inaccessible by the traditional linear optical spectroscopy. However, theoretical studies of polaron dynamics have not received much attention owing to the difficulties in obtaining reliable solutions. To date, only a handful of theories have been developed to simulate the polaron dynamics, such as the time-dependent variant of DMRG, *i.e.*, t-DMRG [99], time-dependent variational methods and time-dependent versions of ED and VED. Due to the limitation of describing high-lying excited states by DMRG, t-DMRG is also not able to simulate the polaron dynamics from an arbitrary initial state accurately.

VED is a powerful approach capable to study the ground- and excited-state properties of the Holstein polaron in 1, 2 and higher dimensions[95]. For much higher excited states, VED suffers from limitation of the computational resource, and its capability has been restricted to small sized lattices. When applied to deal with the ground-state properties, its accuracy and consistency is proved, moreover, the method also provides reliable low-lying excited state for Holstein polaron. The VED method has been applied to the time-dependent case by Ku and Trugman [100, 101] to study the dynamics of Holstein polaron with single phonon mode. The electron–phonon correlation function and the spectral function have also been discussed and a qualitative relation between the polaron formation time and the electron–phonon coupling strength has been given. VED projects an initial quantum state onto a basis consisting of energy eigenstates, which provides the roots for the time evolution of system dynamics. Owing to their highly demanding computational cost, it is only preferable to use ED or VED for small systems, to serve as a

benchmark for checking other numerical approaches.

Variational method usually uses an Ansatz (or in the other word, trial wave function) with a number of variational parameters responsible for describing the system under certain circumstances (such as coherent state and wave packet *etc.*). By introducing a larger number of variational parameters, and varying them in the complex number space, an Ansatz is capable of scanning over a larger subspace of the full Hilbert space. It is also worth noting that the time-dependent variational methods are attractive in being computationally efficient compared to other methods mentioned above, in handling problems associated with polaron dynamics, the capability of treating large systems, *e.g.*, 1000 sites. Davydov soliton [102, 103] proposed in the 1970s was originally designed for explaining energy storage and transport in proteins. Kerr and Lomdahl [104] gave a comprehensive quantum-mechanical derivation for the equations of motion of the Davydov soliton. Localized Davydov Ansätze, such as D_2 and $\tilde{D}$ Ansatz, are suitable candidates to simulate the ultra-fast relaxation process of a photo-excited state in an organic molecular crystal at zero or low temperature. When one or a few molecules in the lattice are excited by an ultra-short laser pulse, an exciton can be generated in the molecules. Due to the low temperature environment, no phonon displacements are generated initially. This initial state is a localized one in real space, which can be approximated by a Davydov Ansatz. Ansätze for solving the ground polaron state variationally with sufficient accuracy have also been constructed in a way that utilize localized states (such as Davydov Ansätze) to construct translationally invariant polaron wave function [86-92]. Although they are solved numerically, the analytical expression of these Ansätze and variational scheme provide a useful platform for further studies of

dynamics of polaron. The first step of solving dynamics for polaron had traditionally been the application of Davydov Ansätze [105], however owing to the limitation of the numerical methods available then, the results were not accurate. Recently, Merrifield Ansatz [106] has been applied to solve the dynamic of polaron variationally, and interesting physics related to the dynamics evolution of variational parameters has been revealed. Observables such as linear absorption spectra have been obtained, suggesting the importance of polaron dynamics in integrating experimental results. However the applicability of the Merrifield Ansatz is restricted to the narrow-band regime when electronic coupling between neighboring molecules is sufficiently weak.

1.2.5 Theory of Polaron Transport in Organic Semiconductors

Many theories of organic molecular crystals have been established to deal with the complexity of charge transport phenomenon from as early as 1950s by Holstein and colleagues [81, 82], where the 1D Holstein polarons were introduced to account for the electron-phonon interaction in the molecular crystals. Charge transport in organic semiconductors is governed by electronic coupling and electron-phonon interactions, and the main transport mechanism can be described by polaron and disorder models as reviewed in Ref. [19].

The most detailed theories on polaron transport are the phenomenological model [107] and the polaron effective mass approach [108]. However, these models are restricted to specific ranges of parameters. More general microscopic model in understanding polaron transport was developed by Munn and Silbey [109-111] in 1980 from a density matrix approach, which is capable of describing electronic coupling, local and nonlocal

electron-phonon interaction of arbitrary strength over full range of temperatures. More recently, microscopic models from generalized master equation approach [112], and dynamical mean-field theory [113] have been developed.

The polaron transport theory developed by Holstein analytically in his seminal works [81, 82] are based on perturbation theory and limited to the case of small transfer integrals. Despite its limitation, this theory has been widely used for qualitative interpretations of experimental data, including the temperature dependence of the band-narrowing effect as well as the crossover from band-like behavior to hopping transport with increasing temperature. Although the qualitative agreement with experimental results of the original theory of Holstein polaron is generally satisfactory, it cannot describe the transport mechanisms in organic crystals, and more general models need to be developed in order to take into the account of both local and nonlocal effects of electron-phonon coupling.

The microscopic transport theory developed by Munn and Silbey [109-111] from a density matrix approach is capable of describing electronic coupling and diagonal and off-diagonal electron-phonon interaction of arbitrary strength over a wide range of temperatures. The effect of off-diagonal coupling poses much more difficulties to tackle than its diagonal counterpart, and as a result, off-diagonal coupling has not been extensively treated before [114]. The off-diagonal coupling was found to increase the polaron binding energy. The bandwidth was also found to be impacted by this type of coupling, and new minima and broadening are introduced to the band shape depending on microscopic parameters. In contrast, the effect of diagonal coupling is always rendered as the narrowing of the band. However, an increase in the off-diagonal coupling also

increases scattering and thereby reduces the band-like contribution to the mobility.

The Yarkony-Silbey variational approach [115, 116] provides an attractive direction to solve the transport problems in organic molecular crystals. This approach has been borrowed to treat two phonon bands in a three-dimensional lattice by Parris and Kenkre [117]. However, as the Yarkony-Silbey approach lacks the flexibility in variational parameters. A more sophisticated approach is needed to capture the correct temperature dependence of diffusion coefficient and mobility. To obtain the optimal basis for a polaron system, the finite-temperature variational method by Cheng and Silbey [118] combining Merrifield's transformation with Bogoliubov's theorem has been recently devised, bringing substantial improvements to earlier results [110]. The theory is able to capture the universal band-like-to-hopping transition as temperature increases, and more importantly, the temperature-independent mobility at extremely low temperature has been found in agreement with a nonperturbative approach recently developed by Ortmann *et al.* [119]

However, Merrifield's transformation itself is applicable only in the small polaron regime, and the off-diagonal exciton-phonon coupling was not accounted for in Ref. [118], making the approach insufficient to describe the phonon assisted transport/tunneling [115] in molecular crystals. Thus, further improvements are necessary for cases with simultaneous diagonal and off-diagonal coupling. Following up on the Munn-Silbey transformation method, Zhao *et al.* [89, 120-122], devised a self-consistent routine to determine the transformation coefficients, demonstrating substantial corrections of the polaron band structures thanks to a built-in momentum dependence of the transformation

coefficients.

An attempt of generalization of the Holstein model to higher dimension with a microscopic model utilizing the generalized master equation approach has been made by Kenkre *et al.* [23] This model was able to reproduce the temperature dependence and anisotropy of experimental mobilities of naphthalene very well. However, the fitting of the experimental data suffers the deficiency of local electron-phonon coupling dependence and small electronic coupling value compared to DFT and INDO estimations, making the model less convincing.

Using master equations, Wang *et al.* [123], developed a non-perturbative method to handle the electron-phonon coupling fully quantum-mechanically and quantify charge-carrier transport properties in organic molecular crystals. A more sophisticated microscopic model based on a Hamiltonian of Holstein-Peierls type has been presented by Bobbert and colleagues [124, 125] recently. Very recently, a theory based on nonperturbative evaluation of Kubo formula for the carrier mobility [119, 126, 127] has been proposed, showing several improvements including the elimination of low-temperature singularity that often appears in theories based on narrow-band approximations. Based on a non-perturbative evaluation of the Kubo formula, calculations have been carried out for durene crystals [128] and guanine based materials [129], and transport channels of charge carriers are revealed by making use of *ab-initio* tools. Coupling to the intermolecular acoustic modes [130] was found to play a significant role in charge transport suggesting that the model presented by Bobbert *et al.* may be improved further. Experimental data of naphthalene could be well reproduced by this

model with microscopic parameters obtained from *ab-initio* calculations. However, it neglected the intramolecular modes as well as the coupling of excitons to the intermolecular acoustic phonons, and only the coupling to the optical modes was accounted for. Moreover, the models developed by Bobbert *et al.*, and by Munn and Silbey, are based on nonlocal canonical transformations with additional approximations. Thus the range of validity of these models still requires further exploration, despite the fact that qualitative results agree well with experiments. Hence, in the context of ongoing discussion, combined with the recent theories by Hultner *et al.* [131] and Troisi *et al.* [132], it is clear that both local and nonlocal exciton-phonon interactions should be taken into account. A comprehensive theory of the charge transport in organic crystals requires treatments of the Hamiltonian having the lattice dealt with quantum mechanically to make itself valid for any temperature of interest, and the Munn-Silbey approach [109-111] combined with the self-consistent routine devised by Zhao *et al.* [89], provides a good opportunity to explore the simultaneous effect of diagonal and off-diagonal exciton-phonon coupling on the transport properties of polaron.

However, theoretical tools that can describe the transport properties in the organic molecular crystals are still not satisfactory despite many attempts of modeling on either charge transport or the optical processes/spectroscopy. As a starting point in this thesis, existing theoretical tools will be applied to specific materials such as rubrene as a representative molecular crystal to find the connections between the charge transport and optical processes.

Chapter 2: Aims and Motivations

2.1 Motivations

To overcome the drawbacks of current organic semiconductors, it is important to further explore new families of materials with better performance and stability or to have guidelines for rationally improving the existing materials. Thus following questions [27] remain to be solved theoretically prior to or along with experimental exploration of new materials and improvement of existing materials: (1) what is the inter-relationship between the molecular properties and the foundation materials? *i.e.*, the molecules constituting the infrastructure of basic functional units; (2) what is the correlation of properties with the spatial arrangements of their different molecular assemblies? and (3) what are their electronic and optical properties? With fundamental understanding of the physical origin of these problems, it could become possible to achieve rational designs of organic semiconductors to some extent. To answer the questions above, we choose to start from the investigation of the optical and transport processes and the properties of these materials that make the organic semiconductors markedly different from their inorganic counterparts such as Si and GaAs. Moreover, an understanding of the underlying physics of both optical and charge carrier transport processes is crucial for the improvements of performance for devices such as thin film transistors, light-emitting diodes, photoconductors, photovoltaic cells and optically pumped light sources based on these materials. Thus the development of a theoretical framework which can provide a general guideline on improving critical material properties is largely needed.

It is well known that electron/exciton-phonon interactions play the central role in

determining the optical and transport properties of organic materials. However the electron/exciton-phonon coupling in organic systems is extremely complicated due to the large amount of intra- and inter-molecular vibrations. In addition, the clear ordering of parameters is also lacking. Both of these difficulties make the thorough understanding of transport and related optical properties in these materials a mission almost impossible to complete.

Emergence of high-quality organic single crystals with semiconducting properties and relatively less amount of defects and impurities provide a natural test-bed to study the underlying physics. Among a variety of material characterization techniques, optical spectroscopy is an excellent tool to study different intrinsic properties related to the electron/exciton-phonon interactions owing to its non-destructive and highly tunable nature. With the aid of optical spectroscopy, it is possible to obtain information about the molecular vibrations with respect to environment parameters such as temperature and pressure, making the technique an ideal one for retrieving physical parameters that are closely related to the transport properties of a material.

Theoretical approaches in their current states, especially those used in obtaining the transport properties, suffer various deficiencies, and even a full understanding regarding how the microscopic material parameters govern the transport processes is still lacking. As the first step of developing a comprehensive approach, it is important to identify the major factors/material parameters governing the transport and optical properties of the organic semiconductors. Thanks to the years of increasing research efforts, we are now able to list some of the most important considerations: (1) Characteristics of electronic

bands (*e.g.*, transfer integral J , dispersion, anisotropy); (2) Forms and strength of electron-phonon coupling (*e.g.*, diagonal coupling strength g and off-diagonal coupling strength ϕ); (3) Characteristics of the phonon bands (*e.g.*, phonon bandwidth Δ , phonon branch, dispersion and characteristic frequency ω_0); (4) Temperature T and; (5) Static disorder resulting from defects and impurities. The theoretical framework sought after in this work thus focuses on elaborating the physical parameters listed above which may help in uncovering relationship between the fundamental atomistic models and the materials properties such as optical spectroscopy and energy/charge transport.

2.2 Objectives

This thesis aims at improving optical and transport performance of organic semiconductors by constructing a theoretical scheme for obtaining certain crucial material parameters through bridging the gaps between optical spectroscopy, quantum chemical calculations and transport properties via polaron dynamics. The objectives of the thesis include the following aspects:

1. To devise computationally affordable quantum chemical methods to tackle the problems of retrieving reliable material parameters from fundamental molecular structures. This study involves a thorough investigation of relationships between the governing material parameters and molecular structure as well as spatial arrangements of the molecules, aiming for a thorough understanding of interplay between molecular and crystal structure in determining the material parameters that are critical towards correct calculation of optical spectra and mobility; at least in a qualitative fashion.

2. To apply the multi-mode Brownian oscillator model (MBO) to fit experimental spectra for the material parameters. Along with this method, independent mode displaced harmonic oscillator model with temperature effect (IMDHO-T) will be used to calculate quantum chemical optical spectra which can be compared to the experimental or MBO spectra. This study focuses on retrieving the material parameters from both experimental and quantum chemical results, thus it plays the part of bridging the gap between realistic materials and fundamental molecule structure. In this study, rubrene is the major material used to demonstrate the idea, where specific structure-property relationship has been discussed in details.

3. The properties of polaron play the central role in this thesis, thus the study of static polaron structure as well as polaron dynamics is critical towards in-depth understanding of the material parameters in determining optical spectroscopy and transport. In this study, the Holstein polaron dynamics using Davydov Ansätze will be studied intensively and in very much detail. With the aid of this study, better understanding of electron/exciton-phonon interaction and its dynamics can be achieved, which is extremely useful in providing guidelines for optimizing material parameters in a rational way.

4. Polaron transport calculations with temperature dependent canonical transformation treatment of Holstein Hamiltonian with both diagonal and off-diagonal electron/exciton-phonon interaction included provide a powerful tool in obtaining important observables such as intrinsic diffusion coefficient and mobility that can be directly compared to experimental results. Such direct comparison is an important criterion to test the applicability of the current theoretical framework. Thus this study

serves as the final test of the whole thesis. Together with the studies above, it is expected a general theoretical framework can be established to study the optical and transport properties of organic semiconductors as a whole, aiming for rational improvement of current materials design of new materials starting from the molecular structures.

Figure 1. A schematic of the hierarchies and relationships between geometry and theoretical tools that are applied to treat the respective problems related. Be noted that the vertical and horizontal axis are only applied for the single molecule, aggregates, mesoscopic and macroscopic identities, where each system has their own theoretical treatment.

The objectives can be summarized with a flow chart as shown in Figure 1, where optical spectroscopy and polaron transport serve as two central lines in this thesis. Bearing in mind the objectives, the rest of the thesis is organized as follows: an overview of theoretical tools used in the thesis is given in Chapter 3. Results and discussions for obtaining material parameters, optical spectra, polaron dynamics and polaron transport properties have been described in details in Chapter 4-6, respectively. Finally, conclusions and recommendations for future works are given in Chapter 7 and 8, respectively.

Chapter 3: Overviews of Theoretical Tools

3.1 Quantum Chemistry Methods

The starting point of the theoretical framework proposed in this work is the molecular structures, which can be specifically designed with currently known building blocks (*e.g.*, functional groups, substitution of atoms *etc.*). The theoretical tools that can be used for dealing with problems at this level are Hatree-Fock self-consistent field method (HF-SCF) [54], density functional theory (DFT) [133] with various approximations, *e.g.*, local density approximation (LDA) [133], grand gradient approximation (GGA) [133] *etc.*, and semi-empirical methods such as INDO [54] and MNDO [54]. With the aid of these approaches and practical approximations, it is possible to describe the ground/excited-state geometry, electronic structures [*e.g.*, molecular orbital, electron density distribution, density of state (DOS) *etc.*], vibrational modes and many other related properties with reasonable accuracy. It has become possible to start looking into various responses (especially optical spectra and charge/energy transport) of these materials by constructing model Hamiltonians such as Holstein Hamiltonian. These model Hamiltonians are enabled to include geometric and electronic structure information that are obtained from the *ab-initio* and semi-empirical calculations of molecules, molecular aggregates and crystals. Details of quantum chemistry and DFT theory will not be fully reviewed here as there are many excellent text books, such as Ref. [133] and [54], to be referred to. Thus we only lay out an infrastructure of quantum chemistry methods to illustrate the contents that are closely related to the theoretical framework of the thesis.

3.1.1 The Hatree-Fock Method

The origin of the Hatree-Fock formalism is the well-known Schrödinger equation, which is regarded as one of the greatest breakthroughs of science in the beginning of the 20th century. The introduction of wave function $\psi(\mathbf{r}, t)$ with its square modulus representing the probability density of the particle at a spatial point $\mathbf{r}$ and at time t makes it possible to access various observables.

In quantum mechanics, particles obey the Schrödinger equation which essentially is a differential equation given as follows:

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{r}, t) = -\frac{\hbar^2}{2m} \Delta \psi(\vec{r}, t) + V(\vec{r}, t) \psi(\vec{r}, t) = H(\vec{r}, t) \psi(\vec{r}, t) \quad (3.1.1)$$

It describes the time evolution of a single particle and its position, velocity as well as the potential that the particle experienced. In most quantum chemistry calculations, ground state properties are more interesting and easier to solve, thus without time evolution, Eqn. (3.1.1) is reduced to its time-independent form as:

$$H\psi(r, R) = E_{tot}\psi(r, R) \quad (3.1.2)$$

where r and R represents the spatial coordinates of electrons and nuclei of a molecular system. From the time-independent equation Eqn. (3.1.1), the total energy of the system E_{tot} can be obtained. For a molecular system, its total Hamiltonian usually includes the kinetic and potential contributions from both electrons and nuclei. Assuming the number of nuclei and electrons to be N and n , respectively, and the electron mass, $\hbar$, Coulomb constant and elementary charge as unity, the total Hamiltonian describing this molecular system can be written as:

$$H = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \sum_{I=1}^N \frac{1}{2m_I} \nabla_I^2 - \sum_{i=1}^n \sum_{I=1}^N \frac{C_I}{r_{i,I}} + \sum_{i=1}^n \sum_{j>i}^n \frac{1}{r_{i,j}} + \sum_{I=1}^N \sum_{J>I}^N \frac{C_I C_J}{r_{I,J}} \quad (3.1.3)$$

or in short,

$$H = K_e + K_N + V_{eN} + V_{ee} + V_{NN} \quad (3.1.4)$$

where K_e and K_N is the kinetic energy for electrons and nuclei, and three parts of the potential energies describe the electron-nuclei (attraction), electron-electron (repulsive) and nuclei-nuclei (repulsive) interactions, respectively. $r_{i,I}$, $r_{i,j}$ and $r_{I,J}$ is the electron-nuclei, electron-electron and nuclei-nuclei distance, respectively, and each nuclei has the charge of C . Current formalism only includes the Columbic interactions, while the importance of spin will be rendered in the later sections.

A very important approximation that assumes the electrons are moving much faster than the nuclei (which is true in quite a lot of cases due to the extreme differences between the mass of electron and proton) is called Born-Oppenheimer (BO) approximation or adiabatic approximation[54]. The solution to the stationary Schrödinger equation now omits the kinetic contribution from the nuclei by fixing them to a given position R in this approximation, thus Eqn. (3.1.4) can be simplified as:

$$H_{el} + H_N = (K_e + V_{eN} + V_{ee}) + V_{NN} \quad (3.1.5)$$

It is also possible to partition the total wave function as: $\Psi(r, R) = \sum_i \psi_i(r, R) \gamma_i(R)$, with this approximation, where ψ is the electronic wave function and γ is the nuclear one, and the summation is carried out over all electronic states. By inserting this wave function in Eqn. (3.1.5), the complicated form [considering the Hamiltonian in Eqn. (3.1.3)] of Eqn. (3.1.2) can be reduced to:

$$H\Psi(r, R) = [H_{el}(R) + V_{NN}] \sum_i \psi_i(r, R) \gamma_i(R) \quad (3.1.6)$$

which naturally leads to:

$$H_{el}\psi_i(r, R) = E_i^{el}(R)\psi_i(r, R) \quad (3.1.7)$$

with $E_i^{el}(R)$ indicating the electronic energy for the i^{th} electronic state. The adiabatic energy instead of total energy can then be derived as:

$$E_{ad} \sum_i \psi_i(r, R)\gamma_i(R) = \sum_i [E_i^{el}(R) + V_{NN}] \psi_i(r, R)\gamma_i(R) \quad (3.1.8)$$

which differs from E_{tot} by neglecting the contribution from nuclear kinetic energy. The essence of the Born-Oppenheimer approximation is the partition of Schrödinger equation into independent electronic and nuclear parts. By decoupling the electron-nuclei interaction, it is possible to solve the electronic equation experiencing the field that is created by the fixed nuclei. Even with such an approximation, exact solvable cases are still lacking. One of the very important cases is the non-interacting model that laid the foundation of quantum chemistry calculations. The model assumes non-interacting electrons, despite not being very realistic, is still meaningful towards the solution of many-electron systems. The model can be described by simply rewriting Eqn. (3.1.7) to a set of n one-electron equations:

$$H_{el}^i \psi_i(r) = \varepsilon_{el}^i \psi_i(r) \quad (3.1.9)$$

where H_i is the single-electron Hamiltonian which composed of electron kinetic energy, electron-nuclei attraction and nuclei-nuclei repulsion operators, *i.e.*, $H_i^{el} = T_e^i + V_{eN}^i$ for electron i , with energy of one electron state $\psi_i(r)$ given by ε_{el}^i . Under this approximation, the many-body problem is simplified to the summation of n set of one electron hydrogenoid model. However due to the Pauli principle, two electrons with same spin cannot occupy same electronic level simultaneously, making it is necessary to introduce spin-orbital which is composed of one-electron orbital and a spin wave function σ . It is

achieved by introducing the Slater determinant and constraining the symmetry to anti-symmetric, and the total wave function of an n -electron system obeying these rules then can be written as:

$$\Psi(1,2,\dots,N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(r_1)\sigma_1(\omega_1) & \dots & \psi_1(r_N)\sigma_1(\omega_N) \\ \vdots & \ddots & \vdots \\ \psi_N(r_1)\sigma_N(\omega_1) & \dots & \psi_N(r_N)\sigma_N(\omega_N) \end{vmatrix} \quad (3.1.10)$$

However, such a crude model is quite insufficient to be applied directly to many problems, it is necessary to introduce a new formalism for better description of a many electron system, for instance, the Hatree-Fock (HF) formalism.

Under the variational principle, it is suggested that disregarding the form of wave function, the energy of a system should obey following relationship:

$$E_{approx} = \frac{\langle \psi_i^{trial} | H | \psi_i^{trial} \rangle}{\langle \psi_i^{trial} | \psi_i^{trial} \rangle} \quad (3.1.11)$$

The Hatree-Fock equations are then derived from the variational principle with the approximation of a total wave function comprised of n one-electron equations. Under this circumstance, each electron is experiencing a mean interacting field due to the existence of all other electrons.

For a closed shell system, the Hatree-Fock equations can be written as:

$$H_i^{HF}(r)\psi_i(r) = \left[H_{el}^i(r) + \sum_j^{n/2} (2J_j(r) - K_j(r)) \right] \psi_i(r) = \varepsilon_i \psi_i(r) \quad (3.1.12)$$

with

$$J_j(r_i) = \langle \psi_j(r_j) | 1/r_{ij} | \psi_j(r_j) \rangle \quad (3.1.13)$$

and

$$K_j(r_i) = \langle \psi_j(r_j) | 1/r_{ij} | \psi_i(r_j) \rangle \quad (3.1.14)$$

Eqn. (3.1.13) and Eqn. (3.1.14) respectively indicate the definition of the Columbic and exchange operators. To solve the HF equations, an iterative scheme to produce self-consistent field should be applied. For dealing with the problems in molecules, it is also helpful to introduce another approximation named linear combination of atomic orbitals (LCAO), which use a linear combination of a set of atomic orbitals to express the spatial orbitals $\phi_i(r)$ in terms of a set of one-electron basis functions χ_s :

$$\psi_i = \sum_s^b C_{is} \chi_s \quad (3.1.15)$$

With the application of this approximation, one can express the one-electron wavefunction with negligible errors if the basis set χ_s is well chosen and the number of basis set b is large enough. Substituting Eqn. (3.1.15) to the Hatree-Fock equations Eqn. (3.1.12), we can get a set of equations named Roothan-Hall equations expressed as:

$$\sum_s^b C_{is} H_i^{HF} \chi_s = \epsilon_i \sum_s^b C_{is} \chi_s \quad (3.1.16)$$

Multiplying the above equation with χ_r^* gives

$$\sum_s^b C_{is} (H_{rs}^{HF} - \epsilon_i S_{rs}) = 0, \quad r = 1, 2, \dots, b \quad (3.1.17)$$

and

$$H_{rs} \equiv \langle \chi_r | H_i^{HF} | \chi_s \rangle, \quad S_{rs} \equiv \langle \chi_r | \chi_s \rangle \quad (3.1.18)$$

Further expansion of the H_{rs} can be written as

$$H_{rs} = \langle \chi_r | -\frac{1}{2} \nabla^2 - \sum_A^N \frac{Z_A}{r_{iA}} | \chi_s \rangle + \sum_j \sum_t \sum_u^{n/2} C_{ij}^* C_{uj} [2 \langle rs | tu \rangle - \langle ru | ts \rangle] \quad (3.1.19)$$

The first term in the bracket in Eqn. (3.1.19) gives the core contribution from the one-electron Hamiltonian, and the next two terms in bracket give the J (Columbic) and K (exchange) two-electron integrals. To have a nontrivial solution, we must have following

secular equation:

$$\det(H_{rs}^{HF} - \varepsilon_i S_{rs}) = 0 \quad (3.1.20)$$

roots of which provide the orbital energies. Iterative process must be applied to determine the unknown coefficients C_{is} , which is the center of the method.

3.1.2 The Semi-empirical Methods

Owing to the two-electron integrals, the computation cost of the HF method grows with the fourth power with the number of basis set. To reduce the computation cost, one way to speed up the HF process is to reduce the number of integrals involved. It is natural to consider only the valence electrons in the calculation as a first step in this direction. The central approximation in semi-empirical methods is the idea of Zero Differential Overlap (ZDO) which can be described as:

$$\chi_s(r) \chi_q(r) = \delta_{sq} \quad (3.1.21)$$

If a full ZDO is applied, the concept of Complete Neglect of Differential Overlap (CNDO) approximation can be introduced. With such an approximation, the overlap S matrix is reduced to the unit matrix, three centre contributions to the one-electron integrals are totally zero and all the integrals involving two electrons or above are neglected, greatly reducing the computation cost. Suitable parameterization has been applied to one-electron integrals to increase the accuracy of calculations, which is usually done by fitting to experimental values. The differences between semi-empirical methods lay on the ways in parameterization and total number of integrals neglected. In our thesis, the ZINDO method[134], or the INDO method parameterized by Zenner and coworkers is applied to

most of the large scale (for instance, molecular aggregates) computations.

3.1.3 The Density Functional Theory

It was the first time that electron density had been used to calculate properties by Enrico Fermi and Paul Dirac that lead to well-known Fermi-Dirac distribution in the 1920's. The advantage of introducing the idea of electron density is in being more intuitive than electron wave function in obtaining various physical properties. It is also true that the introduction of electron density can be very helpful in reducing the number of variables from $4N$ to 3. The actual electron density is related to the number of electrons as:

$$\int \rho(r) dr = N \quad (3.1.22)$$

The method provided by the Thomas-Fermi model[133] laid out the framework of density functional theory of quantum systems. This early model is not accurate enough from current point of view, yet it still provides an insightful framework for the density functional theory (DFT).

The Hohenberg and Kohn theorems that open the gates of the modern DFT, are stated as:

1. Given the exact ground-state density $\rho_0(\mathbf{r})$, all properties of the system can be determined.
2. The exact ground state energy is determined specifically by the exact ground-state density $\rho_0(\mathbf{r})$, which provides the variational principle of the density functional theory.

It was the Ansatz proposed by Kohn and Sham with the replacement of many-body problems by non-interacting particles that initiated the great success of the density functional theory. The Ansatz essentially self-consistently treats the system as

independent particles with interacting density.

To have better description of the Kohn-Sham Ansatz, it is beneficial to start from the Hatree-Fock scheme in describing the density function theory, from which we can write the electronic energy of a molecule (with n electrons and N nuclei) as:

$$E_0[\rho_0] = T_e[\rho_0] + V_{ee}[\rho_0] + V_{eN}[\rho_0] \quad (3.1.22)$$

with each term given as:

$$T_e[\rho_0] = T_s[\rho_0] + T'_e[\rho_0] \quad (3.1.23)$$

$$V_{ee}[\rho_0] = \frac{1}{2} \iint \frac{\rho_0(r_1)\rho_0(r_2)}{r_{12}} dr_1 dr_2 + V'_{ee}[\rho_0] \quad (3.1.24)$$

$$V_{eN}[\rho_0] = \int \rho_0(r) V_{ext}(r) dr \quad (3.1.25)$$

where $T'_e[\rho_0]$ and $V'_{ee}[\rho_0]$ describes the correction to the kinetic and self-interacting energy, respectively. The interaction between electrons and nuclei is now described by an external potential $V_{ext}(r)$. Moreover, $T_s[\rho_0]$ is the kinetic energy of the reference system of non-interacting electrons introduced by Kohn and Sham. Thus one can rewrite Eqn. (3.1.22) as:

$$E_0[\rho_0] = T_s[\rho_0] + \int \rho_0(r) V_{ext}(r) dr + \frac{1}{2} \iint \frac{\rho_0(r_1)\rho_0(r_2)}{r_{12}} dr_1 dr_2 + E_{xc}[\rho_0] \quad (3.1.26)$$

where

$$E_{xc}[\rho_0] = T'_e[\rho_0] + V'_{ee}[\rho_0] \quad (3.1.27)$$

Eqn. (3.1.27) is the so-called exchange-correlation energy, which critically determines the accuracy and robustness of the DFT approach. Thus for decades of development of the theory, extensive efforts have been dedicated to the search of better functional of exchange-correlation (XC). To date, the XC functional can be categorized into three

major approximations, *i.e.*, the local (spin-) density approximation [L(S)DA], the generalized gradient approximation (GGA), and the hybrid functional. Thus it is better to describe the E_{XC} with a new form such that:

$$E_{XC}[\rho_0] = E_X[\rho_0] + E_C[\rho_0] \quad (3.1.28)$$

As the solids are often close to the limit of homogeneous electron gas, the exchange and correlation effects become local, which allows one to have the LDA approximation that can be expressed as:

$$E_{XC}^{LDA}[\rho_0] = \int \rho_0 V_{XC}(\rho_0(r)) dr \quad (3.1.29)$$

More generally, if spin is considered, the LDA becomes LSDA, expressed as following:

$$E_{XC}^{LSDA}[\rho^\uparrow, \rho^\downarrow] = \int \rho_0 V_{XC}(\rho^\uparrow(r), \rho^\downarrow(r)) dr \quad (3.1.30)$$

Now the total density ρ_0 is given by the summation of the electron density with spin up and down. From most of the applications, a systematic overestimation of correlation has been found for the LSDA approximation, which leads to relatively poor description of bond strengths and dissociation energies. However, the LSDA approximation is still a good candidate for predicting certain properties such as geometries and vibrational frequencies of molecules and solids.

Inspired by the LSDA, improved functional based on this approximation can be developed. GGA is one of various improvements based on the LSDA, which relies on both local electron density and density gradient rather than purely local density compared to the LSDA. The general form of GGA can be written as:

$$E_{XC}^{GGA}[\rho^\uparrow, \rho^\downarrow] = \int \rho_0 V_{XC}(\rho^\uparrow(r), \rho^\downarrow(r), \nabla \rho^\uparrow(r), \nabla \rho^\downarrow(r)) dr \quad (3.1.31)$$

Then the correction can be made by including terms related to the density gradient to the exchange and correlation functional.

3.2 Theoretical Optical Spectroscopy Methods

3.2.1 Condon Approximation and Optical Spectroscopy

The absorption transition from electronic-vibrational state a, n to state b, m is proportional to the matrix element of transition dipole as defined below:

$$\langle \psi_b(r_i, Q) \chi_b(m) | \hat{\mu} | \psi_a(r_i, Q) \chi_a(n) \rangle \quad (3.2.1)$$

where $\psi_a(r_i, Q)$, $[\psi_b(r_i, Q)]$ and $[\chi_a(n)]$, $[\chi_b(m)]$ are the electron wave-functions and harmonic oscillator functions at $a(b)$ and $n(m)$, states respectively. The integration is over electronic and vibrational coordinates, and μ is the electric dipole operator. The simplification of this matrix element is carried out under the Born-Oppenheimer approximation, where at very low temperatures, the initial state is $\psi_a \chi_a(0)$ and the harmonic oscillator function $\chi_a(0)$ has maximum amplitude at $Q = Q_0^{(a)}$. With this approximation, this value of Q is actually used as the average in the electronic wave functions. The approximated matrix element can then be expressed as:

$$\langle \psi_b(r_i, Q) | \mu | \psi_a(r_i, Q) \rangle \langle \chi_b(m) | \chi_a(n) \rangle \quad (3.2.2)$$

This type of approximation is also known as Condon approximation. Then the transition probability is defined as:

$$W_{an \rightarrow bm} = P_{ab} \left| \langle \chi_b(m) | \chi_a(n) \rangle \right|^2 \quad (3.2.3)$$

where P_{ab} is the pure electronic transition probability, and is the same for all vibrational states.

The shape of the absorption band is given by:

$$I_{ab}(E) = I_0 A v_n \sum_m \left| \langle \chi_b(m) | \chi_a(n) \rangle \right|^2 \delta(E_{b,m} - E_{a,n} - E) \quad (3.2.4)$$

$A v_n$ in this equation represents a thermal average over the initial vibrational state n , and

$E_{a,n}$ is the energy of the n th vibrational state when the electronic centre is in state a .

The overlap integral is readily expressed in closed form as:

$$\langle \chi_b(m) | \chi_a(n) \rangle = \exp(-A^2/4) \sqrt{\frac{n!}{m!}} \left(-\frac{A}{\sqrt{2}} \right)^{m-n} L_n^{m-n}(A^2/2) \quad (3.2.5)$$

where L_n^{m-n} are the associate Laguerre polynomials.

If temperature is equal to 0 K, the only occupied vibrational state should be $n=0$ state. For this case the values of the overlap between b, m state and $a, 0$ state is of great interest. This overlap is called the zero-temperature Franck-Condon factor [135-137], $F_m(0)$, expressed as:

$$F_m(0) = \left| \langle \chi_b(m) | \chi_a(0) \rangle \right|^2 = \frac{\exp(-A^2/2) (A^2/2)^m}{m!} = \frac{\exp(-S) S^m}{m!} \quad (3.2.6)$$

where S is the Huang-Rhys factor[138] which represents the electron-phonon coupling strength.

Thus for $T=0K$, the absorption band shape function is:

$$\begin{aligned} I_{ab}(E) &= I_0 \sum_m \frac{\exp(-S) S^m}{m!} \delta(E_{b,m} - E_{a,0} - E) \\ &= I_0 \sum_m \frac{\exp(-S) S^m}{m!} \delta(E_0 - m\hbar\omega - E) \end{aligned} \quad (3.2.7)$$

where $E_0 = E_{b,0} - E_{a,0}$ is the energy of the transition between zero vibrational levels of both initial and final states and ω is the phonon frequency of the vibrational mode that coupled to the electronic transition.

Similarly, under these approximations, the shape of the emission band at $T=0K$ can be expressed as:

$$I_{ba}(E) = I_0 \sum_n \frac{\exp(-S) S^n}{n!} \delta(E_0 - n\hbar\omega - E) \quad (3.2.8)$$

The emission and absorption bands will have mirror symmetry separated by the Stokes

shift only when the electronic excited states and ground states have identical parabola as a function of phonon coordinates. However, these crude approximations are far from enough for having realistic spectra. Further improvements based on the theory will be discussed in the next two sessions.

3.2.2 Multi-mode Brownian Oscillator Model

The multi-mode Brownian oscillator model (MBO)[34, 139-148] describes the electronic relaxation of a two level system attached to one (few) primary oscillator(s) which is (are) in turn linearly coupled with a bath of secondary phonons. The coupling of the nuclear coordinates with the optical excitations and electronic relaxation channels in solids can be studied by MBO model. In the MBO model, an electronic two level system interacts linearly with a few primary nuclear coordinates that are in turn coupled linearly to a bath of secondary harmonic oscillators with a given spectral density. The key parameters of the MBO model are the damping coefficient γ , the frequency of the primary oscillators and the Huang-Rhys factor S , with other controlling parameters including the temperature T and the 0-0 transition energy. The damping constant γ , is responsible for the coupling strength of the primary oscillator and the bath modes, therefore it controls the broadening of the zero phonon line (ZPL) and its phonon sidebands. The longitude optical (LO) phonon frequency is assigned to the frequency of the primary oscillator which controls the energy separation between the ZPLs and one phonon peak (and spacing between adjacent phonon side bands) while the Huang-Rhys factor S reflects the electron-LO phonon coupling strength.

In the MBO model, the Hamiltonian of the system can be described by:

$$H = |g\rangle H_g \langle g| + |e\rangle H_e \langle e| + H' \quad (3.2.9)$$

where

$$H_g = \sum_j \left[\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 q_j^2 \right] \quad (3.2.10)$$

$$H_e = \hbar \omega_{eg}^0 + \sum_j \left[\frac{p_j^2}{2m_j} + \frac{1}{2} m_j \omega_j^2 (q_j + d_j)^2 \right] \quad (3.2.11)$$

and

$$H' = \sum_n \left[\frac{P_n^2}{2m_n} + \frac{1}{2} m_n \omega_n^2 \left(Q_n - \sum_j \frac{c_{nj} q_j}{m_n \omega_n^2} \right)^2 \right] \quad (3.2.12)$$

In Eq.(3.2.9)-(3.2.12), P_j (P_n), q_j (Q_n), m_j (m_n) and ω_j (ω_n) are the momentum, coordinate, mass and angular frequency of the j th (n th) nuclear mode of the primary (bath) oscillators, respectively. In Eqn. (3.2.11), d_j is the displacement of the j th nuclear mode in the electronic excited state. The $\hbar \omega_{eg}^0$ term represents the energy difference in the two-level system. H' can be regarded as the coupling between the primary oscillators and bath modes with a coupling strength of c_{nj} . By defining the energy gap operator:

$$U = H_e - H_g - \hbar \omega_{eg}^0 \quad (3.2.13)$$

we can write a correlation function as:

$$C_j(t) = -\frac{1}{2\hbar^2} \left[\langle U(t)U(0) \rho_g \rangle - \langle U(0)U(t) \rho_g \rangle \right] \quad (3.2.14)$$

In this equation, the operator $U(t)$ is the interaction representation of the operator U and ρ_g is the equilibrium ground-state vibrational density matrix defined as

$$\rho_g = \frac{|g\rangle \langle g| \exp(-\beta \hat{H}_g)}{\text{Tr}[\exp(-\beta \hat{H}_g)]} \quad (3.2.15)$$

where $\beta = 1/k_B T$. The correlation function in time-domain, Eqn. (3.2.14), can be transferred into frequency-domain by Fourier transform, with its the imaginary part known as the spectral density

$$\tilde{C}_j''(\omega) = \frac{2\lambda_j \omega_j^2 \omega \gamma_j(\omega)}{\omega^2 \gamma_j^2(\omega) + [\omega_j^2 + \omega \Sigma_j(\omega) - \omega^2]^2} \quad (3.2.16)$$

where $\Sigma_j(\omega)$ is the real part of the self-energy and the Stokes shift contribution of the j^{th} mode; $2\lambda_j$ is described by

$$2\lambda_j = \frac{m_j \omega_j^2 d_j^2}{\hbar} \quad (3.2.17)$$

Alternatively, we can write $\lambda_j = S_j \hbar \omega_j$, where S_j is the dimensionless Huang-Rhys factor describing the electron-LO phonon interaction strength. $\gamma_j(\omega)$ in Eq. (3.2.16) is the spectral distribution function describing the coupling between the primary oscillator and the secondary bath oscillators:

$$\gamma_j(\omega) = \frac{\pi}{m_j} \sum_n \frac{c_{nj}^2}{2m_n \omega_n^2} [\delta(\omega - \omega_n) + \delta(\omega + \omega_n)] \quad (3.2.18)$$

$\Sigma_j(\omega)$ is related to the spectral distribution function by the Kramers-Kronig relations as:

$$\Sigma_j(\omega) = -\frac{1}{\pi} \mathcal{PP} \int_{-\infty}^{\infty} d\omega' \frac{\gamma_j(\omega')}{\omega' - \omega} \quad (3.2.19)$$

where $\mathcal{PP}$ stands for the Cauchy principle part of the integral. A simple form of the BO model in which only a single primary oscillator with frequency ω_l (for example, the LO phonons) is considered and its coupling strength with the bath modes is assumed to be a constant (*i.e.*, $\gamma_j(\omega) = \text{constant}$), called the Markovian or Ohmic limit) to compute PL spectra. For this simple constant damping case, the spectral density function reads

$$\tilde{C}''(\omega) = \frac{2\lambda_l \omega_l^2 \omega \gamma_l}{\omega^2 \gamma_l^2 + (\omega_l^2 - \omega^2)^2} \quad (3.2.20)$$

where the real part of the self-energy $\Sigma_l(\omega)$, is set to zero.

The spectral response function $g(t)$ can be expressed in terms of the frequency-domain correlation function $C''(\omega)$ as

$$g(t) = -\frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{C''(\omega)}{\omega^2} [1 + \cot(\beta\hbar\omega/2)] (e^{-i\omega t} + i\omega t - 1) \quad (3.2.21)$$

The absorption line shape can be then obtained from the spectral response function $g(t)$:

$$\sigma_{abs}(\omega) = \frac{1}{\pi} \text{Re} \int_0^{\infty} \exp[i(\omega - \omega_{eg}^0 - \lambda)t - g(t)] dt \quad (3.2.22)$$

Without the coupling to the bath phonons, the Huang-Rhys theory gives a Poisson distribution for phonon side peaks in the absorption spectrum at zero temperature:

$$\sigma_{abs}(\omega) = \exp(-S_j) \sum_{n=0}^{\infty} \frac{S_j^n}{n!} \delta(\omega - \omega_{eg} - n\omega_j) \quad (3.2.23)$$

S here is the intensity ratio between the first and zero phonon lines, and can also be identified with the average number of phonons emitted. For larger S , the Poisson distribution morphs into a Gaussian centered at S . Upon broadening due to bath dissipation and thermal effects, the well-resolved phonon peaks will acquire widths that increase with phonon occupation number n . Theory at this level is quite useful in obtaining important physically meaningful parameters, *e.g.*, S , γ and ω_l . These parameters can be either obtained from experimental spectra or *ab-initio* spectra (will be discussed in next section).

3.2.3 Displaced Harmonic Oscillator Model

It is well-known that vibrationally-resolved absorption and emission cross sections[149], $\alpha(\omega)$ and $\beta(\omega)$, are defined as the thermal average of the dipole-dipole auto-correlation function as

$$C(t) = \frac{\text{Tr}[e^{-\beta H} \mu(t) \mu]}{\text{Tr}[e^{-\beta H}]} = \frac{\text{Tr}[e^{-\beta H} e^{iHt/\hbar} \mu e^{-iHt/\hbar} \mu]}{\text{Tr}[e^{-\beta H}]} \quad (3.2.24)$$

where $\beta=1/k_B T$, $\text{Tr}[\dots]$ represents the trace over nuclear and electronic degrees of freedom, and μ is the transition-dipole operator defined as

$$\mu = |g\rangle \mu_{ge} \langle e| + |e\rangle \mu_{eg} \langle g| \quad (3.2.25)$$

From the Born-Oppenheimer approximation, the total Hamiltonian for two electronic states $|e\rangle$ and $|g\rangle$ can be written as

$$H = |g\rangle H_g \langle e| + |e\rangle H_e \langle g| \quad (3.2.26)$$

where H_g and H_e denote the nuclear Hamiltonian of electronic ground and excited states, respectively. For linear response spectroscopy, Eqn. (3.2.26) explicitly gives two correlation functions, $C_a(t)$ and $C_e(t)$ as

$$C_a(t) = \frac{\text{Tr} \left[e^{-\beta H_g} e^{iH_g t/\hbar} \mu e^{-iH_e t/\hbar} \mu \right]}{\text{Tr} \left[e^{-\beta H_g} \right]} \quad (3.2.27)$$

and

$$C_e(t) = \frac{\text{Tr} \left[e^{-\beta H_e} e^{iH_e t/\hbar} \mu e^{-iH_g t/\hbar} \mu \right]}{\text{Tr} \left[e^{-\beta H_e} \right]} \quad (3.2.28)$$

where the subscripts “a” and “e” correspond to absorption and emission spectroscopy, respectively. Thus, the optical absorption cross section $\alpha(\omega)$ and emission cross section $\beta(\omega)$ are separately obtained from

$$\alpha(\omega) \propto \omega \int_{-\infty}^{\infty} C_a(t) \exp(i\omega t - \gamma|t|) dt \quad (3.2.29)$$

and

$$\beta(\omega) \propto \omega^3 \int_{-\infty}^{\infty} C_e(t) \exp(-i\omega t - \gamma|t|) dt \quad (3.2.30)$$

Here γ represents the dephasing factor, playing the role of line broadening in spectra obtained. Under the harmonic potential approximation, we can write the vibrational Hamiltonians as

$$H_g^h(q) = \frac{1}{2} \sum_i^n \omega_i^g \left[(p_i^g)^2 + (q_i^g)^2 \right] \quad (3.2.31)$$

and

$$H_e^h(q) = \frac{1}{2} \sum_i^n \omega_i^e \left[(p_i^e)^2 + (q_i^e)^2 \right] + E_{eg} \quad (3.2.32)$$

where E_{eg} is defined as the potential energy minimum difference between two electronic states with the zero-point energy correction, and $\omega_i^g (\omega_i^e)$ is the frequency of the i^{th} phonon at electronic ground (excited) state, which can be readily obtained by doing frequency calculations with *ab-initio* or DFT for the configurations in both states. The dimensionless nuclear coordinates $\mathbf{q}^g$ and $\mathbf{q}^e$ are related with $\mathbf{D}$ and $\mathbf{K}$ as

$$\mathbf{q}^e = \mathbf{K} \mathbf{q}^g + \mathbf{D} \quad (3.2.33)$$

where $\mathbf{D}$ is the displacement between the equilibrium configurations of two electronic states, and $\mathbf{K}$ is the Dushinsky rotation matrix allowing different coordinate systems for the ground state and the excited state, $\mathbf{D}$ and $\mathbf{K}$, both can be obtained by doing DFT calculations. As a result, S can be interpreted as the transformation operator for the dimensionless coordinate q . When the momenta and positions of the nuclei change very little upon photo-excitation, the intensities of vibrationally-resolved electronic absorption or emission spectra can be calculated according to the Franck-Condon (FC) principle. Under Condon approximation, the correlation function $C_{a(e)}(t)$ has been calculated analytically with Green's function approach[150].

Using Eq. (3.2.31) and Eq. (3.2.33) as the starting point, the dimensionless momentum and coordinate vectors p_i and q_i for the i^{th} phonon mode have one to one correspondence to normal modes, which can be described by[151]

$$\begin{cases} p_i = P_i \sqrt{\left(\frac{1}{m_i \omega_i \hbar} \right)} \\ q_i = Q_i \sqrt{\left(\frac{m_i \omega_i}{\hbar} \right)} \end{cases} \quad (3.2.34)$$

P_i and Q_i in the above equation, is the conjugate momentum and the normal coordinate of the i^{th} mode of the corresponding state, respectively. Similar to their counterpart, P_i and Q_i can be related with matrix $\bar{S}$ and $\bar{D}$ as

$$Q_e = \bar{S}Q_g + \bar{D} \quad (3.2.35)$$

$$\bar{S}^T \bar{S} = 1 \quad (3.2.36)$$

where the bar above S and D represents the transformation between the normal modes is orthogonal and $\bar{S}^T$ is the transpose of $\bar{S}$, i.e., $(\bar{S}^T)_{ij} = \bar{S}_{ji}$. The matrix elements of S are related to $\bar{S}$ as

$$S_{ij} = (\omega_e / \omega_g)^{1/2} \bar{S}_{ij} \quad (3.2.37)$$

The components of the dimensionless displacement D are also related to $\bar{D}_j$ as

$$D_j = \left(\frac{m_j \omega_j^e}{\hbar} \right)^{1/2} \bar{D}_j \quad (3.2.38)$$

With all these transformations, we now arrives at the final expression for the absorption spectra (PL is the opposite case)

$$\alpha(\omega) = \omega |\mu_{eg}|^2 \text{Re} \int_0^\infty \sigma(t) \exp[i(\omega - \omega_{eg})t] dt \quad (3.2.39)$$

and $\sigma(t)$ can be expressed as:

$$\sigma(t) = |\psi_T(t)|^{-1/2} \exp[D^T f_T(t) D] \quad (3.2.40)$$

where

$$|\psi_T(t)| = 1/4 (C_+ S' A_- + C_- S A_+) \times (C_+ S A_- + C_- S' A_+) \quad (3.2.41)$$

$$f_T(t) = -S' A_- (C_+ S' A_- + C_- S A_+)^{-1} C_- \quad (3.2.42)$$

with

$$S' = (S_{-1})^T \quad A_\pm = (\bar{n} + 1) \pm \bar{n} \exp(i\omega_g t) \quad C_\pm = 1 \pm \bar{n} \exp(i\omega_e t) \quad (3.2.43)$$

and

$$\bar{n} = [\exp(\hbar\omega_e/kT) - 1]^{-1} \quad (3.2.44)$$

The spectra obtained with this method can also be fitted with MBO model in order to find the critical parameters that are important for the polaron structure and transport calculations. It is also possible to use these parameters as essential indicators to look into the differences between *ab-initio* spectra and experimental spectra.

3.3 Polaron Model

3.3.1 Hamiltonian

Coupling of excitons and phonons is one of the most important interactions in organic molecular crystals. Such interactions often lead to the formation of a quasi-particle named polaron. The polaron motion in molecular crystals is usually described by a Hamiltonian formulated in 1959[81, 82]. In this model, the original concept of polaron in polar crystals is extended to phonon dressed excitons in molecular crystals. The second quantized form of the generalized Holstein Hamiltonian in 1D is described as:

$$\hat{H} = H^{ex} + \hat{H}^{ph} + \hat{H}^{ex-ph}, \quad (3.3.1a)$$

$$\hat{H}^{ex} = \sum_k J_k a_k^\dagger a_k, \quad (3.3.1b)$$

$$\hat{H}^{ph} = \sum_q \omega_q b_q^\dagger b_q, \quad (3.3.1c)$$

$$\hat{H}^{ex-ph} = N^{-1/2} \sum_{kq} \omega_q f_{-k}^q a_{k+q}^\dagger a_k (b_q + b_{-q}^\dagger) \quad (3.3.1d)$$

where the Planck's constant $\hbar=1$ for simplicity. In the above equation, the subscript k and q represents the wave vectors, $a_k^\dagger$, $b_q^\dagger$ (a_k , b_q) are the creation (annihilation) operators for the exciton and phonon respectively, and ω_q is the phonon frequency. J_k is the Fourier transformation of the real space transfer-integral J_n , and f_{-k}^q is the linear exciton-phonon coupling parameter. This one dimensional model is suitable for describing

quasi-one-dimensional crystals (such as naphthalene, rubrene *etc.*) due to the tremendous anisotropy of their electronic transport properties. If the exciton-phonon coupling is limited to the diagonal form, which is the same as Holstein's original treatment, the site-Hamiltonian reads,

$$\hat{H} = \hat{H}^{ex} + \hat{H}^{ph} + \hat{H}^{ex-ph}, \quad (3.3.2a)$$

$$\hat{H}^{ex} = -J \sum_n a_n^\dagger (a_{n+1} + a_{n-1}), \quad (3.3.2b)$$

$$\hat{H}^{ph} = \sum_n \omega b_n^\dagger b_n, \quad (3.3.2c)$$

$$\hat{H}^{ex-ph} = g\omega \sum_n a_n^\dagger a_n (b_n + b_n^\dagger) \quad (3.3.2d)$$

where J is the nearest neighbor transfer integral, g is the on-site exciton-phonon interaction strength, and ω the Einstein phonon frequency.

3.3.2 Ansätze

To treat the Hamiltonian in Eqns. (3.3.1) and (3.3.2), a natural way is the construction of Ansätze with certain approximations of exciton and phonon, *e.g.*, Davydov Ansätze, which have been developed to treat the polaron problem more exactly. The general form of the Ansätze is written as:

$$|D\rangle = \sum_n \psi_n e^{-\hat{S}_n} \hat{a}_n^\dagger |0\rangle_{ex} |0\rangle_{ph} \quad (3.3.3)$$

which is a product state of exciton and phonon. For different forms of the Davydov Ansätze, the Glauber coherent operator $\hat{S}_n$ varies. One can thus define three different types of Ansatz with respect to the operator as:

$$|D_1\rangle = \sum_n \psi_n e^{-\sum_q (\lambda_{nq}^* \hat{b}_q - \lambda_{nq} \hat{b}_q^\dagger)} \hat{a}_n^\dagger |0\rangle_{ex} |0\rangle_{ph} \quad (3.3.4a)$$

$$|\tilde{D}\rangle = \sum_n \psi_n e^{-\sum_q [(\lambda_q^* + \beta_q^* e^{iqn}) \hat{b}_q - (\lambda_q + \beta_q e^{-iqn}) \hat{b}_q^\dagger]} \hat{a}_n^\dagger |0\rangle_{ex} |0\rangle_{ph} \quad (3.3.4b)$$

$$|D_2\rangle = \sum_n \psi_n e^{-\sum_q [\lambda_q^* \hat{b}_q - \lambda_q \hat{b}_q^\dagger]} \hat{a}_n^\dagger |0\rangle_{ex} |0\rangle_{ph} \quad (3.3.4c)$$

It is clear from Eqn. (3.3.4) that $\tilde{D}$ and $D2$ Ansätze are two simplified version of $D1$ Ansatz, where the simplification of the coherent operator with respect to phonon amplitude and displacement related variational parameters λ_{nq} determines the site-correlation between exciton and phonon. The applicability of these Ansätze thus increases with the complexity of λ_{nq} . For example, when the most simplified version of the Davydov Ansätze, *i.e.*, $D2$ Ansatz is to apply to polaron problems, the appropriate quantum systems are those with strongly classical characteristics as each phonon mode in this Ansatz is a single coherent state. In such a case, the solution of the Holstein Hamiltonian is typically a pulse-shaped distribution of phonon amplitudes which represents the deformation localized in the frame of the lattice, which also confines the corresponding pulse-shaped exciton amplitude. As revealed from Eqn. (3.3.4b), the inclusion of local amplitude $\beta_q e^{-iqn}$ helps to extend the spatial correlation between exciton and phonon to more sites, and thus simplifications in the $\tilde{D}$ Ansatz, which can be regarded as a special case of $D1$ Ansatz with spatial variation of λ_{nq} locates around its mean values.

If one wants to further improve the applicability of an Ansatz, it is beneficial to construct their translationally invariant form. Merrifield Ansatz[152], also known as the small-polaron Ansatz, is an example of the simplest form, and is described as

$$|\Psi(\kappa)\rangle = N^{-1/2} \sum_n e^{i\kappa n} a_n^\dagger \exp \left[-\sum_q (\lambda_q^\kappa e^{-iqn} b_q^\dagger + \lambda_q^{\kappa*} e^{iqn} b_q) \right] |0\rangle \quad (3.3.5)$$

where $|0\rangle$ denotes the vacuum state for both the exciton and phonon, and λ_q^κ is the

variational parameter for phonon displacements with wave vector q .

However, this small polaron Ansatz becomes rather inadequate in describing the case of the interacting system when the exciton-phonon coupling strength goes to 0, since this single coherent state gives a poor approximation to a one phonon number state.

To work around this problem, an improved Ansatz state was proposed by Toyozawa[153], expressed as:

$$|\Psi(\kappa)\rangle = |\kappa\rangle \langle \kappa | \kappa \rangle^{-1/2} \quad (3.3.6)$$

$$|\kappa\rangle = N^{-1/2} \sum_{nk} e^{i(\kappa-k)n} \psi_k^\kappa a_k^\dagger \exp \left[-N^{-1/2} \sum_q \left(\lambda_q^\kappa e^{-iqn} b_q^\dagger - \lambda_q^{\kappa*} e^{iqn} b_q \right) \right] |0\rangle \quad (3.3.7)$$

In this expression, λ_q^κ describes the phonon coherent states, and the newly added ψ_k^κ is the exciton amplitude which describes the distribution of the electronic excitation. It can be further observed that the form factor in Eqn. (3.3.7) is the D_2 Ansatz.

Following similar rationale, one can construct translationally invariant versions of $\tilde{D}$ and D_1 , namely global local (GL) Ansatz [85] and delocalized- D_1 [90] Ansatz, respectively. Those can be expressed as:

$$|\kappa^{GL}\rangle = N^{-1/2} \sum_{nlk} e^{i\kappa n - ikl} \psi_{l-n}^\kappa a_k^\dagger \exp \left\{ -N^{-1/2} \sum_q \left[\left(\lambda_q^\kappa e^{-iqn} - \beta_q^\kappa e^{-iql} \right) b_q^\dagger - H.C. \right] \right\} |0\rangle \quad (3.3.8)$$

and

$$|\kappa^{D-D_1}\rangle = N^{-1/2} \sum_{nlk} e^{i\kappa n - ikl} \psi_{l-n}^\kappa a_k^\dagger \exp \left[-N^{-1/2} \sum_q \left(\lambda_{l-n,q}^\kappa e^{-iqn} b_q^\dagger - \lambda_{l-n,q}^{\kappa*} e^{iqn} b_q \right) \right] |0\rangle \quad (3.3.9)$$

The final trial wave function for each Ansatz listed above should be normalized as shown in Eqn. (3.3.6).

3.3.3 Polaron Dynamics

The problem of polaron dynamics can be solved if the time dependencies have been included into the Ansätze given in the previous section. The general formalism of the time-dependent wave function $|\Psi(t)\rangle$ for any given Hamiltonian $\hat{H}$ in Hilbert space can be parameterized by N time-dependent functions $\alpha_n(t)$ ($n = 1, \dots, N$):

$$|\Psi(t)\rangle \equiv |\{\alpha_n(t)\}\rangle \quad (3.3.10)$$

Assuming this wave function satisfies Schrodinger equation:

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle \quad (3.3.11)$$

and by writing the time derivative $\frac{\partial}{\partial t} |\Psi(t)\rangle$ in terms of $\alpha_n(t)$ and their derivatives $\dot{\alpha}_n(t)$, one can obtain:

$$\left(i\hbar \frac{\partial}{\partial t} - \hat{H} \right) |\Psi(t)\rangle = |\{\alpha_n(t)\}, \{\dot{\alpha}_n(t)\}\rangle = 0 \quad (3.3.12)$$

Projecting the time-dependent Schrodinger equation to N different states $|\Psi_n\rangle$ ($n=1, \dots, N$), N equations of motion for N $\alpha_n(t)$ can be derived as:

$$\langle \Psi_n | \{\alpha_n(t)\}, \{\dot{\alpha}_n(t)\} \rangle = 0 \quad (3.3.13)$$

In order to obtain these equations of motion, it is beneficial to introduce Lagrangian formalism established in the Dirac-Frenkel time-dependent variational method[154]. The Lagrangian of the system can be written as:

$$L = \langle \Psi(t) | i\hbar \frac{\partial}{\partial t} - \hat{H} | \Psi(t) \rangle \quad (3.3.14)$$

From which one can obtain the equations of motion for $\alpha_n(t)$ and their time-derivatives $\dot{\alpha}_n(t)$ with:

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{\alpha}_n^*} \right) - \frac{\partial L}{\partial \alpha_n^*} = 0 \quad (3.3.15)$$

As it is preferable to start with a simpler Ansatz, throughout this thesis the Davydov Ansätze will be applied to obtain the equations of motion with the time-dependent variational method introduced in this section. Further derivations of equations of motion *etc.*, will be provided as part of the results in Chapter 6.

3.4 The Munn-Silbey Polaron Transport Model

The Original Munn-Silbey polaron transport model [109-111] was proposed and formulated about two decades ago to address the issue of electronic transport in molecular crystals in the simultaneous presence of local and non-local electron-phonon coupling. The Hamiltonian suitable for describing the behavior of the transport of polaron is a slightly modified form of Eqn. (3.3.1) as:

$$H = \sum_k \varepsilon_k a_k^\dagger a_k + \sum_q \omega_q (b_q^\dagger b_q + 1/2) + N^{-1/2} k \sum_{kq} \omega_q f_{-k}^q a_{k+q}^\dagger a_k (b_q + b_{-q}^\dagger) \quad (3.4.1)$$

where $\varepsilon_k = \varepsilon + J_k$, with

$$J_k = \sum_m e^{i\mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_m)} J_{nm} \quad (3.4.2a)$$

and

$$f_k^q = \sum_m e^{-i\mathbf{k} \cdot (\mathbf{R}_n - \mathbf{R}_m)} f_{n-m}^q \quad (3.4.2b)$$

Eqns. (3.4.2a) and (3.4.2b) describe the relationship between site representation and wave vector representation. Proper transformation of the Hamiltonian in Eqn. (3.4.1) is required in order to yield a weak residual coupling. Since Eqn. (3.4.1) includes both local and non-local coupling, a more general non-local transformation should be applied to obtain the expected Hamiltonian. The Hamiltonian in Eqn. (3.4.1) is transformed according to:

$$H \rightarrow \tilde{H} = e^p H e^{-p} \quad (3.4.3)$$

with

$$p = N^{-1/2} \sum_{kq} A_{-k}^q (b_{-q}^\dagger - b_q) a_{k+q}^\dagger a_k \quad (3.4.4)$$

where

$$A_k^q = \sum_m e^{-i(\mathbf{k}-\mathbf{q}) \cdot \mathbf{R}_m} e^{i\mathbf{k} \cdot \mathbf{R}_m} A_{nm}^q = (A_{k-q}^{-q})^* \quad (3.4.5)$$

describes the transformation parameters.

The phonon operators are changed to:

$$b_q \rightarrow b_q - N^{-1/2} \sum_{nm} A_{nm}^{-q} a_n^\dagger a_m \quad (3.4.6a)$$

$$b_q^\dagger \rightarrow b_q^\dagger - N^{-1/2} \sum_{nm} A_{nm}^q a_n^\dagger a_m \quad (3.4.6b)$$

$$(b_q + b_{-q}^\dagger) \rightarrow (b_q + b_{-q}^\dagger) - 2N^{-1/2} \sum_{nm} A_{nm}^q a_n^\dagger a_m \quad (3.4.6c)$$

according to the transformation.

Eqn. (3.4.4) can also be written as:

$$p = \sum_{kq} a_k^\dagger S_{kk'} a_{k'} \quad (3.4.7)$$

where

$$S_{kk'} = N^{-1/2} A_{-k}^{k-k'} (b_{-k+k'}^\dagger - b_{k-k'}^\dagger) \quad (3.4.8)$$

Thus the excitation operators can be written as:

$$a_k \rightarrow \sum_{k'} \theta_{kk'} a_{k'} \quad (3.4.9a)$$

$$a_k^\dagger \rightarrow \sum_{k'} \theta_{kk'}^\dagger a_{k'}^\dagger \quad (3.4.9b)$$

with

$$\theta_{kk'} = [\exp(-\mathbf{S})]_{kk'} \quad (3.4.10a)$$

$$\theta_{kk'}^\dagger = [\exp(\mathbf{S})]_{kk'} \quad (3.4.10b)$$

In Eqn. (3.4.10), $\mathbf{S}$ denotes the matrix $(S_{kk'})$, while the operator $S_{kk'}$ creates a net phonon momentum of $k'-k$.

Thus the final transformed Hamiltonian is:

$$\tilde{H} = H^{ex} + H^{ph} + V \quad (3.4.11a)$$

$$H^{ex} = \sum_k \left(\varepsilon + \tilde{J}_k - N^{-1} \sum_q \omega_q |A_k^q|^2 \right) a_k^\dagger a_k \quad (3.4.11b)$$

where $\tilde{J}_k$ is a renormalized transfer integral that can be described by:

$$\tilde{J}_k = \sum_{k'} J_{k'} \langle \theta_{k'k}^\dagger \theta_{k'k} \rangle \quad (3.4.12)$$

and the phonon Hamiltonian that retains the common form given as:

$$H^{ph} = \sum_q \omega_q \left(b_q^\dagger b_q + \frac{1}{2} \right) \quad (3.4.13)$$

The transformation parameters are determined to prevent divergence of $\tilde{V}$ at high temperature:

$$A_{-k}^q = \sum_{k'} f_{-k'}^q \langle \theta_{k'+q, k+q}^\dagger \theta_{k'k} \rangle \quad (3.4.14)$$

Then the interaction term has the form $\sum_{kk'} V_{kk'} a_k^\dagger a_{k'}$, where

$$V_{kk'} = \sum_k \left\{ J_k \mathbf{T}_{\kappa k; \kappa k'} - N^{1/2} \sum_Q \omega_Q f_{-k}^Q \times \left[2N^{-1/2} A_{-k'}^{-Q} \mathbf{T}_{\kappa+Q, k; \kappa, k'-Q} - \mathbf{T}_{\kappa+Q; \kappa k'} (b_Q + b_{-Q}^\dagger) \right] \right\} \quad (3.4.15)$$

The operators $\mathbf{T}$ are defined as:

$$\mathbf{T}_{kk'; qq'} = \theta_{kk'}^\dagger \theta_{qq'} - \langle \theta_{kk'}^\dagger \theta_{qq'} \rangle \quad (3.4.16)$$

If the residual interaction after transformation is weak, the diffusion coefficient can be expressed as:

$$D = a^2 \left\langle \left\langle v_k^2 / \Gamma_{kk} + \gamma_{kk} \right\rangle \right\rangle \quad (3.4.17)$$

where a is the nearest-neighbor distance and k/a is the wavevector. The double brackets in Eqn. (3.4.17) represent the thermal average over polaron state of energy E_k and v_k is defined as the gradient of E_k . In Eqn. (3.4.17), the contribution to the diffusion coefficient that can be described as scattering and hopping rate Γ_{kk} and γ_{kk} , respectively, are defined as:

$$\Gamma_{kk} = \sum_k W_{kk; k'k'} \quad (3.4.18a)$$

$$\gamma_{kk} = \frac{1}{2} \nabla_q^2 \sum_k' \operatorname{Re} \left(\frac{1}{2} W_{kk; k'+q, k'+q} - W_{k, k+q; k', k'+q} \right) \Bigg|_{q=0} \quad (3.4.18b)$$

The prime in Eqn. (3.4.18a) denotes the sum excluding $k=k'$. And the quantities W are given by:

$$\begin{aligned} W_{k, k+q; k', k'+q} = \int_0^\infty dt \left\{ \langle V_{k'+q, k+q} V_{kk'}(t) \rangle \exp[-i(E_{k'+q} - E_{k+q})t] \right. \\ \left. + \langle V_{k'+q, k+q}(t) V_{kk'} \rangle \exp[-i(E_k - E_{k'})t] \right\} \end{aligned} \quad (3.4.19)$$

The evaluation of D will directly lead to the mobility μ via Einstein relation $\mu = e\beta D$.

Chapter 4: Obtaining Material Parameters with Quantum Chemistry and MBO Optical Spectroscopy

In this chapter, ground- and excited-states of rubrene single molecule, aggregates and crystal will be investigated with the aid of quantum chemical methods. Rubrene is a promising candidate for the application of organic transistors owing to its high hole mobility at room temperature ($10\sim 43\text{cm}^2/\text{Vs}$) [20]. Thus it is crucial to understand the nature of the optical processes and charge carrier transport in rubrene. As a first step towards in-depth understanding, the material parameters closely related to the optical and transport processes should be identified and calculated with the quantum chemical methods at the level of single molecule and molecular aggregates. We have investigated these properties from perspectives of various quantum chemistry calculations, seeking for interconnections between molecular/aggregate geometries and the material parameters. The quantum chemistry calculations include ground state calculations at DFT level, and excited states will be investigated at the level of ZINDO and TDDFT.

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Jun Ye, Andrew C. Grimsdale, and Yang Zhao, *Analyzing the Optical Properties of a Conjugated Polymer by the Multi-Mode Brownian Oscillator Model*, Journal of Physical Chemistry A 114, 504-508 (2010).

4.1 Ground State Properties of Single Molecules, Molecular Aggregates and Crystal

The geometries for both rubrene molecule and crystal have been constructed according to the existing literature [20]. A rubrene monomer can be regarded as a derivative of tetracene with four additional benzene rings (phenyl groups) attached to the backbone.

The geometry of the rubrene molecule is shown in Figure 2(a).

Figure 2. Geometry of (a) a rubrene molecule, where the tetracene backbone is clearly revealed. The isosurfaces of (b) HOMO and (c) LUMO orbital from the optimized rubrene molecule geometry. The green and yellow color represents negative and positive value, respectively. The HOMO and LUMO energy for the rubrene molecule is -4.333eV and -2.865eV, respectively.

Ground state geometry optimization of the rubrene molecule was carried out with the DMol3 package integrated in the Materials Studio software. In order to obtain desired accurate description of molecular geometry, the basis set was chosen as double numerical plus polarization (DNP) with all the electrons considered for the self-consistent calculation. The self-consistent convergence criterion was set as 1.0×10^{-6} Ha. For the

geometry optimization processes, following convergence criteria were chosen: energy difference $< 1.0 \times 10^{-5} \text{ Ha}$, maximum force $< 0.002 \text{ Ha/\AA}$ and maximum displacement $< 0.005 \text{ \AA}$. The HOMO and LUMO orbital were calculated after geometry optimization, and the optimized molecular structure and orbital configuration are given in Figure 2. The GGA functional used to proceed the electronic structures calculation of the rubrene molecular and crystal structure took the form of Perdew Burke Ernzerhof (PBE) [155].

Figure 3. The unit cell of the rubrene crystal, where the three major planes (*ab*, *ac*, *bc*) have one to one correspondence to the synthesized single crystal rubrene as shown in the bottom left corner of the figure. The lattice parameters for the unit cell are: $a=26.789 \text{ \AA}$, $b=7.170 \text{ \AA}$, $c=14.211 \text{ \AA}$, $\alpha=\beta=\gamma=90^\circ$. The space group of the unit cell is CMCA. The red, blue and green arrows indicate three nearest neighbor dimer in a unit cell of crystalline rubrene along different directions. Hydrogen atoms are omitted for clarity.

Geometry optimization was also performed to the rubrene crystalline unit cell shown in Figure 3. To reduce the computation cost, symmetry and lattice parameters of the unit cell were constrained and only allowed variations of the coordinates of the atoms. In

performing the geometry optimization of rubrene unit cell, lattice parameters were retrieved from Ref. [156] and given in the caption of Figure 3.

Figure 4. The (a) HOMO and (b) LUMO orbital contour for the *ab*-plane of a rubrene $2 \times 2 \times 2$ super-cell. The red color and blue color represents positive and negative value of the isosurfaces respectively. It is worth noting that the HOMO energy in crystalline rubrene is now changed to -5.208eV (-4.333eV for single molecule) whereas the LUMO energy is changed -4.095eV (-2.865eV for single molecule). (c) The band structure and partial Density of States (PDOS) chart of a rubrene unit cell.

However, optimization of atom positions still provides useful information such as orbital configuration, density of states and band structures. The optimization was carried out using the same criteria as those adopted for the rubrene molecule. Properties including orbital configurations, band structures and partial density of states (PDOS) were calculated. Schematics of the optimized unit cell are shown in Figure 3 with respect to

three major planes of the synthesized single crystal. The orbital configurations, band structures and partial density of states are shown in Figure 4, where slices of the HOMO and LUMO orbitals are also taken with respect to major crystal planes (for instance, *ab*-plane) to illustrate the most important transition dipoles and the strongest inter-molecular interactions that can be found in the rubrene crystal. The HOMO orbital is shown to have strong overlap in Figure 4a, indicating that the electronic structure of the topmost valence band is favorable for holes transport. This observation agrees well with the experimental facts [20] that rubrene is a very good hole conductor along *a*-direction of the single crystal. Although orbital overlaps are not as strong as those along the *a*-direction, electronic structures of the rubrene crystal still allows substantial potential channels for holes to be transported along *b*-direction. The observed good hole transport capability is closely related to the conjugated backbone of a rubrene molecule and spatial arrangements (especially, the packing) of the molecules which allows for better overlap of the HOMO orbitals. The LUMO configuration in the unit cell also indicates that exciton transfer is more likely to take place along *b*-direction. However, it is noted that the energy difference between the HOMO and LUMO energy of the rubrene crystal is about 1.11eV, which is much smaller than the realistic lowest optical transition energy (~ 2.3 eV). This suggests that excited state calculation should be performed for obtaining accurate optical transition energy, which will be discussed in the next section. The DOS result in Figure 4c also reveals lower population of electrons at HOMO and LUMO levels, while HOMO-1 and LUMO+1 contain much larger populations. Such difference may result in larger oscillator strength for the transitions between HOMO-1 and LUMO+1 level, which also illustrates the importance role of intermolecular interactions. The distance between

HOMO-1 and LUMO+1 level is about twice as large as the HOMO-LUMO gap, which could be an indication that the optically-allowed transitions may not take place between HOMO and LUMO, but rather between HOMO-1 and LUMO+1. Thus it is important to carry out further calculations on the excited states in rubrene aggregates to look into the effects of Van der Waals interactions between molecules. The DFT results obtained so far for both geometry and electronic structures of single molecule and rubrene still provide valuable information such as packing related transport channel in rubrene crystal. But the deficiencies of this method are obvious, especially in regarding the reliability and robustness of the band gap estimation and crystal structure prediction for these materials.

4.2 Excited State Properties of Single Molecules and Molecular Aggregates

The excited-states properties of rubrene monomer and dimers are calculated to facilitate further optical transition analysis. This type of calculations can be performed with *ab-initio* methods such as time-dependent density functional theory (TDDFT) [157] and semi-empirical methods such as ZINDO [134, 158, 159] integrated in many existing commercial or open source software packages. In this thesis, the ground- and excited-states of a rubrene monomer and a few dimers were studied with the semi-empirical ZINDO and first-principle methods (TDDFT) that are implemented in the GAUSSIAN 09 package. The 6-31G basis set was chosen for the calculation of TDDFT and popular B3LYP hybrid exchange-correlation functional was utilized, here we use TDB3LYP as an abbreviation for this method. In performing the TDB3LYP calculations, a self-consistent convergence criterion of 10^{-8} has been applied, and the direct inversion in

the iterative subspace (DIIS) extrapolation method has also been enabled to speed up the convergence processes.

Figure 5. Schematics of the (a) M, N and L axis of a rubrene monomer in planar configuration. (b) Relative orientation of these vectors on the ab -plane of a rubrene unit cell. (c) A rubrene monomer in twisted configuration. Both configurations are obtained with at the level of DFT/B3LYP(6-31G).

The excited-state calculation results for two types of monomers (*c.f.*, Figure 5a and c) and three types of dimers (*c.f.*, Figure 6) are listed in Table 1 and Table 2. From published experimental results, lowest absorption peak for rubrene molecules in chloroform is about 2.35eV [160-164], while 0-0 absorption band in rubrene single crystal is determined as 2.32eV [36]. According to Table 1, the lowest lying optically allowed excited state is identified as a singlet $\pi\pi^*$ state. The energy of this excited state is overestimated by 0.1006eV for ZINDO and 0.019eV for TDB3LYP for planar configuration. For the twisted one, it has been previously determined [165] that for the most stable configuration of rubrene which is in solution or gaseous form, ZINDO shows better performance in predicting energies for interested excited states. It has been observed that the lowest lying optically allowed excited-state energy of the twisted-rubrene is overestimated by 0.0128eV

for ZINDO and underestimated by 0.0791eV for TDB3LYP.

Figure 6. Schematics of three types of dimers used for the excited state calculations, each figure corresponds to the (a) red, (b) blue and (c) green dimers shown in Figure 3. Thus in the following contents, the dimers will be named as R-dimer, B-dimer and G-dimer respectively.

It is also indicated in Table 1 that those obtained with both methods agree well with each other qualitatively, suggesting that ZINDO provides reliable results in predicting excited states for rubrene monomer. Therefore, for calculating reliable excited-state properties without losing much accuracy in the aggregates with much larger number of molecules, computationally cheaper choices such as ZINDO are preferable. Moreover, for the ZINDO results, the first excited-state is characterized as a $\pi\pi^*$ excitation with the largest oscillator strength and with transition dipole moment that lies mostly along the M-axis of the molecule, which is similar to the TDB3LYP results. Thus excited state 1 (ES1) of a rubrene monomer can be regarded as M-polarized (or *c*-polarized from the perspective of crystal structure), in agreement with the experimental results in Ref. [75].

However, the single molecule results are not sufficient to describe realistic situations in a single crystal rubrene, where intermolecular interactions become important. To have better understanding of the effects of intermolecular interactions, three types of rubrene

dimer (*c.f.*, Table 2) shown in Figure 6 have been investigated using TDB3LYP and ZINDO methods, where results from both methods are listed in Table 2. As shown in the table, the trend of excitation energies as well as their corresponding optical transition oscillator strengths and dipole moments obtained from ZINDO is in qualitative agreement with those from TDB3LYP, which further demonstrate the capability of ZINDO in providing reasonable results of excited-state energies of dimers or even aggregates comprised of more molecules. However, caution must be taken in using TDB3LYP, as energies for charge transfer states are clearly underestimated significantly, resulting in unrealistic values just below the first two $\pi\pi^*$ Frenkel exciton states. Calculation results shown in Table 1 and Table 2 also indicate that the most important state involved in optical processes is the ES1 excited-state for a rubrene monomer. However, situation becomes more complicated for the rubrene crystal. As shown in Figure 5, M-polarized transition dipole moments are along a and b directions of a rubrene unit cell which share a same feature of shoulder to shoulder configuration, while the dipole moments along c direction are of head to tail form. For the excited states of dimers, the optically allowed transitions with non-zero oscillator strength are also identified as $\pi\pi^*$ Frenkel exciton states. Such complexity in the dipole moment configurations induces difficulties in identifying their effects on bulk optical transition properties. It can also be deduced from the crystal structure that the center-to-center distance between of two adjacent molecules being the shortest along a -direction, the interaction between them should be the strongest. This is also related to strong π - π interaction between these neighboring molecules owing to molecular packing, which is also responsible for the formation of hole transport channels.

Table 1. The first five singlet excitation states, their corresponding oscillator strengths and transition dipole moments from ZINDO and TDB3LYP for rubrene monomer with planner and twisted configuration. The states with highest oscillator strength have been highlighted in bold font.

ZINDO (planner)	States	E _{ex} (eV)	Oscillator Strength	Transition electric dipole moments (Au)
	1	2.4206	0.4445	(0.0000, 0.0000, 2.7376)
	2	2.8739	0.1723	(-1.5579, 0.1436, 0.0000)
	3	3.3770	0.0000	(0.0000, 0.0000, 0.0000)
	4	3.4882	0.0000	(0.0000, 0.0000, 0.0000)
	5	3.5097	0.1168	(1.1577, -0.1369, 0.0000)
TD-B3LYP (planner)	States	E _{ex} (eV)	Oscillator Strength	Transition electric dipole moments (Au)
	1	2.3390	0.1646	(0.0000, 0.0000, 1.6950)
	2	3.3092	0.0000	(0.0000, 0.0000, 0.0000)
	3	3.3405	0.0007	(0.0454, -0.0808, 0.0000)
	4	3.4676	0.0000	(0.0000, 0.0000, 0.0000)
	5	3.4998	0.0042	(-0.2109, 0.0680, 0.0000)
ZINDO (twisted)	States	E _{ex} (eV)	Oscillator Strength	Transition electric dipole moments (Au)
	1	2.3328	0.4303	(2.7437, 0.0000, 0.0000)
	2	2.7536	0.1238	(0.0000, -1.3545, 0.0000)
	3	3.3437	0.0672	(0.0000, 0.0000, -0.9056)
	4	3.6658	0.0082	(0.0000, 0.0000, 0.3024)
	5	3.7398	0.0323	(0.0000, 0.5933, 0.0000)
TD-B3LYP (twisted)	1	2.2409	0.1729	(1.7744, 0.0000, 0.0000)
	2	3.2798	0.0049	(0.0000, -0.2473, 0.0000)
	3	3.3270	0.0072	(0.0000, 0.0000, -0.2968)
	4	3.4575	0.0002	(0.0000, 0.0509, 0.0000)
	5	3.5648	0.0106	(0.0000, 0.0000, 0.3483)

Table 2. The first five singlet excitation states and their corresponding oscillator strengths from ZINDO and TDB3LYP for three types of rubrene dimer shown in Figure 6. The states with highest oscillator strength have been highlighted in bold font.

ZINDO (dimer R)	States	E _{ex} (eV)	Oscillator Strength	Transition electric dipole moments (Au)
	1	2.3544	0.0000	(0.0000, 0.0000, 0.0000)
	2	2.4154	0.7591	(0.0000, 0.0000, -3.5815)
	3	2.8567	0.0000	(0.0000, 0.0000, 0.0000)
	4	2.8591	0.3512	(-1.1118, -1.9438, 0.0000)
	5	3.1997	0.0000	(0.0000, 0.0000, 0.0000)
TD-B3LYP (dimer R)	States	E _{ex} (eV)	Oscillator Strength	Transition electric dipole moments (Au)
	1	2.0715	0.0597	(0.0000, 0.0000, -1.0842)

	2	2.1421	0.0000	(0.0000, 0.0000, 0.0000)
	3	2.3193	0.0000	(0.0000, 0.0000, 0.0000)
	4	2.4271	0.1988	(0.0000, 0.0000, -1.8286)
	5	3.3160	0.0000	(0.0000, 0.0000, 0.0000)
ZINDO (dimer G)	States	E _{ex} (eV)	Oscillator Strength	Transition electric dipole moments (Au)
	1	2.3702	0.0006	(0.0000, 0.0000, -0.0985)
	2	2.4376	0.8047	(0.0000, 0.0000, -3.6708)
	3	2.8559	0.1232	(0.5451, 1.2096, 0.0000)
	4	2.8748	0.2098	(1.5112, -0.8334, 0.0000)
	5	3.3621	0.0001	(0.0000, 0.0000, 0.0324)
TD-B3LYP (dimer G)	States	E _{ex} (eV)	Oscillator Strength	Transition electric dipole moments (Au)
	1	2.2187	0.0027	(0.0000, 0.0000, 0.2217)
	2	2.2402	0.0029	(0.0000, 0.0000, 0.2305)
	3	2.3115	0.0009	(0.0000, 0.0000, -0.1237)
	4	2.3418	0.2659	(0.0000, 0.0000, 2.1529)
	5	3.2575	0.0000	(0.0000, 0.0000, 0.0184)
ZINDO (dimer B)	States	E _{ex} (eV)	Oscillator Strength	Transition electric dipole moments (Au)
	1	2.4024	0.9576	(3.9494, 0.6891, -0.4437)
	2	2.4368	0.0000	(0.0000, 0.0000, 0.0000)
	3	2.8713	0.0000	(0.0000, 0.0000, 0.0000)
	4	2.8773	0.3257	(-0.4228, 2.1057, -0.0872)
	5	3.3740	0.0000	(0.0000, 0.0000, 0.0000)
TD-B3LYP (dimer B)	States	E _{ex} (eV)	Oscillator Strength	Transition electric dipole moments (Au)
	1	2.3284	0.3903	(2.5673, 0.4280, -0.2611)
	2	2.3471	0.0000	(0.0000, 0.0000, 0.0000)
	3	2.3991	0.0000	(0.0000, 0.0000, 0.0000)
	4	2.3992	0.0004	(0.0738, 0.0200, -0.0116)
	5	3.3092	0.0000	(0.0000, 0.0000, 0.0000)

A semi-quantitative calculation is performed to support this argument. It is well known that the dipole-dipole interaction can be written as:

$$E_{dip-dip} = \frac{1}{R_{AB}^3} \left[\mu_A \cdot \mu_B - 3(\mu_A \cdot \hat{R}_{AB})(\hat{R}_{AB} \cdot \mu_B) \right] \quad (4.2.1)$$

with

$$\begin{aligned} \hat{R}_{AB} \cdot \mu_A &= \mu_A \cos(\theta_A) \\ \hat{R}_{AB} \cdot \mu_B &= \mu_B \cos(\theta_B) \end{aligned} \quad (4.2.2)$$

Amplitude of transition dipole is assumed as $\mu_A = \mu_B = 1$ for convenience, and interaction is only considered among two nearest neighbor molecules.

Case 1: along a -direction:

$$R_{AB}=a=7.187\text{\AA}, \theta_A=\theta_B=90^\circ, \text{ so along } a\text{-direction: } E_{dip-dip} = 1/a^3.$$

Case 2: along b -direction:

$$R_{AB} = \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{b}{2}\right)^2} = \sqrt{\left(\frac{7.187}{2}\right)^2 + \left(\frac{14.430}{2}\right)^2} \text{\AA}, \text{ and } \theta_A=\theta_B=90^\circ, \text{ thus along } b\text{-direction:}$$

$$E_{dip-dip} = -\sqrt[3]{2} \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{b}{2}\right)^2}.$$

Case 3: along c -direction:

$$R_{AB} = \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{c}{2}\right)^2} = \sqrt{\left(\frac{7.187}{2}\right)^2 + \left(\frac{26.901}{2}\right)^2} \text{\AA}, \text{ and } \theta_A=\theta_B=\arctan(a/c), \text{ therefore along}$$

$$c \text{ direction we have: } E_{dip-dip} = -\frac{2c^2 - a^2}{c^2 + a^2} \times \sqrt[3]{2} \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{c}{2}\right)^2}.$$

The absolute values of the interaction are used for comparison. And the amplitude ratio along c -, b - and a -direction is 1: 2.863: 4.038. This ratio proves former conclusion that the interaction along a -direction is the strongest. According to this calculation, with $\mu_A=\mu_B=1.6950$ a.u. as calculated from TDDFT, the dipole-dipole interaction energy along a -direction is found to be: $E_{dip-dip} = 0.024\text{eV}$, which is consistent with the argument above. Semi-empirical ZINDO and TDDFT calculations of three types of dimers along a -, b - and c -direction have also been performed, and the results are listed in Table 2. As shown in the table, the lowest two excited states are identified as $\pi\pi^*$ transitions, moreover, the first excited state possesses the largest oscillator strength, which is in qualitative agreement with the TDDFT results. Combining ZINDO results from Table 1 and Table 2, it can be observed that the excited-state energies increase when dimers are formed, and the amount of increase for ES1 states is 0.0531eV, 0.0373eV and 0.0181eV for dimers along a -, b - and c -direction, respectively. These values further confirm that the dipole-dipole interaction

along a -direction is the strongest, and also of the same magnitude compared to previous qualitative evaluation results. It is also noted that the pointing directions of the transition dipoles of two optical-allowed lowest excited states are along M-axis. Furthermore, the semi-empirical ZINDO calculation results reveal that the dominate transitions from ES0 to ES1 (or ES2) state are composed of those from two highest occupied molecular orbitals (HOMO) to two lowest unoccupied molecular orbitals (LUMO). Since both excited states are identified as Frenkel exciton state, to facilitate the calculation of exciton transfer integral J , one can use the Frenkel exciton model, *i.e.*, $\hat{H}^{ex} = \sum_{nm} J_{nm} a_n^\dagger a_m$ to fit the excited states obtained with ZINDO calculations. Owing to the prominent anisotropy of transport in rubrene as revealed from Figure 4 showing transport channel along a -direction of the crystal, one can simplify the transport in rubrene crystal as a one dimensional problem. Such simplification has been recently demonstrated to be a reasonable one according to Ref. [166], which suggests for the transport in the ab -plane of the rubrene crystal, one-dimensional transport characteristics are well preserved.

Table 3. The first 10 singlet excitation states calculated from ZINDO for a 1D array of 10 rubrene molecules along a -direction. The state with highest oscillator strength has been highlighted in bold font.

States	E _{ex} (eV)	Oscillator Strength
1	2.3219	0.0000
2	2.3261	0.0000
3	2.3334	0.0000
4	2.3436	0.0001
5	2.3566	0.0000
6	2.3723	0.0019
7	2.3895	0.0000
8	2.4067	0.0549
9	2.4215	0.0000
10	2.4319	3.1100

Figure 7 Relative energy plots for the 10 lowest energy states from the ZINDO calculations (squares in black) for an aggregate along a -direction with 10 rubrene molecules and the Frenkel exciton model with $J = 0.031\text{eV}$ (filled circles in red). The energies of the excited states have been subtracted by the average of the 10 ZINDO states. The horizontal axis labels the eigenstate index goes from 1 to 10.

Therefore we follow a strategy of obtaining exciton transfer integral J by fitting the excited state energy of an array of rubrene molecules along a crystallographic direction with Frenkel exciton model, thereby obtaining approximate values of J which are essential to the transport properties. The first ten excited states for the 1D array of 10 molecules along a -direction are listed in Table 3 with the corresponding fittings by the Frenkel exciton model given in Figure 7. As demonstrated in the figure, this simple fitting procedure of singlet excited states energies for arrays of molecules can be very helpful in obtaining the value of exciton transfer integral J in highly anisotropic organic semiconductors. The values of J obtained are comparable to those obtained from much more sophisticated and computationally intensive methods such as TDDFT [64], further strengthening the reliability of semi-empirical methods in obtaining important material parameters for organic semiconductors.

Figure 8. Configurations of rubrene aggregate of different size (in terms of number of molecules) for obtaining excited-state energies using ZINDO.

The ZINDO results of Table 3 and the fitting results in Figure 7 indicate that the rubrene aggregates in *ab*-plane should be H-aggregate. To further support this hypothesis, we performed a series of studies of the effect of aggregation in terms of excited-state energies for rubrene aggregates with various configurations in the *ab*-plane. The configurations of the aggregates with different size are shown in Figure 8. It is obvious from the trend of the excited-state energies listed in Table 4 that packing of the rubrene molecules on the *ab*-plane of rubrene single crystal leads to H-aggregation. Furthermore, the relationship between the packing and symmetry suggests their role in determining excited states of an aggregate. This is well demonstrated by comparing the cases of 7 monomers (7 and 7*), where more symmetric configuration leads to slightly higher excited state energy and oscillator strength.

Table 4. A summary of ZINDO calculated excited states for rubrene aggregates of different size with highest oscillator strength and their corresponding configurations are given in Figure 8.

No.of monomers	Excited State Energy (eV)	Osc. Strength	Transition electric dipole moments (Au)
1	2.3939	0.4402	(-2.7396, -0.0014, 0.0001)
2	2.4238	0.7605	(0.0000, 0.0000, -3.5786)
3	2.4559	1.0523	(0.0000, 0.0000, 4.1821)
4	2.4718	1.3627	(0.0000, 0.0000, -4.7436)
5	2.4628	1.5675	(0.0000, 0.0000, -5.0969)
6	2.4767	1.7924	(0.0000, 0.0000, 5.4351)
7	2.4790	1.9959	(0.0000, 0.0000, -5.7327)
7*	2.4811	2.0022	(0.0000, 0.0000, -5.7392)

Figure 9. Experimental PL spectra from *ab*, *ac* and *bc* surfaces of a rubrene single crystal. The inset is PL spectra of *ab*-plane with different rotating angles of the sample, where the black, green, red and blue curve indicates the initial position, final position, 90° rotation and 180° rotation, respectively. Experimental data are provided by Professor Christian Kloc and Mr. Zhang Keke.

The calculation results of excited states of rubrene monomers, dimers and aggregates help to understand some experimental spectral features shown in Figure 9 for rubrene single crystal. The first band at 2.19 eV can be regarded as a result of the transition in the M-direction, since excitation laser beam is perpendicular to the *ab*-plane of a macroscopic rubrene single crystal. Thus the observation should be along the *c*-direction. In other words, polarization of observed photons should be perpendicular to *c*, resulting in

vanishing of this band in the PL spectrum as shown in the inset of Figure 9. However, as also indicated from the inset of Figure 9, this component does not disappear completely owing to possible optical misalignment and/or the nonzero solid angle of PL collection objective. Thus the PL spectra from *ab*-plane are expected to behave similarly when the sample is rotating around the *c* axis, as indicated in the experimental results (*c.f.*, inset of Figure 9). However, if *ac*- or *bc*-plane is excited, a component from the transition along the *c*-axis will arise accordingly due to the non-vanishing M-transition and its large oscillation strength. Thus the PL intensity in Figure 9 for the *ac*- or *bc*-plane excitations is much stronger as compared to *ab*. Optical anisotropy observed herein the PL behavior relies not only on the effects of transition polarization, but also the symmetry and packing in the rubrene single crystal.

4.3 Quantum Chemical Fitting of the Experimental Spectra

The vibrationally resolved optical absorption and PL spectrum of rubrene monomer has been calculated based on the IMDHO model and excited-state geometry obtained from the TDDFT method. The IMDHO model provides a reasonable approximation for many practical cases, although effects such as Duschinsky rotations and anharmonicities may cause problematic evaluation of certain classes of electronic transitions. The calculated absorption and PL spectra of a single molecule of rubrene are shown in Figure 10, which are compared to the experimental ones obtained in toluene solution. The geometries and vibrational frequencies of ES0 (ground state) and ES1 (first excited state) states are obtained from a hybrid functional of BHandHLYP with def2-TZVP(-f) type of basis implemented in the ORCA package. In performing the calculation of optical spectra, the

linewidth is obtained by assigning a homogeneous broadening factor of 50cm^{-1} to the spectra and a temperature of 300K is also included. Moreover, the 0-0 transition between the ground and excited state is set to 2.32eV.

Figure 10. Comparison of PL and absorption spectra of the single molecule rubrene calculated using TDDFT and IMDHO method with experimental results. A homogeneous broadening factor of 50 cm^{-1} and a temperature of 300K has been applied to the calculations of the spectra. Experimental data are provided by Professor Christian Kloc and Mr. Zhang Keke.

Figure 11. Comparison of the PL spectrum of the single molecule rubrene calculated using TD-B3LYP and IMDHO method with experimental spectrum of single crystal rubrene collected from the *ab*-plane. Experimental data are provided by Professor Christian Kloc and Mr. Zhang Keke.

The TDDFT absorption spectrum agrees well with the experimental result, although the relative intensity of the first three peaks are slightly shifted, which can be regarded as a result of overestimated Huang-Rhys factor for the primary mode that may related to the choice of functional. Although there are 86 vibrational modes in total identified for the molecule, the major phonon sidebands of the absorption spectrum result from one or two modes, as will be further demonstrated in the later section. However, it is also noted from the figure that the PL spectrum in solution differs greatly on the lower energy region, which may have resulted from incorrect excited state geometry or excited state vibrational frequencies owing to neglect of Duschinsky rotations or excited state frequency alterations [65] that may be critical to the PL spectrum of rubrene in solution. Furthermore, it is also possible that lower sensitivity of photodetector above 570nm may be less reliable, making the comparison of PL spectrum less significant [65]. A comparison between TDDFT PL spectrum and the experimental one obtained from the *ab*-plane of a rubrene single crystal is shown in Figure 11. It is interesting to find better agreement between single molecule spectrum and experimental spectrum of single crystal rubrene compared to the case in solution when the temperature is increased 300K. In contrast to the comparisons between theoretical single molecule PL and experimental PL in solution, the agreement between single molecule TDDFT PL spectrum and experimental one in single crystal suggests confinement of molecule distortions in solid state upon excitation. It is also suggested from the figure that the second peak on the lower energy side of the PL spectrum may not necessarily be the phonon side band of the intrinsic rubrene, and that the possibilities of having impurity states cannot be neglected. However, for the current TDDFT + IMDHO method, the drawbacks are also obvious. It is

difficult to apply the method to deal with large number of atoms that are included in a unit cell or even small aggregates due to its computationally intensive nature if one wants to obtain fairly reliable results. However, as is also demonstrated in this section, it is still possible to use *ab-initio* method to find relaxation energy, transfer integral, transition dipoles, strongly coupled phonon modes and to even obtain qualitative fitting of experimental spectra, which will be helpful in interpreting the nature of the excited states for the molecular crystals such as rubrene and providing crucial material parameters.

4.4 MBO Fitting of the Experimental Spectra

As previously demonstrated in Ref. [141-143, 148], the MBO model is a powerful tool for obtaining physically meaningful parameters from experimental spectra of organic, polymeric and inorganic materials. The MBO model contains sophisticated and applicable treatment of thermal bath that is closely related to the lineshape and linewidth of optical spectra of the materials. Thus this model can be regarded as the starting point of understanding the essentials of photophysics. The model deals with the basic optical processes in a two-level system as well as the effects of the environment on this system. Thus it is straightforward to use this method to find material parameters (*e.g.*, ω_{LO} , S and γ) associated with the calculation of polaron dynamics or transport from experimental or *ab-initio* calculated optical spectra. The results of MBO fitting of absorption and PL spectra for rubrene molecules in solutions and in single crystals are shown in Figure 12. The MBO model is also applied to fit the PL spectra for rubrene single crystal; the results of emission signal from different surfaces are given in Figure 13.

Table 5. The MBO parameters used for the calculation of absorption and PL spectra of rubrene in toluene solution

Spectrum	S1(S2)	$\omega_1(\omega_2)/\text{cm}^{-1}$	$\gamma_1(\gamma_2)/\text{cm}^{-1}$	T/K	E_{eg}/eV
Sol-Abs	1.10(4.50)	1375(70)	200(200)	300	2.31
Sol-PL	0.615(2.90)	1000(70)	350(200)	300	2.26
SC-ab-PL	0.34(3.70)	1450(70)	320(200)	300	2.22
Ox-ab-PL ^a	0.69(3.70)	1270(70)	600(200)	300	2.10
SC-ac-PL	0.34(3.70)	1450(70)	700(200)	300	2.22
Ox-ac-PL ^b	0.59(3.70)	1270(70)	350(200)	300	2.10
SC-bc-PL	0.36(3.70)	1450(70)	570(200)	300	2.22
Ox-bc-PL ^c	0.85(3.70)	1270(70)	270(200)	300	2.10

a,b,c: The weighting factors for the rubrene oxide spectra of *ab*, *ac* and *bc* planes are 0.95, 0.44 and 0.33, respectively.

Figure 12. Experimental and MBO absorption and PL spectra of rubrene in toluene solution. The MBO parameters used for the absorption and PL spectra simulation are taken from Table 5. Experimental data are provided by Professor Christian Kloc and Mr. Zhang Keke.

As we can observe from Figure 12, the absorption spectra of rubrene in solution display well-resolved phonon sidebands and the MBO spectra are almost perfectly well overlapped with the experimental spectra except for the high energy region. From the parameters used to calculate the MBO spectra, the primary phonon frequencies for the PL

and absorption spectra are obtained as 1000cm^{-1} and 1375cm^{-1} , respectively. The phonon frequency obtained from the absorption spectrum is in good agreement with experimental value, *i.e.*, 0.167eV or 1347cm^{-1} . Moreover, the difference between the values of primary phonon frequencies obtained with the MBO model for PL and absorption spectrum of rubrene in toluene solution indicates that the flexibility of the rubrene molecules will result in a change in the excited-state geometry compared to that of the ground state. As a result, the complexity of the excitonic dynamics during the PL process as compared to the absorption process is underlined.

Figure 13. Experimental and MBO PL Spectra of rubrene single crystal for *ab*-, *ac*- and *bc*-planes. The MBO parameters for each plane are taken from Table 5. Experimental data are provided by Professor Christian Kloc and Mr. Zhang Keke.

The MBO fittings of the PL spectra of the single crystal rubrene are shown in Figure 13, in which, a good quantitative agreement can be observed. As indicated from Table 5, it is

worth noting that emission features from rubrene oxide(s) have been included into the MBO simulation of the experimental spectra. This is due to the fact that as the spectra measurements were carried out in atmosphere, the oxidation of rubrene is inevitable. The MBO fitting results for the single crystal spectra indicate similar trend as found in Table 5. Since the spectra were normalized when we carried out the MBO fitting, the relative intensity is reflected by the ratio of rubrene oxide emission as shown in the footnote of Table 5. For the *ab*-plane PL spectrum, although there is still some emission from pristine rubrene, the majority of the emission is obtained from the rubrene oxide, in agreement with the direction of the transition dipole moment with largest oscillator strength for *a*- and *b*-dimer on the *ab*-plane (incident light is parallel to the transition dipole moment). When the PL signals were detected from *bc*- and *ac*-plane, the pristine PL features become dominant. However, the MBO model is not capable to identify the form of the rubrene oxide, despite the acquisition of the excited-state energy and exciton-phonon coupling for the oxide. Table 5 also enlists the primary phonon frequency as 1450 cm^{-1} , which is almost exactly the same as that suggested in [75] (0.177 eV or 1452 cm^{-1}). This quantitative agreement suggests applicability of the MBO model as the starting point in resolving photophysics of the organic materials. Moreover, the obtained primary phonon frequency is close to the value corresponding to the absorption spectrum of rubrene in solution, which may relate to the geometry constraints in crystalline environment.

4.5 Comparison of MBO and Quantum-Chemical Results

From the previous sections, it becomes clear that both the methods can reach good agreements with the experiments. This suggests that the spectra calculated using TDDFT

+ IMDHO method contain similar fundamental physical processes as those in the MBO model. In the MBO model, the Huang-Rhys factor S describes the coupling strength of the nuclear degree of freedom and the electronic degree of freedom of a two-level system, and quantum chemical calculations also suggest availability of this model in describing low lying excited states of some realistic systems. By including the damping factor γ which quantifies the dissipative effect of a phonon bath attached to the two-level system, the broadening of the calculated spectra can be achieved. Because of the non-radiative decay after photo-excitation, the emitting states could be different from the absorbing states, as indicated from the difference of the MBO parameters for PL and absorption spectra. Such difference is further supported by the PL and absorption spectrum from TDDFT + IMDHO method, which shows distinct difference in terms of lineshape. Comparison of quantum chemical and MBO results inspires us to introduce an extremely useful idea which will be very helpful in simplifying the situations in the studies later on. Despite large number of vibrational modes and phonon modes that exist in an organic semiconductor, there are always certain modes that are strongly coupled to the excitations which have significant influence in determining photophysics and transport properties. Thus instead of modeling the system with a comprehensive picture, it is beneficial to use a simplified model with one or few modes that are strongly coupled to the excitations. Such simplifications can reduce the efforts of understanding underlying physics. The idea presented here will be repeated in many subsequent contents to emphasize its importance in the studies of optical and transport properties of organic semiconductors.

4.6 Conclusions

In conclusion, a joint experimental and theoretical study has been carried out to unveil the underlying photophysics of the rubrene single crystal grown by physical vapor transport technique. Measured PL spectra are found to be strongly anisotropic with respect to macroscopic morphology of the crystal. DFT calculations provide much useful information regarding the electronic structures of the system, where the band structures of the rubrene crystal has been obtained. DFT calculations also allow for analyzing of possible hole transport channel that is closely connected to the HOMO orbital, from these calculations, it is suggested that the existence of the hole transport channel owing to the overlap of HOMO orbital along *a*-direction is responsible for the high hole mobility in this material. The connection between microscopic crystallographic planes and macroscopic morphology of the single crystal has been established by analyzing polarization of the optical transitions in a rubrene monomer, dimer and aggregates with TDDFT and ZINDO methods. The singlet optical transition with largest oscillator strength is found as M-polarized with respect to the molecular coordinate, which is in agreement with the molecular packing of the single crystal and the PL spectra measured from various macroscopic surfaces. Combining quantum chemical method and Frenkel exciton model, the value of exciton transfer integral can be obtained by fitting the aggregate excited states. Exciton transfer integral J for the rubrene aggregate along the crystallographic *a*-axis is obtained, the value of which is in good agreement with many other studies. Absorption and PL spectrum calculated with the TDDFT + IMDHO method and MBO model are also in good agreement with each other. Furthermore, good agreement with the experimental results has been obtained for both methods. Good

quantitative agreement is found for the MBO fitting of the experimental spectra of rubrene in both solution and single crystal form, which helps to identify the primary phonon mode that is most strongly coupled to the electronic transition in rubrene. It is thus demonstrated that the application of the model in fitting experimental spectra provided a viable way in obtaining material parameters, specifically S and ω_{LO} that are critical to the subsequential polaron dynamics and transport calculations.

Chapter 5: Polaron Dynamics

Part of content in this chapter has been published on the following papers:

Bin Luo, Jun Ye, Chengbo Guan and Yang Zhao, *Validity of time-dependent trial states for the Holstein polaron*, Physical Chemistry Chemical Physics, 12, 15073–15084 (2010).

Bin Luo, Jun Ye, and Yang Zhao, *Variational study of polaron dynamics with the Davydov Ansätze*, Physica Status Solidi C, 8, 70–73 (2011).

5.1 Derivations of Polaron Dynamics using Davydov Ansätze

In this thesis, calculation of polaron dynamics using Davydov Ansätze served as a major research topic for understanding the quasi-particle dynamics in organic semiconductors, thus in the current section and onwards, derivations and numerical studies of equations of motion, deviation vector and linear absorption spectra will be given respectively.

The generalized Holstein Hamiltonian used for simulating polaron dynamics takes the following form:

$$\hat{H} = \hat{H}_{ex} + \hat{H}_{ph} + \hat{H}_{ex-ph}^{diag} + \hat{H}_{ex-ph}^{off-diag} \quad (5.1.1)$$

with

$$\hat{H}_{ex} = -J \sum_n \hat{a}_n^\dagger (\hat{a}_{n+1} + \hat{a}_{n-1}) \quad (5.1.2a)$$

$$\hat{H}_{ph} = \sum_q \omega_q \hat{b}_q^\dagger \hat{b}_q \quad (5.1.2b)$$

$$\hat{H}_{ex-ph}^{diag} = \sum_{n,q} g_q \omega_q e^{iqn} (\hat{b}_q^\dagger + \hat{b}_q) \quad (5.1.2c)$$

$$\hat{H}_{ex-ph}^{off-diag} = \frac{1}{2} \phi \sum_{n,q} \omega_q \left\{ \hat{a}_n^\dagger \hat{a}_{n+1} \left[e^{iqn} (e^{iq} - 1) \hat{b}_q + h.c. \right] + \hat{a}_n^\dagger \hat{a}_{n-1} \left[e^{iqn} (1 - e^{-iq}) \hat{b}_q + h.c. \right] \right\} \quad (5.1.2d)$$

Here $\hat{H}_{ex}$ defines the Hamiltonian for a single Frenkel exciton band in a rigid chain, and $\hat{a}_n^\dagger$ ($\hat{a}_n$) represents Pauli creation (annihilation) operator for an exciton at site n .

Throughout the derivation and calculations, the value of $\hbar$ is set to 1. At the current stage, nearest-neighbor exciton transfer integral is assumed although it is more realistic to have a full matrix of the transfer integral. $\hat{H}_{ph}$ denotes the phonon Hamiltonian which takes the form of harmonic oscillators, and $b_q^\dagger(b_q)$ is the boson creation (annihilation) operator for a phonon with momentum q and frequency dispersion ω_q . For the sake of simplicity, the zero-point energy is neglected. $\hat{H}_{ex-ph}^{diag}$ and $\hat{H}_{ex-ph}^{off-diag}$ describes the linear coupling of the exciton with the phonon field in site diagonal and off-diagonal forms, respectively. Moreover, to facilitate the comparison with experiments, our discussion is confined to the one-exciton subspace thanks to exciton number conservation in the Hamiltonian (5.1.1).

Without off-diagonal exciton-phonon coupling, the spectral density[106] can be defined as:

$$C_{mn}(\omega) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \hat{V}_m(t) \hat{V}_n(0) \rangle_{ph} e^{i\omega t} dt \quad (5.1.3)$$

Here $\hat{V}_n(t)$ is the Heisenberg representation of the exciton-phonon interaction at site n , which is readily written as:

$$\hat{V}_n(t) = \sum_{q} g_q \omega_q \hat{a}_n^\dagger \hat{a}_n (\hat{b}_q^\dagger e^{-iqn} + \hat{b}_q e^{iqn}) \quad (5.1.4)$$

For zero temperature, one has:

$$C_{mn}(\omega) \equiv \sum_q g_q^2 \omega_q^2 e^{iq\pi(m-n)} \delta(\omega - \omega_q) \quad (5.1.5)$$

as a result of the vanish of the thermal average in Eqn. (5.1.3).

Assuming the form[106] of the spectra density as:

$$C_{00}(\omega) = \sum_q g_q^2 \omega_q^2 \delta(\omega - \omega_q) = \frac{2S\omega^2}{\pi W^2} \sqrt{W^2 - (\omega - \omega_0)^2} \quad (5.1.6)$$

one can define the relaxation energy as:

$$E_r \equiv \int_{-\infty}^{\infty} \frac{C_{00}(\omega)}{\omega} d\omega = \sum_q g_q^2 \omega_q = S \omega_0 \quad (5.1.7)$$

Here S is the well-known Huang-Rhys factor that characterizes the strength of exciton-phonon coupling, ω_0 is the central frequency of the phonon band which is set as the energy unit, *i.e.*, $\omega_0 = 1$, and W is the width of the phonon band taking the form of liner dispersion as given by:

$$\omega_q = \omega_0 + 2W \left(\frac{|q|}{\pi} - \frac{1}{2} \right) \quad (5.1.8)$$

Since the D1 Ansatz is the most general form of the Davydov Ansätze, the derivation of the equations of motion will be performed with it, while special results for the cases with the $\tilde{D}$ and D2 Ansätze will also be provided separately. To arrive at the equations of motion for the variational parameters, a starting point is the application of the time-dependent form of Eqn. (3.3.4a) to Eqn. (3.3.10), from which one obtains the Lagrangian for the D1 Ansatz:

$$L = \langle D_1 | i\hbar \frac{\vec{\partial}}{\partial t} - \hat{H} | D_1 \rangle = i \frac{\hbar}{2} \left[\langle D_1 | i\hbar \frac{\vec{\partial}}{\partial t} | D_1 \rangle - \langle D_1 | i\hbar \frac{\vec{\partial}}{\partial t} | D_1 \rangle \right] - \langle D_1 | \hat{H} | D_1 \rangle \quad (5.1.9)$$

Further expansion using the specific form of D1 Ansatz gives:

$$L = i \frac{\hbar}{2} \left[\sum_n (\dot{\psi}_n \psi_n^* - \dot{\psi}_n^* \psi_n) + \sum_{nq} |\psi_n|^2 (\dot{\lambda}_{nq} \lambda_{nq}^* - \dot{\lambda}_{nq}^* \lambda_{nq}) \right] - \langle D_1 | \hat{H} | D_1 \rangle \quad (5.1.10)$$

The last term of Eqn. (5.1.10) can be separated into four independent contributions:

$$\langle D_1 | \hat{H} | D_1 \rangle = \langle D_1 | \hat{H}_{ex} | D_1 \rangle + \langle D_1 | \hat{H}_{ph} | D_1 \rangle + \langle D_1 | \hat{H}_{ex-ph}^{diag} | D_1 \rangle + \langle D_1 | \hat{H}_{ex-ph}^{off-diag} | D_1 \rangle \quad (5.1.11)$$

Further expansion of each term in Eqn. (5.1.3) gives

$$E_{ex} \equiv \langle D_1 | \hat{H}_{ex} | D_1 \rangle = -J \sum_n \psi_n^* (\psi_{n+1} S_{n,n+1} + \psi_{n-1} S_{n,n-1}) \quad (5.1.12)$$

$$E_{ph} \equiv \langle D_1 | \hat{H}_{ph} | D_1 \rangle = N^{-1} \sum_n |\psi_n|^2 \sum_q \omega_q |\lambda_{nq}|^2 \quad (5.1.13)$$

$$E_{ex-ph}^{diag} \equiv \langle D_1 | \hat{H}_{ex-ph}^{diag} | D_1 \rangle = N^{-1/2} \sum_n |\psi_n|^2 \sum_q g_q \omega_q (\lambda_{nq}^* e^{-iqn} + \lambda_{nq} e^{iqn}) \quad (5.1.14)$$

$$\begin{aligned}
E_{ex-ph}^{off-diag} &\equiv \langle D_1 | \hat{H}_{ex-ph}^{off-diag} | D_1 \rangle \\
&= \frac{1}{2} \phi N^{-1/2} \left[\sum_n \psi_n^* \sum_q \omega_q \left(\psi_{n+1} S_{n,n+1} \Lambda_{n+1}^* + \psi_{n-1} S_{n,n-1} \Lambda_n \right) \right]
\end{aligned} \tag{5.1.15}$$

where $S_{n,m}$ is the Debye-Waller factor defined as

$$S_{n,m} = \exp \left[-\frac{1}{2} \sum_q \left(|\lambda_{nq}|^2 + |\lambda_{mq}|^2 - 2\lambda_{nq}^* \lambda_{mq} \right) \right] \tag{5.1.16}$$

and

$$\Lambda_n = \sum_q \left[(1 - e^{iq}) \lambda_{n-1,q} e^{iqn} + (e^{iq} - 1) \lambda_{nq}^* e^{-iqn} \right] \tag{5.1.17}$$

Following the Hamiltonians given in Eqn. (5.1.1) and (5.1.2), and using the Lagrangian formalism shown in Eqn. (5.1.10), the equations of motion for the time-dependent variational parameters can be readily obtained:

$$iN^{-1} \dot{\psi}_n \dot{\lambda}_{nq}^{D1} = \dot{\lambda}_{nq}^{lag} \tag{5.1.18}$$

where

$$\begin{aligned}
\dot{\lambda}_{nq}^{lag} &= JN^{-1} \left[\psi_{n+1} S_{n,n+1} (\dot{\lambda}_{nq} - \dot{\lambda}_{n+1,q}) + \psi_{n-1} S_{n,n-1} (\dot{\lambda}_{nq} - \dot{\lambda}_{n-1,q}) \right] \\
&\quad + N^{-1} \dot{\psi}_n \omega_q \left(N^{1/2} g_q e^{-iqn} - \dot{\lambda}_{nq} \right) \\
&\quad + \frac{1}{2} \phi N^{-1/2} \omega_q \left\{ \psi_{n+1} S_{n,n+1} \left[\Lambda_{n+1}^* (\dot{\lambda}_{n+1,q} - \dot{\lambda}_{nq}) - (e^{-iq} - 1) e^{-iqn} \right] \right. \\
&\quad \left. + \psi_{n-1} S_{n,n-1} \left[\Lambda_n (\dot{\lambda}_{n-1,q} - \dot{\lambda}_{nq}) + (e^{iq} - 1) e^{-iqn} \right] \right\}
\end{aligned} \tag{5.1.19}$$

and

$$\begin{aligned}
i\dot{\psi}_n^{D1} &= -J \left(\psi_{n+1} S_{n,n+1} + \psi_{n-1} S_{n,n-1} \right) - \frac{i}{2} \dot{\psi}_n N^{-1} \sum_q \left(\dot{\lambda}_{nq} \dot{\lambda}_{nq}^* - \dot{\lambda}_{nq}^* \dot{\lambda}_{nq} \right) \\
&\quad + N^{-1} \dot{\psi}_n \sum_q \omega_q |\dot{\lambda}_{nq}|^2 - N^{-1/2} \dot{\psi}_n \sum_q g_q \omega_q \left(\dot{\lambda}_{nq}^* e^{-iqn} + \dot{\lambda}_{nq} e^{iqn} \right) \\
&\quad + \frac{1}{2} \phi N^{-1/2} \sum_q \omega_q \left(\psi_{n+1} S_{n,n+1} \Lambda_{n+1}^* + \psi_{n-1} S_{n,n-1} \Lambda_n \right)
\end{aligned} \tag{5.1.20}$$

For clarity, all time dependencies of the parameters are hidden. To solve these equations of motion, one can apply the commonly used Runge-Kutta method in solving first-order differential equations. Simplified versions of the D1 Ansatz can also be contemplated. For example, the equations of motion for the simplest D2 Ansatz are now given by

$$i\dot{\lambda}_q^{D2} = \omega_q \left[\frac{1}{2} \phi(e^{-iq} - 1) \sum_n (\psi_n^* \psi_{n+1} + \psi_n \psi_{n-1}^*) e^{-iqn} + g_q \sum_n |\psi_n|^2 e^{-iqn} - \lambda_q \right] \quad (5.1.21)$$

and

$$\begin{aligned} i\dot{\psi}_n^{D2} = & -J(\psi_{n+1} + \psi_{n-1}) + \psi_n \sum_q \omega_q |\lambda_q|^2 - \psi_n \sum_q g_q \omega_q (\lambda_q e^{iqn} + \lambda_q^* e^{-iqn}) \\ & + \frac{1}{2} \phi \sum_q \omega_q \left\{ \psi_{n+1} (1 - e^{-iq}) [\lambda_q e^{iq(n+1)} - \lambda_q^* e^{-iqn}] \right. \\ & \left. - \psi_{n-1} (1 - e^{iq}) [\lambda_q e^{iq(n-1)} - \lambda_q^* e^{-iqn}] \right\} - \frac{i}{2} \psi_n \sum_q (\dot{\lambda}_q \lambda_q^* - \dot{\lambda}_q^* \lambda_q) \end{aligned} \quad (5.1.22)$$

When the $\tilde{D}$ Ansatz is used, for time-dependent parameters λ_q , β_q and ψ_n , one has

$$\dot{\lambda}_{n,q=0}^{\tilde{D}} = i\omega_{q=0} (N^{-1/2} g_{q=0} - \lambda_{n,q=0}) \quad (5.1.23)$$

$$\dot{\lambda}_q^{\tilde{D}} = iN \left(\frac{1}{1 - \gamma_{-q} \gamma_q} \right) (\lambda_q^{lag} - \beta_q^{lag} \gamma_q), \quad \gamma_q = \sum_n |\psi_n|^2 e^{iqn}, \quad \gamma_{-q} = \gamma_q^* \quad (5.1.24)$$

and

$$\dot{\beta}_q^{\tilde{D}} = iN \beta_q^{lag} - \dot{\lambda}_q \gamma_{-q} \quad (5.1.25)$$

where:

$$\begin{aligned} \lambda_q^{lag} = & JN^{-1} \sum_n \psi_n^* \left[\psi_{n+1} S_{n,n+1} (\lambda_{nq}^{\tilde{D}} - \lambda_{n+1,q}^{\tilde{D}}) + \psi_{n-1} S_{n,n-1} (\lambda_{nq}^{\tilde{D}} - \lambda_{n-1,q}^{\tilde{D}}) \right] \\ & - N^{-1} \sum_n |\psi_n|^2 \omega_q \lambda_{nq}^{\tilde{D}} + N^{-1/2} \sum_n |\psi_n|^2 g_q \omega_q e^{-iqn} \\ & + \frac{1}{2} \phi N^{-1/2} \sum_n \psi_n^* \omega_q \left\{ \psi_{n+1} S_{n,n+1} \left[\Lambda_{n+1}^{\tilde{D}*} (\lambda_{n+1,q}^{\tilde{D}} - \lambda_{nq}^{\tilde{D}}) - (e^{-iq} - 1) e^{-iqn} \right] \right. \\ & \left. + \psi_{n-1} S_{n,n-1} \left[\Lambda_n^{\tilde{D}} (\lambda_{n-1,q}^{\tilde{D}} - \lambda_{nq}^{\tilde{D}}) + (e^{iq} - 1) e^{-iqn} \right] \right\} \end{aligned} \quad (5.1.26)$$

and

$$\begin{aligned}
\beta_q^{lag} = & JN^{-1} \sum_n \psi_n^* \left\{ \psi_{n+1} S_{n,n+1} \left[\lambda_{n+1,q}^{\tilde{D}} e^{iqn} - \frac{1}{2} \lambda_{nq}^{\tilde{D}} e^{iqn} - \frac{1}{2} \lambda_{n+1,q}^{\tilde{D}} e^{iq(n+1)} \right] \right. \\
& + \psi_{n-1} S_{n,n-1} \left[\lambda_{n-1,q}^{\tilde{D}} e^{iqn} - \frac{1}{2} \lambda_{nq}^{\tilde{D}} e^{iqn} - \frac{1}{2} \lambda_{n-1,q}^{\tilde{D}} e^{iq(n-1)} \right] \Big\} \\
& - N^{-1} \sum_n |\psi_n|^2 \omega_q \lambda_{nq}^{\tilde{D}} + N^{-1/2} \sum_n |\psi_n|^2 g_q \omega_q e^{-iqn} \\
& + \frac{1}{2} \phi N^{-1/2} \sum_n \psi_n^* \omega_q \left\{ \psi_{n+1} S_{n,n+1} \left[\Lambda_{n+1}^{\tilde{D}*} \left(\lambda_{n+1,q}^{\tilde{D}} e^{iqn} - \frac{1}{2} \lambda_{nq}^{\tilde{D}} e^{iqn} - \frac{1}{2} \lambda_{n+1,q}^{\tilde{D}} e^{iq(n+1)} \right) - (e^{-iq} - 1) \right] \right. \\
& + \psi_{n-1} S_{n,n-1} \left[\Lambda_n^{\tilde{D}} \left(\lambda_{n-1,q}^{\tilde{D}} e^{iqn} - \frac{1}{2} \lambda_{nq}^{\tilde{D}} e^{iqn} - \frac{1}{2} \lambda_{n-1,q}^{\tilde{D}} e^{iq(n-1)} \right) + (e^{iq} - 1) \right] \Big\}
\end{aligned} \tag{5.1.26}$$

Here the superscript $\tilde{D}$ in $\lambda_{nq}^{\tilde{D}}$ denotes λ_{nq} takes the following form:

$$\lambda_{nq}^{\tilde{D}} = \lambda_q + \beta_q e^{-iqn} \tag{5.1.27}$$

And the equation of motion for exciton amplitude ψ_n is expressed as:

$$\begin{aligned}
i\dot{\psi}_n^{\tilde{D}} = & -J(\psi_{n+1} S_{n,n+1} + \psi_{n-1} S_{n,n-1}) - \frac{i}{2} \psi_n N^{-1} \sum_q \left(\dot{\lambda}_{nq}^{\tilde{D}} \lambda_{nq}^{\tilde{D}*} - \dot{\lambda}_{nq}^{\tilde{D}*} \lambda_{nq}^{\tilde{D}} \right) \\
& + N^{-1} \psi_n \sum_q \omega_q \left| \lambda_{nq}^{\tilde{D}} \right|^2 - N^{-1/2} \psi_n \sum_q g_q \omega_q \left(\lambda_{nq}^{\tilde{D}*} e^{-iqn} + \lambda_{nq}^{\tilde{D}} e^{iqn} \right) \\
& + \frac{1}{2} \phi N^{-1/2} \left(\psi_{n+1} S_{n,n+1} \Lambda_{n+1}^{\tilde{D}*} + \psi_{n-1} S_{n,n-1} \Lambda_n^{\tilde{D}} \right)
\end{aligned} \tag{5.1.28}$$

Here we conclude the discussions of polaron dynamics using the Davydov Ansätze. Derivations of the deviation vector, autocorrelation functions and linear absorption spectra will be given in later sections.

For further discussion, one needs to introduce the reduced single exciton density matrix $\rho_{mn}(t)$ defined as:

$$\rho_{mn}(t) = \text{Tr} \left[\rho(t) \hat{a}_m^\dagger \hat{a}_n \right] \tag{5.1.29}$$

where $\rho(t) = |\Psi(t)\rangle\langle\Psi(t)|$ is the full density matrix at zero temperature, and $|\Psi(t)\rangle$ is the total polaron wave function at time t after photo excitation. Substituting the detailed form of the Davydov Ansätze into the polaron wave function, one obtains the reduced

density matrices of the D1, $\tilde{D}$ and D2 Ansatz, respectively, as

$$\rho_{mn}^{D_2} = \langle D_2 | \hat{a}_m^\dagger \hat{a}_n | D_2 \rangle = \psi_m^*(t) \psi_n(t) \quad (5.1.30)$$

$$\begin{aligned} \rho_{mn}^{\tilde{D} \text{ or } D_1} &= \langle \tilde{D} \text{ or } D_1 | \hat{a}_m^\dagger \hat{a}_n | \tilde{D} \text{ or } D_1 \rangle \\ &= \psi_m^*(t) \psi_n(t) S_{m,n} \end{aligned} \quad (5.1.31)$$

As revealed from the expression of the reduced density matrices shown above, for the D2 Ansatz, the reduced exciton density matrix only contains the exciton amplitude, without any information on the phonon manifold. In contrast, the more sophisticated trial states, the D1 and $\tilde{D}$ Ansätze all include the Debye-Waller factor $S_{n,m}$ in their expressions of the reduced exciton density matrices. The Debye-Waller factor has a substantial effect on determining time evolution of the polaron as it described the detailed scattering information of excitons the phonons.

Previously, for translationally invariant states, a definition of the characteristic coherence size, L_ρ , in terms of the density matrix was introduced using the inverse participation ratio which is a concept commonly used in the theory of quantum localization,

$$L_\rho \equiv \left[L_0 \sum_{mn} |\rho_{mn}|^2 \right]^{-1} \left[\left(\sum_{mn} |\rho_{mn}| \right)^2 \right] \quad (5.1.32)$$

Eqn. (5.1.32) can be utilized to quantify the excitonic delocalization despite both of our Ansätze possessing the localized form.

5.2 Effects of Materials Parameters in Polaron Dynamics using Various Ansatz

5.2.1 Effects of J in the Polaron Dynamics using Bare Exciton Dynamics

It is always a good idea to start with the simplest model. Thus, we chose to start with free

Figure 14. Dynamics of bare exciton amplitude $|\psi_n|^2$ calculated from the Lagrangian formalism with (a) $J=0.1$, (b) $J=0.3$, (c) $J=0.5$. Total number of sites for the molecular chains is 32 and total evolution time is 12.5 phonon periods.

exciton dynamics obtained with previously introduced Lagrangian formalism. Omitting the coupling between exciton and phonon, the bare exciton dynamics can be obtained by simply solving:

$$\dot{\psi}_n(t) = iJ[\psi_{n+1}(t) + \psi_{n-1}(t)] \quad (5.2.1)$$

which describes the free exciton migration in an N -site 1-dimensional lattice with periodic boundary condition (or a N -site ring). Despite the simplicity of the equation of motion, the underlying physics is still interestingly complex. Figure 14a reveals the wave-like propagation of free exciton in a ring system with 32 sites. The propagation speed of the exciton is found to be linearly proportional to the exciton transfer integral J before the collision as shown in Figure 14b and c. Taking the case with $J = 0.3$ as an example, the time required for the main exciton wave front to reach the first collision point is 4 phonon periods, thus the speed here is about 4 sites/phonon period considering the spreading only in one direction. Detailed structures suggest interference between wave fronts leads to the formation of a ripple-like structure. It is also very interesting to observe constructive and destructive interference which appears in an alternating fashion, with constructive ones on even-number sites and destructive ones on odd-number sites. Figure 14b and c show more interesting cases when the exciton wave packet travels in opposite directions after collide at the opposite site to that on which exciton is initially situated. It is noted from the figure that constructive interference also propagate in a way similar to the wave fronts, where collisions and scattering of the wave fronts due to interference of the parent wave fronts lead to multiple secondary wave fronts. As noted from the figure that after the first collision, the secondary wave packets have slower travelling speed compared to their parents, indicating multiple collisions taking place at around 4 phonon periods. However

it is worth noting that for the J value chosen in Figure 14b, a possible revival appears after 8 phonon periods, at $n = -1$, the initial excitation site. This type of revival is however weak compared to the initial excitation, and the oscillation period of the revival increases with time, reflecting the quantum nature of the dynamics. From this point of view, a complete revival is next to impossible as the quantum quasi-particle always tends to spread out in space. Interestingly, the phenomenon observed here is similar to the 2D quantum billiard problem[167], whereas in our treatment, only 1-dimensional collisions exist in the system. But quantum chaos is still expected in our system. When the value of J is increased with corresponding results depicted in Figure 14c, the revival phenomenon becomes pronounced as the travelling speed of wave fronts is increased. Within the time window of our calculation, the first possible revival appears after of 5 phonon periods. Similarly, for smaller J values, the intensities of the first revival are not very strong, and two wave packets with similar intensity also reappear after one phonon period following the first revival. The second revival appears at the time around 11 phonon periods, which is slightly smaller than twice of the time for the first revival. For the first two revivals, we can at least regard them as periodic, where the period between the revivals is roughly 5 phonon periods.

5.2.2 Effects of g and ϕ in the Polaron Dynamics Using the D2 Ansatz

Figure 15. Dynamics of D2 and effect of g , only diagonal coupling is considered here. (a)-(c) is the exciton amplitude $|\psi_n|^2$ and (d) –(f) is the phonon displacement ξ_n with $g = 0.1, 0.3$ and 0.5 respectively. The other parameters are fixed to $J = 0.3$, $W = 0.5$ and $\phi = 0.0$.

The localized D2 Ansatz involves two sets of variational parameters for independent descriptions of exciton and phonon. By studying the time evolution of the exciton amplitude ψ_n given earlier and phonon displacement ξ_n defined here as

$$\xi_n = \langle \Psi_D | \frac{\hat{b}_n^\dagger + \hat{b}_n}{2} | \Psi_D \rangle \quad (5.2.2)$$

it is possible to probe the polaron dynamics following photoexcitation at a single-site of a one dimensional molecular chain (ring) with respect to the time-dependent variational parameters. The simplest initial state can be constructed as follows: at $t=0$, the exciton is generated on one site with no initial phonon displacements. Due to the exciton transfer integral and the exciton-phonon coupling in the Holstein Hamiltonian, the spreading of the exciton amplitude and the growth of phonon deformations around the initial excited site ensues. As shown in Figure 15 for three g values, representing diagonal

exciton-phonon coupling strengths from weak to strong, the exciton amplitude propagates from the initial site $n=0$ to the entire chain with a speed proportional to the transfer integral J .

Figure 16. Dynamics of D2 with $J = 0.1$, $S = 2.88$ ($g=0.3$), $W=0$, and increasing value of ϕ . (a)-(b) is the exciton $|\psi_n|$ and phonon amplitude $|\lambda_n|$ for $\phi = 0.1$, (b)-(c) is $|\psi_n|$ and $|\lambda_n|$ for $\phi = 0.3$ and (b)-(c) is $|\psi_n|$ and $|\lambda_n|$ for $\phi = 0.7$.

However, the propagation speed is much smaller if compared to the bare exciton case with the same value of J (*c.f.*, Figure 14b) as a result of the localization effect of g . The case with $g = 0.1$ for sufficient weak diagonal exciton-phonon coupling shown in Figure

15a resembles bare exciton dynamics. Further increase of g leads to a much more localized exciton amplitude. When $g = 0.5$, the exciton is almost localized on site 0, whereas the phonon wave packets still travel with a speed proportional to the value of W . It is also noted from the figure that for stronger exciton-phonon coupling, the phonon displacement also shows a localized feature, which is directly correlated to the localization of exciton. This indicates that strong exciton-phonon coupling not only leads to the localized exciton, but also induces large lattice distortion.

Inclusion of off-diagonal exciton-phonon coupling in addition to its diagonal counterpart uncovers previously unseen polaron dynamics with interesting physics, as shown in Figure 16. For example, asymmetric propagations of both exciton and phonon amplitudes can be observed. The phenomenon becomes more pronounced with increasing off-diagonal coupling strength. More importantly, it should be pointed out that the off-diagonal coupling exists only when the exciton amplitudes are non-zero on at least two adjacent sites as indicated by Eqn. (6.1.2d).

It is quite interesting to observe the two-sided nature of the off-diagonal exciton-phonon coupling. As the value of J is very small in these cases, the dominant terms in the Hamiltonian are the exciton-phonon interactions. It can be observed that the off-diagonal exciton-phonon coupling becomes the sole transport mechanism while it also tends to localize the exciton amplitude. When ϕ is small, as shown in Figure 16a and b, exciton hopping always takes place in the middle of one phonon period, where the phonon amplitude reaches its maximum. As ϕ is increased to take on larger values, stronger off-diagonal coupling between the exciton and phonons leads to severer lattice distortions

and much faster hopping motion of exciton during first phonon period. The exciton amplitude and phonon amplitude are well correlated according to Figure 16c, d and Figure 16e, f. In these figures, the exciton always hops from right to left, which is attributed to the sign of J (as off-diagonal exciton-phonon coupling intrinsically is the second derivative of J with respect to phonon coordinates).

5.2.3 Effects of Initial States on the $\tilde{D}$ /D1 Dynamics

When migrating from the D2 Ansatz to the $\tilde{D}$ or D1 Ansatz, one is expected to encounter new physics that is rooted in the fundamental differences among Ansätze. The time evolution of the variational parameters for the $\tilde{D}$ Ansatz is shown in Figure 17 and Figure 18 obtained for four different types of initial states. Calculations of polaron dynamics using the D1 Ansatz is also carried out and the results are given in Figure 19. The cases with evenly or nearly evenly excited chains are studied, revealing many interesting phenomenon when compared to the D2 results. Inclusion of longer spatial exciton-phonon correlation between exaction and phonon by writing the variational parameters in the form shown in Eqns. (3.3.4b) and (3.3.4c) helps to extend the applicability range. This allows for exploration on how initial states affect polaron dynamics.

Four different initial states introduced are: 1) single excitation of one site without any initial phonon displacement, 2) the initial excitation is evenly distributed among the entire chain, but there is also initial phonon displacement on one site, 3) an evenly excited chain without any initial phonon displacement and 4) nearly evenly excited chain with one site unexcited. The effects of the initial state lead to distinct polaron dynamics of $\tilde{D}$ and D1.

Figure 17. Dynamics of $\tilde{D}$ with different initial states. In (a)-(c), the initial state is a single excitation of site 0 without any initial phonon displacement. In (d)-(f), the initial excitation is evenly distributed among the entire chain, but there is also initial phonon displacement on site 0. For all calculations, the other parameters are fixed to: $S = 1.44$, $J = 0.3$, $W = 0.1$.

Dynamics of the two Ansätze share similar features with those obtained with the D2 Ansatz for single-site excitation. However there are some interesting characteristics emerged in the polaron dynamics of the $\tilde{D}$ and D1 Ansätze. As shown in Figure 17a, the step-wise propagation of the exciton wave packets is obvious, which has a period similar to that of the optical phonon, and the phonon displacement shown in Figure 17b also displays similar behavior. The synchronized dynamics between the exciton and phonons suggests that during the propagation of exciton wave packets, the exciton-phonon coupling could lead to localization of the exciton amplitude, and exciton hopping only

becomes possible when the overall lattice distortion is at minimum after one phonon period.

Figure 18. Dynamics of $\tilde{D}$ with different initial states. In (a)-(c), the initial state is an evenly excitation chain without any initial phonon displacement. In (d)-(f), the initial excitation a nearly evenly excitation chain with site 8 untouched. For all calculations, the other parameters are fixed to: $S = 1.44$, $J = 0.3$, $W = 0.1$.

It is even more interesting to observe the effect of localization due to the exciton-phonon coupling when inspecting Figure 17d-e. With number of phonons equal to 1, the system which is initially completely delocalized quickly becomes localized. The step-wise behavior observed for single-site excitation case is also shown in Figure 17d-e, although the overall pattern is completely different from the previous case shown in Figure 17a-c.

Figure 19. Dynamics of D1, with (a)-(c) using single-site excitation initial state, and (d)-(f) initial state with nearly evenly excitation except site 8. (a) and (d) are the exciton amplitude for the two initial states. (b) and (e) are the phonon displacements. (c) and (f) are the energies and coherence size of two dynamic runs. $S = 0.5$, $J = 0.3$, $W = 0.1$.

The major difference is obviously related to the initial state used to perform the dynamics calculation, where non-zero initial number of phonons for a system that is initially completely delocalized (one of the eigen states of the bare exciton Hamiltonian) is found as a source of destruction of coherence within the system through the diagonal exciton-phonon coupling as shown in Figure 17f. It is worth noting in Figure 18a and b that without the addition of initial phonon displacement, the coherence size of the system is also reduced as a result of exciton-phonon coupling even though the exciton dynamics remain evenly distributed. From this point of view, it is important to compare the

dynamics in this case to those obtained with $\kappa=0$ Merrifield Ansatz [106]. A simple comparison of the time-dependant variational parameters describing phonon suggests similarity between two approaches [*i.e.*, Eqn. (3.3.4b) and (3.3.5)] when the initial state of the $\tilde{D}$ dynamics takes the form of evenly excited chain. It is therefore reasonable to suspect that $\kappa=0$ Merrifield Ansatz could be a special case of $\tilde{D}$. Slight change of this evenly distributed initial state by reducing the total number of excited sites to 15 has a dramatic effect on the polaron dynamics, as demonstrated in Figure 18c and d. As a result of the exciton-phonon coupling, the exciton amplitude quickly becomes localized and begins its propagations in a similar manner as the single-site excitation case. Results of coherence size shown in Figure 18e also provide evidence of temporal localization of the exciton amplitude, suggesting that for certain states with much larger exciton span in real space, it is also possible to have a localized state owing to the exciton-phonon interaction. Thus, one cannot simply use the degree of delocalization of exciton as the only criterion of characterizing the size of a polaron; further information is needed for a rigorous assessment of the polaron size.

Sophistication of the D1 Ansatz results in improved description in the polaron dynamics, as shown in Figure 19. Owing to the matrix form of the phonon-part variational parameters in the D1 Ansatz, richer information of exciton coherence can be extracted. From Figure 19c and f, the coherence size are generally very large in the D1 dynamics, which is related to the smaller value of S and more importantly, the further sophistication of λ_{nq} .

5.4 Deviation Vector

Since a trial wave function $|\Psi(t)\rangle$ does not necessarily obey the Schrödinger equation, and to qualify the accuracy of an Ansatz, one can define a deviation vector $|\delta(t)\rangle$

$$|\delta(t)\rangle \equiv i \frac{\partial}{\partial t} |\Psi(t)\rangle - \hat{H} |\Psi(t)\rangle \quad (5.4.1)$$

A quantitative measure of the Ansatz deviation from exact wave function of the Schrodinger equation can be proposed in the form of the amplitude of the deviation vector $\Delta(t)$

$$\Delta(t) \equiv \sqrt{\langle \delta(t) | \delta(t) \rangle} \quad (5.4.2)$$

Here $|\delta(t)\rangle$ can be derived as follows:

$$\begin{aligned} |\delta(t)\rangle &= \sum_{n,q} \left\{ i \frac{1}{N} \dot{\psi}_n - i \psi_n \text{Re} [\dot{\lambda}_{nq} \lambda_{nq}^*] + \psi_n g_q \omega_q \lambda_{nq} e^{iqn} \right. \\ &\quad + \left(i \psi_n \dot{\lambda}_{nq} - \psi_n \omega_q \lambda_{nq} + \psi_n g_q \omega_q e^{-iqn} \right) \hat{b}_q^\dagger \left. \right\} e^{-\hat{S}_n} \hat{a}_n^\dagger |0\rangle_{ex} |0\rangle_{ph} \\ &\quad + J \frac{1}{N} \sum_n \left(\psi_{n+1} e^{-\hat{S}_{n+1}} + \psi_{n-1} e^{-\hat{S}_{n-1}} \right) \hat{a}_n^\dagger |0\rangle_{ex} |0\rangle_{ph} \\ &\quad - \frac{1}{2} \phi \left\{ \sum_{n,q} \psi_{n+1} \omega_q \left[e^{iqn} (e^{iq} - 1) \lambda_{n+1,q} + e^{-iqn} (e^{-iq} - 1) \hat{b}_q^\dagger \right] e^{-\hat{S}_{n+1}} \hat{a}_n^\dagger |0\rangle_{ex} |0\rangle_{ph} \right. \\ &\quad \left. + \sum_{n,q} \psi_{n-1} \omega_q \left[e^{iqn} (1 - e^{-iq}) \lambda_{n-1,q} + e^{-iqn} (1 - e^{iq}) \hat{b}_q^\dagger \right] e^{-\hat{S}_{n-1}} \hat{a}_n^\dagger |0\rangle_{ex} |0\rangle_{ph} \right\} \\ &= \sum_{n,q} \left\{ \left(A_{nq} + B_{nq} \hat{b}_q^\dagger \right) e^{-\hat{S}_n} + \left(V_{nq} + W_{nq} \hat{b}_q^\dagger \right) e^{-\hat{S}_{n+1}} + \left(X_{nq} + Y_{nq} \hat{b}_q^\dagger \right) e^{-\hat{S}_{n-1}} \right\} \hat{a}_n^\dagger |0\rangle_{ex} |0\rangle_{ph} \end{aligned} \quad (5.4.3)$$

with

$$\begin{aligned} A_{nq} &= i \frac{1}{N} \dot{\psi}_n - i \psi_n \text{Re} [\dot{\lambda}_{nq} \lambda_{nq}^*] + \psi_n g_q \omega_q \lambda_{nq} e^{iqn} \\ B_{nq} &= i \psi_n \dot{\lambda}_{nq} - \psi_n \omega_q \lambda_{nq} + \psi_n g_q \omega_q e^{-iqn} \\ V_{nq} &= J \frac{1}{N} \psi_{n+1} - \frac{1}{2} \phi \psi_{n+1} \omega_q e^{iqn} (e^{iq} - 1) \lambda_{n+1,q} \\ W_{nq} &= -\frac{1}{2} \phi \psi_{n+1} \omega_q e^{-iqn} (e^{-iq} - 1) \\ X_{nq} &= J \frac{1}{N} \psi_{n-1} - \frac{1}{2} \phi \psi_{n-1} \omega_q e^{iqn} (1 - e^{-iq}) \lambda_{n-1,q} \\ Y_{nq} &= -\frac{1}{2} \phi \psi_{n-1} \omega_q e^{-iqn} (1 - e^{iq}) \end{aligned} \quad (5.4.4)$$

As a result, one arrives at the expression for $\langle \delta(t) | \delta(t) \rangle$, derived as follows

$$\begin{aligned}
& \langle \delta(t) | \delta(t) \rangle \\
&= \sum_{n,q,q'} \left[A_{nq}^* A_{nq} + A_{nq}^* B_{nq} \lambda_{nq}^* + B_{nq}^* A_{nq} \lambda_{nq} + B_{nq}^* B_{nq} (\delta_{qq'} + \lambda_{nq}^* \lambda_{nq'}) \right] \\
&+ \sum_{n,q,q'} \left[V_{nq}^* V_{nq} + V_{nq}^* W_{nq} \lambda_{n+1,q}^* + W_{nq}^* V_{nq} \lambda_{n+1,q'} + W_{nq}^* W_{nq} (\delta_{qq'} + \lambda_{n+1,q}^* \lambda_{n+1,q'}) \right] \\
&+ \sum_{n,q,q'} \left[X_{nq}^* X_{nq} + X_{nq}^* Y_{nq} \lambda_{n-1,q}^* + Y_{nq}^* X_{nq} \lambda_{n-1,q'} + Y_{nq}^* Y_{nq} (\delta_{qq'} + \lambda_{n-1,q}^* \lambda_{n-1,q'}) \right] \quad (5.4.5) \\
&+ 2 \operatorname{Re} \sum_{n,q,q'} S_{n,n+1} \left[A_{nq}^* V_{nq} + A_{nq}^* W_{nq} \lambda_{nq}^* + B_{nq}^* V_{nq} \lambda_{n+1,q'} + B_{nq}^* W_{nq} (\delta_{qq'} + \lambda_{nq}^* \lambda_{n+1,q'}) \right] \\
&+ 2 \operatorname{Re} \sum_{n,q,q'} S_{n,n-1} \left[A_{nq}^* X_{nq} + A_{nq}^* Y_{nq} \lambda_{nq}^* + B_{nq}^* X_{nq} \lambda_{n-1,q'} + B_{nq}^* Y_{nq} (\delta_{qq'} + \lambda_{nq}^* \lambda_{n-1,q'}) \right] \\
&+ 2 \operatorname{Re} \sum_{n,q,q'} S_{n+1,n-1} \left[V_{nq}^* X_{nq} + V_{nq}^* Y_{nq} \lambda_{n+1,q}^* + W_{nq}^* X_{nq} \lambda_{n-1,q'} + W_{nq}^* Y_{nq} (\delta_{qq'} + \lambda_{n+1,q}^* \lambda_{n-1,q'}) \right]
\end{aligned}$$

Figure 20. Energy components and Δ for the D2, $\tilde{D}$ and D1 Ansätze with (a) $S = 0.16$, $J = 0.3$, $W = 0.5$; (b) $S = 0.16$, $J = 0.1$, $W = 0.5$; (c) $S = 1.44$, $J = 0.1$, $W = 0.5$; (d) $S = 4$, $J = 0.1$, $W = 0.5$.

With these variational parameters, it becomes possible to calculate various properties such as components of the system energy and the amplitude of deviation vector $\Delta(t)$ for the Ansätze. Figure 20 shows $\Delta(t)$ and system energies for four different parameter sets (S, J, W) using the Davydov Ansätze. For each calculation, the initial exciton state is localized at the site $n = 0$ in a 1D molecular ring, and no phonons have been excited initially. From Figure 20, it is a fact that the $\tilde{D}$ and D1 Ansätze are more accurate than the D2 Ansatz when the exciton–phonon coupling strength g is relatively small. On the other hand, for large S (*i.e.*, $S=4$) and small J (*i.e.*, $J = 0.1$), all three Ansätze provide solutions with almost identical accuracy. However, the information provided by these simple comparisons are far from sufficient to have a better understanding of the applicability of the Ansätze. We thus have carried out a detailed mapping of $\Delta(t)$ of these Ansätze over a large region of the (S, J, W) parameter space. For simplicity, we define the relative deviation of an Ansatz as $\sigma \equiv \max\{\Delta(t)\} / \text{avg}\{E_{ph}(t)\}$ where t runs from 0 to $t_{\max}$, covering the entire duration of simulated time evolution. In this work, the total time used is $t_{\max} = 8(2\pi/\omega_0)$. According to the above discussions, a smaller relative deviation σ indicates a better accuracy of an Ansatz in describing the system dynamics. By exploring the (S, J, W) parameter space, σ as a function of S and J can be obtained for different values of W , which provides a reliable way of finding applicable regimes of an Ansatz. Figure 21 display σ for D2 Ansatz with $W = 0.1$ and $W = 0.8$ for the Davydov Ansätze.

Figure 21 implies that the suitability of D1 Ansatz to be applied over a relatively large parameters regime as compared to the D2 Ansatz. Generally speaking, the relative deviation σ increases as S decreases or as J increases, indicating complicated relationships between the exciton and the phonons at weak coupling, which may require

more sophistication in trial states in order to have a better description. For the cases with small S (e.g., $S=0.16$) and large J (e.g., $J=0.8$), all the Ansätze investigated have failed to deliver an adequate description of the system dynamics. For strong coupling ($S = 4.0$) cases, irrespective of the values J and W all the three Ansätze deviate little from the exact solutions for the time-dependent Schrödinger equation of the Holstein system.

Figure 21. Relative deviation vector σ for the (a)-(b) D_2 , (c)-(d) $\tilde{D}$ and (e)-(f) D_1 Ansatz with single-site excitation as the initial state. The phonon bandwidth W takes on values of 0.1 and 0.8, as indicated in the Figures. For all figures, diagonal exciton-phonon coupling strength S ranges from 0.5 to 6 and exciton transfer integral J also ranges from 0.1 to 1.

The initial state used in all the simulations for the Ansätze is an exciton localized on one site of the molecular ring. Interestingly, if the initial state of an Ansätze consists of evenly distributed exciton, the relative deviation σ will adopt a different dependence on J and S as shown in Figure 22. Such an initial state is usually true for realistic scenarios with a large excitation wavelength and a small system size. One can also introduce a Gaussian distribution or other forms of initial states to approximate realistic situations.

Figure 22. Relative deviation vector σ for the (a)-(b) D_2 , (c)-(d) $\tilde{D}$ and (e)-(f) D_1 Ansatz with evenly excited chain as the initial state. The phonon bandwidth W takes on values of 0.1 and 0.8, as indicated in the Figures. For all figures, diagonal exciton-phonon coupling strength S ranges from 0.5 to 6 and exciton transfer integral J also ranges from 0.1 to 1.

In these cases, both the D1 and $\tilde{D}$ Ansätze can provide description of a polaron system within a large span of parameter regimes. In contrast, the D2 Ansatz fails in most regions even for very strong exciton-phonon coupling. It should be pointed out that for the biologically interesting parameter regimes as well as those are important for organic semiconductors, both S and J are usually small, J usually ranges from 0.1 to 0.5 and S usually ranges from 0.2 to 4.0. From the relative deviation σ as displayed in Figure 21, it is obvious that the D2 Ansatz is invalid in this region. For most cases, the D1 Ansatz can provide a relatively accurate solution to the Schrödinger equation due to more sophisticated variational parameters used to describe the phonons in the Holstein system. Although the D1 Ansatz is not sufficiently accurate when J is larger than 1, it still provides a qualitative description for the quantum dynamics of the Holstein system. In order to have a better description of the systems for small S and large J , more sophisticated Ansätze such as Toyozawa Ansatz, global-local (GL) Ansatz and delocalized D1 Ansatz should be considered. It is worthwhile to note that the simpler Ansätze investigated here can also provide fundamental insights into interactions between the excitation and the lattice deformation that have dramatic impact in the optical and transport properties of materials. The drawbacks owing to the simplicity of the Ansätze can overcome by choosing parameter regimes that are specifically suited for their application by looking into their relative deviation σ . In the other words, it is possible to apply the results of the relative deviation σ obtained in this section to justify the applicability of an Ansatz in describing material systems characterized by specific sets of S , J and W .

5.5 Linear Absorption Spectroscopy

In an exciton–phonon system the autocorrelation function $F(t)$ is defined as

$$F(t) = {}_{ph} \langle 0 | {}_{ex} \langle 0 | \hat{P} e^{-i\hat{H}t} \hat{P}^\dagger | 0 \rangle_{ex} | 0 \rangle_{ph} \quad (5.5.1)$$

where $\hat{P}$ is the polarization operator defined by

$$\hat{P} = \mu \sum_n \left(\hat{a}_n^\dagger | 0 \rangle_{ex} \langle 0 | + | 0 \rangle_{ex} \langle 0 | \hat{a}_n \right) \quad (5.5.2)$$

with μ the transition dipole matrix element for a single-site. In the time-dependent variational methods, once the variational parameters of the Ansätze are obtained by solving the time evolution equations, various physical quantities such as the autocorrelation function $F(t)$ can be easily calculated. Exact expressions of $F(t)$ for the Davydov Ansätze are given in following:

$$F(t) = \mu^2 \sum_n \sum_m {}_{ph} \langle 0 | {}_{ex} \langle 0 | \hat{a}_m e^{-i\hat{H}t} \hat{a}_n^\dagger | 0 \rangle_{ex} | 0 \rangle_{ph} \quad (5.5.3)$$

For the periodic Hamiltonian, one has

$$\begin{aligned} & \sum_m {}_{ph} \langle 0 | {}_{ex} \langle 0 | \hat{a}_m e^{-i\hat{H}t} \hat{a}_n^\dagger | 0 \rangle_{ex} | 0 \rangle_{ph} \\ &= \sum_m {}_{ph} \langle 0 | {}_{ex} \langle 0 | \hat{a}_{m-n} e^{-i\hat{H}t} \hat{a}_{n-n}^\dagger | 0 \rangle_{ex} | 0 \rangle_{ph} \\ &= \sum_m {}_{ph} \langle 0 | {}_{ex} \langle 0 | \hat{a}_m e^{-i\hat{H}t} \hat{a}_0^\dagger | 0 \rangle_{ex} | 0 \rangle_{ph} \end{aligned} \quad (5.5.4)$$

Thus, one can obtain

$$F(t) = \mu^2 N \sum_m {}_{ph} \langle 0 | {}_{ex} \langle 0 | \hat{a}_m e^{-i\hat{H}t} \hat{a}_0^\dagger | 0 \rangle_{ex} | 0 \rangle_{ph} \quad (5.5.5)$$

wherein $e^{-i\hat{H}t} \hat{a}_0^\dagger | 0 \rangle_{ex} | 0 \rangle_{ph}$ is the time evolution from the initial state $\hat{a}_0^\dagger | 0 \rangle_{ex} | 0 \rangle_{ph}$, and

this time evolution can be approximated with the Davydov Ansätze:

$$e^{-i\hat{H}t} \hat{a}_0^\dagger | 0 \rangle_{ex} | 0 \rangle_{ph} \approx \sum_n \psi_n(t) \hat{a}_n^\dagger \exp \left\{ \sum_q \left[\lambda_{nq}(t) \hat{b}_q^\dagger - \text{H.c.} \right] \right\} | 0 \rangle_{ex} | 0 \rangle_{ph} \quad (5.5.6)$$

where the variational parameters are initialized using $\psi_{n=0}(t=0)=1$ and $\lambda_{nq}(t=0)=0$

provided and then solved with the Lagrangian formalism. Furthermore,

$$\begin{aligned}
F(t) &= \mu^2 N \sum_m \psi_m(t) {}_{\text{ph}} \langle 0 | {}_{\text{ex}} \langle 0 | \exp \left\{ \sum_q [\lambda_{mq}(t) \hat{b}_q^\dagger - \text{H.c.}] \right\} | 0 \rangle_{\text{ex}} | 0 \rangle_{\text{ph}} \\
&= \mu^2 N \sum_m \psi_m(t) \exp \left[-\frac{1}{2} \sum_q |\lambda_{mq}(t)|^2 \right]
\end{aligned} \tag{5.5.7}$$

where λ_{nq} take the forms from the D2, $\tilde{\text{D}}$ and D1 Ansätze as given in Eqn. (3.3.4).

Polaron dynamics is closely related to the optical spectroscopy. As the spectroscopy can provide valuable information on various correlation functions, optical spectra shall reveal quantum dynamics of the exciton–phonon system. In this study, the linear absorption spectra for the polaron dynamics calculated with different Ansätze have been studied to check the validity of these trial wave functions in various parameter regimes. The linear absorption spectrum $\tilde{F}(\omega)$ can be obtained by the Fourier transformation of the autocorrelation function $F(t)$:

$$\tilde{F}(\omega) = \frac{1}{\pi} \text{Re} \int_0^\infty F(t) e^{i\omega t} dt \tag{5.5.8}$$

The ability of the Ansätze in providing reliable dynamical information can also be gauged by the accuracy of optical spectra calculated from the trial states, as analytical expressions for the absorption and fluorescence spectra were well-known if the transfer integral J and the phonon bandwidth W are negligible. As a starting point of this study, three representative parameter regimes, corresponding to weak exciton–phonon coupling, intermediate coupling and strong coupling, were selected to compare the absorption spectra of these Ansätze according to the $\Delta(t)$ studies. The parameters are chosen to keep $\Delta(t) < 0.2$, and therefore ensure a relatively accurate description of polaron dynamics. According to the results on $\Delta(t)$, the $\tilde{\text{D}}$ Ansatz is found to have better performance compared to the D2 Ansatz, and hence expected to generate better spectra. Three different types of initial states, viz., single-site excitation, uniformly distributed excitation, and

excitation with a Gaussian-type distribution spanned on 7 sites, have been applied in the study of optical spectra. Here only the $\tilde{D}$ and D2 Ansätze are investigated, as they differ by one array of variational parameters in describing the phonon behavior.

Figure 23. Absorption spectra of the $\tilde{D}$ (a, b, c) and D2 Ansätze (d, e, f) for $W = 0.1$ and $J = 0.1$. Three kinds of initial exciton distributions: single-site excitation, Gaussian and uniform distributions are used for the initial states, and the HR factor ranges from 0.64 to 2.56, as indicated in the Figures. For (a), (b) and (c), the damping factor used to do the Fourier transformation of the autocorrelation function is chosen as 0.07, while for (d), (e) and (f), the damping factor is 0.08.

To facilitate comparisons, spectral maxima are normalized to 1. Figure 23, Figure 24 and Figure 25 demonstrate that the linear absorption spectra can be a very useful indicator of

the Ansatz validity in the investigation of the dynamics of a polaron system. For example, in the D2 Ansatz, the phonon displacement is only described by one set of variational parameters, leading to problems in its description of polaron correlations.

Figure 24. Absorption spectra of the $\tilde{D}$ (a, b, c) and D2 Ansätze (d, e, f) for $W = 0.1$ and $J = 0.2$. Three kinds of initial exciton distributions: single-site excitation, Gaussian and uniform distributions are used for the initial states, and the HR factor ranges from 0.64 to 2.56, as indicated in the Figures. For (a), (b) and (c), the damping factor used to do the Fourier transformation of the autocorrelation function is chosen as 0.07, while for (d), (e) and (f), the damping factor is 0.08.

When the initial state is a δ -function at site $n = 0$, Figure 23a–c reproduce the correct spectral features. The lack of accuracy for the D2 Ansatz is clearly reflected by its

inability to capture vibronic spectra as shown in Figure 23d–f when the initial electronic excitations adopt a uniform or Gaussian distribution. Such behavior is mainly due to the lack of correlation between exciton and phonon as one may observe in the structure of the D2 Ansatz, which will eventually lead to the absence of long range correlation in the autocorrelation function, and yield an inaccurate description of optical spectra.

Figure 25. Absorption spectra of the $\tilde{D}$ (a, b, c) and D2 Ansätze (d, e, f) for $W = 0.1$ and $J = 0.3$. Three kinds of initial exciton distributions: single-site excitation, Gaussian and uniform distributions are used for the initial states, and the HR factor ranges from 0.64 to 2.56, as indicated in the Figures. For (a), (b) and (c), the damping factor used to do the Fourier transformation of the autocorrelation function is chosen as 0.07, while for (d), (e) and (f), the damping factor is 0.08.

The inability of the D2 Ansatz is alleviated only for strong coupling and small- J cases where the exciton is sitting on one site during most of the dynamical evolution. The sensitivity of the spectral behavior towards the accuracy of an Ansatz and the initial state is clearly revealed by comparing Figure 23a–c with d–f. In contrast, using the Huang–Rhys theory[138] as a reference, the $\tilde{D}$ Ansatz can provide smooth and accurate absorption spectra with a tiny damping factor value added to the Fourier transformation of the autocorrelation function. The superior performance of the $\tilde{D}$ Ansatz originates in its correlated structure, which guarantees the long range correlation between exciton and phonon. Moreover, the $\tilde{D}$ phonon sidebands obey a Poisson distribution well described by the Huang–Rhys theory, which is a useful check for the accuracy of the results obtained. However, for the $\tilde{D}$ spectra with δ -function initial electronic excitations, additional side peaks appear besides the major phonon sidebands as shown in Figure 23a–c, Figure 24a–c and Figure 25a–c. Such an effect can be eliminated only when the value of J is close or equal to zero. In the DCPA[168] and DMFT[143] study of the polaron system, no such effect can be found with finite value of J . Thus it is suspected this kind of lineshape is unphysical. Moreover, as J increases, the spectra calculated from the $\tilde{D}$ Ansatz in Figure 23 - Figure 25 show notable changes in the ratio between the intensities of the 0–0 zero-phonon line and the 0–1 phonon sideband. This phenomenon has been extensively discussed [169-171], where the two-particle approximation has been used to obtain highly accurate absorption spectra. The two-particle approximation may also be used to check the accuracy of time-dependent trial states such as those developed in this thesis by absorption spectral comparisons.

Furthermore, it is worth mentioning that excitonic coupling to multiple phonon modes has

been included in accounting the spectral features recently [172, 173]. Thus, polaron dynamics studies such as ours are expected to reveal more interesting features by introducing multiple phonon modes. One can also observe the deterioration of the performance for both $\tilde{D}$ and D2 Ansätze as J increases, which is in agreement with the trend of the σ results. However, it is also indicated from the figures that the $\tilde{D}$ state has a much better performance compared to D2, a result in good agreement with the earlier conclusions. Such agreement is a crucial test of the sensitivity of the optical spectroscopy as an indicator of a sound trial state. More importantly, the trends obtained from the spectroscopy as well as the σ calculations provide rational criteria on further improving the performance of an Ansatz.

Figure 26. Comparisons of Absorption spectra obtained with different Davydov Ansätze for (a) $g = 0.1, J = 0.3, W = 0.5$; (b) $g = 0.1, J = 0.1, W = 0.5$; (c) $g = 0.3, J = 0.1, W = 0.5$; (d) $g = 0.5, J = 0.1, W = 0.5$. Throughout the figure, a damping factor used to do the Fourier transformation of the autocorrelation function is chosen as 0.1.

Figure 26 depicts the linear absorption spectra calculated from the D2, $\tilde{D}$ and D1 Ansätze obtained using four different sets of (g , J and W) parameters. The spectrum calculated from an Ansatz should be a curve above the zero line if the Ansatz is accurate. Negative values in absorption spectra originate from aperiodicity of the autocorrelation functions [Eqn. (5.5.7)] when performing Fourier transformations to them. Spatial correlation between exciton and phonon is closely related to the form of λ_{nq} , which specifically determines periodicity of an autocorrelation function. Thus better spatial exciton-phonon correlation descriptions in more sophisticated Ansätze such as $\tilde{D}$ and D1 will lead to improved periodicity and much fewer negative values in linear absorption spectra. In Figure 26a, the spectrum by the D2 Ansatz shows negative values in some region. Such phenomenon is also clearly revealed in certain spectra obtained with the $\tilde{D}$ Ansatz. This result is consistent with the σ study in the previous section. In Figure 26b, both the $\tilde{D}$ Ansatz and the D1 Ansatz yield good spectral features, while the spectrum by the D2 Ansatz still has negative values. In Figure 26c, although the spectrum by the D2 Ansatz is nearly free of negative values, but there exist several peaks with no physical meaning, which are caused by the inaccuracy of the Ansatz. As revealed by Figure 26, the magnitudes of the negative values of the spectra decrease with increasing g or decreasing J . In all the four parameter sets investigated in Figure 26, the D1 spectra are all free of negative values and with smoothest lineshape, thereby establishing firmly, its superiority for investigating various problems.

5.6 Conclusions

Polaron dynamics in a one-dimensional molecular chain under the Dirac-Frenkel

time-dependent variational approach has been investigated in detail in this chapter. Effects of physical parameters (*i.e.*, J , g or S and ϕ) and initial exciton state, in determining time-evolution of variational parameters and related quantities (*i.e.*, deviation vector and linear absorption spectroscopy) for different Ansätze applied are discussed thoroughly. Without coupling to phonon, exciton undergoes a quantum mechanical wave-like dynamics, where interference plays an essential role in determining the time-evolution patterns. Based on the Holstein Hamiltonian, time-evolution of the exciton amplitude, phonon displacements, system energies, coherence size, deviation vector and linear optical absorption spectra have been investigated for three types of variational wave functions, namely, the Davydov D2 Ansatz, a simplified variant of Davydov D1 Ansatz, also known as the $\tilde{D}$ Ansatz and finally Davydov D1 Ansatz. Following the equations of motion derived from the time-dependent variational approach, the exciton amplitude will transfer from the site of creation to neighboring sites with propagation velocity proportional to J , as revealed from the bare exciton dynamics. Furthermore, interference of exciton wave function induces interesting patterns, from which possible quantum chaos is expected. For the adopted Ansätze, formation of exciton induced lattice deformations can be found around the sites with considerable exciton amplitude. Propagation to the entire aggregate can be observed if there is sufficient phonon dispersion enabling mobility.

The validity of three variations of Davydov Ansätze, namely, D2, $\tilde{D}$ and D1 has been examined in detail with regards to their deviation from the exact solutions to the time-dependent Schrödinger equation for the Holstein Hamiltonian. The relative deviation σ has been introduced as the major quantity of characterizing validity of an Ansatz, which

is defined as the ratio between the deviation vectors $\Delta(t)$ and the average phonon energy of the polaron system. By mapping the parameter space of the Ansätze and plotting the relative deviation vector σ as a function of S , J and W , the D1 Ansatz is found to have much better performance than the D2 and $\tilde{D}$, indicating the importance of accurate description of phonons. In general, the relative deviation σ increases as S decreases or J increases. For the cases with small S and large J , all the Ansätze investigated have failed to describe the system dynamics adequately. Under different initial states, *i.e.*, single-site and evenly excited states, σ has different behavior. Compared to single-site excitation, when the initial state takes the form of evenly distributed excitation, both D1 and $\tilde{D}$ Ansatz can provide good results in describing a polaron system within a larger span of parameter regimes, while D2 fails in most regions even at a very strong exciton-phonon coupling regime.

Linear absorption spectra have been calculated to support the validity study. Such spectra are calculated from the autocorrelation function directly linked to polaron dynamics, providing a convenient comparison with experiment. The sensitivity of linear absorption spectra to the detailed dynamics of polaron formation and excited-state relaxation enables us to study the applicability of D2, $\tilde{D}$ and D1 Ansatz in the weak, intermediate and strong exciton–phonon coupling regimes. The superior performance of the $\tilde{D}$ and D1 Ansätze have been shown in all three regimes. The lineshapes of absorption spectra also suggest importance of initial exciton states, where δ -function, Gaussian and uniform initial exciton amplitude result in similar spectra only when J is small. Studies carried out in this work also provide valuable information on improving the description of Holstein polaron dynamics in a systematic manner.

The dramatic contrast between D1, $\tilde{D}$ and D2 spectra originates in their analytical expressions, where D1 and $\tilde{D}$ has superior description of phonons compared to D2. However, such improvement is limited by the coherent nature of the phonons' parts as first presented in Davydov's original formalism. The static performance of the various polaron Ansätze has revealed limitations of the coherent phonon description in dealing with the situations of very weak exciton–phonon coupling ($S < 0.5$). Thus one may apply routines such as gradually increased basis size during the time evolution of a polaron, coupling of multiple phonon modes *etc.*, to improve the performance of an Ansatz at the very weak exciton–phonon coupling regimes.

Overall it is found that $\tilde{D}$ and D1 are more flexible Ansätze while the D2 Ansatz is rather efficient in terms of numerical calculations, and its extension to higher spatial dimensions is a feasible generalization of our approach. Our Ansätze adopted in this chapter are both localized, while detailed dynamics of their translationally invariant counterparts, *e.g.*, the Toyozawa Ansatz and GL Ansatz can be derived in a similar fashion to further improve the accuracy of our current approach. The approach developed in this chapter so far can also readily be extended to include other forms of exciton-phonon interactions, such as asymmetric and symmetric off-diagonal coupling, and higher-order couplings.

Lastly, it should be mentioned that the Holstein polaron model can be readily applied to real systems such as rubrene and even the light-harvesting system II (LH2)[174, 175] in purple bacteria, and the time-dependent Ansätze investigated here can be used for various time-resolved spectral calculations. Effects of temperature and multiple phonon modes can be included in the model for more realistic descriptions of the polaron systems.

Chapter 6: Polaron Transport

Part of content of this chapter has been published on following paper:

Dongmeng Chen, Jun Ye, Haijun Zhang, and Yang Zhao, *On the Munn-Silbey Approach to Polaron Transport with Off-Diagonal Coupling and Temperature-Dependent Canonical Transformations*, Journal of Physical Chemistry B: Shaul Mukamel Festschrift, 115, 5312–5321 (2011).

6.1 Derivations

The generalized Holstein Hamiltonian incorporating simultaneous diagonal and off-diagonal coupling[109] has the form

$$H = \sum_n \epsilon a_n^\dagger a_n + \sum_{n,m} J_{nm} a_n^\dagger a_m + \sum_q \omega_q \left(b_q^\dagger b_q + \frac{1}{2} \right) + N^{-1/2} \sum_{nmq} \omega_q f_{nm}^q a_n^\dagger a_m (b_q + b_{-q}^\dagger) \quad (6.1.1)$$

here $a_n^\dagger(a_n)$ is the creation (annihilation) operator of an excitation (*i.e.*, exciton or charge carrier) with energy ϵ at site n , and $b_q^\dagger(b_q)$ creates (destroys) a phonon with frequency ω_q and wave vector q . J_{nm} stands for the electronic transfer integral between sites n and m . In this study, the discrepancies between molecules have been neglected; thus the on-site energies are set to ϵ , as shown in Eqn. (6.1.1). Finally, the exciton-phonon coupling is described by the last term of Eqn. (6.1.1), where the coupling strength f_{nm}^q must satisfy the relationship $(f_{n-m}^q)^* = e^{-i\mathbf{q} \cdot (\mathbf{R}_n - \mathbf{R}_m)} f_{n-m}^{-q}$, to make H Hermitian and translationally invariant. A unitary transformation can be applied to the Hamiltonian, as shown below:

$$H \rightarrow \tilde{H} = U^\dagger H U, \quad (6.1.2)$$

$$U = \exp \left[N^{-1/2} \sum_{nmq} A_{nm}^q (b_{-q}^\dagger - b_q) a_n^\dagger a_m \right]$$

The transformation requires $U^\dagger = -U$ to keep the translational symmetry of A_{nm}^q , similar to f_{nm}^q . Details of the transformation have been explicitly introduced in elsewhere. Moreover, the Hamiltonian in momentum representation is more convenient than the site representation due to the translational symmetry. Eqn. (6.1.1) can be written in the momentum representation as

$$H = \sum_k \epsilon_k a_k^\dagger a_k + \sum_q \omega_q (b_q^\dagger b_q + 1/2) + N^{-1/2} \sum_{kq} \omega_q f_{-k}^q a_{k+q}^\dagger a_k (b_q + b_{-q}^\dagger) \quad (6.1.3)$$

with $\epsilon_k = \epsilon + J_k$ and

$$J_k = \sum_m e^{ik \cdot (\mathbf{R}_n - \mathbf{R}_m)} J_{nm} \quad (6.1.4)$$

where $J_{n,m} = J(\delta_{n,m+1} + \delta_{n,m-1})$, and ω_q is the phonon frequencies. The exciton-phonon coupling coefficients can also be written as

$$f_k^q = \sum_m e^{-ik \cdot (\mathbf{R}_n - \mathbf{R}_m)} f_{n-m}^q \quad (6.1.5)$$

with the following coupling geometry:

$$f_k^q = g - i\phi[\sin(k) - \sin(k - q)] \quad (6.1.6)$$

this indicates that the anti-symmetric type of coupling is used throughout this work. Now the transformation takes the following form in the momentum representation:

$$U = \exp \left[N^{-1/2} \sum_{kq} A_{-k}^q (b_{-q}^\dagger - b_q) a_{k+q}^\dagger a_k \right] \quad (6.1.7)$$

and

$$A_k^q = \sum_m e^{-i(\mathbf{k}-\mathbf{q}) \cdot \mathbf{R}_n} e^{i\mathbf{k} \cdot \mathbf{R}_m} A_{nm}^q = (A_{k-q}^{-q})^* \quad (6.1.8)$$

The transformation can then also be written as

$$U = \exp \left(\sum_{kk'} a_k^\dagger \mathbf{S}_{kk'} a_{k'} \right), \quad \mathbf{S}_{kk'} = N^{-1/2} A_{-k}^{k-k'} (b_{k'-k}^\dagger - b_{k-k'}) \quad (6.1.9)$$

where $\mathbf{S}_{kk'}$ is an operator creating a net phonon with momentum $\mathbf{k}' - \mathbf{k}$. This operator is essential toward the evaluation of a series of important matrices, where

$$\begin{aligned} a_k &\rightarrow \sum_{k'} \theta_{kk'} a_{k'} \\ a_k^\dagger &\rightarrow \sum_{k'} \theta_{kk'}^\dagger a_{k'}^\dagger \end{aligned} \quad \text{with} \quad \begin{aligned} \theta_{kk'} &= [\exp(-\mathbf{S})]_{kk'} \\ \theta_{kk'}^\dagger &= [\exp(\mathbf{S})]_{kk'} \end{aligned} \quad (6.1.10)$$

where $\mathbf{S}$ stands for matrix $\mathbf{S}_{kk'}$. The transformed Hamiltonian can be partitioned into H_0 terms (zeroth-order part) and the perturbative V terms. The thermal average of the $\theta_{kk'}$ operator has the property:

$$\langle \theta_{k,k+q}^\dagger \theta_{k',k'+q} \rangle = \langle \theta_{k,k+q}^\dagger \theta_{k',k'+q} \rangle \delta_{qq'} \quad (6.1.11)$$

which ensures the correct thermal equilibrium behavior of H_0 by keeping it diagonal in excitation wave vector. H_0 here has following expression:

$$\begin{aligned} \tilde{H}_0 = \sum_q \omega_q \left(b_q^\dagger b_q + \frac{1}{2} \right) + \sum_k a_k^\dagger a_k \left\{ \left(\epsilon - \tilde{J}_k \right) + N^{-1} \sum_q \omega_q \left| A_{-k}^{-q} \right|^2 \right. \\ \left. - 2N^{-1} \sum_{qk'} \omega_q f_{-k'}^q A_{-k}^{-q} \left\langle \theta_{k'+q,k}^\dagger \theta_{k',k-q} \right\rangle + N^{-1/2} \sum_{qk'} \omega_q f_{-k'}^q A_{-k}^{-q} \left\langle \theta_{k'+q,k}^\dagger \theta_{k',k} \left(b_q + b_{-q}^\dagger \right) \right\rangle \right\} \end{aligned} \quad (6.1.12)$$

here $\tilde{J}_k$ represents the renormalized transfer integral which can be expressed by

$$\tilde{J}_k = \sum_{k'} J_{k'} \langle \theta_{k'k}^\dagger \theta_{k'k} \rangle \quad (6.1.13)$$

The perturbation parts of the transformed Hamiltonian can be written as

$$\begin{aligned} V = \sum_{kk'k''} \left\{ J_k T_{kk';kk''} - 2N^{-1} \sum_q \omega_q f_{-k'}^q \left(A_{-k}^q \right) T_{k+q,k';k,k''-q} \right. \\ \left. + N^{-1/2} \sum_q \omega_q f_{-k}^q a_k^\dagger a_{k''} \left[T_{k+q,k';kk''} \left(b_q + b_{-q}^\dagger \right) - \left\langle T_{k'+q,k';kk''} \left(b_q + b_{-q}^\dagger \right) \right\rangle \right] \right\} \\ + N^{-1/2} \sum_{qk} \omega_q \left[A_{-k}^q - \sum_{k'} f_{-k'}^q \left\langle \theta_{k'+q,k}^\dagger \theta_{k',k-q} \right\rangle \right] \left(b_q + b_{-q}^\dagger \right) a_{k+q}^\dagger a_k \end{aligned} \quad (6.1.14)$$

where

$$T_{kk';uu'} = \theta_{kk'}^\dagger \theta_{uu'} - \langle \theta_{kk'}^\dagger \theta_{uu'} \rangle \quad (6.1.15)$$

However, the last term of V has the potential to grow with increasing temperature, motivating the choice of A_k^q :

$$A_{-k}^q = \sum_{k'} f_{-k'}^q \langle \theta_{k'+q,k}^\dagger \theta_{k',k-q} \rangle \quad (6.1.16)$$

to curb this possible uncontrolled growth of $\theta_{kk'}$. By applying the thermal average

routine shown in [109], we can write the transformed Hamiltonian in a simpler form, which facilitates the numerical calculations. The zeroth-order Hamiltonian H_0 now can be written as

$$\tilde{H}_0 = \sum_k \tilde{\epsilon}_k a_k a_k + \sum_q \omega_q \left(b_q^\dagger b_q + \frac{1}{2} \right) \quad (6.1.17)$$

with

$$\tilde{\epsilon}_k = \epsilon + \tilde{J}_k - N^{-1} \sum_q |A_k^q|^2 \omega_q \quad (6.1.18)$$

The renormalized transfer integral in Eqn. (6.1.18) is given by

$$\tilde{J}_k = \sum_{k'} \langle \theta_k \rangle^2 \left[\exp(E^q) \right]_{kk'} J_{k'} \quad (6.1.19)$$

where the triadic $E_{kk'}^q$ is a quantity introduced to yield a simpler form of the transformed Hamiltonian, with the following relationship:

$$E_{kk'}^q = N^{-1} (2n_{k-k'} + 1) (A_{k-q}^{k-k'})^* A_k^{k-k'} \quad (6.1.20)$$

here n_q is the Bose-Einstein distribution, with $2n_q + 1 = \coth\left(\frac{1}{2}\beta\hbar\omega\right)$. With the form of

A_k^q shown in Eqn. (6.1.16), the perturbation part V of $\tilde{H}$ can be written as

$$\begin{aligned} V = \sum_{kk'k''} \left[J_k T_{kk';kk''} - 2N^{-1} \sum_q \omega_q f_{-k}^q A_{-k''}^{-q} T_{k+q,k';k,k''-q} \right. \\ \left. + N^{-1/2} \sum_q \omega_q f_{-k}^q T_{k+q,k';kk''} (b_q + b_{-q}^\dagger) a_{k'}^\dagger a_{k''} \right] \end{aligned} \quad (6.1.21)$$

In this study, the transformation coefficients A_k^q (A-matrix) will be obtained variationally prior to the calculations of the transport properties. The detailed numerical variational procedures can be found in [89]. In performing the variational calculations, the transformation coefficients must satisfy following self-consistency equations together with Eqn. (6.1.20):

$$\langle \theta_k \rangle = \exp \left[-\frac{1}{2} \sum_{k'} E_{kk'}^0 \right] \quad (6.1.22)$$

$$A_k^q = \langle \theta_{k-q} \rangle \langle \theta_k \rangle \sum_{k'} f_{k'}^q \left[\exp(E^q) \right]_{kk'} \quad (6.1.23)$$

The self-consistency equations above follow the Munn-Silbey secular elimination scheme. In [109], this set of equations was solved upon further approximations on A_k^q , whereas in this thesis, it is solved numerically with an accuracy unavailable previously. In the Munn-Silbey approach, the transformation coefficients A_k^q were at first approximated by the scaling parameters ξ and η as

$$A_k^q = g\xi - i\phi\eta[\sin(k) - \sin(k-q)] \quad (6.1.24)$$

Numerical evaluation of the Eqns. (6.1.20)-(6.1.23) is facilitated by rewriting the Eqn. (6.1.24) with real matrices ξ_k^q and η_k^q in the following form:

$$A_k^q = g\xi_k^q - i\phi\eta_k^q[\sin(k) - \sin(k-q)] \quad (6.1.25)$$

In the equation above, the sine function leads to zero imaginary part along the line with $q = 0$, $q = 2k \pm \pi$. In the numerical calculation, the lines with $q = 0$ and $q = 2k \pm \pi$ are treated as removable singularities. Moreover, the values of η_k^q along these lines are chosen to be analytically connected with neighboring values. The variational matrices ξ_k^q and η_k^q chosen can preserve the symmetry properties of A_k^q in a way such that $\xi_k^q = \xi_{k-q}^{-q}$ and $\eta_k^q = \eta_{k-q}^{-q}$. The self-consistency approach shown in this thesis is largely limited by the secular elimination scheme that is independent of the rigid-lattice tunneling matrix elements “ $\mathcal{J}$ ”. However, since “ $\mathcal{J}$ ” determines the rigid-lattice band structures and related quantities such as effective mass and density of states, this approach only applies for the narrow (rigid) band regime where the traditional small polaron theory is still available. The wide (rigid) band systems are beyond the scope of the approach discussed in this work. Based on the simple introduction and discussion of the Hamiltonian and transformation schemes, the parameters used for our numerical calculations are limited to

the regime that holds the traditional small polaron scenario. The diffusion coefficient is closely related to the mean square displacement of an excitation in a given period of time.

For the transformation scheme shown in this thesis, the mean square displacement can be calculated from the excitation density matrix. Approximations have been made to reduce the complexity of the exact formalism of the mean diffusion coefficient by neglecting small terms of the perturbation V as shown in the section above. The diffusion coefficient can then be expressed as

$$D = a^2 \left\langle \left\langle \mathbf{v}_k^2 / \Gamma_{kk} + \gamma_{kk} \right\rangle \right\rangle \quad (6.1.26)$$

where a is the nearest neighbor distance, $\mathbf{k}$ is the wave vector, and $\mathbf{v}_k = \nabla_{\mathbf{k}} E_k$. The double bracket denotes the thermal average of the polaron states E_k , where Γ_{kk} and γ_{kk} are the scattering and hopping rates expressed as

$$\begin{aligned} \Gamma_{k'k'} &= N^{-1} \sum_{k \neq k'} W_{k,k;k',k'}, \\ \gamma_{kk} &= \frac{1}{2} \nabla_q^2 \sum_k \text{Re} \left(\frac{1}{2} W_{k,k;k'+q,k'+q} - W_{k,k+q;k',k'+q} \right) \Big|_{q=0} \end{aligned} \quad (6.1.27)$$

where $W_{k,k;k',k'}$, crucial to the calculation of diffusion coefficient, are given by

$$\begin{aligned} W_{k,k+q;k',k'+q} &= \int_0^\infty dt \left\{ \left\langle V_{k'+q,k+q} V_{k,k'}(t) \right\rangle \exp \left[-i(E_{k'+q} - E_{k+q})t \right] \right. \\ &\quad \left. + \left\langle V_{k'+q,k+q}(t) V_{kk'} \right\rangle \exp \left[-i(E_k - E_{k'})t \right] \right\} \end{aligned} \quad (6.1.28)$$

here the single angular bracket denotes the average of the residual interaction $V_{kk'}(t)$ over phonon states. Using the formalism above, the evaluation of D will be done numerically here without introducing further approximations as in [111] and [109]. With the diffusion coefficient D , the mobility can be easily obtained with the Einstein relation $\mu = e\beta D$.

As inferred from the expression of the diffusion coefficient, the central problem is the

evaluation of the correlation functions $\langle V_{k'+q,k+q} V_{k,k'}(t) \rangle$ since both the scattering and the hopping rates are determined by the W quantities. It is indicated from the previous formalism that the residual interaction $V_{kk'}(t)$ is closely related to the transformation coefficients A_k^q . Hence, the problem of evaluating D ultimately hinges on the solution of the self-consistency equations, *i.e.*, Eqns. (6.1.20), (6.1.22), and (6.1.23). In this thesis, the transformation coefficients that determine the structure of polaron states and energy bands are solved numerically, which provide new information about the transport properties of polarons in molecular crystals. Without the analytical approximation form of η carried out in [110], the important quantity $\langle \theta_{k,k'}^\dagger \theta_{q,q'} \rangle$ can be derived as

$$\langle \theta_{k,k'}^\dagger \theta_{q,q'} \rangle = \langle \theta_{-k'} \rangle \exp(D^{k-q})_{k,k'} \langle \theta_{-q'} \rangle \delta_{k-k', q-q'} = \langle \theta_{-k'} \rangle \exp(E^{k-q})_{-q',-q} \langle \theta_{-q'} \rangle \delta_{k-k', q-q'} \quad (6.1.29)$$

and

$$(E^q)_{k,k'}[t] = \frac{1}{N} P_{k-k'}(t) (A_{k-q}^{k-k'})^* A_k^{k-k'} \quad (6.1.30)$$

$$(D^q)_{k,k'}[t] = \frac{1}{N} P_{k-k'}(t) (A_{-k'}^{k-k'})^* A_{-k'+q}^{k-k'} \quad (6.1.31)$$

where the expression of $\langle \theta_k \rangle$ is given by Eqn. (6.1.22). The factors $P_Q(t)$ are the characteristics of correlation functions for linear exciton-phonon coupling[176], which may take the form

$$\begin{aligned} P_Q(0) &= (2n_Q + 1) / N \\ P_Q(t) &= [(2n_Q + 1) \cos(\omega t) + i \sin(\omega t)] / N \end{aligned} \quad (6.1.32)$$

where n_Q is also the Bose-Einstein distribution, with $(2n_Q + 1) = \coth(\frac{1}{2} \beta \hbar \omega)$ and ω is the mean phonon frequency. For the correlation to decay to zero at long times, $P_Q(t)$ should be multiplied by a decay factor $A(t)$, defined as the Fourier transform of the phonon density of states, which takes a Gaussian form as given by

$$A(t) = \exp(-\Delta^2 t^2 / 4) \quad (6.1.33)$$

where Δ is the phonon bandwidth taken much less than ω . For the convenience of

numerical calculations, the mean phonon frequency ω is set to 1. For all calculations performed in this thesis, Δ is set to be 0.1, indicating a rather narrow phonon band. A number of factors can result in a finite bandwidth in the phonon density of states, and as pointed out by other authors, the inclusion of the phonon bandwidth ensures the long-time decay of correlation functions.

In the evaluation of $\langle V_{k'+q, k+q} V_{k, k'}(t) \rangle$, an important quantity is the four θ_k correlation function which is given by:

$$\begin{aligned} & \langle \theta_{k_1, k_2}^\dagger \theta_{k_3, k_4} \theta_{q_1, q_2}^\dagger(t) \theta_{q_3, q_4}(t) \rangle \\ &= \sum_{r_1, r_2, r_3} \langle \theta_{k_2+r_1, k_2}^\dagger \theta_{k_3, k_3-r_1} \rangle \langle \theta_{q_2+r_2, q_2}^\dagger \theta_{q_3, q_3-r_2} \rangle [\exp(-E^{k_1+q_4+r_3-q_2-q_3}(t))]_{k_3+r_3-q_1-k_4-r_1, -q_2-r_2} \\ & \times [\exp(E^{k_1+r_2-q_3}(t))]_{-q_4-r_3, r_2-q_3} [\exp(E^{k_3-q_1-r_1}(t))]_{-q_1, k_3+r_3-q_1-k_4-r_1} \\ & \times [\exp(-E^{k_4-q_4-r_3}(t))]_{-q_4, -q_4-r_3} \delta_{k_1+q_1+k_4+q_4, k_2+q_2+k_3+q_3} \end{aligned} \quad (6.1.34)$$

Now we can derive the expression for $\langle V_{k'+q, k+q} V_{k, k'}(t) \rangle$, which is the core item of W. Here we first express $V_{k, k'}$ as follows:

$$\begin{aligned} V_{k, k'} = \sum_{\kappa} \left\{ J_{\kappa} T_{\kappa k, \kappa k'} - \frac{1}{\sqrt{N}} \sum_q \omega_q f_{-\kappa}^q \left[\frac{1}{\sqrt{N}} \left(A_{-k}^{-q} T_{\kappa+q, k; \kappa, k'-q} + A_{-k}^{q*} T_{\kappa+q, k+q; \kappa, k'} \right) \right. \right. \\ \left. \left. - \frac{1}{2} \left(T_{\kappa+q, k; \kappa, k'} \psi_q + \psi_q T_{\kappa+q, k; \kappa, k'} \right) \right] \right\} \end{aligned} \quad (6.1.35)$$

and $J_k = J \cos(k)$ denotes the polaron band with its width determined by J . As described in the previous section, the currently applied approach is only applicable for narrow band rigid lattice system. Consequently, the value of J should not be too large to guarantee the accuracy of the transport results obtained. The correlation function is now given by

$$\begin{aligned}
& \langle V_{k_1, k_2} V_{q_1, q_2}(t) \rangle \\
&= \left\langle \sum_{k_3} \left\{ J_{k_3} T_{k_3, k_1; k_3, k_2} - \frac{1}{\sqrt{N}} \sum_{Q_1} \omega_{Q_1} f_{-k_3}^{Q_1} \left[\frac{1}{\sqrt{N}} \left(A_{-k_1}^{-Q_1} T_{k_3+Q_1, k_1; k_3, k_2-Q_1} + A_{-k_1}^{Q_1*} T_{k_3+Q_1, k_1+Q_1; k_3, k_2} \right) \right. \right. \right. \\
&\quad \left. \left. - \frac{1}{2} \left(T_{k_3+Q_1, k_1; k_3, k_2} \psi_{Q_1} + \psi_{Q_1} T_{k_3+Q_1, k_1; k_3, k_2} \right) \right] \right\} \\
&\quad \times \sum_{k_4} \left\{ J_{k_4} T_{k_4, q_1; k_4, q_2} - \frac{1}{\sqrt{N}} \sum_{Q_2} \omega_{Q_2} f_{-k_4}^{Q_2} \left[\frac{1}{\sqrt{N}} \left(A_{-q_1}^{-Q_2} T_{k_4+Q_2, q_1; k_4, q_2-Q_2} + A_{-q_1}^{Q_2*} T_{k_4+Q_2, q_1+Q_2; k_4, q_2} \right) \right. \right. \\
&\quad \left. \left. - \frac{1}{2} \left(T_{k_4+Q_2, q_1; k_4, q_2} \psi_{Q_2} + \psi_{Q_2} T_{k_4+Q_2, q_1; k_4, q_2} \right) \right] \right\} \right\rangle
\end{aligned} \tag{6.1.36}$$

The expression of the correlation functions $\langle V_{k'+q, k+q} V_{k, k'}(t) \rangle$ is mainly composed of three parts as:

$$\langle V_{k_1, k_2} V_{q_1, q_2}(t) \rangle = X_{k_1, k_2; q_1, q_2} + Y_{k_1, k_2; q_1, q_2} + \Lambda_{k_1, k_2; q_1, q_2} \tag{6.1.37}$$

First of all, the expression of $X_{k_1, k_2; q_1, q_2}$ is given by:

$$\begin{aligned}
& X_{k_1, k_2; q_1, q_2} \\
&= \sum_{k_3, k_4} \left[J_{k_3} J_{k_4} \langle T_{k_3, k_1; k_3, k_2} T_{k_4, q_1; k_4, q_2} \rangle - \frac{1}{N} \sum_{Q_2} J_{k_3} \omega_{Q_2} f_{-k_4}^{Q_2} \left(A_{-q_1}^{-Q_2} \langle T_{k_3, k_1; k_3, k_2} T_{k_4+Q_2, q_1; k_4, q_2-Q_2} \rangle \right. \right. \\
&\quad \left. \left. + A_{-q_1}^{Q_2*} \langle T_{k_3, k_1; k_3, k_2} T_{k_4+Q_2, q_1+Q_2; k_4, q_2} \rangle \right) - \frac{1}{N} \sum_{Q_1} J_{k_4} \omega_{Q_1} f_{-k_3}^{Q_1} \left(A_{-k_1}^{-Q_1} \langle T_{k_3+Q_1, k_1; k_3, k_2-Q_1} T_{k_4, q_1; k_4, q_2} \rangle \right. \right. \\
&\quad \left. \left. + A_{-k_1}^{Q_1*} \langle T_{k_3+Q_1, k_1+Q_1; k_3, k_2} T_{k_4, q_1; k_4, q_2} \rangle \right) + \frac{1}{N^2} \sum_{Q_1, Q_2} \omega_{Q_1} \omega_{Q_2} f_{-k_3}^{Q_1} f_{-k_4}^{Q_2} \left(A_{-k_1}^{-Q_1} A_{-q_1}^{-Q_2} \right. \\
&\quad \times \langle T_{k_3+Q_1, k_1; k_3, k_2-Q_1} T_{k_4+Q_2, q_1; k_4, q_2-Q_2} \rangle + A_{-k_1}^{-Q_1} A_{-q_1}^{Q_2*} \langle T_{k_3+Q_1, k_1; k_3, k_2-Q_1} T_{k_4+Q_2, q_1+Q_2; k_4, q_2} \rangle \\
&\quad \left. \left. + A_{-k_1}^{Q_1*} A_{-q_1}^{-Q_2} \langle T_{k_3+Q_1, k_1+Q_1; k_3, k_2} T_{k_4+Q_2, q_1; k_4, q_2-Q_2} \rangle + A_{-k_1}^{Q_1*} A_{-q_1}^{Q_2*} \langle T_{k_3+Q_1, k_1+Q_1; k_3, k_2} T_{k_4+Q_2, q_1+Q_2; k_4, q_2} \rangle \right) \right]
\end{aligned} \tag{6.1.38}$$

where

$$\langle T_{k_1, k_2; k_3, k_4} T_{q_1, q_2; q_3, q_4}(t) \rangle = \langle \theta_{k_1, k_2}^\dagger \theta_{k_3, k_4} \theta_{q_1, q_2}^\dagger(t) \theta_{q_3, q_4}(t) \rangle - \langle \theta_{k_1, k_2}^\dagger \theta_{k_3, k_4} \rangle \langle \theta_{q_1, q_2}^\dagger \theta_{q_3, q_4} \rangle \tag{6.1.39}$$

and the expression for $\langle \theta_{k_1, k_2}^\dagger \theta_{k_3, k_4} \theta_{q_1, q_2}^\dagger(t) \theta_{q_3, q_4}(t) \rangle$ and $\langle \theta_{k_1, k_2}^\dagger \theta_{k_3, k_4} \rangle \langle \theta_{q_1, q_2}^\dagger \theta_{q_3, q_4} \rangle$ has been given by Eqn. (6.1.34) and Eqn. (6.1.29), respectively. Here and onwards, N represents the total number of sites used in the transport calculation.

Now we turn to the expression of $Y_{k_1, k_2; q_1, q_2}$, which is written as:

$$\begin{aligned}
& Y_{k_1, k_2, q_1, q_2} \\
&= \sum_{k_3, k_4} \left\{ \frac{1}{\sqrt{N}} \left[\sum_Q J_{k_3} \omega_Q f_{-k_4}^Q \langle Z_{k_1, k_3, k_3, k_2} \psi_Q(t) \rangle \langle T_{k_3, k_1, k_3, k_2} T_{k_4+Q, q_1, k_4, q_2}(t) \rangle \right. \right. \\
&\quad - \frac{1}{N} \sum_{Q_1, Q_2} \omega_{Q_1} \omega_{Q_2} f_{-k_3}^{Q_1} f_{-k_4}^{Q_2} \left(A_{-k_1}^{-Q_1} \langle Z_{k_1, k_3+Q_1, k_3, k_2-Q_1} \psi_{Q_2}(t) \rangle \langle T_{k_3+Q_1, k_1, k_3, k_2-Q_1} T_{k_4+Q_2, q_1, k_4, q_2}(t) \rangle \right. \\
&\quad \left. \left. + A_{-k_1}^{Q_1*} \langle Z_{k_1+Q_1, k_3+Q_1, k_3, k_2} \psi_{Q_2}(t) \rangle \langle T_{k_3+Q_1, k_1+Q_1, k_3, k_2} T_{k_4+Q_2, q_1, k_4, q_2}(t) \rangle \right) \right] \\
&\quad + \frac{1}{\sqrt{N}} \left[\sum_{Q_1} J_{k_4} \omega_{Q_1} f_{-k_3}^{Q_1} \langle \psi_{Q_1} Z_{q_1, k_4, k_4, q_2}(t) \rangle \langle T_{k_3+Q_1, k_1, k_3, k_2} T_{k_4, q_1, k_4, q_2}(t) \rangle \right. \\
&\quad - \frac{1}{N} \sum_{Q_1, Q_2} \omega_{Q_1} \omega_{Q_2} f_{-k_3}^{Q_1} f_{-k_4}^{Q_2} \left(A_{-q_1}^{-Q_2} \langle \psi_{Q_1} Z_{q_1, k_4+Q_2, k_4, q_2-Q_2}(t) \rangle \langle T_{k_3+Q_1, k_1, k_3, k_2} T_{k_4+Q_2, q_1, k_4, q_2-Q_2}(t) \rangle \right. \\
&\quad \left. \left. + A_{-q_1}^{Q_2*} \langle \psi_{Q_1} Z_{q_1+Q_2, k_4+Q_2, k_4, q_2}(t) \rangle \langle T_{k_3+Q_1, k_1, k_3, k_2} T_{k_4+Q_2, q_1+Q_2, k_4, q_2}(t) \rangle \right) \right] \Big\}
\end{aligned} \tag{6.1.40}$$

where

$$\begin{aligned}
& \langle C_{k_1, k_2, k_3, k_4} \psi_q(t) \rangle \\
&= \frac{1}{\sqrt{N}} \left\{ A_{-k_2}^{k_1-k_2} \left[n e^{-i\omega t} - (1+n) e^{i\omega t} \right] \delta_{-k_1+k_2, q} - A_{-k_4}^{k_3-k_4} \left[n e^{-i\omega t} - (n+1) e^{i\omega t} \right] \delta_{-k_3+k_4, q} \right\}
\end{aligned} \tag{6.1.41}$$

and

$$\begin{aligned}
& \langle \psi_q Z_{k_1, k_2, k_3, k_4}(t) \rangle \\
&= \frac{1}{\sqrt{N}} \left\{ A_{-k_2}^{k_1-k_2} \left[(n+1) e^{i\omega t} - n e^{-i\omega t} \right] \delta_{q, -k_1+k_2} - A_{-k_4}^{k_3-k_4} \left[(n+1) e^{i\omega t} - n e^{-i\omega t} \right] \delta_{q, -k_3+k_4} \right\}
\end{aligned} \tag{6.1.42}$$

here n is the Bose-Einstein distribution, with $2n+1 = \coth(\frac{1}{2} \beta \hbar \omega)$.

Finally we give the expression of $\Lambda_{k_1, k_2, q_1, q_2}$:

$$\begin{aligned}
& \Lambda_{k_1, k_2, q_1, q_2} \\
&= \sum_{k_3, k_4} \frac{1}{N} \left\{ \sum_{Q_1, Q_2} \omega_{Q_1} \omega_{Q_2} f_{-k_3}^{Q_1} f_{-k_4}^{Q_2} \left\{ \frac{1}{N} \left(-A_{-k_3-Q_1}^{k_1-k_3-Q_1} A_{-k_4-Q_2}^{q_1-k_4-Q_2} \delta_{k_1-k_3-Q_1, -Q_2} \delta_{-Q_1, q_1-k_4-Q_2} \right. \right. \right. \\
&\quad \left. \left. + A_{-k_3-Q_1}^{k_1-k_3-Q_1} A_{-q_2}^{k_4-q_2} \delta_{k_1-k_3-Q_1, -Q_2} \delta_{Q_1, q_2-k_4} + A_{-k_2}^{k_3-k_2} A_{-k_4-Q_2}^{q_1-k_4-Q_2} \delta_{k_2-k_3, Q_2} \delta_{-Q_1, q_1-k_4-Q_2} \right. \right. \\
&\quad \left. \left. - A_{-k_2}^{k_3-k_2} A_{-q_2}^{k_4-q_2} \delta_{k_2-k_3, Q_2} \delta_{Q_1, q_2-k_4} \right) \left[n e^{-i\omega t} - (n+1) e^{i\omega t} \right]^2 \right. \\
&\quad \left. + \langle \psi_{Q_1} \psi_{-Q_2}(t) \rangle \delta_{Q_1, -Q_2} \right\} \langle T_{k_3+Q_1, k_1, k_3, k_2} T_{k_4+Q_2, q_1, k_4, q_2} \rangle \Big\}
\end{aligned} \tag{6.1.43}$$

6.2 Effects of Physical Parameters on Transport Calculation

The numerical evaluation of transformation coefficients A_k^q involves the solution of the self-consistency equations Eqns. (6.1.20), (6.1.22), and (6.1.23). Details of the evaluation

procedures have been discussed in detail in [89] here we only revisit some important issues related to the transport properties, especially the role of off-diagonal coupling. For moderate temperature with $k_{\text{B}}T = \hbar\omega$, the self-consistency method applied in this thesis tends to fail in strong coupling regimes; this is attributed to the failure to minimize errors to desired precision or to convergence to multiple solutions that are sensitive to procedure initialization. It is also possible for the convergence to fail in strong coupling regimes for solely numerical reasons. This problem increases with increasing exciton-phonon coupling, which leads to large positive and negative eigenvalues for the exponential matrices, thus to the possible failure of obtaining reliable diffusion coefficient. Due to the problems of convergence and possible multiple solutions of the method applied, we restricted our studies in the weak and intermediate coupling regimes to ensure the robustness of the results obtained. As demonstrated in [89], A-matrix parameters ξ_k^q and η_k^q in Eqn. (6.1.25) obtained with the self-consistency procedure have a significant wave vector dependence, which is lacking in the original treatment of Munn and Silbey, as indicated in (6.1.24). In addition, the Munn-Silbey parameterization of the A-matrix, η and ξ , can be regarded as the lower bounds of ξ_k^q and η_k^q rather than the average values.

Figure 27. A-matrix parameters ξ_k^q (a)-(c) and η_k^q (d)-(f) as functions of increasing diagonal coupling strength g^2 . $g^2 = 0.1$ for (a) and (d), 0.3 for (b) and (e), and 1.0 for (c) and (f). Other parameters are $J = 0.1$, $\phi^2 = 0.3$, and $T = 1.0$.

More importantly, the wave vector dependence of the variational parameters leads to significant changes in the structure of polaron energy band E_k , where the bimodal variation of E_k can be always found. Such changes in the structure of polaron states and the energy band lead to critical modifications of the transport properties, which will be

explicitly examined in the next section. In this section, we present detailed structures of A-matrix parameters as well as the corresponding polaron bands obtained with the self-consistency routines, to facilitate understanding of calculated transport properties, which are deferred to the next subsection. As shown in Figure 27, the two sets of A-matrix parameters in Eqn. (6.1.25), ξ_k^q and η_k^q , differ in their wave vector dependence. In the vicinity of $q=0$, ξ_k^q is weakly structured and relatively flat with respect to k , while the wave vector dependence of η_k^q is much more pronounced than that of ξ_k^q . Regardless of coupling strength, the wave vector dependence of ξ_k^q and η_k^q has a characteristic “manta-ray” shape, a fact that may be understood through an examination of the real-space structure of the A-matrix. As revealed in Figure 27, the A-matrix parameters tend to have less wave vector dependence for larger g . If diagonal coupling strength exceeds that of off-diagonal coupling, the parameters lose most of the q dependence. Thus, the transformation coefficients in Eqn. (6.1.24), as approximated by Munn and Silbey, represent the A-matrix in Eqn. (6.1.25) in the limit of strong diagonal coupling. It is also interesting to look into the change of the polaron band structures (especially, band narrowing) as a function of the temperature, which may provide an intuitive understanding of the difference between transport properties obtained here and those by Munn and Silbey using Eqn. (6.1.24).

Figure 28. Polaron bandwidths (a) as functions of temperature, and band structures (b) and (c) comparisons between this work and the Toyozawa variational method with off-diagonal coupling strength (b) $\phi^2 = 0.1$ and (c) $\phi^2 = 0.3$ at $T = 0$, where g^2 and J are both set to 0.1 for all calculations. The inset of (a) is the band structure comparison between the result from [109] by Munn and Silbey and that from this work at $T = 1$ with $g^2 = \phi^2 = J = 0.1$.

Variance of the polaron bandwidth as well as the entire band with respect to temperature has been obtained with our numerically determined A-matrix and is illustrated in Figure 28. It is also indicated in the inset of Figure 28a that the polaron band obtained with the transformation coefficients of Munn and Silbey lacks a bimodal structure and has a much larger bandwidth than that from the current approach. It is indeed counterintuitive to see that the greater momentum-space variability we find in our transformation coefficients should translate into a narrower polaron band. The explanation lies in that the binding energy is proportional to the average of $|A_k^q|^2$. Compared with results from [109], the average binding energy obtained in the current approach is significantly larger and the average Debye-Waller factor significantly smaller, which eventually leads to the narrower band. To lend further support to the polaron band structures calculated here, it is helpful to introduce the Toyozawa Ansatz for zero-temperature band comparisons. As shown in Figure 28b, c, good agreement between the current method and the Toyozawa Ansatz has been found. For weak diagonal and off-diagonal coupling, as is the case in Figure 28b, the Toyozawa method yields a larger bandwidth, and with increasing ϕ , the bimodal structure appears and the agreement between the two approaches improves. The concurrence provides legitimacy to the current approach in finding reliable polaron bands, a step that is essential for the transport calculations. Moreover, the band narrowing effect is in good qualitative agreement with those obtained with the Holstein-Peierls model and *ab-initio* calculations in [124]. As can be readily seen from Figure 28a, the off-diagonal coupling strength helps boost the bandwidth for temperatures lower than ω , $g^2 = 0.1$, and $J = 0.1$.

$\tilde{J}_k$ is proportional to the exponential value of the amplitude of the A-matrices according to Eqn. (6.1.20) when $q=0$, thus the value of the renormalized transfer integral now can be

regarded as directly proportional to the value of ϕ , thus at lower temperature, higher value of ϕ will eventually result in higher value of bandwidth as shown in Figure 28.

Figure 29. A-matrix parameters ξ_k^q (a)-(c) and η_k^q (d)-(f) as functions of increasing temperature. $T = 0.2$ for (a) and (d), 1.3 for (b) and (e), and 4.0 for (c) and (f). Other parameters are $J = 0.1$, $g^2 = 0.1$, and $\phi^2 = 0.3$.

The differences in polaron band-narrowing effect due to inclusion of non-local exciton-phonon coupling between current approach and those from [124] may closely related to the chosen form of off-diagonal coupling, where in the later approach, the

coupling is treated more generally to facilitate the *ab-initio* calculations. Thus it is possible in [124] and many others; the diagonal exciton-phonon coupling strength has also been increased due to the inclusion of many other components of exciton-phonon coupling matrix in real space for specific phonon momentum, resulting in overall enhancement of polaron band-narrowing.

To better understand the bandwidth narrowing effect, the parameter matrices ξ_k^q and η_k^q have been plotted in Figure 29 for three temperatures, $T = 0.2, 1.3$, and 4.0 in unit of ω . Other control parameters in Figure 29 are set to be the same as those for Figure 28c. As temperature increases, the wave vector variations grow for both ξ_k^q and η_k^q , while in Figure 27, the variations are reduced as g increases. As explained in [89], a larger wave vector variation in ξ_k^q and η_k^q is transformed into a weaker distortion of the energy band, which explains the temperature dependence in Figure 28a. In contrast to an overall enhancement of polaron band-narrowing by including off-diagonal coupling in [124], our model demonstrates the possibility that at low temperatures off-diagonal coupling may increase the bandwidth while at high temperature the effect is reversed. Such an effect can be understood from Eqns. (6.1.18)-(6.1.23), as well as from Figure 30, where the bandwidth is shown to be closely related to the renormalized transfer integral $\tilde{J}_k$ and the polaron binding energy, which is the third term on the right-hand side of Eqn. (6.1.18). At lower temperatures, the binding energy dominates in Eqn. (6.1.18) in the presence of off-diagonal coupling strength ϕ , resulting in a bandwidth that increases with ϕ . However, at high temperatures the renormalized transfer integral $\tilde{J}_k$ dominates at weak off-diagonal coupling, and the bandwidth derived from the $\tilde{J}_k$ term shrinks with increasing ϕ . While diagonal exciton-phonon coupling always acts as a localization factor,

off-diagonal exciton-phonon coupling is a transport mechanism as it is an agent for polaronic localization. At low temperatures, the former trait of the off-diagonal coupling is more evident as the off-diagonal coupling alone can generate a polaron-bandwidth through the off-diagonal polaron binding energy term even in the absence of the transfer integral ($J = 0$).

Figure 30. The (a) polaron binding energy and (b) renormalized transfer integral $\tilde{J}_k$ as function of temperature and ϕ . Other parameters are given as: $g^2=0.1$ and $J=0.1$.

Figure 31. Diffusion coefficient D versus scaled temperature $k_B T / \omega$ for a 1-dimensional chain with 4, 6, and 8 sites, where the diagonal coupling strength $g^2 = 0.1$ for (a)-(c) and $g^2 = 0.5$ for (d)-(f). The off-diagonal coupling strength ϕ^2 is equal to 0.0 for (a) and (d), 0.3 for (b) and (e), and 0.7 for (c) and (f). Finally, the transfer integral $J = 0.1$ for all cases.

The influence of the diagonal coupling strength g and off-diagonal coupling strength ϕ (especially the latter) is substantial in determining momentum space modulations of

transformation coefficients A_k^q , which in turn determine the structure of polaron states and the energy bands. For all calculations here, the number of sites is equal to 6 and the hopping integral J is 0.1 in units of ω unless specified otherwise. Comparisons between the results obtained here and those from [110] have been made to illustrate the importance of the A-matrix momentum dependence as well as the straightforward numerical evaluation of transport properties sans additional approximations. In the calculations of the transport properties, computation time increases dramatically with the number of sites. Our existing computational capabilities allow only calculations for less than 10 sites without overshooting memory requirements. To ensure the robustness of the results obtained with current method, we computed the diffusion coefficient D for 1D lattices of 4, 6, and 8 sites. The results with various lattice sizes and control parameters are displayed in Figure 31, indicating that almost identical results are obtained for lattices of 6 and 8 sites in the absence of off-diagonal coupling. Hence, in such a scenario, calculations with 6 sites are expected to give sufficiently reliable values of D at affordable computational cost. As ϕ^2 increases, however, the number of sites becomes an issue in determining the value of D due to exciton-phonon correlation spans over longer distances. The effect of the lattice size is more prominent in the low temperature regime as shown in Figure 31b, c, where the transport properties are dominated by coherent or band-like contributions. At higher temperatures, the hopping contribution eventually dominates the transport and the results become less sensitive to the system size. This can also be understood from polaron band narrowing at high temperatures and a reduced effective transfer integral with increasing temperature. As the diagonal coupling strength g increases, the difference between the results obtained with 4 sites and 6 sites becomes less

obvious than the weak coupling cases. Even better agreement is reached for $\phi^2=0$, and the results are found to be almost identical from 4 to 8 sites, as shown in Figure 31d. It is also interesting to spot nonmonotonic changes of the diffusion coefficient (*i.e.*, a “hump”) as a function of the temperature, in the absence of any size dependence, in the low temperature regime for $g^2 = 0.5$ and nonzero ϕ^2 , as shown in Figure 31e, f. Such a hump also appears in Figure 31c for $g^2 = 0.1$ and $\phi^2 = 0.7$ despite a slightly visible size dependence of the diffusion coefficient. For a fixed value of g^2 , the “hump” becomes more pronounced with increasing ϕ^2 , underlying the partial role of off-diagonal coupling.

The role of the off-diagonal coupling can be understood by combining previous discussions of its role in generating polaron-bandwidth. It was known previously that the off-diagonal coupling term is not only a localization factor but also a transport mechanism. Inclusion of the off-diagonal coupling term facilitates transport, a fact that is evident if one looks into the D2 dynamics with off-diagonal exciton-phonon coupling discussed in detail in Chapter 4. It is found that exciton hopping is always observed in the middle of one phonon period, when the phonon amplitude reaches its maximum, indicating an increased probability of tunneling through the potential barrier between neighboring sites. This observation is also in agreement with the appearance of new energy minima in the polaron band structure, and is further supported by the fact [89] that with only off-diagonal coupling, a bimodal variation of the band structure can be obtained. This is a very important aspect of how off-diagonal exciton-phonon coupling determines polaron transport behavior.

In the absence of diagonal-coupling, at the center and boundary of the Brillouin zone, the

exciton is equally shared by two sites with phonon displacements of equal magnitudes and opposite signs. When the diagonal coupling is included, the aforementioned bond-centered structure will be substituted with a site-centered one, leading to the shift of the exciton and the accompanied phonon cloud to one of the two neighboring sites (with exact location depending on the sign of J).

Increase in temperature in general leads to decrease of the polaron bandwidth, as shown in Figure 28, due to increasing phonon scattering of the exciton. In general, increasing temperature deprives the polaron of its quantum characteristics, and shifts polaron transport to the regime of classical diffusion as the quasi-particle gains in thickness of its phonon cloud. As a result, the transition from band-like (coherent) to hopping transport (incoherent) can be observed.

It is also interesting to look into the effect of other parameters in determining polaron transport properties. As shown in Figure 32, increasing the phonon bandwidth Δ leads to an increase in the band-like contribution to the diffusion coefficient, and a decrease in the relative importance of the hopping contribution. These findings from our numerical calculations for a case of diagonal exciton-phonon coupling are in good agreement with analytical results from [111]. Qualitatively similar results can be obtained with the inclusion of off-diagonal coupling.

Figure 32. Effects of phonon bandwidth Δ on (a) total diffusion coefficient, (b) band-like contribution, and (c) hopping contribution. Other parameters are $g^2 = 0.5$, $\phi^2 = 0.0$, and $J = 0.1$.

Figure 33. Comparisons of the logarithm diffusion coefficient of this work and those from [110], where both diagonal and off-diagonal couplings are limited to a moderate value to guarantee the definiteness of our results.

In the original work of Munn and Silbey, the diffusion coefficient as a function of temperature have been studied with structure-less A-matrix parameters ξ and η . The detailed structure for the A-matrix parameters is found to have a substantial impact on the transport properties, as revealed in Figure 33 by comparing the diffusion coefficients from [110] with those obtained here. Moreover, we would like to note that in the absence of off-diagonal coupling our results are in good agreement with those from [112] and [118]. The results in this thesis can be compared with those obtained using other methods such as a Green's function approach and variational exact diagonalization with a better construction of phonon states. For example, with an improved numerical technique in [177], the 1D polaron mass and radius are studied for an expanded parameter regime, where comparisons with our approach are especially convenient. Despite the discrepancies between our results and those of Munn and Silbey in the high temperature regime where hopping transport dominates, agreement is found in the low temperature regime where band-like transport prevails. This can be understood as follows. As discussed in [89], the transformation coefficients obtained self-consistently are shown to have stronger wave vector dependencies as ϕ increases. For weak off-diagonal coupling, however, the average values of ξ_k^q and η_k^q generated by the self-consistency procedure are in reasonable agreement with those by Munn and Silbey despite some systematic deviations, which leads to the aforementioned low-temperature agreement. As shown in Figure 28 and Figure 29, a higher temperature induces higher amplitude of wave vector variations of the A-matrix parameters together with a much flatter polaron band as compared with its Munn-Silbey counterpart, resulting in a diminished diffusion coefficient. Finally, the diffusion coefficients obtained here in the absence of the

off-diagonal coupling are shown to have qualitative agreements with those from Ref. [110]. The differences between the two can be ascribed to a series approximations made in Ref. [110] leading to the calculation of the diffusion coefficient, which in this work are substituted with numerically exact evaluations.

6.3 Mobility Calculation using Quantum-Chemical and MBO Material parameters and Comparisons to the Experimental Results

The transport calculation was carried out based on the parameters obtained from spectra fitting with MBO model or calculated from TDDFT. The input parameters for the transport calculation of temperature dependence of mobility are, characteristics phonon frequency ω_{LO} , the diagonal exciton-phonon coupling strength g , off-diagonal exciton-phonon coupling strength ϕ , exciton transfer integral J , temperature range (usual scaled with k_B/ω_{LO}), and phonon bandwidth $\Delta\omega$. The diagonal exciton-phonon coupling strength g can be directly related to the parameters obtained from the spectra fitting and *ab-initio* calculation with the relationship $S = g^2$, where S is the Huang-Rhys factor. Other parameters such as ϕ and J require specific DFT or semi-empirical calculations with respect to the geometry of the molecular crystals. The characteristic phonon frequency found from the spectra fitting can also be used as the input parameter of the transport calculation. The phonon bandwidth $\Delta\omega$ is related to the density of states of the characteristic phonon, which can also be obtained with DFT or semi-empirical methods. After finding the parameters needed, the transport calculation can be performed. In this work, we will perform a simple demonstration of calculation transport properties with parameters from fitting of rubrene single crystal PL spectra and quantum chemical

calculations. For the transport calculations, we use a diagonal exciton-phonon coupling strength $g = 0.92$, an exciton transfer integral $J = 0.17\omega_{LO}$ and an off-diagonal exciton-phonon coupling strength with $\phi = 0.0$. Here the values of g and J are obtained from the fitting of experimental optical spectra and excited-state energy calculations, respectively, from the previous chapters. The LO-phonon frequency ω_{LO} is adjusted to 1450cm^{-1} according to the spectral fitting. The value of $\Delta\omega$ takes on one tenth of ω_{LO} , indicating the characteristic phonon is nearly dispersion-less. Finally, the calculated results of mobility versus temperature are compared to the published results. The dependence of the total mobility (*c.f.*, Figure 34) on temperature agrees well with the experimentally measured Hall mobility [30], which suggests the applicability of current approach in finding the intrinsic transport properties of the organic semiconductor.

Figure 34. Comparison of theoretical and experimental mobility dependence on temperature, where the experimental data is obtained from [30]. The parameters used for the theoretical calculation are: $g = 0.92$, $\phi = 0.0$, $J = 0.17\omega_{LO}$ and $\Delta\omega = 0.1\omega_{LO}$. Contributions from theoretical band-like and hopping mobility have also been illustrated as comparisons.

However, the results calculated by the Munn-Silbey model requires further justifications due to deviation of exciton-phonon coupling strength used for transport calculations from those previously obtained from the optical spectra. Moreover, the electronic processes in a molecular crystal are complicated by the presence of interface, oxide layer and disorder such as grain boundaries and so on. The microscopic model used in this work can successfully predict the temperature dependence of carrier mobility quantitatively, indicating the basic physical picture of the charge carrier/energy transport in rubrene single crystal is in agreement with the model. Other issues, such as the role of the off-diagonal exciton-phonon coupling and disorder that may lead to different temperature related transport behaviors, need to be addressed in the future.

6.5 Conclusions

Following the Munn-Silbey approach to polaronic transport in organic molecular crystals, diffusion coefficients have been computed by numerical means while taking into account simultaneously diagonal and off-diagonal exciton-phonon coupling for a wide range of temperatures. The transformation coefficients for appropriate zeroth-order polaron states have been determined self-consistently without additional approximations. Calculated transport properties exhibit substantial corrections on those obtained previously thanks to the added momentum dependence of the A-matrix parameters and numerically exact evaluation of many essential quantities. The A-matrix which define the structure of polaron states and energy band structures in this approach respond to increasing diagonal exciton-phonon coupling by developing dramatic momentum-space modulations. A spreading of exciton-phonon correlations in real space is responsible towards these

distortions, suggesting coherent phonon-assisted exciton transfers could be important to a polaron state based on an extended exciton structure.

The general transport properties obtained are also in good qualitative agreement with those obtained with the Holstein-Peierls model and *ab-initio* calculations, demonstrating robustness of the current approach. Comparisons between this work and the one in Ref. [110] reveal the importance of the electron-phonon correlations and the polaron band structures to transport properties of the extended Holstein molecular crystal model. By treating the diagonal and off-diagonal exciton-phonon coupling on an equal footing in our self-consistency procedure, the current approach is one of the few capable to model realistically the transport phenomenon in organic molecular crystals, for which the effect of off-diagonal coupling often cannot be neglected. Off-diagonal coupling, in itself, is a transport mechanism, as it is an agent for polaronic localization. Inclusion of off-diagonal coupling in the current approach allows us to see the critical role it plays in determining both polaron structures and transport properties over a wide range of temperatures. Of course, just as any other treatment of transport, the current approach can be improved, especially in the low temperature regime, where the temperature-independent mobility has recently been found.

Mobility as a function of temperature for rubrene has been evaluated using refined material parameters obtained from both MBO fitting of experimental optical spectra (PL and absorption), as well as *ab-initio* calculations. Quantitative agreements have been reached, showing applicability of the current approach in predicting important material properties for organic semiconductors with intermediate excitonic coupling strength.

Chapter 7: Summaries

The application of existing theoretical tools in investigating the optical and electronic processes in organic molecular crystals helps resolve basic physical pictures. *Ab-initio* electronic structure calculations using DFT and semi-empirical methods provide relatively accurate results on both ground- and excited-states of rubrene single molecules. The results obtained allow a basic understanding of important spectroscopy quantities such as optically allowed transition states, transition dipole moments, and so on. With the aid of the Frenkel exciton model, the value of the transfer integral J along a -direction is extracted by fitting the rubrene aggregate.

The independent mode displaced harmonic oscillator (IMDHO) model connects *ab-initio* results, such as ground/excited state geometry, singlet states, transition dipole moments and ground/excited state normal modes, with optical spectroscopy (*i.e.*, PL and absorption). Good qualitative agreements between *ab-initio* and measured spectra of rubrene have been achieved using TDDFT+IMDHO. The approach we used in calculating the PL and absorption spectra are relatively simple and straight-forward. MBO provides a pathway to describe the optical processes by introducing a phonon bath and a few essential parameters which can be determined by the spectra, and be directly applied to calculations of polaron dynamics and polaron transport. Thus the application of the MBO model in extracting physical meaningful parameters from PL and absorption spectra can be viewed as a prerequisite for further investigations with more complicated models. Moreover, the results obtained from the MBO model can also be used as a basic reference for qualitative comparisons.

Polaron dynamics have been studied with the Dirac-Frenkel time-variational method using Davydov Ansätze for the Holstein molecular crystal Hamiltonian. Effects of control parameters, such as g , J , ϕ and W , on the polaron dynamics as well as physical observables closely related to the dynamics have been discussed in length. For the adopted Ansätze, formation of exciton induced lattice deformations can be found around the sites with considerable exciton amplitude. By mapping the parameter space of the Ansätze and plotting the relative deviation vector σ as a function of S , J and W , the D1 Ansatz is found to have much better performance than the D2 and $\tilde{D}$ Ansätze, indicating the importance of accurate description of phonons. Sensitivity of linear absorption spectra to detailed dynamics of polaron formation and excited-state relaxation enables us to study the applicability of D2, $\tilde{D}$ and D1 Ansätze in the weak, intermediate and strong exciton–phonon coupling regimes. The superior performance of the $\tilde{D}$ and D1 Ansätze have been shown in all three regimes.

Following Munn-Silbey’s approach, the microscopic model with an improved description of off-diagonal exciton-phonon coupling has been introduced in this thesis. This model is capable of addressing the issues of charge carrier transport in organic molecular crystals. Effects of various control parameters, especially the role of off-diagonal exciton-phonon coupling strength on mobility calculation, have been discussed. For rubrene single crystal, satisfactory results have been reached for mobility calculations using parameters from MBO fitting of measured PL and absorption spectra, and *ab-initio* calculations. Thus a general theoretical framework of rational design of organic semiconductors starting from molecule structures can be summarized with the schematics shown below in Figure 35.

Figure 35. Schematics of the theoretical framework of rational design and improvement of organic semiconductors.

The loop starts from the fundamental building blocks such as functional groups, backbones, and so on, for a molecule. With the assistance of *ab-initio* and semi-empirical quantum chemistry methods, ground/excited-state structures, and vibrational modes of the

molecule and aggregates can be obtained. After this step, information (optical transition energy, electronic structures, characteristic phonon frequency *etc.*) is fed to the IMDHO model and the MBO model to find the control parameters, such as g , J , ϕ , ω_{LO} and $\Delta\omega$, from optical spectra (*e.g.*, PL and absorption spectra) of the molecule and its aggregates/crystal. The final step is the calculation of intrinsic transport properties using the Munn-Silbey polaron transport model. Moreover, polaron dynamics calculated with the control parameters also provide valuable information in interpreting optical and transport processes. Thus a theoretical framework has been developed in this thesis to facilitate rational design and development of new organic materials for applications in electronic and optoelectronic devices.

Chapter 8: Recommendations for Future Works

7.1 Obtaining Material Parameters from *ab-initio*/Semi-empirical Calculations

The computationally intensive nature of *ab-initio* calculations limits their application in obtaining excited-states for aggregates or crystals containing a large number of atoms. However, the intermolecular van der Waals interactions are important in determining macroscopic properties of organic semiconductors. This is especially true when excitations are taking place on different crystallographic planes. In future research, anisotropic behavior of excitations will be further explored with the help of *ab-initio* and semi-empirical methods by simplifying excitations under experimental conditions to special dimers or aggregates according to packing of molecules in rubrene crystal or any other materials. More precise optical spectra from aggregates can also be calculated and compared with measured ones. Further extension to large aggregates may be needed if simplifications are not sufficient. In this case, one can tackle the problem of scaling by developing more efficient codes that can be parallelized and perform calculations with graphic processing unit (GPU). It is also possible to develop model Hamiltonians that can be incorporated with quantum mechanical methods to treat critical problems of excited states self-consistently.

7.2 Optical Spectroscopy

Despite that good results have been obtained through the MBO model and the IMDHO model, ample room remains to be explored for both methods. The MBO model is too

simple to be used in interpreting more complicated systems with multiple energy levels, charge transfer, nonlinear exciton-phonon coupling, inharmonic vibrational modes, and so on. Thus in future studies, it is beneficial to combine the merits of the MBO model in treating a dissipative bath with more sophisticated methods in dealing electronic structures and exciton-phonon coupling to have better understanding of optical processes of organic semiconductors. Additionally, the bath behavior can also be explored with the assistance of classical or quantum molecular dynamics. Owing to the complexity and computational intensive nature of *ab-initio* calculations, it is difficult to consider the dissipation effects due to a phonon bath in the IMDHO model directly. In the current IMDHO calculations, broadenings of the spectra are achieved through inclusion of arbitrary factors, which is insufficient for describing the phonon bath. Thus, the merits of the *ab-initio* calculations + the IMDHO model may be combined with the elegant treatment of the phonon bath in the MBO model to form a new approach that can interpret measured optical spectra in greater depth. It is also possible to utilize molecular dynamics to find the critical parameters that can determine the dissipative behavior of a phonon bath. Furthermore, consideration of charge and energy transfer processes during optical transition is an important aspect of future research. In-depth exploration of the off-diagonal exciton-phonon coupling in determining spectral features can also be an interesting direction.

7.3 Polaron Dynamic

The studies of polaron dynamics in this thesis only cover localized Ansätze, however, for a wide range of applications, translationally invariant Ansätze will become important.

Thus efforts can be devoted to the development of time-dependent formalisms for translationally invariant Ansätze such as the Toyozawa and GL wavefunctions. The approach only deals with 1D lattice, thus it is natural to go to higher dimensions, allowing for studies of polaron dynamics in materials like graphene, and so on. Important nonlinear optical spectroscopy such as 2D correlation spectroscopy and time-resolved spontaneous emission spectroscopy can also be derived from the current approach. Moreover, questions related to the transition between large and small polaron is still open. One may study this problem with the assistance of quantum information techniques such as entanglement and fidelity. Finding relationships between entanglement/fidelity and optical spectroscopy can be a very attractive direction. To have tight connections with experiments, studies of polaron dynamics, optical spectroscopy, entanglement and fidelity with temperature effects considered remain interesting and urgent in the future.

7.4 Polaron Transport

Validity of the polaron transport model still requires substantial works to verify. Thus a thorough scan over the parameters space is critical as part of the future work. The current approach only treat 1D systems, thus for future studies, extension of current approach to higher dimension is a feasible task. This extension allows for full consideration of electronic band structures of realistic materials. Effects of external fields as well as disorder (due to the presence of impurities, defects and grain boundaries) can also be considered. The current approach is limited to small system size owing to algorithms employed, thus, improvements can be made along this direction to raise the efficiency in calculating the transport properties in large systems.

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List of Publications during the PhD Candidature

1. X.C. Dong, Y.M. Shi, Y. Zhao, D.M. Chen, **J. Ye**, Y.G. Yao, F. Gao, Z.H. Ni, Y. Ting, Zexiang Shen, Peng Chen, and Lance Li, *Symmetry Breaking of Graphene Monolayers by Molecular Decoration*, Physical Review Letters **102**, 135501 (2009).
2. **Jun Ye**, Yang Zhao, Nathaniel Ng, and Jianshu Cao, *Width of Phonon Sidebands in the Brownian Oscillator Model*, Journal of Physical Chemistry B **113**, 5897 (2009)
3. Fuming Chen, **Jun Ye**, Ming Yong, Yang Zhao, Lay Poh Tan, Yuan Chen, Mary Chan-Park, and Lain-Jong Li, *Species-Dependent Energy Transfer of Surfactant-Dispersed Semiconducting Single-Walled Carbon Nanotubes*, Journal of Physical Chemistry C **113**, 20061–20065 (2009).
4. **Jun Ye**, Andrew C. Grimsdale, and Yang Zhao, *Analyzing the Optical Properties of a Conjugated Polymer by the Multi-Mode Brownian Oscillator Model*, Journal of Physical Chemistry A **114**, 504-508 (2010).
5. Y. Y. Tay, T. T. Tan, F. Boey, M. H. Liang, **J. Ye**, Y. Zhao, T. Norby and S. Li, *Correlation between the characteristic green emissions and specific defects of ZnO*, Physical Chemistry Chemical Physics **12**, 2373-2379 (2010).
6. Qingmei Liu, **Jun Ye** and Yang Zhao, *Vibronic spectra of molecular crystals by dynamical mean field theory*, Physical Chemistry Chemical Physics **12**, 6045-6053 (2010).
7. Bin Luo, **Jun Ye**, Chengbo Guan and Yang Zhao, *Validity of time-dependent trial states for the Holstein polaron*, Physical Chemistry Chemical Physics **12**, 15073 (2010).
8. Bin Luo, **Jun Ye**, and Yang Zhao, *Variational Study of Polaron Dynamics with the Davydov Ansätze*, physica status solidi (c), (EXCON'10 Proceedings or special issue) **8**, 70 (2011).
9. Chen Rui, Tay Yee, **Ye Jun**, Zhao Yang, Xing Guo Zhong, Wu Tom, Sun Handong, *Investigation of Structured Green Band Emission and Electron-Phonon Interactions in Vertically Aligned ZnO Nanowires*, Journal of Physical Chemistry C, **114**, 17889 (2010).
10. Prathamesh M Shenai, **Jun Ye** and Yang Zhao, *Sustained smooth dynamics in short sleeved nanobearings based on double walled carbon nanotubes*, Nanotechnology, **21**, 495303 (2010).
11. Dongmeng Chen, **Jun Ye**, Haijun Zhang and Yang Zhao, *On the Munn-Silbey approach to polaron transport with off-diagonal coupling and*

temperature-dependent canonical transformations, Journal of Physical Chemistry B: Shaul Mukamel Festschrift, **115**, 5312 (2011).

12. Zhongcheng Mu, Qi Shao, **Jun Ye**, Zebing Zeng, Huey Hoong Hng, Yang Zhao, Jishan Wu, and Xiaodong Chen, *Effect of Intermolecular Dipole-Dipole Interactions on Interfacial Supramolecular Structures of C₃-Symmetric Hexa-peri-hexabenzocoronene Derivatives*, Langumir ASAP, **27**, 1314 (2011) (Supramolecular Chemistry at Interfaces special issue).
13. Liap Tat Su, **Jun Ye**, Jun Guo, Siva Krishna Karuturi, Lijun Liu, Alfred Tok Iing Yoong and Yang Zhao, *High index, reactive facets controlled synthesis of one-dimensional single crystalline rare earth hydroxide nanobelts*, CrystEngComm, **13**, 5367 (2011).
14. Junling Song, Zongyou Yin, Zijiang Yang, Pitchamuthu Amaladass, Shixin Wu, **Jun Ye**, Yang Zhao, Wei-Qiao Deng, Hua Zhang and Xue-Wei Liu, *Enhancement of Photogenerated-Electron Transport in Dye-Sensitized Solar Cells with Introduction of Reduced Graphene Oxide-TiO₂ Junction*, Chemistry - A European Journal, **17**, 10832-10837, (2011).
15. **Jun Ye**, Kewei Sun, Yang Zhao, Yunjin Yu, Chee Kong Lee, and Jianshu Cao, *Excitonic energy transfer in light-harvesting complexes in purple bacteria*, submitted to Physical Chemistry Chemical Physics.
16. **Jun Ye**, Dongmeng Chen, and Yang Zhao, *Off-diagonal carrier-phonon coupling and polaron transport*, submitted to Journal of Physics: Conference Series.