

Computational Modelling of Electronic States, Charge Transfer and Charge Transport in Organic Semiconductors

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Declaration

The work described in this thesis was undertaken from June 2014 – November 2017, under the supervision of Professor Jenny Nelson, Dr Jarvist Frost and Dr Kim Jelfs. Unless explicitly stated otherwise, the results presented herein are the product of my own work.

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Abstract

In this thesis, we model electronic states, charge transfer and charge transport in organic semiconductors (OSCs). We are interested in the effect of chemical structure, molecular packing and different types of disorder on the charge transport in these materials, which is an important factor determining the efficiencies of devices made with OSCs. This is an intrinsically multiscale problem, and we use computational methods than span length and time-scales.

We investigate the effect of molecular packing and crystal structure on charge carrier mobility in molecular crystals. We also model the electron mobility in disordered small molecules containing different defects to find the effect of these defects on the performance of devices. We perform electronic structure calculations to investigate the HOMO and LUMO levels in the presence of different defects, as well as to generate absorption, photoluminescence and infrared spectra to compare to experimental spectra.

We develop a computationally efficient method for modelling polarons in organic semiconductors within a tight-binding framework. We apply the method to large assemblies of fullerene molecules generated with coarse-grained molecular dynamics. The method allows us to explore the effect of energetic and configurational disorder, as well as polaron formation, on the density of states and size of charge states in these systems.

We further develop a method for calculating transfer integrals between molecules or molecular fragments, based on performing calculations of molecular orbitals in a counterpoise basis set. We apply it to calculating intramolecular transfer integrals and transfer integrals between donor and acceptor molecules at interfaces in organic photovoltaics, and between dopant and host molecules.

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Symbols and abbreviations

OSC	Organic semiconductor
OPV	Organic photovoltaics
OFET	Organic field effect transistor
OLED	Organic light emitting diode
m_e	Electron mass
ω_0	Resonant frequency
$\mathcal{E}$	Electric field
P	Polarisation field
D	Displacement field
q	Electronic charge
ϵ_0	Vacuum permittivity
ϵ_r	Relative permittivity
f	Oscillator strength
μ_D	transition dipole moment
ω	frequency
χ	Electric susceptibility
ϵ_{opt}	Optical dielectric constant
ϵ_{stat}	Static dielectric constant
$\hbar$	Reduced Plancks constant
$N(E)$	Density of states (DOS)
σ	Standard deviation
E	Energy
n	Electron density

α	Electron-phonon coupling constant
m^*	Reduced mass
k	Wave vector
W_p	Small polaron formation energy
μ	Mobility
D	Diffusion coefficient
k_B	Boltzmann constant
T	Temperature
v	Velocity
a	Acceleration
$\vec{F}$	Force
v_g	Group velocity
Ψ	Total wavefunction
ψ	Electronic wavefunction
ϕ	Electronic wavefunction in frozen orbital approximation
Ω	Nuclear wavefunction
Z	Nuclear charge
τ	Relaxation time
Γ	Rate
$\hat{H}$	Hamiltonian
$\hat{H}_{TB}$	Tight-binding Hamiltonian
J_{ij}	Transfer integral (electronic coupling)
λ	Reorganisation energy
λ_{inner}	Inner reorganisation energy

λ_{outer}	Outer reorganisation energy
ΔE	Change in energy
S^{eff}	Effective Huang-Rhys factor
$\hbar\omega^{eff}$	Effective mode energy
d_m	Spatial dimensionality

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1

Introduction

1.1 Organic semiconductors

Organic semiconductors (OSCs) are a class of material that combine semiconducting properties with flexibility, light weights and solution processibility, which is hoped to translate to lower costs than their inorganic counterpart when commercialised [1]. They are π -conjugated molecular materials that include molecular crystals, disordered molecular materials and conjugated polymers. OSCs have applications in molecular electronics, such as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs) and organic photovoltaics (OPV). Due to the number of potential molecular constituents of OSCs, they can possess a huge variety of properties, which have the potential to be tuned depending on the desired applications [2].

As well as their advantages, there are many challenges still faced by OSCs. The first is the efficiency of devices made with OSCs, which is generally less than that of analogous inorganic devices. The second is their lifetime, as some OSC materials degrade in the presence of air and water, which can affect their properties [3]. Understanding the factors that influence both the efficiency and lifetime of OSCs is hence vital for designing better devices. This means understanding the mechanisms that influence the efficiency or lifetime as well as identifying materials that have potential for a specific applications.

There are a huge number of possible materials for OSC-based devices, with properties determined by chemical structure as well as bulk packing and disorder. Computational modelling of OSCs can therefore play a major role alongside experiments in studying and understanding these materials, both in terms of identifying desirable properties and pre-screening potential materials. This approach requires knowledge of atomic- or electronic-scale processes, but should also be able to access macro-scale properties that can be measured [4].

There are many factors influencing the efficiency of devices made with OSCs. Here, we focus specifically on understanding charge transport, and therefore the electronic states in these materials. We model electronic states, charge transfer and charge transport in different types of organic semiconductors, including disordered small molecules, disordered small molecules with chemical defects, and molecular crystals. We also develop methods to calculate microscopic charge transport parameters that can be applied to a range of different systems relevant to OSC applications. In this thesis, we are particularly interested in applications to solar energy conversion.

1.2 Organic photovoltaics

One of the major challenges of the 21st century is providing the world's growing population with energy that is sustainable and that does not contribute to climate change. Solar power could be a significant part of the solution, with 3,850,000 exajoules (EJ) of solar energy reaching the Earth every year [5]. Solar photovoltaic (PV) currently accounts for 300,000 MW of installed capacity worldwide, which is only 1% of the total power generation, but this has been growing exponentially [6].

Traditional photovoltaic (PV) devices are based on doped inorganic semiconductors. The advantages of OPVs over these devices include their lower cost and low temperature solution processability, as well as being made from earth abundant materials. They can be manufactured using roll-to-roll production, so have the potential for large area devices, and are light-weight, flexible and can be made semi-transparent [7].

All PV devices are based on the photovoltaic effect. This is where a photon is absorbed, exciting an electron, which then moves through the material because of an in-built asymmetry in the device [8]. The separation of charges results in a potential difference (voltage) between the contacts

and the device can be connected to an external load where it can do electrical work. When OPV materials absorb light, an electron is excited, but the binding energy between the electron and hole (exciton) is usually too large for them to spontaneously dissociate.

In the simplest type of OPV device, an organic semiconducting material is sandwiched between two different conducting contacts. The difference in work function between these electrodes results in an electric field that drives the charge carriers (electron and hole) to the contacts. However, the electric field is not usually sufficient to dissociate the exciton, and since exciton diffusion lengths are relatively short, the exciton may recombine which results in low power conversion efficiency for these devices (<1%).

This problem was solved by the development of heterojunction devices, where two different OSC materials with different electron affinities and ionisation potentials make up the active layer. Electrostatic forces are generated at the interface between the two materials, an electron donor and electron acceptor, which allows the exciton to dissociate much more efficiently. The charge carriers can then diffuse to their respective contacts.

To maximise the interface between donor and acceptor materials, bulk heterojunction (BHJ) devices were developed, where the active layer is a nanoscale blend of donor and acceptor materials [9] [1]. The donor and acceptor domains are on the order of the exciton diffusion length, maximising the size of excitons that dissociate into free charge carriers. These are currently the most common type of OPV cell. The mechanism by which BHJ OPV devices convert solar energy into electricity is illustrated in Figure 1.1, and described below.

1. A photon of light is absorbed in the active layer, exciting an electron and creating an electron-hole pair, or exciton.
2. Exciton diffuses to an interface between the donor and acceptor material.
3. Exciton dissociates into an electron and hole.
4. Charge transport of the electron (in acceptor material) and hole (in donor material) to the contacts.
5. Current generated.

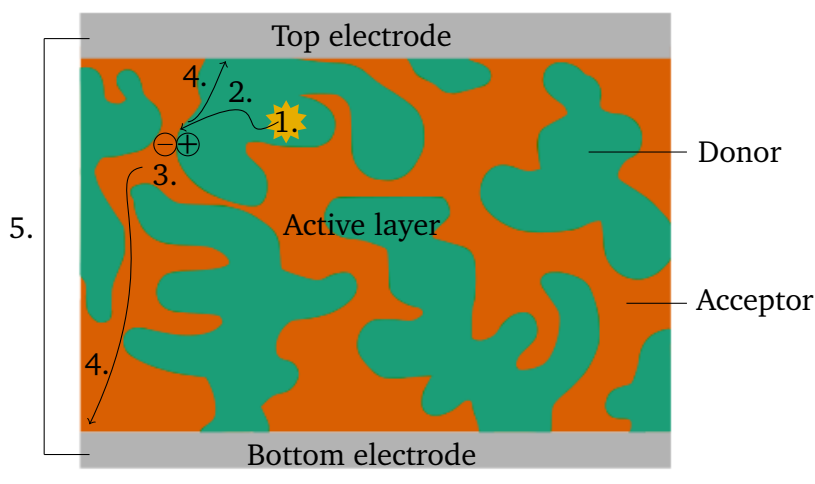


Figure 1.1: OPV architecture and mechanism in a bulk heterojunction.

Since 2002 the maximum power conversion efficiency (PCE) of OPV devices has increased from 2% to 11.51% for a single junction device [6]. Increasing OPV efficiency further, as well as extending the device lifetime, is the key to producing commercially competitive devices. One of the key determining factors influencing the efficiency is the rate of charge transport through the device, which we focus on in this thesis.

1.3 Understanding Charge Transport

The optoelectronic performance of devices based on OSCs is directly related to their charge transport properties. This is a function of the chemical structure, microstructure, chemical and physical properties, and the dynamics of the material. The nature of charge transport also depends on the electronic states. In the majority of OSCs, the electronic states are not Bloch states with a well-defined momentum, meaning charge transport is rarely in the regime where band transport models are valid. In the other limit, charge transport in some OSCs can be treated with a hopping model, where charge moves between sites via thermally activated hops. Charge transport can also fall into an intermediate regime between these two limits.

In section 2.6, we outline these three regimes and the methods currently used to approach them. Marcus theory for calculating the rates of charge carriers hopping between molecules or molecular segments is well-established for modelling charge transport in OSCs [10]. However, it is not always valid and part of the work is understanding where it can be applied, which means understanding the electronic states.

To model charge transport, assemblies of many hundreds of molecules are required, since experimental films are on the order of 100 nm thick. Models of charge transport require knowledge of the electronic structure of the system, which is informed by both the chemical structure of individual molecules and the interactions between molecules in the assemblies. The disordered nature of many OSC films also means that multiple realisations of the same system must be generated. This motivates the need for computationally efficient methods that span length and time scales (section 2.1).

1.4 Aims

In this thesis, we aim to apply multiscale methods for modelling electronic states, charge transfer and charge transport in OSCs to interesting systems where we can add insight to work by experimental collaborators. We also aim to develop computationally efficient methods for modelling both electronic states and charge transfer. This is to pave the way towards charge transport models in systems where established methods are not applicable, or where methods cannot access large enough systems relevant to applications.

Here, we give an outline of the chapters in this thesis in which we hope to achieve these aims.

1.5 Thesis outline

Chapter 2 describes the theoretical background underpinning the work of thesis. This includes the origin of conjugation in OSCs from atomic orbitals; theories of disorder and localisation; the physical and mathematical understanding of polarons; and our current understanding of charge transport based on the literature.

In chapter 3, the existing methods used in this thesis are explained and/or derived, including coarse-grained molecular dynamics, electronic structure methods such as DFT and tight-binding, quantum chemical calculations and Marcus theory to obtain the charge mobility. We also review previous work that has used these methods, and indicate where they have been built on.

In chapter 4, we study a system where Marcus theory is valid: crystal structures of helicene molecules. We explore how the chirality of the molecule affects the crystal structure, and therefore

the mobility between different crystal structures. We investigate the difference between enantiopure (molecules of all one handedness) and racemic (a 50:50 mix of left- and right-handed molecules) aza[6]helicene structures in terms of their mobility, prompted by experimental measurements and characterisation by collaborators. We apply the same method to a set of low-energy crystal structures of [6]helicene and investigate the correlation between high hole and electron mobilities with density, energy and anisotropy. We identify substructures that exist in high mobility structures to aid future synthesis of these structures.

In chapter 5, we investigate the effect of chemical defects in PCBM, the most popular electron acceptor in OPVs. This work was done in collaboration with experimentalists to explore the types of defects that can form in PCBM films under exposure to oxygen, as well as the effects on their optical and electronic properties. We compare experimental FTIR spectra with modelled IR spectra from hybrid DFT vibrational calculations of PCBM with different defect types. We also compare experimental absorption and photoluminescence measurements with those modelled using TD-DFT calculations. We measure the effect of the different defects on the HOMO and LUMO levels of the molecules to see if traps are likely to form and affect the device performance. Finally, we calculate the mobility of electrons in PCBM assemblies with different densities of defected molecules.

In chapter 6, we develop a way to model polaron states in organic semiconductors, within a molecular tight-binding framework. We base it on a continuum approximation, which results in a computationally efficient method that can be applied to large, disordered assemblies. These polaron states are electronic states that are important for understanding the nature of charge transport and whether a hopping model is valid.

We apply this model to three-dimensional disordered assemblies of fullerene adducts - that is C60, PCBM and PCBM with increasing numbers of sidechains (up to six). We generate the assemblies with coarse-grained molecular dynamics, and take advantage of the fact that electronic coupling in these systems is isotropic to populate the tight-binding Hamiltonian. The different adducts allow us to explore configurational disorder, while the tight-binding framework allows us to easily explore energetic disorder. We calculate the density of states and spatial extent of the electronic states in each of the adducts with increasing energetic disorder. We apply the polaron formation model to these systems and carefully calculate the appropriate parameters for C60, PCBM and bis-PCBM. Finally, we do a variational analysis with different values of the key polaron parameter

for all of the fullerene adducts, and look at the effect of varying both the energetic disorder and strength of the polaron formation together, to explore the relative localising effects of these different processes.

In chapter 7, we further develop a method to calculate transfer integrals in a range of different systems, based on a counterpoise basis set. The method is transparent, widely applicable and straightforward to implement. It allows us to calculate transfer integrals between unlike molecules, as well as bonded molecules, increasing the scope of the types of systems we can investigate. We first validate the model with simple, well-studied systems, and then apply it to intramolecular transfer integrals, transfer integrals between donor and acceptor molecules, and transfer integrals between a dopant and host.

For the intramolecular transfer integrals, we compare our calculations to analytic dihedral dependent approximations. For the donor-acceptor systems, we also explore the rates of charge separation and charge recombination based on the calculated transfer integrals and the energies of the initial and final states. In the dopant and host system, we use the transfer integrals to infer whether the charge transfer is likely to be integer or partial. We therefore show the utility of this counterpoise method for calculations beyond transfer integrals between pairs of like molecules, usually used as inputs to the Marcus equation.

Finally, in chapter 8, we summarise our findings and suggest possible next steps for this research.

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2

Theoretical background

2.1 Multiscale modelling

Charge transport in organic semiconductors involves many processes occurring on different length and time-scales. Modelling these processes involves using theory and simulation techniques that span these. The different length- and time-scales used for studying OSCs are illustrated in the schematic in Figure 2.1. Those we use in this thesis are highlighted in bold.

Macroscopic material properties that are of interest for devices based on OSCs can be understood via quantum mechanics, molecular models and mesoscale dynamics. To model charge transport, we need relatively large systems of many hundreds of molecules, since thin films used in devices are of order 100 nm thick. Disorder in the films also means that we must sample many realisations of the system in order to get good statistics. This motivates the need for computationally efficient methods to access large assemblies of molecules that are based on molecular or electronic scale calculations.

As Figure 2.1 shows, we use methods that span length scales from angstroms to cm, and time scales from femtoseconds to 10s of seconds. The different length- and time-scale simulations inform each other, for example DFT can be used to calculate parameters for tight-binding, and

structures obtained from coarse grained molecular dynamics can inform electronic structure calculations.

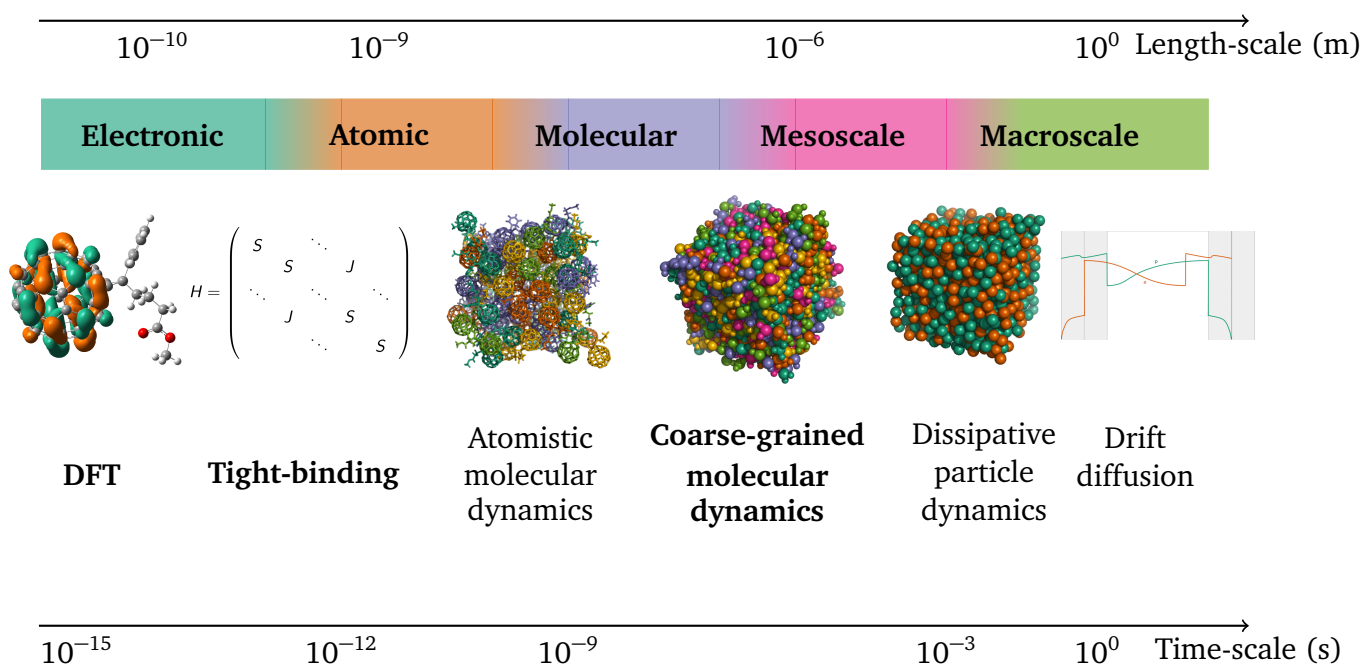


Figure 2.1: Schematic showing the different length- and time-scales relevant to modelling OSCs. The methods that are used are illustrated, with the ones we use in this thesis in bold.

In chapter 3 we explain the methods used in this thesis that are highlighted in bold here. In this chapter, we describe the theoretical background underpinning these methods as well as the processes that give OSCs their properties. We also give an overview of methods that are used to model charge transport, to situate our work within the context of research in the field.

2.2 Conjugated organic molecules

OSCs are based on conjugated organic molecules, which are carbon-based molecules containing alternating single and double bonds that results in delocalisation of the orbitals. This bonding is a result of sp^2 hybridisation and it is this hybridisation that leads to delocalisation of the orbitals and the extended π -conjugated system. The sp^2 hybridisation is illustrated in Figure 2.2, along with the resultant bonding in an ethene molecule. The $2s$ orbital hybridises with two p_x and p_y orbitals in different combinations to result in three sp^2 hybridised orbitals, while the p_z orbital remains unhybridised (shown in (a)). In the simple case of an ethene molecule, this results in the two carbon molecules having both a π and σ bond joining them. Electrons in the π bond are more weakly bound and therefore delocalise (see (b)).

Conjugated organic molecules act as semiconductors due to this delocalisation of their frontier orbitals, which can spatially overlap with those of neighbouring molecules. For electron transport the important orbital is the lowest unoccupied molecular orbital (LUMO) and for hole transport it is the highest occupied molecular orbital (HOMO) [1].

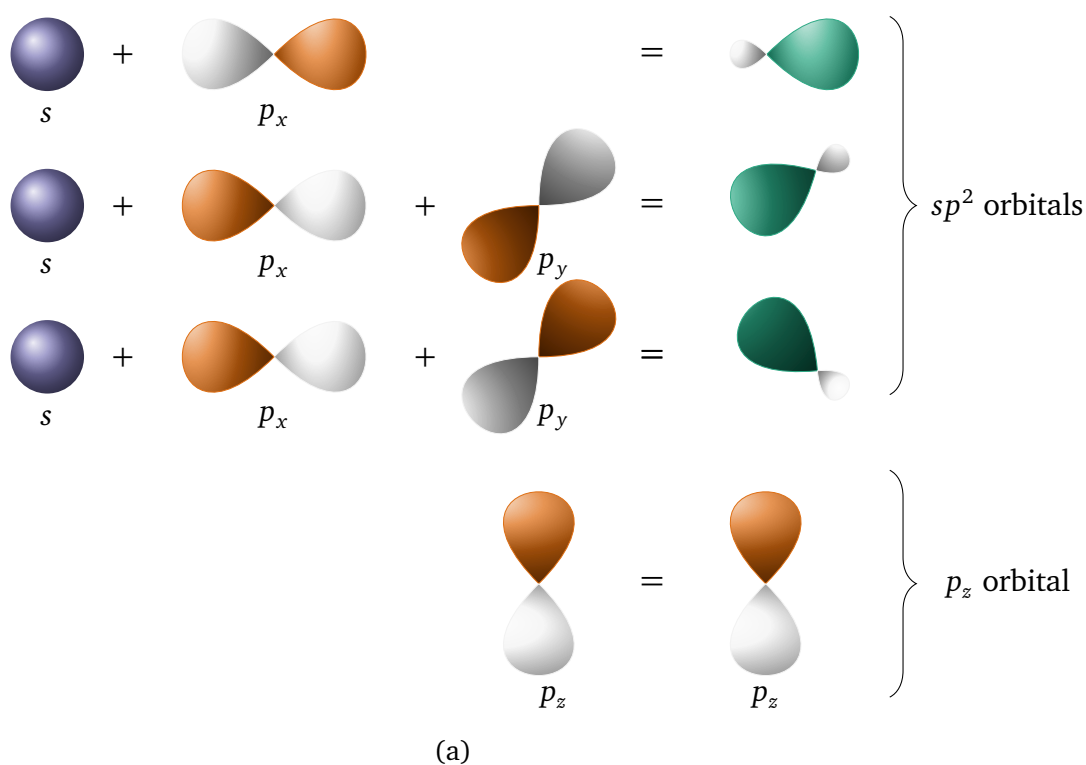
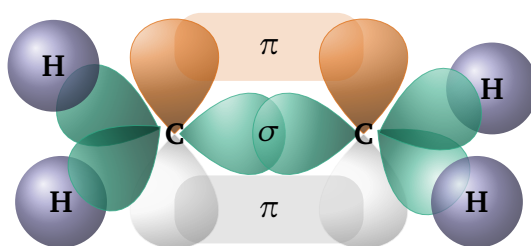


Figure 2.2: (a) Formation of the three sp^2 orbitals from one s and two p orbitals, along with the unhybridised p_z orbital. (b) sp^2 hybridised orbitals along with the remaining p_z orbital forming π – and σ – bonds in ethene.

2.3 Optical properties

To understand charge transport in these systems, we first need to understand how light interacts with electrons, i.e. the optical properties of the materials.

The interaction between a light wave and an atom can be considered with a Lorentz oscillator model, where the displacements of the atomic dipoles are treated as damped harmonic oscillators. The damping term takes into account the fact that the oscillating dipoles can lose their energy through collisions [2].

The electric field of the light wave induces oscillations in the atomic dipoles via the electrons. Since the nuclear mass is much greater than the electronic mass, nuclear motion is not included in the model (Born–Oppenheimer approximation). The displacement of the electron, x , is described by the following equation of motion:

$$m_e \frac{d^2x}{dt^2} + m_e \gamma \frac{dx}{dt} + m_e \omega_0^2 x = -q\mathcal{E}, \quad (2.1)$$

where m_e is the mass of the electron, γ is the damping term, ω_0 is the resonant frequency, q is charge of an electron, and $\mathcal{E}$ is the electric field of the light wave. The terms on the left hand side correspond to the acceleration, the damping, and the restoring force, respectively. The term on the right hand side corresponds to the driving force due to the electric field of the light wave.

The time dependence of the electric field is given by

$$\mathcal{E}(t) = \mathcal{E}_0 \cos(\omega t + \Phi) = \mathcal{E}_0 \operatorname{Re}(e^{-i(\omega t + \Phi)}), \quad (2.2)$$

where ω is the frequency of the light, $\mathcal{E}_0$ is the amplitude of the light and Φ is the phase of the light. Substituting equation 2.2 into equation 2.1, and looking for solutions of the form $x(t) = X_0 e^{-i\omega t}$, gives

$$-m_e \omega^2 X_0 e^{-i\omega t} - i m_e \gamma \omega X_0 e^{-i\omega t} + m_e \omega_0^2 X_0 e^{-i\omega t} = -q \mathcal{E}_0 e^{-i\omega t}. \quad (2.3)$$

This implies that

$$X_0 = \frac{-q\mathcal{E}_0/m_e}{\omega_0^2 - \omega^2 - i\gamma\omega}, \quad (2.4)$$

and therefore

$$x(t) = \frac{-q\mathcal{E}_0/m_e}{\omega_0^2 - \omega^2 - i\gamma\omega} e^{-i\omega t}. \quad (2.5)$$

The magnitude of the time-dependent atomic dipole, $p(t)$, relates to the time-dependent displacement with

$$p(t) = -qx(t). \quad (2.6)$$

The polarisation can be split into a non-resonant background term ($\mathbf{P}_{bg}$) and a resonant term ($\mathbf{P}_{res}$), where the frequency is close to the resonant frequency. Substituting equation 2.5 into equation 2.6, and defining the number of atoms per unit volume as N , gives the resonant polarisation as

$$\mathbf{P}_{res} = -Nqx = \frac{Nq^2}{m_e} \frac{1}{(\omega_0^2 - \omega^2 - i\gamma\omega)} \mathcal{E}. \quad (2.7)$$

The background polarisation term is defined as:

$$\mathbf{P}_{bg} = \epsilon_0 \chi \mathcal{E}, \quad (2.8)$$

where ϵ_0 is the vacuum permittivity and χ is the electric susceptibility that accounts for all higher frequency contributions to the polarisability of the system [3].

The electric displacement $\mathbf{D}$ of a medium is related to the electric field $\mathbf{E}$ and polarisation $\mathbf{P}$ through [2]:

$$\mathbf{D} = \epsilon_0 \mathcal{E} + \mathbf{P}, \quad (2.9)$$

$$\mathbf{D} = \epsilon_0 \mathcal{E} + \mathbf{P}_{bg} + \mathbf{P}_{res}. \quad (2.10)$$

Assuming the material is isotropic, the relative dielectric constant can be defined through the relationship:

$$\mathbf{D} = \epsilon_0 \epsilon_r \mathcal{E}. \quad (2.11)$$

If the material is anisotropic, then ϵ_r is a tensor.

Combining equations 2.9 to 2.11 gives:

$$\epsilon_r(\omega) = 1 + \chi + \frac{Nq^2}{\epsilon_0 m_e} \frac{1}{(\omega_0^2 - \omega^2 - i\gamma\omega)}. \quad (2.12)$$

This equation holds when there is a single resonance. For multiple resonances a similar treatment would give:

$$\epsilon_r(\omega) = 1 + \chi + \frac{Nq^2}{\epsilon_0 m_e} \sum_j \frac{f_j}{(\omega_{0j}^2 - \omega^2 - i\gamma_j\omega)}, \quad (2.13)$$

where an oscillator strength f_j has been assigned to each transition j . The oscillator strength of an electronic transition at ω_0 is defined as

$$f = \frac{2}{3} \frac{m_e \omega_0}{\hbar q^2} \mu_D^2, \quad (2.14)$$

where m_e is the mass of an electron and μ_D is the transition dipole moment.

Taking the high and low frequency limits yields the optical (ϵ_{opt}) and static (ϵ_{stat}) dielectric constants respectively:

$$\epsilon_r(0) \equiv \epsilon_{stat} = 1 + \chi + \frac{Nq^2}{\epsilon_0 m_e} \sum_j \frac{f_j}{\omega_{0j}^2}, \quad (2.15)$$

$$\epsilon_r(\infty) \equiv \epsilon_{opt} = 1 + \chi. \quad (2.16)$$

These constants are important when considering the formation of polarons, which is discussed in section 2.5.

2.4 Disorder and localisation

Organic semiconductors are relatively disordered, due to relatively weak intermolecular bonds and processing conditions. Thermal energy with soft structures leads to thermal disorder even in single crystals. The different types of disorder include: (i) conformational (structural); (ii) configurational (e.g. different isomers of the same molecule); (iii) packing (e.g. amorphous assemblies or different polymorphs in a crystal). Disorder affects both the site energies and the interactions between molecules.

Disorder can localise free charges. This is known as Anderson localisation and is expanded on below. On a simple level, localisation of a charge can be thought of as a competition between an electrostatic potential term, tending to localise it, and its kinetic energy tending to delocalise it [4].

2.4.1 Anderson localisation

In one-dimension, any amount of disorder fully localises the charge carriers and mobility drops to zero. This isn't necessarily true for two- or three-dimensional systems. Anderson's theorem (1958) [5] states that "*the eigenfunctions are localised if the 'strength' of the disorder exceeds some definite value*" [6]. Using a tight-binding model, Anderson proved in his 1958 paper that the states at the centre of the band must be localised when the energy of the individual atomic states varies at random over a range greater than the width of the band produced by the overlap between adjacent atomic orbitals. Tight-binding describes electronic structure starting with a basis of localised electronic states. We expand on the theory of tight-binding in section 3.3.3.

The density of states (DOS) of a system is the distribution of available electronic states at each energy interval. With disorder, it can be classified as extended and localised states, separated by mobility edges (see Figure 2.3). The mobility edges are the point below and above which

the states are localised. A ‘localised’ state does not contribute to the electrical conductivity at absolute zero. The external states beyond the mobility edge form the ‘tails’ of the density of states distribution. They are important since charges can be trapped in the low energy tail states.

For small values of disorder δ , some states at the edges of the spectrum may be localised, while those at the centre of the band are extended. As δ increases, tails of localised states are produced at the edges of the band, which become larger with δ . Once it reaches some critical value, δ_c , the mobility edges coalesce at the centre of the band, and all states are localised. This *Anderson transition* is illustrated in Figure 2.4 [6].

In the Anderson model, all states becoming localised means that the material becomes an insulator at 0 K, since the electrons cannot escape the region they have been localised to. At finite temperatures, charges can move between localised states via thermally activated hopping [4].

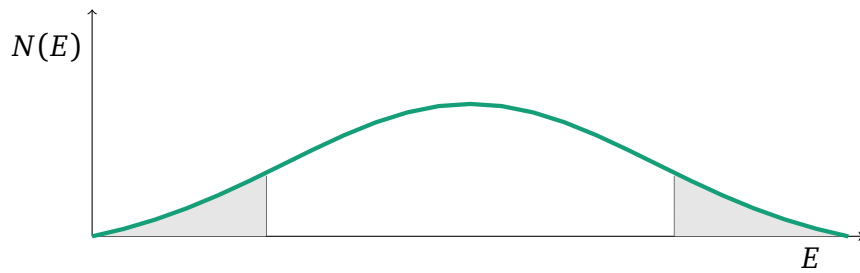


Figure 2.3: Localised states and mobility edges. The shaded region shows the localised states, and the line separating these from the extended states is the mobility edge

The Anderson transition is one example of a metal-insulator transition. Here, a metal is defined as a material with electronic conductivity at 0 K. Another metal-insulator transition is the Mott transition [7], which is outlined below.

2.4.2 Mott transition

In a semiconductor, as more donor material is added, the density of electrons is increased. During this process, the interaction between these electrons and the charged donor gets screened by electron-electron interactions. Eventually, the screening causes the donor binding energy to vanish, and the semiconductor becomes metallic [8]. The Mott transition is defined by the critical number of donors at which the transition from insulating at low temperature (insulator) to conducting at low temperature (metal) happens.

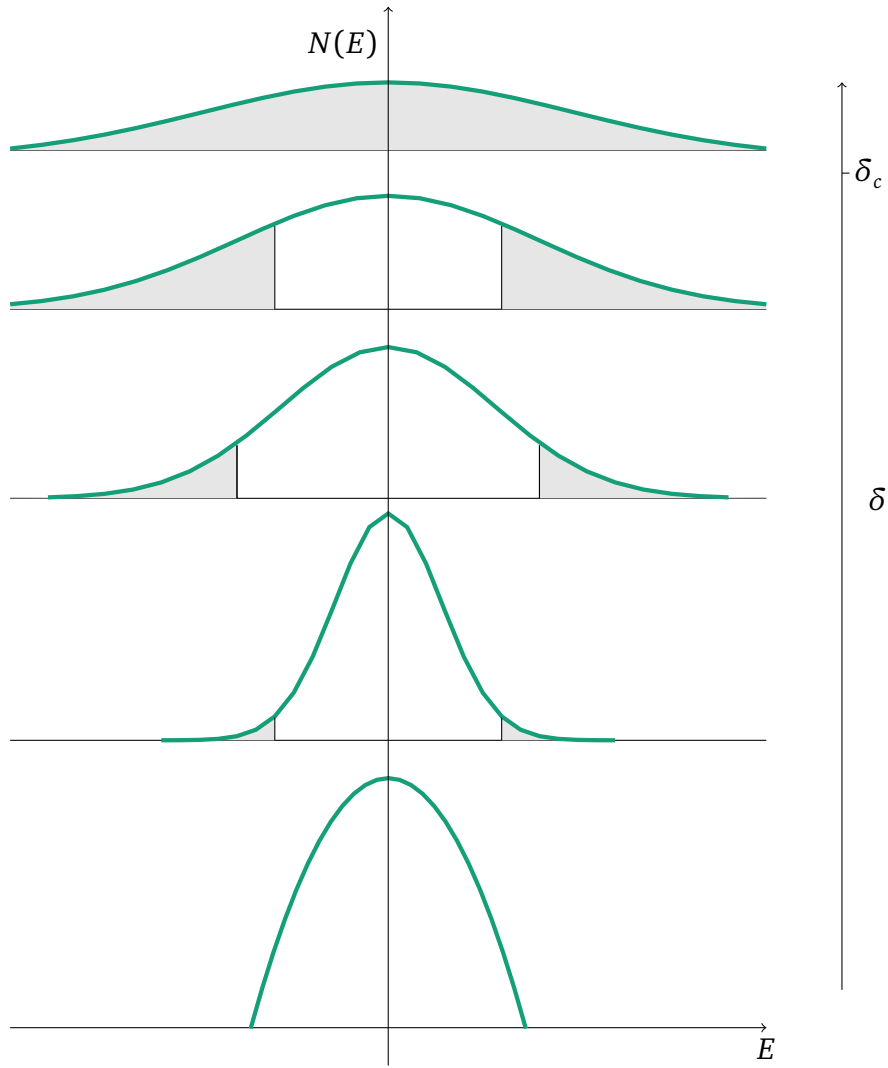


Figure 2.4: Anderson model showing how as disorder, δ , increases more states are localised (shown by shading). After the *Anderson transition*, δ_c , the mobility edges coalesce and all states are localised.

The screened potential of each centre in the Thomas-Fermi approximation is

$$V_{sc}(r) = -\frac{e^2}{4\pi\epsilon_0\epsilon_r} \exp(-k_{TF}r), \quad (2.17)$$

where k_{TF}^{-1} is the Thomas-Fermi screening length

$$k_{TF}^{-1} = \frac{4n^{1/3}}{a_0^*}, \quad (2.18)$$

where n is the density of free electrons and a_0^* is the effective Bohr radius. The condition for metallic behaviour is that the screening length is less than a_0^* , and therefore that

$$n^{1/3}a_0^* \geq 0.25. \quad (2.19)$$

2.4.3 Description of band tails

In OSCs, the distribution of states below the mobility edge (shaded states in Figure 2.3) is typically approximated as an exponential or a Gaussian.

Assuming an exponential band tail, the density of states $N(E)$ is given by [9]

$$N(E) = N_0 \exp\left(\frac{E - E_0}{E_{ch}}\right), \quad (2.20)$$

where E_0 is a reference energy where electrons are free to move (i.e. the mobility edge), N_0 is the density of states at E_0 , and E_{ch} is the characteristic energy of the tail [10].

The exponential band tail approximation is analogous to the Urbach tail in optical absorption spectra [11]. The evidence of "Urbach tails" was first documented in the optical absorption spectra of ionic crystals by Urbach in 1953 [12], and they have since been found in a wide range of organic materials, both in the optical absorption and in the density of states [13] [14] [15] [16].

There has also been evidence of the density of states being approximately Gaussian, having the following form:

$$N(E) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{E^2}{2\sigma^2}\right), \quad (2.21)$$

where σ is the standard deviation.

The Gaussian Disorder Model (GDM), developed by Bässler (1993) [17], assumes this functional form for disordered organics semiconductors. This model has been successfully used to explain a number of experimental observations relating to charge transport in conjugated polymers [18].

2.5 Polaron theory

When a charge carrier (electron or hole) is put into a system, the atoms surrounding it will deform, tending to form a potential well for the electron. The electron along with its self-induced polarisation is a quasi-particle called a polaron (Figure 2.5). This displacement of nuclei is described in terms of phonons, and when electrons interact with these displacements it is known as electron-phonon coupling. The “self-trapping” of the electron is a result of the coupling of the electron wavefunction with a set of harmonic oscillators (associated with the normal modes of vibration) [19]. Polarons are important in ionic crystals or polar semiconductors, such as conducting polymers or fullerenes [20].

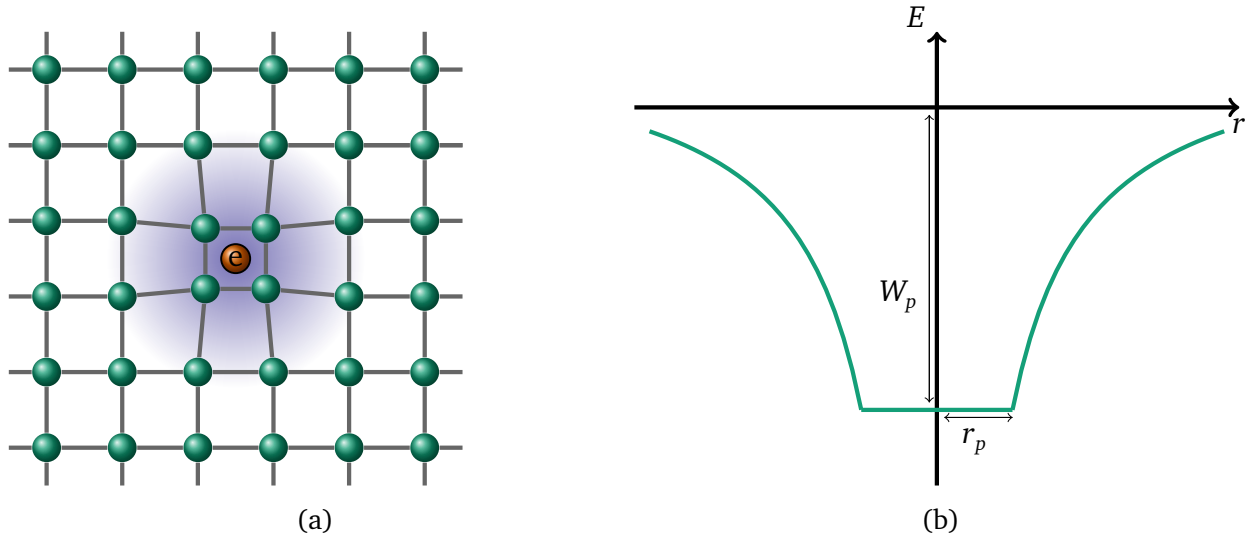


Figure 2.5: (a) A schematic of a polaron (purple), showing the electron along with the induced distortion of the lattice. (b) A plot of the energy of a small polaron versus distance r from its centre, with the depth of the potential well, W_p , and radius of the polaron, r_p , indicated.

The work of Landau and Pekar [21] forms the basis for polaron theory and many have built on this since. Pekar studied the polaron in the continuum approximation, i.e. a free electron that interacts with a dielectric polarisable continuum, which is described by the static and optical dielectric constants [22]. This model is applicable when the self-trapped state is large compared to the lattice constant [23].

Fröhlich introduced a model Hamiltonian for such a polaron so its dynamics can be described quantum mechanically [24]. The longitudinal optical phonons carry the polarisation and are represented by a set of quantum oscillators. The interaction between the charge and the polarisation field is linear in the field. The dimensionless electron-phonon coupling constant α describes the

strength of the interaction, i.e. whether there is strong or weak coupling [25].

$$\alpha = \frac{1}{4\pi\epsilon_0} \frac{q^2}{\hbar} \sqrt{\frac{m^*}{2\hbar\omega_{LO}}} \left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon_{stat}} \right), \quad (2.22)$$

where ϵ_{opt} and ϵ_{stat} are the optical and static dielectric constants, respectively, q is the charge on the electron, $\hbar\omega_{LO}$ is the energy of the longitudinal optical phonons, ϵ_0 is the vacuum permittivity and m^* is the effective mass of the electron, which is given by [26],

$$m^* = \hbar^2 \left(\frac{d^2E}{dk^2} \right)^{-1}, \quad (2.23)$$

where the term d^2E/dk^2 is the curvature of the band structure, E is the energy and k is the wavevector. This can only be defined in periodic media, so is not applicable for our disordered materials.

The Fröhlich polaron model can be used to described both small and large polarons [27]. A small Fröhlich polaron is formed by a long-range interaction as described by the Hamiltonian, in contrast to a small Holstein polaron, formed by short-range electron-phonon interactions, which takes into account the discrete nature of the lattice.

As the polaron radius approaches the dimensions of the lattice constant, the continuum approximation used in the theory of large polarons is no longer valid. Holstein was the first to describe the “small polaron”, which means one that is confined to a unit cell, with a theory which takes into account the discrete nature of the lattice [28]. It has been shown that there exists a critical value of the electron-phonon coupling constant below which self-trapping of Holstein polarons does not occur [29], and also that there is a crossover regime between large and small polarons [30].

To determine the potential energy of the electron in its self-induced well, we consider the potential

energy of an electron in a rigid lattice and in a lattice with deformation. In these two limits, we use the optical and static dielectric constants as these are the two limits of the dielectric spectrum (see section 2.3). In a rigid lattice where ions are fixed, only the electrons can move so the potential energy is $q^2/\epsilon_{opt}r$, where ϵ_{opt} is the optical dielectric constant (since it is the high frequency limit of the dielectric spectrum), and r is a displacement. Now, considering a deformation so the ions are free to move as well as the electrons, the potential energy is $q^2/\epsilon_{stat}r$, where ϵ_{stat} is the static dielectric constant. Taking the difference between these gives a potential energy of the electron due to the displacement of ions as [31]

$$W_{electron} = -\frac{q^2}{4\pi\epsilon_0 r} \left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon_{stat}} \right). \quad (2.24)$$

This is the potential that leads to the “self trapping” of the electron. The radius of the polaron, r_p , is the region in which this potential holds. There are two different cases to consider: a “small polaron”, where r_p is on the order of the lattice spacing, and a “large polaron” where r_p is larger than the lattice spacing. In organic semiconductors, charge transport is often modelled as a small polaron hopping between molecular sites.

2.5.1 Small polaron

In the case of a small polaron, the effective mass m^* is assumed to be so high that the kinetic energy due to its localisation is negligible [32]. The energy of a small polaron is therefore the sum of the energy required to polarise the medium and the lowering of the potential energy of the electron. The energy required to polarise the medium is given by

$$W_{medium} = \frac{1}{2} \int \mathbf{E} \cdot \mathbf{D} dV \quad (2.25)$$

where $\mathbf{E}$ is the electric field and $\mathbf{D}$ is the displacement field, defined by $\mathbf{D} = \epsilon_0 \epsilon_r(\omega) \mathbf{E}$. ϵ_r is the frequency dependent dielectric constant given in 2.12. Substituting this in and using the fact that $\mathbf{E} = (q/4\pi\epsilon_0\epsilon_r)\mathbf{r}/|\mathbf{r}|^3$, and integrating over the whole sphere ($dV = 4\pi r^2 dr$) gives

$$W_{medium} = \frac{1}{2} \int \frac{q^2}{4\pi\epsilon_0\epsilon_r r^2} dr. \quad (2.26)$$

Now, considering the limits of integration. The integral is taken over all of the polarised surroundings,

i.e. over the radius of the polaron

$$W_{medium} = \frac{1}{2} \int_0^{r_p} \frac{q^2}{4\pi\epsilon_0\epsilon_r r^2} dr \quad (2.27)$$

$$= \frac{q^2}{8\pi\epsilon_0 r_p} \frac{1}{\epsilon_r} \quad (2.28)$$

Taking the frequency dependent dielectric constant at its limits, i.e. the static and optical dielectric constants, yields the final energy to polarise the medium as

$$W_{medium} = \frac{q^2}{8\pi\epsilon_0 r_p} \left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon_{stat}} \right). \quad (2.29)$$

The lowering of the potential energy of the electron is given in equation 2.24 above. Summing this with the change in potential energy of the medium in equation 2.29 gives the total polaron energy (which is also the depth of the potential well) as

$$W_p = -\frac{q^2}{8\pi\epsilon_0 r_p} \left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon_{stat}} \right). \quad (2.30)$$

This is illustrated in Figure 2.5(b).

2.5.2 Large polaron

For a large polaron, the effective mass is not large, meaning that the kinetic energy $\hbar^2/2m^*r_p^2$ due to localisation cannot be ignored. This gives the polaron energy as

$$W_p = -\frac{e^2}{8\pi\epsilon_0 r_p} \left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon_{stat}} \right) + \frac{\hbar^2}{2m^*r_p^2}. \quad (2.31)$$

This is minimised when

$$r_p^{-1} = \frac{m^*e^2}{8\pi\epsilon_0\hbar^2} \left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon_{stat}} \right), \quad (2.32)$$

and therefore

$$W_p = -\frac{e^2}{16\pi\epsilon_0 r_p} \left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon_{stat}} \right). \quad (2.33)$$

2.5.3 Polarons in disordered systems

In disordered organic semiconductors, polaron theory becomes more complicated since there are different processes that tend to localise the electron: (1) the response of the lattice; (2) local fluctuations in the potential, i.e. on site disorder resulting in Anderson localisation (section 2.4.1); and (3) disorder in off-diagonal (electronic coupling) elements, which can be induced by thermal fluctuations [33]. It is important to understand the nature of polaron formation in these systems because charge carriers in organic semiconductors have been found to form polarons [34] [35] and this self-trapping tends to localise the charge, which can inhibit its mobility.

Polarons have been modelled in OSCs with the Holstein-Peierls Hamiltonian [36]

$$\hat{H} = \sum_{ij} \epsilon_{ij} a_i^\dagger a_j + \sum_{\lambda} \hbar \omega_{\lambda} (b_{\lambda}^\dagger b_{\lambda} + \frac{1}{2}) + \sum_{ij\lambda} \hbar \omega_{\lambda} g_{\lambda ij} (b_{\lambda}^\dagger + b_{-\lambda}) a_i^\dagger a_j, \quad (2.34)$$

where the first term is the electronic part of the Hamiltonian ($\hat{H}_e$), the second term is the phonon part ($\hat{H}_p$) and the third term is the electron-phonon coupling part ($\hat{H}_{e-p}$). ϵ_{ij} is the energy, $a^{(+)}$ and $b^{(+)}$ are the (creation) and annihilation operators, ω is the frequency, $g_{\lambda ij}$ is the dimensionless electron-phonon coupling constant, λ refers to the mode index and i and j refer to site indices.

This model assumes that the potential energy surfaces (PES) are harmonic, the electron-phonon couplings are linear and that the electron-electron interactions can be treated statically. It is not exactly solvable (due to the interaction of particles and phonons) and there are no efficient numerical solvers for the general case [36].

The calculation of the Hamiltonian involves many parameters, which increases with the number of phonons considered. Therefore, it has only been applied to small or simple systems, such as naphthalene crystals [37], a 2D molecular lattice [38], and in anisotropic 2D molecular crystals [39].

Hannewald *et al.* [40] [41] have derived a mobility formula within the Holstein-Peierls framework

based on evaluation of the Kubo formula for mobility [42]

$$\mu_{\alpha\beta} = \frac{1}{qN_c} \frac{1}{2k_B T} \int_{-\infty}^{\infty} dt \langle j_{c,\alpha}(t) \mathfrak{x}_{c,\beta}(0) \rangle_H, \quad (2.35)$$

where N_c is the number of charge carriers, and $j_{c,\alpha}$ and $j_{c,\beta}$ are elements of the current operator

$$\mathbf{j}_c = \frac{d\mathbf{P}}{dt} = \frac{1}{i\hbar} [\mathbf{P}, \hat{H}], \quad (2.36)$$

where $\mathbf{P}$ is the polarisation operator and $\hat{H}$ is given in equation 2.34.

Since the Hamiltonian in equation 2.34 cannot be diagonalised exactly, to evaluate equation 2.35, a canonical transformation is performed on the Hamiltonian to obtain a transformed "polaron" Hamiltonian. This can be separated into phonon and polaron parts by replacing the operator coupling electron and phonon operators in the new Hamiltonian with a thermal average over the phonon part in the original Hamiltonian. This gives an approximate polaron Hamiltonian

$$\tilde{H} = \sum_{ij} a_i^\dagger \tilde{\epsilon}_{ij} a_j + \sum_{\lambda} \hbar \omega_{\lambda} (b_{\lambda}^\dagger b_{\lambda} + \frac{1}{2}), \quad (2.37)$$

where $\tilde{\epsilon}_{ij}$ are the polaron transfer integrals. Assuming a low charge carrier concentration, the new approximate polaron Hamiltonian can be used to evaluate the Kubo formula for mobility, giving

$$\mu_a(T) = \frac{e_0}{2k_B T \hbar^2} \sum_{j \neq i} R_{aij}^2 \int_{-\infty}^{\infty} dt e^{-\Gamma^2 t^2} \left[\epsilon_{ij}^2 + (\epsilon_{ij} - \Delta_{ij})^2 + \frac{1}{2} \sum_q (\hbar \omega_{qij})^2 \Phi_q(t) \right] \exp \left(-2 \sum_{\lambda} G_{\lambda} [1 + 2N_{\lambda} - \Phi_{\lambda}(t)] \right), \quad (2.38)$$

where $\Delta_{ij} = \frac{1}{2} \sum_{\lambda} \hbar \omega_{\lambda} [g_{\lambda ij} (g_{\lambda ii} + g_{\lambda jj}) + \frac{1}{2} \sum_{k \neq i,j} g_{\lambda ik} g_{\lambda kj}]$. R_{aij} is the distance between site i and j in the a direction, G_{λ} is the effective coupling constant of mode λ , N_{λ} is the phonon occupation of mode λ , $\Phi_q(t)$ describes incoherent scattering events caused by phonon number changes, and Γ is a line broadening term.

This has been applied to a simple model crystal and to naphthalene crystals, where it was shown to

give an improved low temperature description of mobility compared with previous models [43]. More recently, polarons have been modelled classically with Langevin molecular dynamics (LMD), treating the polaron as a pseudo atom in a system of a pair of PCBM molecules [44], so it is still limited to a very small system. Modelling polarons in large systems is computationally expensive. In chapter 6, we develop a tight-binding model that includes polaron formation, which can be applied to large disordered semiconductors.

2.6 Charge transport

Charge carrier mobility, μ , is a phenomenological property of a material that can be measured, through time-of-flight (TOF) [45] [46] [47], field effect transistor (FET) [48] [49], space charge limited current (SCLC) [50] [51] or time-resolved microwave conductivity (TRMC) [52] [53]. It is therefore a useful measure to be able to simulate or calculate in materials.

The different experimental measurements of mobility have different advantages and shortcomings, and can give different results for measurements on the same device. In TOF, charges are generated in a thin layer on one side of the film and then drift under an applied electric field until they are collected on the opposite side. As the charges drift across the film they induce a photocurrent in an external circuit [54] [55]. In a trap-free material, there is a characteristic plateau in the photogenerated transient current [56] where the charge carriers move with a constant velocity, which eventually drops off as the charge carriers are collected. The point at which this drops off is the transit time, which is inversely proportional to the mobility. TOF directly probes the bulk mobility and is the method that is most comparable to our mobility simulations (see section 3.5).

FET measurements involve depositing the semiconductor on a patterned substrate. These measurements tend to overestimate the mobility since they only probe the first few nm of the material [57]. A space charge limited current depends on the mobility via Child's law ($j_{SCL} = 9\epsilon_0\epsilon_r\mu V^2/8d^3$) [58], so the mobility can be inferred from a J-V curve, as long as the current is space charge limited. TRMC does not require contacts and can be used to obtain the change in conductivity over time, which is used to infer a mobility by estimating the number of free charges [59]. It can be used to probe the transport properties on a very local spatial scale.

The charge carrier mobility is directly related to the electrical conductivity ($\sigma_{c,ij}$), a second-rank tensor, of the material through [60]

$$\sigma_{c,ij} = q\rho\mu_{ij}, \quad (2.39)$$

where q is the charge of the carrier and ρ is the density of charge carriers. The mobility tensor, μ_{ij} , is defined as the velocity response of a charge carrier to an external electric field

$$\mu_{ij} = \frac{\langle v \rangle_i}{\mathcal{E}_j}, \quad (2.40)$$

where $\langle v \rangle_i$ denotes the i^{th} component of the average velocity of charge carriers in the direction of the field, and $\mathcal{E}_j$ is the j^{th} component of the electric field vector $\vec{\mathcal{E}}$. In this thesis, we use isotropic form of the mobility and reduce to a scalar

$$\mu = \frac{\langle v \rangle}{\mathcal{E}}, \quad (2.41)$$

where $\langle v \rangle$ is the magnitude of the average velocity and $\mathcal{E}$ is the magnitude of the electric field.

Another definition of mobility from kinetic theory is based on a random walk model and is known as the Einstein relation [61]

$$\mu = \frac{qD}{k_B T}, \quad (2.42)$$

where D is the diffusion coefficient, k_B is the Boltzmann constant and T is the temperature.

To determine the charge carrier mobility from either equation 2.41 or 2.42, we first need to understand the charge transport mechanism. There are three main regimes for charge transport, which depend on the localisation of the charge carriers. These are: (i) the band regime where charge carriers are fully delocalised at the valence or conduction band edges, motion is well-correlated and momentum is well-defined; (ii) the hopping regime where charge carriers are localised to individual sites due to strong scattering and move between them via thermally activated hops; (iii) the intermediate regime where the charge carrier is not in either of these limiting approximations.

Experimentally, the regimes are often distinguished by their temperature dependence [62]. Hopping

is thermally activated, so there is a positive correlation with temperature. Band transport displays a negative correlation as temperature activates additional scattering processes.

2.6.1 Band regime

In the band regime, charge carriers are fully delocalised in periodic bands, the valence or conduction bands for holes and electrons respectively. As such, band-like transport is a model applicable in crystalline periodic solids, and is generally applied to inorganic materials for this reason. However, it could also be relevant to highly pure organic molecular crystals which have strong coupling between molecules.

Band theory is based on Bloch's theorem, which states that the wavefunction of an electron in a periodic potential is given by

$$\psi_k(\mathbf{r}) = u_k(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (2.43)$$

where $u(\mathbf{r})$ has the periodicity of the potential, $u(\mathbf{r}) = u(\mathbf{r} + \mathbf{R})$, where $\mathbf{R}$ is the length of the unit cell.

When an electric field $\vec{\mathcal{E}}$ is applied to an electron, the force is given by

$$\vec{F} = q\vec{\mathcal{E}} = \left(\frac{1}{m^*}\right)^{-1} \frac{d\mathbf{v}_g}{dt}, \quad (2.44)$$

where m^* is the effective mass of the electron and $\mathbf{v}_g$ is the group velocity. The effective mass is defined in equation 2.23.

Equation 2.44 implies an indefinite acceleration of the charge in response to an electric field. In real crystals, scattering processes would impede acceleration, a . This can be approximated by introducing a relaxation time, τ . This is defined as the average time between scattering events that reset the carrier distribution in the band [63]. The maximum instantaneous velocity is therefore $v = a\tau$.

Relating a to the force F via Newton's second law gives

$$a = \frac{q\mathcal{E}}{m^*}. \quad (2.45)$$

Therefore,

$$v = \frac{q\mathcal{E}\tau}{m^*}, \quad (2.46)$$

so mobility is

$$\mu = \frac{q\tau}{m^*}. \quad (2.47)$$

Note that there is no explicit dependence on the applied electric field $\mathcal{E}$. However, this may influence the relaxation time τ .

Band-like transport characteristics (i.e. a negative temperature dependence of mobility) have been found in organic semiconductors, such as pentacene [64] [65], and other oligoacene crystals [66] [67].

2.6.2 Hopping regime

Organic semiconductors are typically too disordered to be treated with a band transport model. A hopping model assumes that charge carriers are localised and move via thermally-activated hops. The sites can be defined as individual molecules, a group of molecules, or molecular segments (such as monomer units in a polymer), but they must have weak coupling between them. The charge transport is then described by hopping rates between these sites.

Marcus theory

One of the most popular methods applied to charge transport in OSCs was derived by Marcus (1964) [68] [69]. It is a non-adiabatic, semi-classical theory for the rate of charge hopping between weakly coupled sites. An outline of the derivation (as proposed by Jortner *et al.*) is given below [70].

The Marcus equation describes a charge transfer event from site i to site j , where the following assumptions are made:

- The nuclear and electronic motion of molecules can be separated, where the electronic wavefunction depends parametrically on the nuclear positions (Born-Oppenheimer approximation).
- Nuclear coordinates are invariant during charge carrier transfer (Franck Condon principle).
- The transition is semiclassical in the sense that the vibronic energy scale is smaller than the other energy scales, such as the barrier height and the energy difference of the two states.
- There is weak electronic coupling between sites and a non-adiabatic intersection between potential energy curves (solid curve in Figure 2.6), so the interaction between the initial and final states is small enough to be treated as a perturbation.

The last assumption means that Fermi's Golden Rule [71] can be taken as the starting point:

$$\Gamma_{ij} = \frac{2\pi}{\hbar} |\langle \Psi_i | \hat{H} | \Psi_j \rangle|^2 \delta(E_i - E_j) \quad (2.48)$$

where Γ_{ij} is the rate of hopping between sites i and j , $\hat{H}$ is the perturbed Hamiltonian and $\delta(E_i - E_j)$ is the infinitesimal difference in energies. Using the Born-Oppenheimer approximation to split the wavefunction into its electronic (ψ) and nuclear (Ω) components, and assuming that the perturbation only acts on the electronic part leads to

$$\langle \Psi_i | \hat{H} | \Psi_j \rangle = \langle \psi_i | \hat{H} | \psi_j \rangle \langle \Omega_i | \Omega_j \rangle. \quad (2.49)$$

Defining the transfer integral (electronic coupling) as

$$J_{ij} = \langle \psi_i | \hat{H} | \psi_j \rangle, \quad (2.50)$$

gives

$$\Gamma_{ij} = \frac{2\pi}{\hbar} |J_{ij} \langle \Omega_i | \Omega_j \rangle|^2 \delta(E_i - E_j). \quad (2.51)$$

Assuming the system is initially in a thermal average of vibronic states, and taking a sum over the initial vibronic states, weighting each term by the Boltzmann probability of being in that state gives

$$\Gamma_{ij} = \frac{2\pi}{\hbar} |J_{ij}|^2 \sum_{ij} \langle \Omega_i | \Omega_j \rangle^2 \delta(E_i - E_j) \exp(-E_i/k_B T) Z^{-1}, \quad (2.52)$$

where $Z = \sum_i \exp(-E_i/k_B T)$ is the partition function. To simplify this equation, the δ function is treated using Fourier Transforms and an analytical form of the vibrational coupling is obtained, with the assumption that the vibrational modes are quadratic and have the same angular frequency. Finally, it is assumed that $\hbar\omega \ll kT$, i.e. the high temperature (semi-classical) limit, and that there is weak coupling, which requires that $|J_{ij}| \ll \lambda$.

$$\Gamma_{ij} = \frac{|J_{ij}|^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{(\Delta E_{ij} + \lambda)^2}{4\lambda k_B T}\right) \quad (2.53)$$

where Γ_{ij} is the rate of hopping between sites i and j ; J_{ij} is the transfer integral (electronic coupling) between these sites; λ is the reorganisation energy, which is the energy cost associated with the rearrangement of the molecules and their surroundings during charge transfer; and ΔE_{ij} is the energy difference between the initial and final states.

Figure 2.6 shows J_{ij} , λ and ΔE with non-adiabatic (solid) and adiabatic (dashed) potential energy curves of the reactants and products, plotted against the reaction coordinate Q_r .

Marcus theory has been applied to charge transport between polymer chains [72] [73] [74], as well as intrachain charge transport in polymers [75]. It has also been applied to p-type organic crystals, such as pentacene [76], rubrene [77], oligothiophenes, and n-type organic crystals [78] [79]. Disordered organic semiconductors have also been treated with Marcus theory, for example Alq₃ [55], fullerenes [80], as well as DNA segments [81] [82].

2.6.3 Intermediate regime

There are many organic semiconductors that fall into neither the band or hopping limiting regimes, where the charge is neither fully localised to one site or fully delocalised in a band. To tackle this problem without assuming anything about the nature of the charge states, we can directly

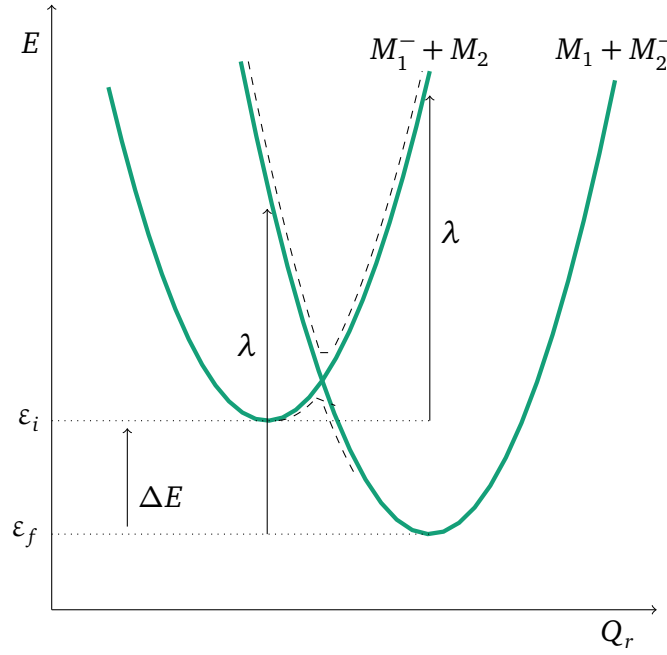


Figure 2.6: Potential energy curves for $M_1^- + M_2$ and $M_1 + M_2^-$ where Q_r is the reaction coordinate and E is the energy. λ and ΔE are shown on the curves.

propagate the charge carrier wavefunction in time, i.e. solve the time-dependent Schrödinger equation for the nuclear-electronic system. Two of the methods used for this are Ehrenfest dynamics and surface hopping, which are both semiclassical approaches where the electronic wavefunction is propagated with the time-dependent Schrödinger equation and the nuclear degrees of freedom follow classical trajectories [83].

The time-dependent Schrödinger equation (TDSE) is given by

$$\hat{H}(\mathbf{r}, \mathbf{R})\Psi(\mathbf{r}, \mathbf{R}, t) = i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, \mathbf{R}, t), \quad (2.54)$$

where $\Psi(\mathbf{r}, \mathbf{R}, t)$ is the total wavefunction of the system (nuclear and electronic), depending on $\mathbf{r}$ the electronic coordinates, $\mathbf{R}$ the nuclear coordinates and time t , and $\hat{H}$ is the Hamiltonian for the system given by

$$\hat{H}(\mathbf{r}, \mathbf{R}) = -\sum_{\alpha} \frac{\hbar^2}{2M_{\alpha}} \nabla_{\alpha}^2 - \sum_i \frac{\hbar^2}{2} \nabla_i^2 + \sum_{i < j} \frac{1}{|r_i - r_j|} - \sum_{\alpha, i} \frac{Z_{\alpha}}{|R_{\alpha} - r_i|} + \sum_{\alpha < \beta} \frac{Z_{\alpha} Z_{\beta}}{|R_{\alpha} - R_{\beta}|}. \quad (2.55)$$

Here M is the mass of the nucleus, Z is the nuclear charge, α and β denote a sum over nuclei and i and j denote a sum over electrons.

Ehrenfest dynamics

Ehrenfest dynamics [84] is a mean field approach where the classical nuclear propagation is governed by the gradient of the expectation value of the total energy of the system. The method is based on a single mean potential energy surface (PES), obtained by averaging over all adiabatic states weighted by their population [85] [86]. The two main approximations of Ehrenfest dynamics are: (i) the electrons influence the nuclei through a classical field generated by the time-dependent electron density (a mean field approximation); (ii) the nuclei follow classical (Newtonian) mechanics on this PES [87].

Ehrenfest dynamics is derived by inserting the following ansatz for the wavefunction in the TDSE in equation 2.54 above [88]

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \Phi(\mathbf{r}; \mathbf{R}, t) \Omega(\mathbf{R}, t) \exp \left[\frac{i}{\hbar} \int_{t_0}^t dt' E_{el}(t') \right], \quad (2.56)$$

where $\Phi(\mathbf{r}, \mathbf{R}, t)$ is the electronic wavefunction and depends parametrically on $\mathbf{R}$. $E_{el}(t)$ is given by

$$E_{el}(t) = \int \int d\mathbf{r} d\mathbf{R} \Phi^*(\mathbf{r}, t) \Omega^*(\mathbf{R}, t) \hat{H}_{el}(\mathbf{r}, \mathbf{R}) \Phi(\mathbf{r}, t) \Omega(\mathbf{R}, t) \quad (2.57)$$

where $\hat{H}_{el}$ is the electronic parts of the total Hamiltonian, i.e. the middle three terms in equation 2.55.

In the classical $\hbar \rightarrow 0$ limit for the nuclear wavefunction, this gives

$$M_\alpha \ddot{\mathbf{R}}_\alpha = -\nabla_\alpha \langle \hat{H}_{el}(\mathbf{r}, \mathbf{R}) \rangle. \quad (2.58)$$

For the electronic wavefunction this gives

$$\hat{H}_{el} \Phi(\mathbf{r}, t) = i\hbar \frac{\partial}{\partial t} \Phi(\mathbf{r}, t). \quad (2.59)$$

The combined system can be propagated with a suitable integration scheme. To get a diffusion

coefficient and therefore a mobility with this method, the mean-squared displacement (MSD) of a number of trajectories is calculated with [89]

$$MSD(t) = \frac{1}{N} \sum_n [\langle \Phi^{(n)}(\mathbf{r}, t) | r^2 | \Phi^{(n)}(\mathbf{r}, t) \rangle - \langle \Phi^{(n)}(\mathbf{r}, t) | r | \Phi^{(n)}(\mathbf{r}, t) \rangle^2], \quad (2.60)$$

where N is the total number of trajectories and $\Phi^{(n)}$ denotes the wavefunction of the n^{th} trajectory. The diffusion coefficient relates to the MSD with [90]

$$D = \frac{1}{2d_m} \lim_{t \rightarrow \infty} \frac{dMSD(t)}{dt}, \quad (2.61)$$

where d_m is the spatial dimensionality. Finally, the Einstein relation can be used to obtain a mobility

$$\mu = \frac{qD}{k_B T}, \quad (2.62)$$

where q is the electronic charge, k_B is the Boltzmann constant and T is the temperature.

There are a number of shortcomings of Ehrenfest dynamics for charge transport simulations in OSCs. The back-action of the electrons on the nuclear dynamics is through one average PES, which means that the molecular structure cannot relax down to a single adiabatic state [91]. Therefore, relaxation of the molecular structure will be progressively underestimated with the increasing degree of delocalisation, and the electrons are progressively heated up via molecular vibrations. This means that the model gets worse over longer timescales and the mobility incorrectly increases with simulation time [92].

This issue also means that the mobility for thermally activated polaron hopping cannot be accessed with Ehrenfest dynamics. For polaron formation, the back-reaction to the nuclear motions should be larger than in the mean-field Ehrenfest method. Starting from a localised polaron state, Ehrenfest dynamics allows it to be propagated over short timescales, but this cannot be sustained over longer timescales due to the fact that the average wavefunction of many localised states would tend to be delocalised.

Wang and Beljonne [89] came across this issue when they found that Ehrenfest dynamics does not yield the correct temperature dependence of mobility. They attributed this to the fact that an average PES is used, which implies an infinite decoherence time of the charge carrier states. In the charge carrier hopping limit of many OSCs this assumption will not hold.

Despite this, it has been successfully applied under specific conditions to model stacks of OSCs [93], as well as hexabenzocoronene (HBC) [91], anthracene [94], pentacene and PPV [87]. One method to overcome some of the shortcomings of Ehrenfest dynamics is the surface hopping approach developed by Tully [95] .

Surface hopping

The surface hopping approach allows nuclei to propagate on an ensemble of single PES at a time, but can make stochastic transitions between different PES. This allows ground and excited PES to be considered [96].

Starting from the Born-Huang expansion of the total wavefunction [88]

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_{i=1}^{\infty} \Omega_i(\mathbf{R}, t) \Psi_i(\mathbf{r}; \mathbf{R}), \quad (2.63)$$

Tully derived an equation for the state amplitudes ($C_j(t)$) that replace the nuclear wavefunctions $\Omega(\mathbf{R}, t)$

$$i\hbar \dot{C}_j(t) = \sum_{i=1}^{\infty} C_i(t) [E_i^{el}(\mathbf{R}^{(\alpha)}) \delta_{ij} - i\hbar \sum_{\alpha} \mathbf{d}_{ji}^{\alpha}(\mathbf{R}) \cdot \dot{\mathbf{R}}_{\alpha}], \quad (2.64)$$

where $\mathbf{d}_{ji}(\mathbf{R}) = \langle \Phi_j(\mathbf{r}; \mathbf{R}) | \nabla_{\alpha} \Phi_i(\mathbf{r}; \mathbf{R}) \rangle$ is the non-adiabatic coupling vector (NACV). Defining the matrix elements of the electronic coupling in the adiabatic basis as $H_{ji}^{ad} = E_i^{el}(\mathbf{R}^{(\alpha)}) \delta_{ij}$, and using the chain rule so that $\mathbf{d}_{ji}^{\alpha}(\mathbf{R}) \cdot \dot{\mathbf{R}}_{\alpha} = \langle \Phi_j | \frac{d\Phi_i}{dt} \rangle = d_{ji}^{ad}$, this simplifies to [97]

$$i\hbar \dot{C}_j(t) = \sum_{i=1}^{\infty} C_i(t) (H_{ji}^{ad} - i\hbar d_{ji}^{ad}). \quad (2.65)$$

The nuclear degrees of freedom propagate adiabatically on a single PES j until a "hop" to a different PES i . The nuclear trajectories follow Newton's equations of motion, and the "hop"

occurs with a probability that is calculated with

$$g_{ji} = \frac{-2 \operatorname{Re}(a_{ji}^* d_{ji}^{ad}) \Delta t}{a_{ii}}, \quad (2.66)$$

where $a_{ji} = C_j C_i^*$ and Δt is the molecular dynamics time step.

The feedback from the electronic to the nuclear system is incorporated through this stochastic "hopping" between PES. In the surface hopping method, multiple trajectories are calculated to obtain the nuclear dynamics and ultimately a mobility, with the same MSD described for Ehrenfest dynamics above.

The surface hopping method has been compared to Ehrenfest dynamics for modelling charge transport in 1D molecular stacks [90] [93], and been applied to tetracene stacks [98], linear chains [99], and ethylene-like molecules [97], using a fragment-orbital based method for calculating couplings ("FOB-SH").

There remain shortcomings of the surface hopping method, including the so-called "decoherence problem", unavoided crossings between PES, and maintaining detailed balance [98]. Work has also been done to ensure detailed balance is obtained by incorporating energy forbidden hops [100]. However, there are some outstanding issues and the method is currently limited to smaller systems. To access larger assemblies of molecules, we pursue other methods for modelling electronic states and charge transport in the intermediate regime.

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3

Methods

3.1 Introduction

In this thesis we use computational methods that span length and time-scales. We are interested in the chemical structure and electronic structure (section 3.3) of individual molecules, which we calculate with density functional theory (DFT). DFT is also used to calculate parameters that feed into other aspects of our models, such as the tight binding model or the Marcus equation.

We are also interested in the interactions between pairs of molecules, in particular charge transfer between these pairs. In weakly coupled pairs, the rate of charge transfer can be calculated with Marcus theory (see section 2.6.2). In chapter 7, we outline an additional method to calculate transfer integrals and apply it to a range of systems not accessible with the method described in this chapter.

To understand electronic states and charge transport in OSC assemblies, we need to obtain structures of the systems of interest. In crystalline structures, we use crystal structure databases or crystal structure predictions and build up supercells of the complete structure (section 3.2.1). For disordered systems, we use molecular dynamics- more specifically coarse grained molecular dynamics- to obtain these structures (section 3.2.2).

With assemblies of disordered molecules, we use a tight-binding model in the basis of molecular orbitals to investigate electronic states and polaron formation. This is to gain information about the density of states and extent of delocalisation of the electronic states. The extent of delocalisation is one factor determining which models of charge transport are valid.

In assemblies where charge localises to individual sites and the sites are weakly coupled, we calculate microscopic hopping rates with Marcus theory. We outline the methods used to calculate the parameters for the Marcus equation in section 3.4, which include the reorganisation energy, transfer integrals and the energy difference between sites. We use a master equation approach to convert the set of rates into a direction-dependent charge carrier mobility, which is a macroscopic property that can be measured experimentally.

Depending on the properties of the OSC materials we are interested in, we use a subset of these methods to investigate the electronic states, charge transfer and charge transport in them.

3.2 Assemblies of molecules

3.2.1 Crystal structures

For crystalline OSCs, we use crystal structures from the Cambridge Structural Database (CSD) [1] where they exist, which contains a complete record of all published organic and metal–organic small-molecule crystal structures. In this thesis, where there are no published crystal structures for a particular molecule, we use crystal structure predictions from Dr Kim Jelfs.

Crystal structure prediction (CSP) is a technique to identify the most likely polymorphs of solids by searching the potential energy landscapes and energetically ranking the structures [2]. The structures used in this thesis were generated with CrystalPredictor software [3] [4] and lattice energy minimised with DMACRYS [5].

A crystal structure for a molecule contains the number of molecules per unit cell, the atomic positions of one molecule in the unit cell, the symmetry operations required to obtain the other molecules in the unit cell, and the lattice constants of the unit cell. The symmetry operations are defined by the space group of the crystal structure.

Given these crystal structures, we calculate transfer integrals between pairs of molecules in the structure. We optimise one molecule in the unit cell and use the symmetry operations to generate the other molecules in the unit cell. We translate it in 26 different directions to get a $3 \times 3 \times 3$ supercell, and calculate the transfer integrals between molecules in the unit cell with all other molecules in the supercell. We use the symmetry of the unit cell to obtain the complete set of transfer integrals between each molecule and every other (within some distance cut-off). This set of transfer integrals can be used to obtain a set of rates with Marcus theory (section 3.4), and finally to obtain a direction dependent mobility with the master equation (section 3.5).

3.2.2 Molecular Dynamics

In amorphous OSCs, there are no well defined structures of molecules that can be used. Therefore, we use molecular dynamics to generate assemblies of molecules.

Molecular dynamics (MD) allows detailed microscopic modelling on the molecular scale. This gives us an insight into the way bulk properties are influenced by microstructure and interactions between molecules [6].

In MD, the dynamics follow a numerical, step-by-step solution of Newton's equations of motion

$$\mathbf{f}_i = m_i \ddot{\mathbf{r}}_i, \quad (3.1)$$

$$\mathbf{f}_i = -\frac{\partial U}{\partial \mathbf{r}_i}. \quad (3.2)$$

where $\mathbf{f}_i$ are the forces, m_i are the masses, $\mathbf{r}_i$ are the positions and U is the potential, that contains the force-field (see below). In *ab initio* MD, the force-field is calculated with DFT (section 3.3.1). This is only feasible for small systems and therefore the force-field is usually based on empirical or experimental results.

The trajectories of individual atoms are propagated in time with a symplectic integrator, for example the Verlet algorithm [7], which conserves the total energy of the system. The time-step of this integration must be chosen to be small enough to ensure energy is conserved, while a smaller time-step increases the computational time required.

The force-field describes the intra- and intermolecular (or bonded and non-bonded) forces in the system. The intermolecular part of the force-field is a sum of Van der Waals and Coulomb interactions between molecules. The Van der Waals (VDW) interactions are often based on a Lennard-Jones potential [8]. This is true for the coarse-grained molecular dynamics in this thesis. The Lennard-Jones potential for two atoms a distance r_{ij} apart is

$$U(r_{ij})_{VDW} = -4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^6 - \left(\frac{\sigma}{r_{ij}} \right)^{12} \right], \quad (3.3)$$

where ϵ is the depth of the potential well and σ is a characteristic length scale. The Coulomb interactions are given by

$$U_{Coulomb}(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0\epsilon_r r_{ij}}, \quad (3.4)$$

where q_i and q_j are the charges on atoms i and j , ϵ_0 is the vacuum permittivity, and ϵ_r is the relative permittivity. In the coarse grained molecular dynamics that is used in this thesis, the (pseudo) atoms are neutral so this term is zero.

The intramolecular part describes the bonds between atoms

$$U(r_{ij})_{bonded} = U_{bond} + U_{angle} + U_{dihedral} + U_{remainder}, \quad (3.5)$$

where U_{bond} is the energy cost associated with atoms moving away from each other, U_{angle} is the energy cost of atoms bending away from each other, $U_{dihedral}$ is the energy cost of atoms moving out of plane, and $U_{remainder}$ is anything not included in the previous terms. The exact definitions of these terms depends on the force-field chosen.

A thermostat and barostat are applied to the system to reproduce thermodynamic observables. The Berendsen thermostat used in our simulations works by scaling velocities by a constant λ given by [9]

$$\lambda = \left[1 + \frac{\delta t}{\tau} \left(\frac{T_0}{T} - 1 \right) \right]^{1/2}, \quad (3.6)$$

where T is the temperature, T_0 is the target temperature, τ is a relaxation time constant and t is the time. Similarly, the Berendsen bath used as a barostat works by rescaling each dimension by μ given by

$$\mu = \left[1 - \frac{\beta \delta t}{\tau} (P_0 - P) \right]^{1/3}, \quad (3.7)$$

where P is the pressure, P_0 is the target pressure, and β is the isothermal compressibility.

When obtaining realistic structures of assemblies of molecules it is necessary to find a configuration that minimises the energy of the system according to the force field. In MD, this is done using algorithms such as the steepest descent algorithm or conjugate gradient method [10].

For disordered systems, such as the small molecule OSCs we are interested in, we require multiple realisations of the same system to enable us to average over a statistically representative sample to calculate properties. One method to obtain these is simulated annealing [11]. Simulated annealing is a method to obtain minimum energy configurations when the phase space is too large to explore all possible configurations. It doesn't necessarily result in the global minimum, but can find many local minima without getting trapped in them [12]. In practise, it involves ramping up the temperature of the system and then cooling it to the chosen temperature, to efficiently find minimum energy configurations at this chosen temperature.

The number of timesteps and particles that can be simulated with MD are limited by computational power. The timestep used to integrate the equations of motion is determined by the fastest motion in the system. This can be up to 3000 cm^{-1} for hydrogen vibrations, a period of 10 fs. This typically requires a timestep for correct integration on the order of a femtosecond. We can calculate up to 10^6 – 10^8 timesteps, which means we can simulate processes for 1–100 ns. The size of the cell that can be studied is limited by the number of atoms that can be studied, which is on the order of 10^4 to 10^8 atoms. This corresponds to a simulation cell with lengths on the order of 10s of nm.

To overcome this limitation in system size and timescales, in this thesis, we use coarse grained molecular dynamics to generate large assemblies of molecules. The coarse grained force fields used were developed by Steiner *et al.* [13], where free parameters were fitted by comparing

radial distribution functions of (atomistic) molecular dynamics generated assemblies with those generated with coarse grained molecular dynamics.

3.2.3 Coarse grained molecular dynamics

Coarse graining the MD allows us to explore systems of more molecules for longer times. This involves grouping atoms together and treating them as one “pseudo-atom”, and building a force field based on pseudo-atoms. It allows us to access systems of more molecules for longer time-scales because (i) there are fewer atoms to calculate forces between and (ii) the atoms are more massive, so the fastest motion is slower and we can use a larger timestep.

Methods to parameterise the force-field for coarse grained MD include both top down and bottom up approaches. Bottom up approaches start from atomistic MD, and include force-matching [14], where atomic forces are used to derive the pseudo-atom forces. Top down approaches involve finding a potential that reproduces experimental or simulated material properties, and include iterative Boltzmann inversion [15] and reverse Monte Carlo [16] [17]. Both of these methods generate a coarse grained potential that exactly matches the input distribution function (e.g. a chosen pair correlation function).

One example of coarse graining is the Girifalco potential developed for the C60 molecule [18]. Girifalco assumes that carbon atoms interact with a Lennard-Jones potential, with the constants fitted to experiment. He then approximates the C60 molecule as a sphere with the carbon atoms ‘smeared out’ uniformly across its surface. Finally, he calculates the potential between two C60 spheres with surface integration. This is a bottom up approach in that the coarse grained potential is derived from the potential between atoms, but constants for the interaction terms are obtained from experiment.

In chapters 5 and 6, we generate structures of PCBM molecules and higher fullerene adducts (PCBM with additional sidechains) with coarse grained molecular dynamics. We use a force field based on this Girifalco potential, with additional terms introduced for interactions with and between pseudo-atoms representing the side chains. The force fields for the side chains were developed by scaling the C60 force field by Steiner *et al.* [13].

3.3 Electronic structure

The physical structure, response and chemistry of a material arises due to the (quantum) mechanics of the electrons. These mechanics are described by the Schrödinger equation. Electronic structure theory is the study of approximate solutions to this equation with numeric and computational methods. We are interested in charge transport and therefore the nature of the charge carrier (electron or hole) in the material, along with its relationship with the chemical structure, defects and disorder, and how it changes in time.

In this thesis, we calculate electronic structure with density functional theory (DFT) and tight-binding (TB) methods. These are approximate solutions to the time-independent Schrödinger equation. We calculate optical properties of molecules with linear response time-dependent DFT (TD-DFT) to calculate excitation energies of molecules.

3.3.1 Density functional theory (DFT)

Density Functional Theory (DFT) is a theory to describe the electronic structure of correlated many-body systems. It is based on the central tenet that any property of a system of many interacting particles can be viewed as a functional of the ground state electron density $n_0(\mathbf{r})$. With an exact functional, DFT gives an exact solution for the ground state energy. There are no exact functionals known for any system of more than one electron, but the work of Kohn and Sham has allowed ground state functionals of many electrons to be approximated [19].

The key ansatz of the Kohn-Sham approach was to replace the many body problem with an auxiliary independent particle problem, i.e. assuming that the ground state of an interacting system is equal to that of a non-interacting system. It is a self-consistent method that involves independent particles but an interacting density. The Kohn-Sham ansatz is an exact rewriting of the many body Schrödinger equation.

Starting with the time-independent Schrödinger equation that the electronic ground state ψ_0 is satisfied by

$$\left[-\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_\alpha \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{d}_\alpha|} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_\alpha \sum_{\beta \neq \alpha} \frac{Z_\alpha Z_\beta}{|\mathbf{d}_\alpha - \mathbf{d}_\beta|} \right] \psi_0 = E_0 \psi_0, \quad (3.8)$$

where i and j denote electron indices and α and β denote nuclear indices, Z_α and Z_β are the nuclear charges, $\mathbf{r}_i$ are the electronic positions, $\mathbf{d}_\alpha$ are the nuclear positions, and E_0 is the ground state energy. The Born-Oppenheimer approximation separates the nuclear and electronic components of the wavefunction and means that the nuclear positions $\mathbf{d}_\alpha$ are constant vectors that the electronic positions depend on parametrically.

This can be written in operator form as

$$(\hat{T} + \hat{V}_{en} + \hat{V}_{ee} + E_{nn})\psi_0 = E_0\psi_0, \quad (3.9)$$

where $\hat{T}$ is the kinetic energy operator, $\hat{E}_{en}$ is the electron-nuclear interaction operator, $\hat{E}_{ee}$ is the electron-electron interaction operator, and E_{nn} is the nuclear-nuclear interaction energy.

The central quantity in DFT is the electron density defined as

$$n(\mathbf{r}) = \int |\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 \left(\sum_i \delta(\mathbf{r} - \mathbf{r}_i) \right) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \quad (3.10)$$

The variational principle ensures that the minimum value of the energy functional occurs when the electron density $n(\mathbf{r})$ is equal to the ground state electron density $n_0(\mathbf{r})$. This means that the ground state energy is a functional of the ground state electron density

$$E_0 = E[n_0] = \text{Min}_{\psi \rightarrow n_0} \langle \psi | E | \psi \rangle = \langle \psi_0 | E | \psi_0 \rangle \quad (3.11)$$

In the Kohn-Sham approach, the energy functional is defined as [20]

$$E[n] = T[n] + E_H[n] + E_{en}[n] + E_{nn} + E_{xc}[n], \quad (3.12)$$

where the terms are defined as follows:

- $T[n]$ is the kinetic energy functional, which is the ground-state kinetic energy of a gas of non-interacting electrons, defined as

$$T[n] = -\frac{1}{2} \sum_i \langle \psi_i | \nabla^2 | \psi_i \rangle. \quad (3.13)$$

- $E_H[n]$ is the Hartree energy functional, which is the mean-field interaction energy of the electrons, defined as

$$E_H[n] = \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r'. \quad (3.14)$$

- $E_{en}[n]$ is the electron-nuclear interaction functional, defined as

$$E_{en}[n] = \int V_{ext}(\mathbf{r})n(\mathbf{r})d^3r, \quad (3.15)$$

where V_{ext} is potential due to the nuclei and other external fields.

- E_{nn} is the nuclear-nuclear (classical) interaction energy.
- $E_{xc}[n]$ is the exchange-correlation functional, which includes all the many body effects. The origin of the exchange-correlation term is the fact that given an electron at position $\mathbf{r}_0$, then other electrons are kept away due to both the necessary antisymmetry of the wavefunction (exchange) and because of the Coulomb repulsion (correlation).

The first four terms can be evaluated exactly, but the exchange-correlation functional, containing the many-body terms, must be approximated. The accuracy of the ground state energy and density is limited by the approximate form of this exchange-correlation functional.

Functionals

There are many approximate exchange-correlation functionals:

- **Local density approximation (LDA)**

This approximates $E_{xc}[n]$ as the exchange-correlation energy of a homogeneous electron gas of the same density

$$E_{xc}^{LDA}[n] = \int \varepsilon_{xc}(n(\mathbf{r}_0))n(\mathbf{r}_0)d^3r_0, \quad (3.16)$$

where $\varepsilon_{xc}(\mathbf{r}_0)$ is the exchange-correlation energy per electron in a uniform electron gas of density n .

- **Generalised gradient approximation (GGA)**

This assumes that close to $\mathbf{r}_0$, the electron density $n(\mathbf{r})$ can be approximated using the first few terms of a Taylor series and E_{xc} is then a function of those terms, i.e. $n(\mathbf{r})$ and its first few spatial derivatives evaluated at $\mathbf{r}_0$:

$$E_{xc}^{GGA}[n] = \int \varepsilon_{xc}(n(\mathbf{r}_0), |\nabla n(\mathbf{r}_0)|, \nabla^2 n(\mathbf{r}_0) \dots) n(\mathbf{r}_0) d^3r_0, \quad (3.17)$$

- **Hybrid functionals**

Hybrid functionals add the correlation energy from the LDA or GGA approximation to the exchange energy made up of a combination of the Hartree-Fock exchange energy and LDA or GGA approximated exchange energy. The Hartree-Fock exchange energy arises as a result of enforced antisymmetry of the wavefunction. We can calculate this by

$$E_x^{HF} = -\frac{1}{2} \sum_{i,j}^{N'} \sum_{s,s'} \int \frac{\psi_i^*(\mathbf{r},s)\psi_j^*(\mathbf{r}',s')\psi_j(\mathbf{r},s)\psi_i(\mathbf{r}',s')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' \quad (3.18)$$

In this thesis, we primarily use hybrid functionals for our DFT calculations, particularly the B3LYP functional [21]

$$E_{xc}^{B3LYP} = E_x^{LDA} + a_0(E_x^{HF} - E_x^{LDA}) + a_x(E_x^{GGA} - E_x^{LDA}) + E_c^{LDA} + a_c(E_c^{GGA} - E_c^{LDA}), \quad (3.19)$$

where $a_0 = 0.20$, $a_x = 0.72$ and $a_c = 0.81$. The B3LYP functional has been shown give good results for organic molecules, particularly for geometry optimisations and total energies, at reasonable computational cost [22]. The B3LYP functional does not capture long range dispersion effects

and fails to predict the properties of charge transfer processes [23]. Other functionals such as CAM-B3LYP [24] and ω B97XD [25] have been developed to overcome these problems.

Basis sets

The wavefunction is typically numerically represented as a linear combination of basis functions. These can be atomic orbitals (linear combination of atomic orbitals, or LCAO), or plane waves [26]. For the LCAO approach, Slater-type orbitals, numerical-type orbitals, or Gaussian-type orbitals can be used.

Slater-type orbitals are solutions to the Schrödinger equation for hydrogen-like atoms which decay exponentially with distance from the nucleus. This is a physically intuitive representation of atomic orbitals. However, integrating over orbitals in a Slater-type orbital basis becomes very computationally expensive [27].

Slater-type orbitals can be approximated as a linear combination of Gaussian-type orbitals. As the Gaussian-Gaussian overlaps are analytic (because a product of two Gaussians can be written as a Gaussian), the expansion in the size of the basis set is more than compensated for by the computational savings. In this thesis, we primarily use the *Gaussian* [28] software package for DFT calculations, which uses Gaussian-type orbitals, as the name suggests.

In order to recognise the fact that valence electrons are the main electrons involved in bonding, a split-valence basis set represents valence electrons by multiple basis functions. For the majority of calculations, we use the 6-31g* basis set. In this, 6 refers to the number of Gaussians representing the core atomic orbitals; 3 and 1 mean that the valence orbitals are composed of two basis functions each, one with a linear combinations of 3 Gaussians, one with 1 Gaussian; the * means that additional polarisation functions are included on heavy atoms only [29].

This basis set represents a compromise between accuracy and computational time [30], and the combination of it with the B3LYP functional is widely used in the literature of organic semiconductors [31] [32] [33] [34]. This means although there are limitations, both with accuracy (compared to larger basis sets or better functionals), and with the lack of diffuse basis functions, we can benchmark our calculations against other published work that uses the same functional and basis set.

3.3.2 Time-dependent DFT

Time-dependent density functional theory (TD-DFT) uses the same Kohn-Sham approach in DFT of replacing interacting particles with independent particles with an interacting density. It is described by a time-dependent Schrödinger-like equation

$$i\hbar \frac{d\psi_i(t)}{dt} = \hat{H}(t)\psi_i(t), \quad (3.20)$$

where $\psi_i(t)$ is the electronic wavefunction at a particular time t , and $\hat{H}$ is the electronic Hamiltonian. The effective time-dependent Hamiltonian is [19]

$$\hat{H}_{eff} = -\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}, t) + \int \frac{n(\mathbf{r}, t)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + E_{xc}[n](\mathbf{r}, t), \quad (3.21)$$

where $E_{xc}[n](\mathbf{r}, t)$ is a function of $\mathbf{r}$ and t and a functional of $n(\mathbf{r}', t)$, so is a functional of t' for all times $t' < t$. Many TD-DFT methods use an adiabatic approximation so that the exchange-correlation potential is a time-independent functional of the density $E_{xc}[n(\mathbf{r})]$.

In this work we use TD-DFT to calculate excitation energies of molecules. These calculations are based on the fact that the frequency dependent linear response function (i.e. how the electron density changes when the external potential change) has poles at the exact excitation energies of the system [35].

3.3.3 Tight-binding

Tight-binding is a further approximation to describe electronic structure, based on localised electronic states, i.e. electronic states that are "tightly bound" to sites. It was developed by Bloch in 1928 based on only s-orbitals, and later expanded to other atomic orbitals by Jones, Mott and Skinner in 1934 [19].

Tight-binding can be directly deduced as a rigorous approximation to DFT and is the limit of DFT with no electron correlation [36] [37] [38] [39]. The method is linear, and can be solved directly without iterative (self-consistent) methods.

Tight-binding was initially based on atomic orbitals. However, in molecular systems, since there

are very different interactions between atoms in the same and different molecules, a natural extension of the atomic orbital based tight-binding method is to “coarse-grain” groups of atoms in a conjugated segment into a single unit. This requires that only the energies of these units and the direction and orientation dependent interactions (or electronic coupling) between them must be known.

An excess charge carrier in a molecular system can be described by the tight-binding Hamiltonian

$$\hat{H}_{TB} = \sum_m \epsilon_m a_m^\dagger a_m + \sum_{m \neq n} J_{mn} a_m^\dagger a_n, \quad (3.22)$$

where $a_m^\dagger$ and a_m are the creation and annihilation operators, respectively, for a charge carrier on molecular site m , ϵ_m is the charge carrier site energy, and J_{mn} is the electronic coupling (transfer integral) between sites m and n [40].

In the molecular tight-binding model, the sites are conjugated segments, e.g. monomers from a polymer or organic small molecules, so are described by the frontier molecular orbitals rather than atomic orbitals. The model generally has one molecular orbital per site. If the excess charge carrier is an electron, this is taken as the LUMO of the molecule and if the excess charge carrier is a hole it is the HOMO of the molecule. Section 3.4 details the calculations required to obtain parameters for the tight-binding Hamiltonian.

Tight-binding models have been applied to molecular semiconductors [41], such as for hole transport in DNA [42], charge transport along PPV wires [43] and in organic crystals [44], and the electronic structure of fullerenes [45].

In chapter 6, we use this molecular tight-binding framework to develop a model of polaron formation in disordered molecular assemblies.

3.4 Microscopic charge transfer rates

Marcus theory (section 2.6.2) provides microscopic charge carrier hopping rates between two weakly coupled sites. The Marcus equation for the rate of charge transfer in the high temperature, non-adiabatic limit is given by

$$\Gamma_{ij} = \frac{|J_{ij}|^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{(\Delta E_{ij} + \lambda)^2}{4\lambda k_B T}\right), \quad (3.23)$$

where Γ_{ij} is the rate of hopping between sites i and j ; λ is the reorganisation energy, which is the energy cost associated with the rearrangement of the molecules and their surroundings during charge transfer; J_{ij} is the electronic coupling between these sites; and ΔE_{ij} is the energy difference between the initial and final states. In the following sections we detail how we calculate these three parameters.

3.4.1 Reorganisation energy

As shown in Figure 2.6, the reorganisation energy λ is the difference in energy between the initial electronic state in the final nuclear coordinates and in the initial electronic state's minimum energy coordinates. This is equivalent to the difference in energy between the final electronic state in the initial nuclear coordinates and the final states minimum energy coordinates [46].

This energy difference contains contributions from the energies and nuclear coordinates of the molecules involved in the hop (inner sphere reorganisation energy, λ_{inner}), and the polarisation of the surrounding environment (outer sphere reorganisation energy, λ_{outer}).

The inner reorganisation energy can be calculated with a four-point method. Single point energy calculations are performed on charged and neutral molecules in the charged and neutral geometry [33]. This assumes that the interaction between the molecules is unchanged after a charge transfer event, which means the orientation of the molecules relative to each other does not matter and the calculation can be applied to a single molecule in vacuum (as long as charge transfer is between identical molecules). An outline of the derivation is given below.

The contributions to be considered are the relaxation of the neutral molecule and the relaxation of the charged molecule, referred to here as λ_{inner}^0 and λ_{inner}^+ .

The relaxation of the neutral molecule is given by

$$\lambda_{inner}^0 = E_{charged_geom}^0 - E_{neutral_geom}^0, \quad (3.24)$$

where E^0 is the total energy of the neutral molecule, and *neutral_geom* and *charged_geom* indicate that the energy is computed in the ground state geometry of the neutral or charged molecule.

The relaxation of the charged molecule is given by

$$\lambda_{inner}^+ = E_{neutral_geom}^+ - E_{charged_geom}^+, \quad (3.25)$$

where E^+ is the total energy of the charged molecule. The two contributions are summed to give the total inner reorganisation energy.

$$\lambda_{inner} = E_{neutral_geom}^+ - E_{charged_geom}^+ + E_{charged_geom}^0 - E_{neutral_geom}^0, \quad (3.26)$$

where E^+ and E^0 are the total energies of the charged and neutral systems respectively, and *neutral_geom* and *charged_geom* indicate that the energy is computed in the ground state geometry of the neutral or charged system.

In this thesis, we obtain these energies and geometries using hybrid DFT: two geometry optimisations are needed to get the neutral and charged geometries, then four single point energy calculations are needed to get the four values required for equation 3.26.

The outer sphere reorganisation energy is difficult to quantify, since it involves the contributions of all of the surrounding molecules. Methods exist for calculating it when it is a molecule in solvent (i.e. in dye-sensitised solar cells) [47] [48], but it is more difficult to calculate for molecular crystals or disordered molecular materials. As long as it is the case that $J \ll \lambda$, the reorganisation energy will just act as a scaling factor. Therefore, charge carrier mobilities from a Marcus theory approach should not be taken as absolute values, but as values that can be compared to each other when the reorganisation energy is the same or similar.

3.4.2 Transfer integrals

There are multiple different methods that are used to calculate the transfer integrals between sites, which vary in their accuracy, applicability and computational expense [49]. Here, a subset of the

methods are summarised. In this thesis we primarily use the projective method for the calculation, but we introduce an additional method in Chapter 7 that broadens the range of different charge transfer processes we can explore.

The transfer integral between two sites A and B is given by

$$J_{AB} = \langle \psi_A | \hat{H} | \psi_B \rangle, \quad (3.27)$$

where $\hat{H}$ is the Hamiltonian of the system, and ψ_A and ψ_B are the full electronic wavefunctions for the electron localised on molecule A or molecule B . The following methods differ in the ways the diabatic states ψ_A and ψ_B are defined as well as the definition of the Hamiltonian $\hat{H}$.

We are generally interested in the absolute magnitude of J as it is squared in any rate equation based on Fermi's Golden Rule. However, J can take both positive and negative values. A positive value for J indicates that a negative combination of the two states results in the most stable state in the pair (i.e. HOMO-1 or LUMO). Likewise, a negative J means that a positive combination of the two states results in the most stable state in the pair [50], i.e. bonding versus anti-bonding orbital combinations.

Generalised Mulliken-Hush

The Generalized Mulliken-Hush method was developed by Cave and Newton [51] [52], and is based on work by Mulliken [53] [54] and Hush [55], as the name suggests. One of the assumptions of the Mulliken-Hush model is that transition dipole moments connecting diabatic states localised on different sites are zero. This provides a general method for defining diabatic states for charge transfer processes in terms of purely adiabatic quantities. When the transformation that diagonalises the adiabatic dipole moment matrix is applied to the adiabatic (diagonal) Hamiltonian, the transfer integral is obtained from

$$J_{ij} = \frac{\mu_{ij}^D \Delta E_{ij}}{\sqrt{(\mu_{ii}^D - \mu_{jj}^D)^2 + 4|\mu_{ij}^D|^2}}, \quad (3.28)$$

where ΔE_{ij} is the splitting between ground and excited states and μ_{ab}^D are the elements of the dipole moment matrix.

The parameters in this expression can be calculated with TD-DFT. Since it involves the dipole moment matrix and the excited state splitting, it is computationally expensive for large systems. This approach also relies on the assumption of zero spatial overlap, which may not be valid.

Constrained Density Functional Theory (CDFT)

The CDFT method applied to calculating transfer integrals in molecular systems is often based on the work of Wu *et al.* [56]. CDFT involves finding an effective external potential that is added to the electronic Hamiltonian so that the resulting ground-state density, n , satisfies a specific density constraint [57] [58]. The energy functional then becomes

$$F[n, V_c] = E[n] + V_c \int w(\mathbf{r})n(\mathbf{r})d\mathbf{r} = E + V_c N_c \quad (3.29)$$

where the first term is the unconstrained DFT functional (see section 3.3.1), n is the electron density as before, V_c is the strength of the external potential, $w(\mathbf{r})$ is the weight function that defines the area the charge is constrained to, and N_c is the charge constraint defined as $\int w(\mathbf{r})n(\mathbf{r})d\mathbf{r}$ [59].

To find the transfer integral, for an electron transfer event, for example, different states with the electron localised on either the donor or acceptor molecule are constructed using the constraints. The transfer integral between these two states ψ_i^c and ψ_j^c is then given by

$$J_{ij} = (E + V_c N_c) \langle \psi_i^c | \psi_j^c \rangle - V_c^j \langle \psi_i^c | w | \psi_j^c \rangle. \quad (3.30)$$

The constrained states are not generally orthogonal since they are not eigenfunctions of the same Hamiltonian. Therefore, they are usually transformed in order to diagonalise their overlap matrix and the weight matrix [49].

Fragment Orbital methods

Fragment orbital methods are based on the assumption that only the frontier orbitals are involved in the charge transfer change between the initial and final states (the frozen orbital approximation). This specific formulation of the method was originally proposed by Senthilkumar *et al.* [60] [42].

They used the ADF program [61] with a basis set consisting of atomic orbitals to obtain the HOMOs of the individual molecules. They then used these molecular orbitals (referred to as “fragment orbitals”) as a basis set in calculations of hole transfer on the pair. They were interested in hole transfer integrals so used the HOMOs, but the approach can equally be applied to electron transfer integrals by using the LUMOs.

The Hamiltonian for the two-site system is

$$\hat{H} = \begin{pmatrix} e_A & j_{AB} \\ j_{AB} & e_B \end{pmatrix}, \quad (3.31)$$

where the matrix elements are evaluated as

$$j_{AB} = \langle \phi_A | \hat{H} | \phi_B \rangle, \quad (3.32)$$

$$e_A = \langle \phi_A | \hat{H} | \phi_A \rangle, \quad (3.33)$$

$$e_B = \langle \phi_B | \hat{H} | \phi_B \rangle. \quad (3.34)$$

Here, ϕ_A and ϕ_B are the HOMOs or LUMOs (for hole or electron transfer integrals), from the frozen orbital approximation.

The characteristic equation for the Hamiltonian is

$$\hat{H}\mathbf{C} - E\hat{S}\mathbf{C} = \mathbf{0}, \quad (3.35)$$

where $\mathbf{H}$ is the Hamiltonian for the two-site system and $\mathbf{S}$ is the overlap matrix, both in the basis of the relevant frontier orbitals (HOMO or LUMOs for hole and electron transfer, respectively), and $\mathbf{C}$ are the expansion coefficients of the wavefunctions. The overlap matrix is defined as

$$\hat{S} = \begin{pmatrix} 1 & S_{AB} \\ S_{AB} & 1 \end{pmatrix}, \quad (3.36)$$

where

$$S_{AB} = \langle \phi_A | \phi_B \rangle. \quad (3.37)$$

The Hamiltonian, and therefore the relevant matrix elements, can be evaluated with

$$\hat{H} = E \hat{S} C C^{-1}. \quad (3.38)$$

The expansion coefficients C , overlaps S and diagonal matrix containing the eigenvalues E are outputted in the ADF program.

The matrix elements j_{AB} are only equal to the transfer integrals J_{AB} from equation 7.1 if they are given in an orthogonal basis. Valeev *et al.* [62] identified that because in general the molecular orbitals of the individual molecules are not orthonormal, i.e. $S_{AB} \neq 0$, equation 3.35 must first be transformed into a standard eigenvalue problem of the form

$$\hat{H}^{eff} C = E C, \quad (3.39)$$

which can be achieved via Löwdin orthogonalisation. This gives

$$\hat{H}^{eff} = S^{-1/2} \hat{H} S^{-1/2}. \quad (3.40)$$

The effective Hamiltonian is then

$$\hat{H}^{eff} = \begin{pmatrix} e_A^{eff} & j_{AB}^{eff} \\ j_{AB}^{eff} & e_B^{eff} \end{pmatrix}, \quad (3.41)$$

and $j_{AB}^{eff} = J_{AB}$, which is explicitly

$$J_{AB} = j_{AB}^{eff} = \frac{j_{AB} - \frac{1}{2}(e_A + e_B)S_{AB}}{1 - S_{AB}^2}. \quad (3.42)$$

Since the original formulation, other fragment orbital approaches have been developed that use different numbers of electrons for the donor, acceptor or Hamiltonian [63] [59]. These different “flavours” of fragment orbital DFT have been compared by Schober *et al.* [64].

Energy splitting in dimer (ESID)

Solving for the determinant of 3.41

$$E_{\pm} = \frac{e_A + e_B}{2} \pm \frac{1}{2} \sqrt{(e_A - e_B)^2 + (2J_{AB})^2}, \quad (3.43)$$

where these two solutions are the degenerate energy levels of the isolated molecules and the splitting is due to the interaction. Taking the difference of these two solutions, which are the HOMO and HOMO-1 (or LUMO and LUMO+1) of the pair, gives

$$E_{splitting} = \sqrt{(e_A - e_B)^2 + (2J_{AB})^2}. \quad (3.44)$$

Note that this is for orthogonal molecular orbitals. If non-orthogonal, a process of Lowdin orthogonalisation is applied to the orbitals [65].

In the case where there is no difference in the site energies, J_{AB} can be approximated [66] as

$$J_{AB} = \frac{E_{splitting}}{2}. \quad (3.45)$$

This can be calculated with a simple hybrid DFT calculation to obtain the Kohn-Sham orbital energies [62].

Figure 3.1 illustrates this method. The levels labelled with E_+ and E_- are the HOMO and HOMO-1 (or LUMO and LUMO+1) of the pair of molecules and result solely from the interaction of the diabatic states (HOMOs or LUMOs) of the two molecules.

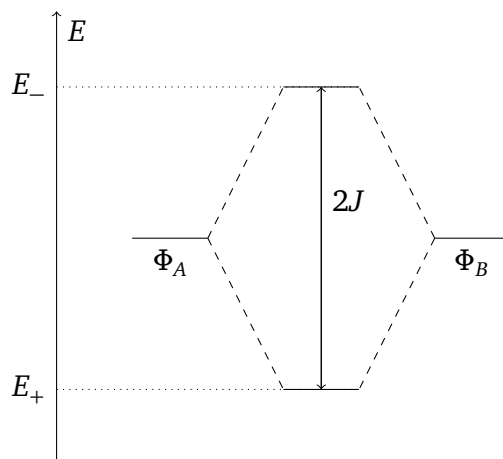


Figure 3.1: Diagram showing the interaction between the wavefunction of the diabatic states of the two molecules.

The ESID method is limited since it relies on the two site energies being identical. This means that the two molecules must be symmetric in such a way that ensures they do not polarise each other differently. In practise, this limits the ESID method to very simple systems with C2 symmetry [66].

Molecular Orbital Overlap

In large disordered molecular assemblies, many transfer integrals must be calculated to obtain a mobility, prompting the need for efficient methods to calculate them. The Molecular Orbital Overlap method (MOO) has been developed for this purpose by Kirkpatrick [67]. It is similar to the Analytic Overlap Method (AOM) developed by Gajdos *et al.* [68]. Both are based on the observation that in certain systems the transfer integral is approximately proportional to the overlap of the two diabatic frontier molecular orbitals.

Projective method

This is the principle method used to calculate transfer integrals in this thesis, so here we outline the method in detail. The initial theoretical underpinning is the same as the fragment orbital method in that the same assumptions are made: (i) the full electronic wavefunction can be considered to be a determinant of one-electron wavefunctions, ϕ_i , and (ii) the wavefunctions only differ by their frontier orbital during the charge transfer event: the "frozen orbital" approximation. Therefore, we begin with equation 3.32

$$J_{AB} = \langle \phi_A | \hat{H} | \phi_B \rangle, \quad (3.46)$$

where $\hat{H}$ is the Hamiltonian for the system and ϕ_i is the electronic wavefunction of site i in the frozen orbital approximation. In the projective method, the Hamiltonian is given by the Fock matrix, F .

To obtain this set of transfer integrals, we project the molecular orbitals of the pair of molecules onto a basis set defined by the molecular orbitals of the individual molecules. We then use the energy eigenvalues of the pair of molecules to reconstruct the Fock matrix in the basis set of the individual molecules. The transfer integral between any orbital of A with any orbital of B can then be read off with the appropriate matrix indices.

Practically, we obtain the molecular orbitals (MOs) of molecule A , molecule B , and molecules A and B together ("molecule AB "), along with the atomic orbital overlaps and energies of molecule AB , via a single point energy *Gaussian* calculation [28] on the optimised molecules. We specify the internal options `IOP(3/33=1,6/7=3)` to ensure the relevant orbitals and energies are outputted.

The method applied once we have these MOs is outlined below [69]. The orbitals of the pair of molecules are written as a matrix $\mathbf{C}_{pair}$, with each column corresponding to a molecular orbital (MO) and each row corresponding to an atomic orbital (AO). This is to be projected onto a basis set defined by the orbitals of the individual molecules, which is written as a matrix $\mathbf{C}_{mol}$. This has the first $N/2$ columns corresponding to the molecular orbitals of molecule A (ϕ_A) and the second $N/2$ columns corresponding to the molecular orbitals of molecule B (ϕ_B). The first $N/2$ rows correspond to the atomic orbitals of molecule A and the second $N/2$ rows correspond to the atomic orbitals of molecule B .

$$\mathbf{C}_{mol} = \begin{pmatrix} c_1^1 & c_1^2 & \dots & c_1^{\frac{N}{2}} & 0 & 0 & 0 & 0 \\ c_2^1 & c_2^2 & \dots & c_2^{\frac{N}{2}} & 0 & 0 & 0 & 0 \\ \dots & \dots & \dots & \dots & 0 & 0 & 0 & 0 \\ c_{\frac{N}{2}}^1 & c_{\frac{N}{2}}^2 & \dots & c_{\frac{N}{2}}^{\frac{N}{2}} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{\frac{N}{2}+1}^1 & c_{\frac{N}{2}+1}^2 & \dots & c_{\frac{N}{2}+1}^{\frac{N}{2}} \\ 0 & 0 & 0 & 0 & c_{\frac{N}{2}+1}^{\frac{N}{2}+1} & c_{\frac{N}{2}+1}^{\frac{N}{2}+2} & \dots & c_{\frac{N}{2}+1}^N \\ 0 & 0 & 0 & 0 & c_{\frac{N}{2}+2}^{\frac{N}{2}+1} & c_{\frac{N}{2}+2}^{\frac{N}{2}+2} & \dots & c_{\frac{N}{2}+2}^N \\ 0 & 0 & 0 & 0 & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & 0 & c_{\frac{N}{2}}^{\frac{N}{2}} & c_{\frac{N}{2}}^{\frac{N}{2}} & \dots & c_N^N \end{pmatrix} \quad (3.47)$$

If the AOs are orthogonal, the orbitals of the pair can be written in the new basis set by calculating the dot product,

$$\mathbf{C}_{pair}^{mol} = \mathbf{C}_{mol}^T \mathbf{C}_{pair}. \quad (3.48)$$

Then the Fock matrix can be reconstructed for the pair of molecules (using the spectral theorem) as,

$$\mathbf{F}_{pair}^{mol} = \mathbf{C}_{pair}^{mol T} \epsilon_{pair} \mathbf{C}_{pair}^{mol}. \quad (3.49)$$

Here, ϵ_{pair} is a diagonal matrix containing the molecular orbital energies of the pair of molecules. The off-diagonal elements of this matrix $\mathbf{F}_{mn}$, $m \neq n$, are the electronic couplings (transfer integrals) between molecular orbitals m and n of the isolated molecules.

If the AOs are not orthogonal, they can be orthogonalised with Löwdin orthogonalisation. Defining a matrix $\mathbf{D}$ as

$$\mathbf{S} = \mathbf{D}^T \mathbf{D}, \quad (3.50)$$

where $\mathbf{S}$ is the overlap matrix with each element $S_{i,j}$ being the integral over all space of the product of the i^{th} and j^{th} atomic orbitals. The non-orthogonal orbitals $\mathbf{C}'_{mol}$ can then be orthogonalised with

$$\mathbf{C}_{mol} = \mathbf{D} \mathbf{C}'_{mol}. \quad (3.51)$$

The procedure can then be followed from equation 3.48.

We use the projective method for the majority of the transfer integral calculations in this thesis. However, it is limited to transfer integrals between molecules of the same type and cannot be used for intramolecular transfer integrals. We introduce a further method in chapter 7 which allows us to calculate intramolecular transfer integrals and transfer integrals for a larger variety of systems of interest.

3.4.3 Energy difference

The difference in energy between the two sites (ΔE_{ij}) is influenced by the chemical structure of the molecule as well as relative orientation and electric field. To calculate this, multipole analysis of the neutral and charged molecules can be used to calculate the interaction energy [41]. If the two molecules are identical, to a first approximation the energy difference can be assumed to be negligible. If an electric field is applied to the system, the energy difference is

$$\Delta E_{ij} = \varepsilon_i - \varepsilon_j - q \vec{\mathcal{E}} \cdot \vec{r}_{ij}, \quad (3.52)$$

where ε_i and ε_j are the energies of the two sites, q is the charge of an electron, $\vec{\mathcal{E}}$ is the field vector and $\vec{r}_{ij}$ is the distance vector between sites i and j .

3.5 Mobility

The Marcus equation provides a set of microscopic rates for charge transfer between every molecular pair. This defines a master equation [70] [71] [72]

$$\frac{dP_n}{dt} = \sum_{m \neq n} [\Gamma_{mn} P_m(t) - \Gamma_{nm} P_n(t)]. \quad (3.53)$$

Here, P_m are the set of occupation probabilities, and Γ_{mn} the rate of charge transfer between sites m and n . The master equation is a first order differential equation describing a Markov chain process where memory of the system is lost after every event. This equation is applicable in the low charge carrier limit, since with higher charge densities it is non-linear.

By considering a matrix A defined as

$$A_{mn} = \begin{cases} \Gamma_{mn} & m \neq n \\ -\sum_{m \neq n} \Gamma_{nm} & m = n \end{cases} \quad (3.54)$$

it can be seen that in the steady state solving equation 3.53 is equivalent to solving equation 3.55.

$$A\vec{P} = 0 \quad (3.55)$$

This is solved by finding the null space of the matrix A , which is done using singular value decomposition (SVD). If A is an $M \times N$ matrix, then it can be decomposed as

$$A = U\Sigma V^T, \quad (3.56)$$

where U is an orthogonal $M \times M$ matrix, Σ is a diagonal matrix containing the singular values, and V is an orthogonal $N \times N$ matrix. The null space required is the columns of V that correspond to singular values equal to zero. In practice, these are singular values which are below some threshold, $\epsilon \ll 1$. In the case where there are multiple null spaces, we choose the one that is consistent with a set of probabilities, i.e. all positive, and scale so they sum to 1.

The solution of the Master equation gives a steady state occupation of the sites, P_i . It can be used

to find the mobility in the direction of a field $\vec{F}$. The field is introduced into the Marcus equation (equation 3.23) via the change in energy term with

$$\Delta E_{ij} = \varepsilon_i - \varepsilon_j - q\vec{F} \cdot \vec{r}_{ij}, \quad (3.57)$$

where ε_i and ε_j are the energies of the two states, q is the charge of an electron, $\vec{F}$ is the field vector and $\vec{r}_{ij}$ is the distance vector between sites i and j .

The steady state occupation probabilities can then be used to find the average velocity of charges, with [71]

$$\vec{v} = \sum_{m \neq n} \vec{r}_{mn} A_{mn} P_n, \quad (3.58)$$

Assuming a linear regime, the mobility is therefore

$$\mu = \frac{\langle v \rangle}{F}, \quad (3.59)$$

where $\langle v \rangle$ is the average velocity of charges in the direction of a field, and F is the magnitude of the field.

The mobility can also be related to the diffusion coefficient D , by the Einstein relation [73]:

$$\mu = \frac{qD}{kT}. \quad (3.60)$$

The diffusion coefficient is calculated from the rate matrix and distance matrix, using the following expression, derived from the random walk model and adapted to our purposes [71]:

$$D = \frac{1}{2d_m} \sum_{i,j} P_i A_{ij} (\vec{r}_{ij} \vec{e})^2 \quad (3.61)$$

where $\vec{e}$ is the direction the diffusion coefficient D is measured in, and d_m is the spatial dimensionality. The second equation for mobility allows us to calculate the mobility without applying an electric

field.

The mobility can also be calculated from a set of microscopic hopping rates with kinetic Monte Carlo (kMC) [74]. This method has been applied to assemblies of fullerene molecules [13], AlQ_3 [75] [76], and conjugated polymers [77].

3.6 Summary

The methods described here allow us to model electronic states and charge transport in OSCs, covering length scales that range from angstroms at the electronic structure level to cm for the mobility which is a device level property. We use coarse grained molecular dynamics to generate large assemblies of molecules. These structures can feed into a tight-binding Hamiltonian in the basis of molecular orbitals to investigate the electronic structure of large systems. DFT calculations of electronic structure allow us to obtain the parameters to generate microscopic charge transfer rates. These can then feed into a master equation to get a phenomenological device-scale measure of mobility.

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4

Relating crystal structure to electronic properties and mobility

We investigate the charge carrier mobility in crystal structures of helicene molecules: polyaromatic, helical molecules that are chiral. This chirality means that depending on the chiral mix (enantiopure or racemic), different crystal structures are available. For aza[6]helicene, we collaborate with experimentalists to explain their observation that the racemic form has a hole mobility that is almost two orders of magnitude greater than for the enantiopure form. We investigate 28 low-energy crystal structures of [6]helicene to identify specific motifs or substructures that exist in high electron or hole mobility structures.

4.1 Introduction

Part of the work presented in this chapter has been published in *ACS Nano* [1]. A further part has been published in *Nanoscale* [2].

In molecular materials that are weakly coupled- that is the electronic coupling is much less than the reorganisation energy- the rate of charge transfer can be calculated with non-adiabatic Marcus

theory (see section 2.6.2). This can be applied to intra- or intermolecular charge transport. The site energies, reorganisation energy and transfer integrals between all sites must be calculated for the Marcus equation of rates. Once a set of hopping rates between all sites and every other has been calculated, the mobility can be calculated in a number of ways. One of these is the Master equation approach detailed in section 3.5.

In crystal structures, assuming charge transfer between a limited number of neighbours (specifically between sites in neighbouring unit cells only), the periodicity means that only a subset of all of the transfer integrals needs to be calculated explicitly. Taking a unit cell and then calculating the transfer integrals between the molecules in this unit cell and all others in a $3\times 3\times 3$ supercell suffices to find the crystal mobility in any direction [3].

This chapter is focussed on calculating the electron and hole mobilities in crystal structures of helicene molecules. We investigate the structure-property relationships in these materials, and how the chirality of the molecules influences this. The methods in this chapter can be applied to any molecular crystal systems that have weak coupling between molecules. We focus on helicenes as an interesting system where the bulk properties are influenced solely by differences in crystal structure, the range of which is induced by by chirality.

4.2 Helicenes

Helicenes are *ortho*-fused polyaromatic helical molecules that are chiral, which means that they can exist in two non-superimposable isomers, i.e. left and right-handed helices that are mirror images of each other. This means that crystal structures of helicenes can be both enantiopure (containing molecules of one handedness) or racemic (containing molecules of both handedness) [4].

This class of materials make interesting systems to study since the chiral isomers are chemically identical and will have the same molecular properties. Therefore, any difference in properties is entirely due to the different bulk packing which is induced by the chiral composition. This opens up the possibility of using different chiral compositions of the same molecule to influence its material properties.

We investigated two different helicenes: aza[6]helicene and [6]helicene, shown in Figure 4.1,

which differ only by a nitrogen atom. We were interested in how the different crystal structures induced by their chiral composition (enantiopure or racemic in a 50:50 mix) affected the charge carrier mobility. For aza[6]helicene we collaborated with experimentalists who had the molecules synthesised, carried out structural characterisation of single crystals and thin films, and made OFET devices from them to measure the mobility. We investigated one racemic and one enantiopure crystal of aza[6]helicene that was identified from characterisation measurements together with crystal structure prediction [1].

For [6]helicene we compared a range of low-energy crystal structures to investigate structure-property relationships, such as how energy, density and anisotropy changed with structure and how this affected the mobility. We also identified packing motifs within the structures to see if the existence of any particular substructure could be associated with high hole or electron mobility [2].

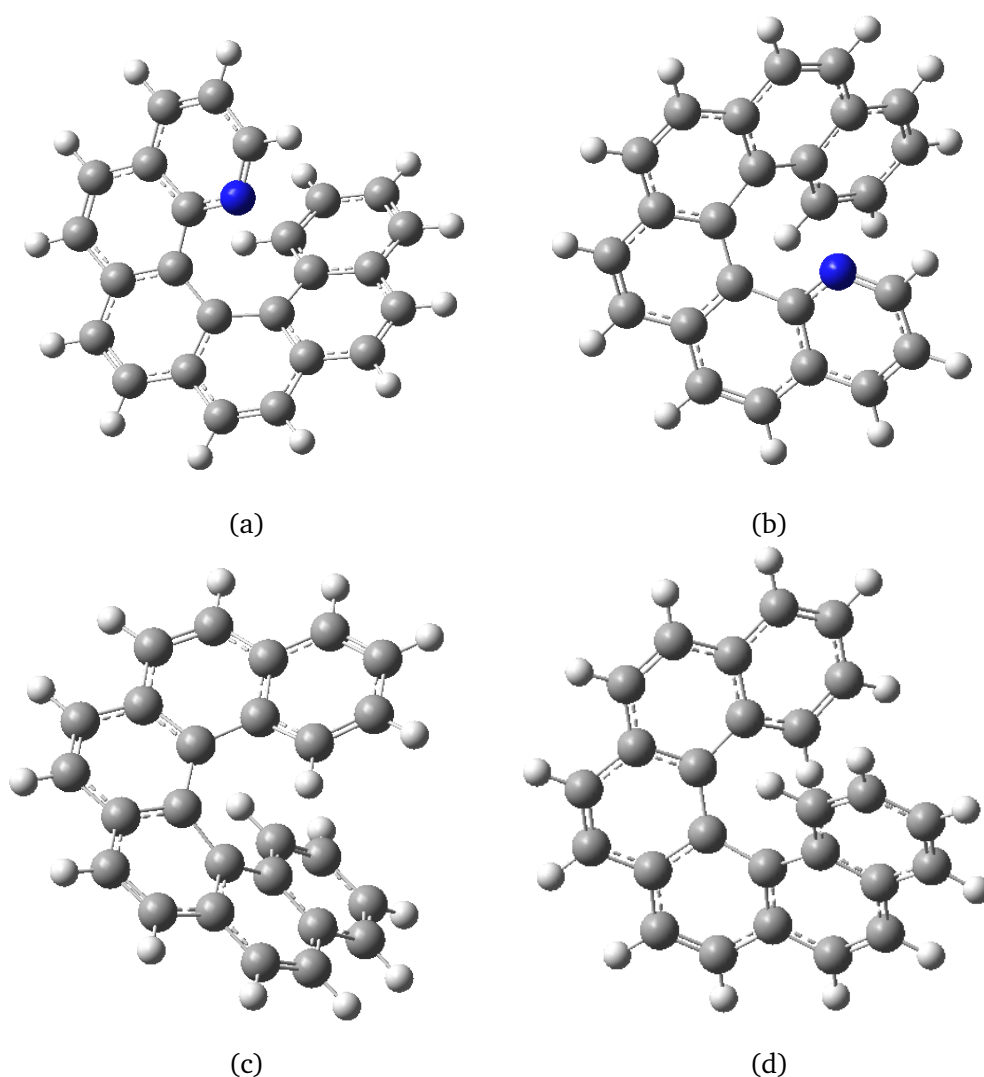


Figure 4.1: (a) Left and (b) right handed aza[6]helicene molecules and (c) left and (d) right handed [6]helicene molecules

4.3 Methodology

4.3.1 Crystal structures

We used predicted crystal structures generated by Dr Kim Jelfs in the department of Chemistry at Imperial College and calculated the transfer integrals between all molecules in a unit cell to all others in a $3 \times 3 \times 3$ supercell with the projective method (section 3.4.2). Stehr *et al.* [3] confirmed that using a larger supercell does not effect the value of the mobility. We then used Marcus theory (section 2.6.2) to calculate a set of rates and a Master equation approach (section 3.5) to obtain the hole and electron mobility.

By using the space group symmetry operations for each crystal structure prediction, we projected one molecule from the unit cell to its equivalent positions, having first geometrically optimised it. The optimisation was done in *Gaussian* with a B3LYP functional and 6-31g* basis set. Having generated the unit cell, we translated this in 26 directions to generate a $3 \times 3 \times 3$ supercell.

4.3.2 Transfer integrals

The most computationally expensive step for obtaining a set of rates with Marcus theory is calculating the set of transfer integrals between the molecular sites. There are many methods to do this which are outlined in more detail in section 3.4.2. Once a set of rates have been obtained, a mobility can be calculated with a Master equation approach [5] [6] [7] (see section 3.5 or section 4.3.4 below). In highly crystalline organic semiconductors an expression for mobility can be obtained that depends only on the angles and distances between molecules [8] [9]. In more disordered semiconductors, a Monte Carlo approach can be used [10] [11].

The Marcus equation for rates requires transfer integrals (or electronic couplings) between each site in the unit cell and all others in the supercell. These were calculated using the projective method, the theory of which is detailed in section 3.4.2. A crystal structure with m molecules per unit cell requires $(m-1) + 27m^2$ calculations if the symmetry is utilised, as opposed to $27^2m^2 - 1$ calculations, reducing the computational cost. The symmetry of the supercell can then be used to populate a matrix J_{ij} for every site i and j in the supercell.

Gaussian [12] was used to calculate the molecular orbitals, orbital overlaps, and energies of each

of the optimised molecules, as well as each required pair of molecules. The pair is made up of one molecule from the unit cell with every other possible molecule within a specified cut-off distance. These were obtained with a single point energy calculation ensuring the molecular orbitals and atomic orbital overlaps were outputted by specifying internal options 6/7=3 and 3/33=1, respectively. The calculations were performed with the B3LYP functional and 6-31g* basis set. We set the separation cut-off between molecules to 18 Å, which in this system means that we don't calculate transfer integrals less than 1×10^{-9} eV as they would contribute very little to the overall mobility.

4.3.3 Marcus equation for rates

The Marcus equation for non-adiabatic charge transfer defines the rate of charge hopping between sites i and j as

$$\Gamma_{ij} = \frac{|J_{ij}|^2}{\hbar} \sqrt{\frac{\pi}{\lambda k_B T}} \exp\left(-\frac{(\Delta E_{ij} + \lambda)^2}{4\lambda k_B T}\right), \quad (4.1)$$

where J_{ij} is the transfer integral between these sites; λ is the reorganisation energy, which is the energy cost associated with the rearrangement of the molecules and their surroundings during charge transfer; and ΔE_{ij} is the energy difference between sites i and j .

The electronic coupling J_{ij} is calculated with the projective method, as explained above and in section 3.4.2. We calculate the inner reorganisation energy for one molecule from the unit cell with the 4-point method (section 3.4.1), with each of the calculations at the B3LYP level of theory with the 6-31g* basis set.

The energy difference is given by $\Delta E_{ij} = \varepsilon_i - \varepsilon_j - q\vec{F} \cdot \vec{r}_{ij}$, where q is the charge of an electron, $\vec{F}$ is the applied electric field and $\vec{r}_{ij}$ is the distance vector between the two sites.

We calculate this matrix of rates for an applied field, here taken as 10000 V cm^{-1} , applied at 10 degree intervals in each of the three orthogonal planes, and then use the Master equation approach to find a mobility in each of these directions.

4.3.4 Master equation for mobility

The Master equation approach (section 3.5) for charge transport in the low density limit means constructing a matrix defined by

$$A_{mn} = \begin{cases} \Gamma_{mn} & m \neq n \\ -\sum \Gamma_{nm} & m = n \end{cases} \quad (4.2)$$

The steady state occupation probabilities P are then found by solving

$$\mathbf{A}\vec{P} = 0. \quad (4.3)$$

This is solved by finding the null space of the $\mathbf{A}$ matrix, as in section 3.5.

Once we have a set of occupation probabilities, we find the average velocity of charges in the direction of the applied field, $\langle v \rangle$, and then find the mobility μ with

$$\mu = \frac{\langle v \rangle}{F}, \quad (4.4)$$

where F is the magnitude of the field.

4.4 Results

Aza[6]helicene

We investigated the crystal structure dependence of hole mobility in aza[6]helicene molecules (Figure 4.1). This was prompted by experimental work by Dr Matthew Fuchter to characterise the molecules, measurements by Prof Alasdair Campbell and Dr Ying Yang, and crystal structure prediction (CSP) by Dr Kim Jelfs. They found that field effect transistor (FET) measurements showed an improvement in the mobility of almost two orders of magnitude for the racemic structure ($2.0 \times 10^{-3} \text{ cm}^2/\text{Vs}$) compared to enantiopure ($2.4 \times 10^{-5} \text{ cm}^2/\text{Vs}$) [1].

The crystal structures we investigated were chosen from a selection of low energy crystal structures

predicted by Kim Jelfs, which were then compared with crystal structures defined using Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS) measurements of the actual experimental films by Prof Alasdair Campbell and co-workers at Cornell. GIWAXS is a method that allows the unit cell parameters of crystal structures to be deduced from the scattering pattern. We chose the racemic and enantiopure crystal structures that best matched the GIWAXS patterns of the thin films. This means those that best matched the unit cell parameters of the thin films from GIWAXS.

We calculated a set of transfer integrals for each of the crystal structures, that ranged from 2.72×10^{-9} to 0.039 eV for the enantiopure structure and 6.96×10^{-9} to 0.052 eV for the racemic structure. A histogram of the transfer integrals for each crystal structure is given in Figure 4.2. It should be noted that there are 4 molecules per unit cell in the racemic crystal structure and 8 molecules per unit cell in the enantiopure crystal structure, which is why the two plots do not integrate to the same value. The figures show that the racemic crystal structure has a greater proportion of larger transfer integrals.

We used the Marcus equation for rates (section 2.6.2) to obtain a set of rates in the crystal structure with a field of 10000 V cm^{-1} applied at 10 degree intervals in the three orthogonal planes. We calculated the inner reorganisation energy (λ_{inner}) to be 0.171 eV and approximated the outer reorganisation energy (λ_{outer}) to give a total reorganisation energy of $\lambda = 0.3 \text{ eV}$. The reported mobility values depend strongly on the value of λ . As long as the transfer integral are much less than the reorganisation energy, the values are useful to give a qualitative description.

Figure 4.3 shows the angular dependent mobility in each of the three orthogonal planes for the predicted racemic and enantiopure structures. The maximum mobility for the racemic structure is $0.14 \text{ cm}^2/\text{Vs}$ and for the enantiopure structure it is $0.052 \text{ cm}^2/\text{Vs}$. It can be seen that in two of the planes the mobility for the racemic structure is more than double that of the enantiopure structure. Experimental evidence suggests that the preferential plane of mobility (i.e. the plane that is most likely to lie parallel to the substrate of the FET device) is the bc-plane for the enantiopure structure and that there is not a preferred crystal orientation for the racemic structure.

We further investigated the transfer integrals for each structure and found that there is a high coupling path through differently-handed molecules for the racemic structure, which cannot exist in the enantiopure structure. This is illustrated in Figure 4.4 and may explain the large difference in mobilities in the two structures. We don't find as large a difference in the calculated hole

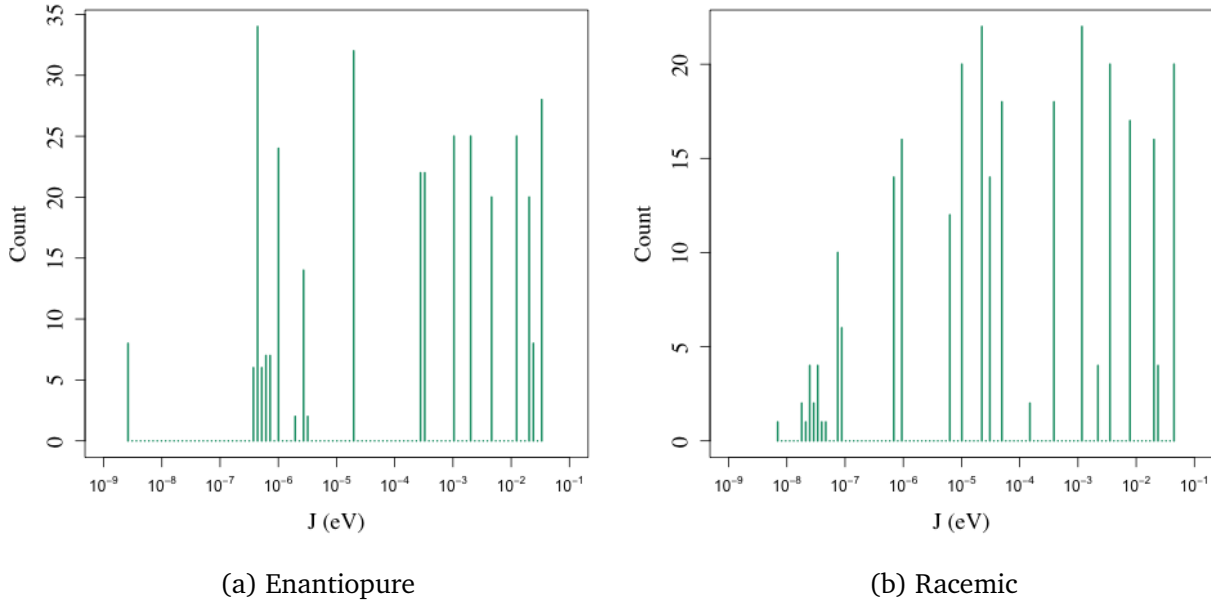


Figure 4.2: Histograms of the transfer integrals for enantiopure and racemic crystal structures.

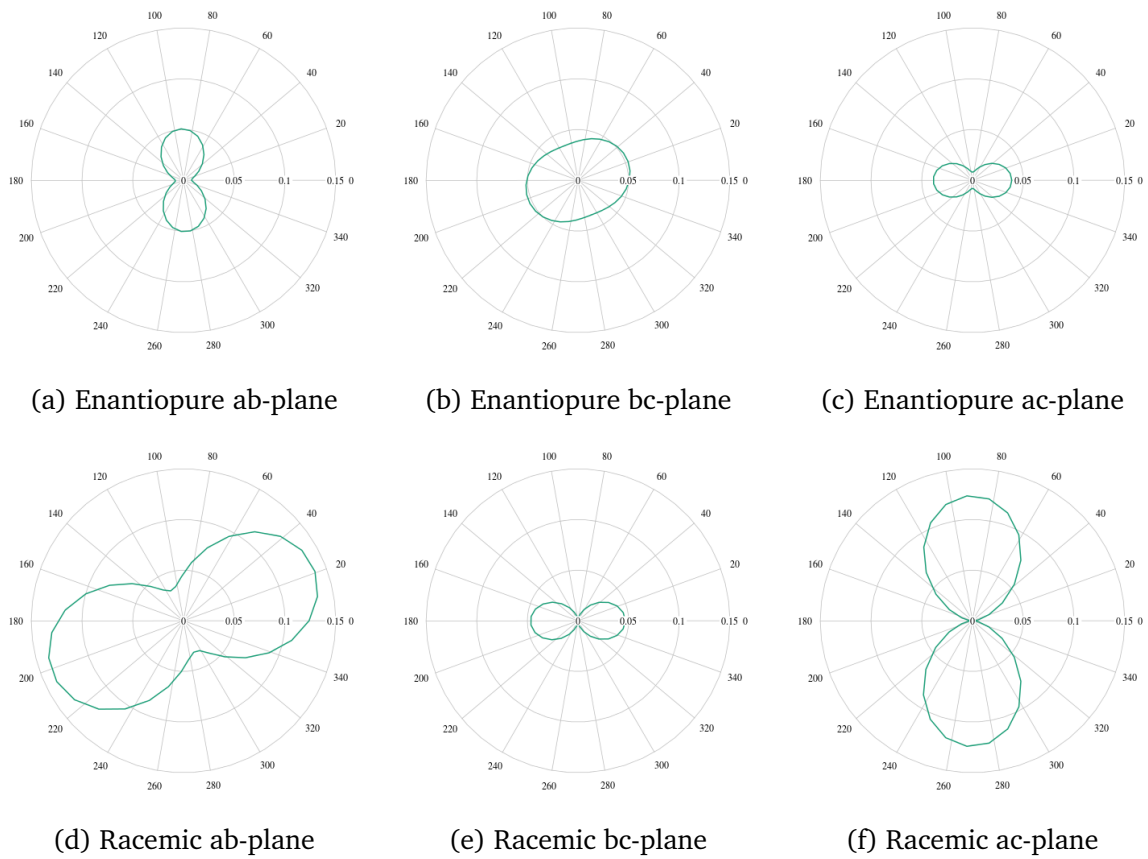


Figure 4.3: Angular plot of mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) in each plane for predicted enantiopure and racemic crystal structures.

mobility as the experimental FET measurements. We propose that the larger difference observed experimentally could be due to other factors such as polymorphism in the films.

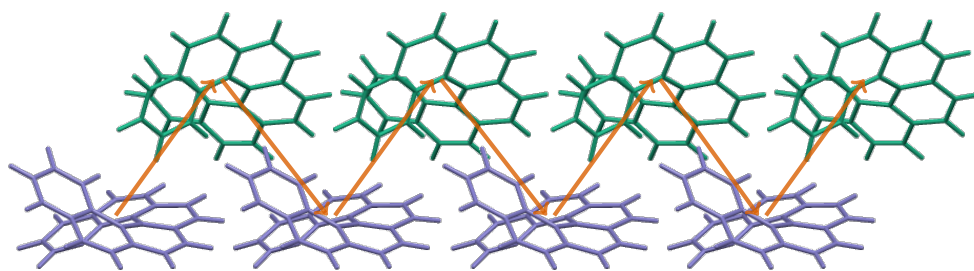


Figure 4.4: An illustration of the high-coupling path that exists between different handed molecules in the racemic form of aza[6]helicene.

[6]helicene

We are also interested in the difference in mobility for different crystal structures of the same molecule, to explore the interplay between structure, substructures and properties. For the case of the [6]helicene structures, we used crystal predictions from Kim Jelfs, where 28 low energy structures were identified (low energy is defined as within 7.2 kJ/mol of the minimum energy structure). Three of the structures were enantiopure, one was intergrowth (which means a unit cell that is doubled in one direction and two opposite handed enantiopure structures side by side), and the rest were racemic.

With the same method outlined above, and a total reorganisation energy of 0.3 eV, we calculated the mobility in each of these to explore trends that lead to higher electron or hole mobilities. We looked for macroscopic properties that could be measured that correlated with electron or hole mobility, including total energy (i.e. the thermodynamic stability), density, anisotropy, and whether the structure was enantiopure or racemic. In Figure 4.5, different symbols correspond to different substructures identified by Kim Jelfs using the COMPACK procedure [13] to construct a similarity tree in Mercury [14] [15].

The charge mobility obtained for the 28 low energy structures ranges from 0.0015 to 2 cm²V⁻¹s⁻¹ for hole mobility and 0.14 to 2.9 cm²V⁻¹s⁻¹ for electron mobility. From Figure 4.6, it can be seen that there is no significant correlation between electron or hole mobility versus the maximum calculated electronic coupling for the structure. There is stronger correlation with the maximum transfer integral for electron mobility compared to hole mobility, but it is not predictive in either case.

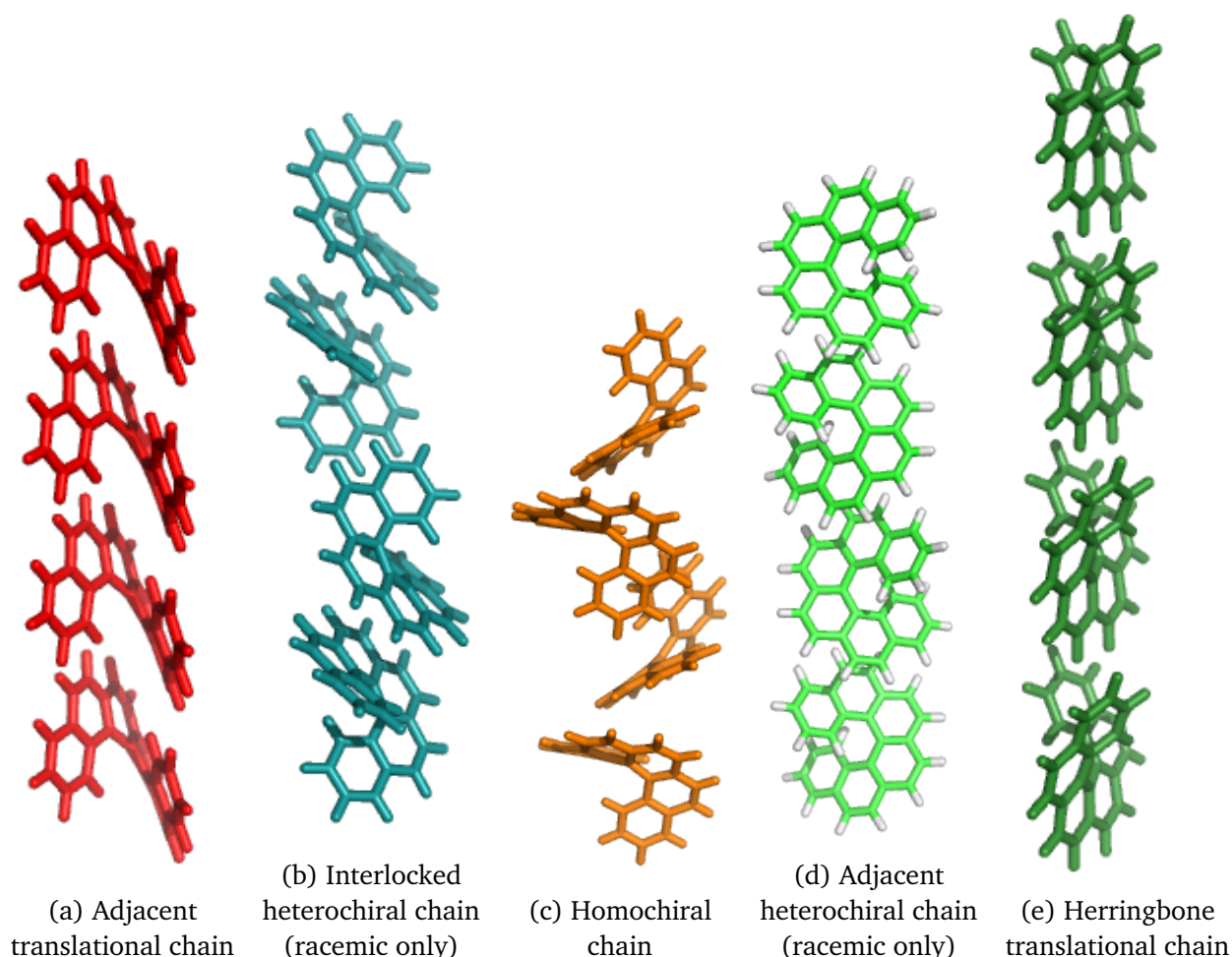


Figure 4.5: The substructures identified in the larger crystal structures.

There are more racemic structures that are at the higher end for hole mobility and lower end for electron mobility. This gives a broader picture for a trend that was identified by Hatakeyama *et al.* [16]. They showed that in two particular structures for azaboradibenzo[6]helicene the racemic form had higher hole mobility than the enantiopure form, and that it had undetectable electron mobility, while the enantiopure form had higher electron mobility than hole mobility. Our results suggest that the specific structure is more important than whether the structure is racemic or enantiopure.

As shown in Figure 4.7, there is no strong correlation with any of the properties- energy, density and anisotropy- with mobility. However, out of all of these density shows the strongest correlation: higher density indicates that molecules are closer together which would tend to increase transfer integrals. However, this is not the complete picture, as can be seen from the fact that structures with approximately the same density have a range of electron or hole mobilities.

On the other hand, the existence of some substructures does seem to correlate with higher mobilities.

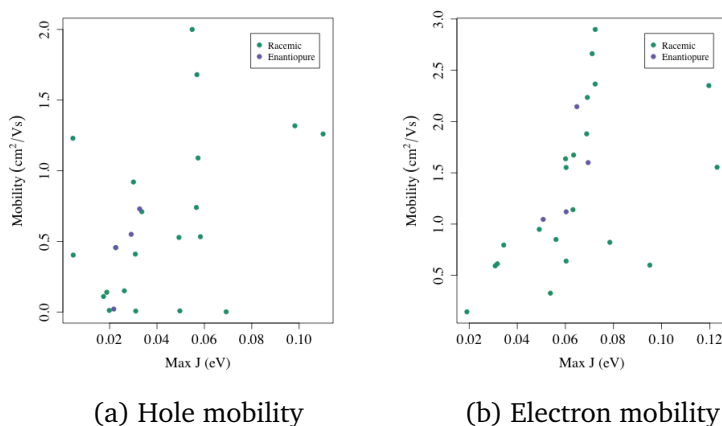


Figure 4.6: Hole and electron mobility versus the maximum HOMO-HOMO or LUMO-LUMO coupling, respectively.

We found that the adjacent heterochiral chain and herringbone translational chain substructures were present in three of the five structures with the highest hole mobility. These substructures always appear together due to the nature of the packing.

The angular dependent mobility in each of the three planes for the highest hole mobility structure is shown in Figure 4.8, along with the identified substructures. Looking at the direction of maximum mobility, as well as the values for the transfer integrals between molecules, we can see that it is the herringbone translational chain substructure that results in the high hole mobility for the structure.

These high hole mobility structures have relatively low electron mobility. The structure with the highest electron mobility contains the adjacent translational homochiral chain substructure. The high electron mobility direction is along this substructure where it exists, but this substructure is contained in many of the structures with a range of electron mobility values.

Figure 4.9 shows the angular dependent mobility in each of the three planes for the highest electron mobility structure, along with the adjacent translational chain substructure and the transfer integral along the chain in this particular structure. In other structures containing this substructure, the distance between molecules in the chain is greater, reducing the magnitude of the transfer integral, and therefore the rate of charge transport along the chain. For high mobilities, more important than having an individual high maximum transfer integral is having a high coupling pathway through the crystal.

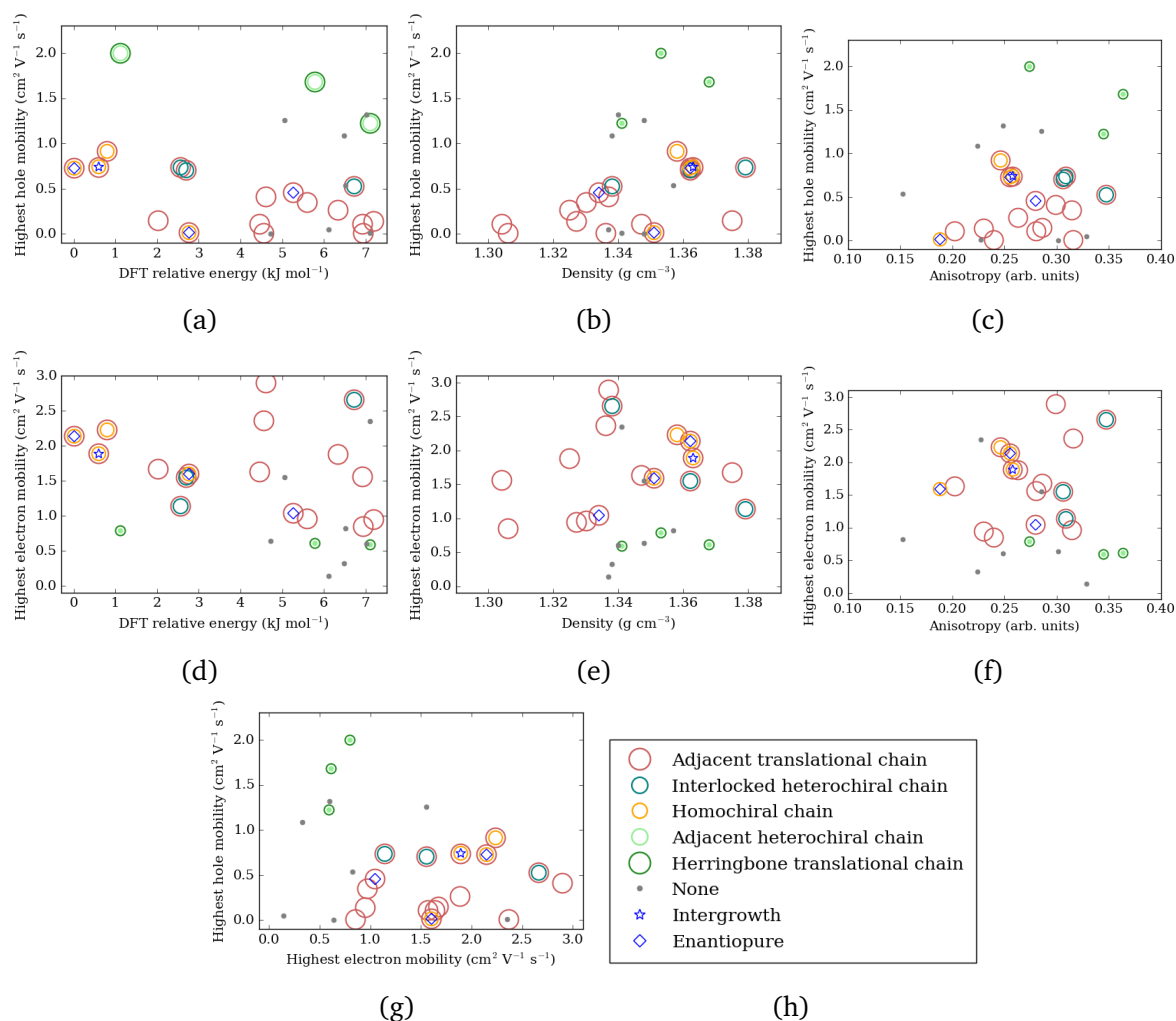


Figure 4.7: Electron and hole mobility versus different properties. The substructures present in each of the structures are indicated in the legend, and are cross-referenced by colour in Figure 4.5. Note the herringbone translational chain and adjacent heterochiral chain substructures that result in high hole mobility, and the adjacent translational chain that is present in the structure with the highest electron mobility.

4.5 Conclusions

We have explored the effect of chirality on the mobility in helicene molecular crystals, via an understanding of the effect of the chiral composition on the crystal structures that can form. We calculated the transfer integrals from one unit cell to all other molecules in a $3 \times 3 \times 3$ unit cell, and used these to calculate a matrix of hopping rates with Marcus theory, with a mobility calculated using the Master equation.

By calculating the hole mobility in racemic and enantiopure crystal structures of aza[6]helicene, we showed that the racemic crystal structure has a higher hole mobility than the enantiopure crystal structure. Here, the unit cell and space group was identified by collaborators through GIWAXS measurements alongside crystal structure prediction calculations. We also identified

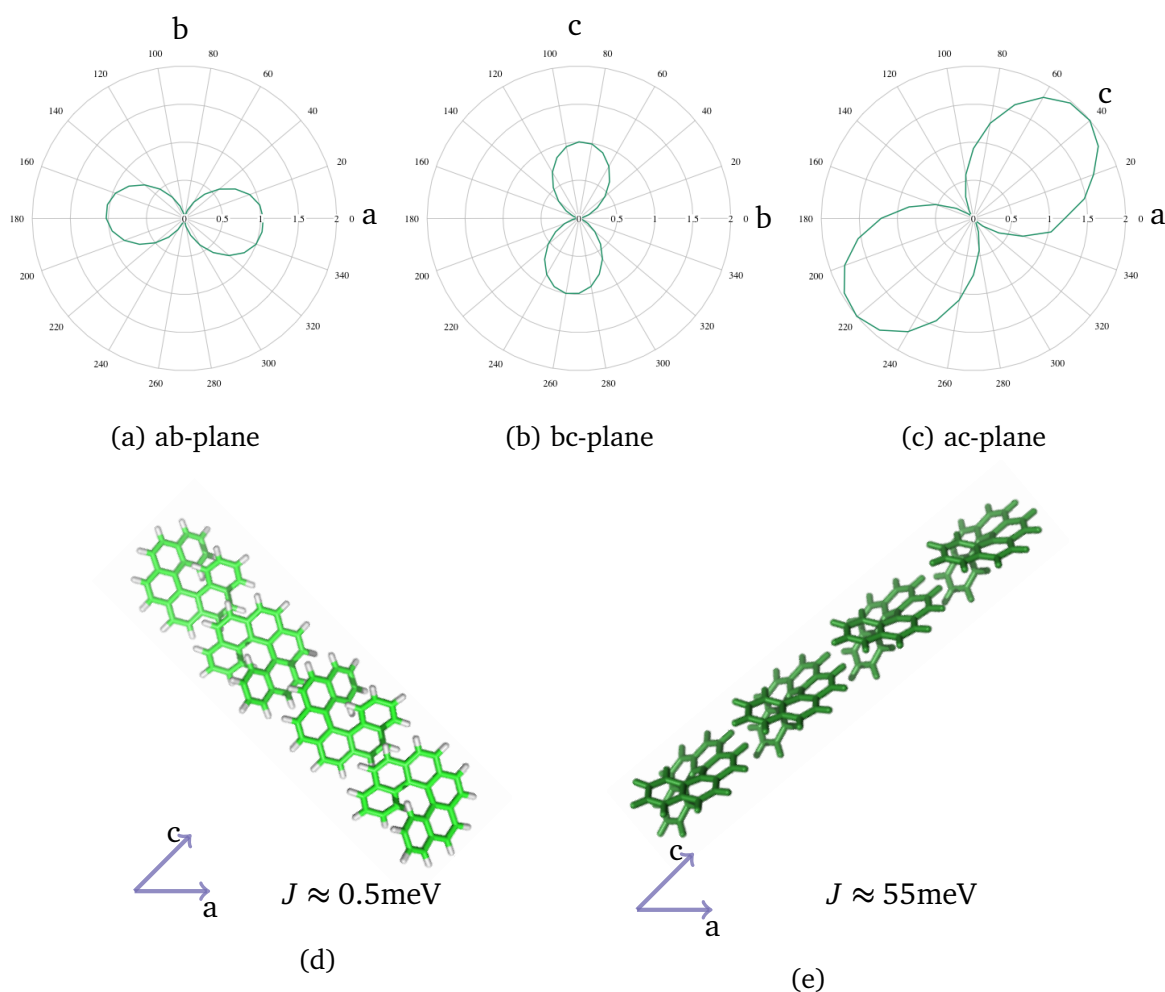


Figure 4.8: (a)-(c) Angular plot of mobility in each plane for maximum hole mobility structure. (d) The adjacent heterochiral chain substructure, with approximate intermolecular J value for the chain. (e) The herringbone translational chain substructure, with approximate intermolecular transfer integral for the chain.

the high coupling pathway in the racemic crystal, which was between molecules of different handedness, so could not exist in the enantiopure structure. The difference in hole mobility between the racemic and enantiopure structures was not as great as what was found with FET measurements, but there could be other factors, such as polymorphism in experimental films, that could influence the values.

For [6]helicene molecules, we investigated the mobility, energy, density and anisotropy in 28 low energy crystal structures, of which three were enantiopure, one was an intergrowth structure and the rest were racemic. Because there are more racemic structures compared to enantiopure, any comparison between the two is somewhat difficult. However, our results showed the enantiopure structures tended to have higher electron mobilities and lower hole mobilities. This trend was not absolute, and the actual structure mattered a lot more than whether it was racemic or enantiopure,

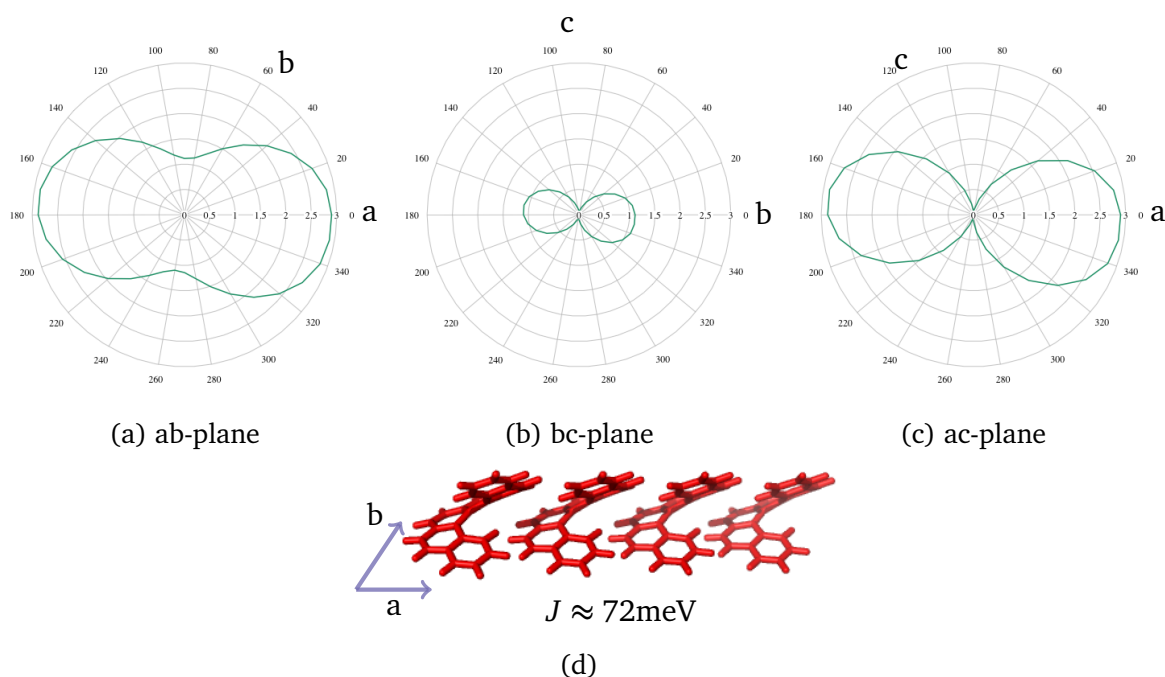


Figure 4.9: Angular plot of mobility in each plane for (a)-(c) maximum electron mobility structure. The adjacent translational chain substructure with the approximate intermolecular transfer integral for the chain.

although of course this influences which structures can form.

There were no strong correlations for hole or electron mobility with any of the other properties (energy, density, anisotropy), although density showed more of a correlation than the others. Higher density suggests that molecules are closer together which tends to produce larger transfer integrals, but this is not a complete picture. To gain a greater understanding, we investigated substructures that were present in multiple structures to see if the existence of a particular substructure predicted higher hole or electron mobility.

We found that the herringbone translational chain substructure was present in three of the five structures with the highest hole mobility, and was only present in these high hole mobility structures. The high coupling pathway is along this chain. Although the adjacent heterochiral chain also exists in these structures, the coupling along this chain is not strong. It appears that this substructure always exists with the herringbone translational chain substructure due to the packing, but does not contribute to the high mobility pathway.

High electron mobility did not correlate with high hole mobility. In fact, the three high hole mobility structures mentioned above had some of the lowest electron mobilities. We found that

the adjacent translational chain substructure was present in the three structures with the highest electron mobility. However, it was less predictive of high electron mobility because it was also present in many structures with a range of electron mobilities.

This method can be applied to any crystal structures where there is weak coupling between molecules, so the Marcus equation can be used. The symmetry of the unit cell limits the number of transfer integrals that must be calculated. However, it could also be applied to amorphous materials but this becomes much more computationally expensive. The direction dependent mobility is an important property for many organic semiconductor devices, and an understanding of the interplay between the chemical structure, bulk packing and properties paves the way for tunable devices.

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5

Defects in PCBM: insights from modelling

We work with experimentalists to investigate the types of defects that may form in PCBM films, and their effect on the performance of devices. We use electronic structure methods to obtain spectra of PCBM with different defects, which we compare to the spectroscopic and characterisation work of our experimental collaborators to identify which defects are likely to form. We calculate the HOMO and LUMO levels of PCBM with different defects with electronic structure techniques and use these to simulate the electron mobility in PCBM films that contain different proportions of defects, and show the negative effect of defects on electron mobility. This is supported by SCLC measurements of mobility by our collaborators on PCBM films with different proportions of degraded PCBM.

5.1 Introduction

Part of this work in this chapter has been published in *ACS Applied Materials & Interfaces* [1]. A further part has been published in *Energy & Environmental Science* [2].

The operational lifetime of OPVs and other organic semiconductor devices is a key factor that determines how successful the technology will be. Therefore, it is important to understand degradation in the materials, both in terms of mechanism and what effect it has on the properties

of the devices.

Most studies of OPV degradation involve measurements of devices under ageing in harsh environments (exposure to any of light, oxygen, water, heat and electrical stress) [3] [4] but without isolating the effect of those stress factors on different components (donor or acceptor material, or contacts with electrodes) and therefore it is difficult to identify degradation mechanisms. Studies on degradation of individual components so far have mainly focussed on conjugated polymers, the donor material [5] [6].

Here, we focus on PCBM as the most common electron acceptor in OPV. Xiao et al. [7] proposed the degradation mechanism for PCBM given in Figure 5.1. It shows a PCBM molecule being oxidised to form an epoxide defect, then a diol defect and finally a carbonyl defect.

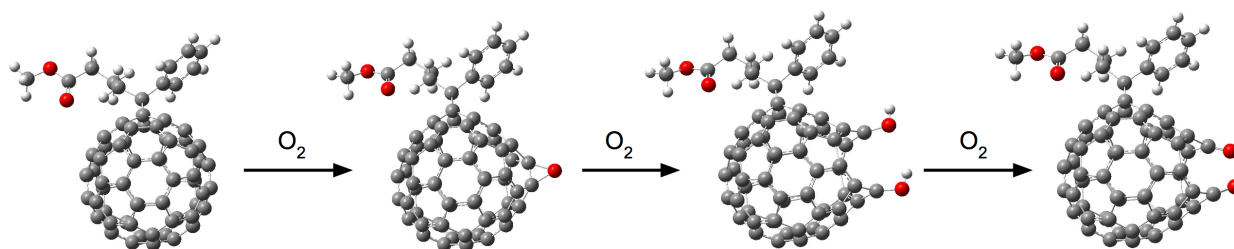


Figure 5.1: Degradation mechanism proposed by Xiao et al. [7]. The PCBM molecule is oxidised to an epoxide, then a diol, then a carbonyl.

In this chapter, we take advantage of experimental work by Wing C. Tsoi, Emily Speller and others at Swansea University, along with Dr Andrew Telford, Jason Rohr and others at Imperial, to understand degradation in PCBM. In this study, PCBM was selectively degraded by exposure to light and oxygen prior to device fabrication, and the material then used in devices, as well as being characterised by chemical and spectroscopic techniques [1] [2]. This allowed the specific oxygen induced defects to be identified so their properties could then be calculated.

Here we will present calculations of the electronic structure of the defects, their effect on IR and UV-visible spectra and photoluminescence, and their effect on electron mobility via the trapping of charge.

5.2 Summary of experimental results

In the first experimental study, Speller and co-workers [1] selectively degraded PCBM with exposure to light and oxygen prior to device fabrication. The PCBM films were characterised with UV-vis absorption, XPS, photoluminescence (PL) and FTIR measurements.

These experimental results are given in Figure 5.2. The FTIR measurements for fresh PCBM and PCBM after exposure to light and oxygen show a peak appearing at $\approx 1750\text{cm}^{-1}$, which corresponds to an additional carbonyl. The large peak that appears in both spectra corresponds to the carbonyl in the PCBM sidechain. An epoxide would be expected at $\approx 900\text{ cm}^{-1}$ and it does not appear to be in the spectrum of the defected PCBM. However, this may be due to the sensitivity of the measurement. XPS measurements in the paper are consistent with C-O-C (epoxide) species, which supports the proposed mechanism.

The UV-vis spectrum shows a small decrease in the absorbance for PCBM films after photoaging and exposure to air, which indicates photobleaching of the film. The PL spectrum shows a red shift of the peak with increasing exposure, indicating the generation of intraband defect states that are radiatively coupled to ground states.

In the second experimental study, Lee and co-workers [2] systematically investigated the effect of introducing minor fractions (0.2 to 3.6%) of deliberately photo-oxidised PCBM on the transport and recombination mechanisms in OPV devices. They found a significant decrease in the power conversion efficiency (PCE) with increasing fraction of degraded PCBM. They also used space charge limited current (SCLC) measurements to find the mobility and trap density in devices containing an increasing fraction of degraded PCBM (see Figure 5.3).

The SCLC measurements show that the band mobility obtained by fitting drops by between one and three orders of magnitude when the fraction of degraded PCBM is increased from 0% to 3.6%. Note that the range of fitted parameters increases with degradation, due to the microstructural variations resulting from the degradation process.

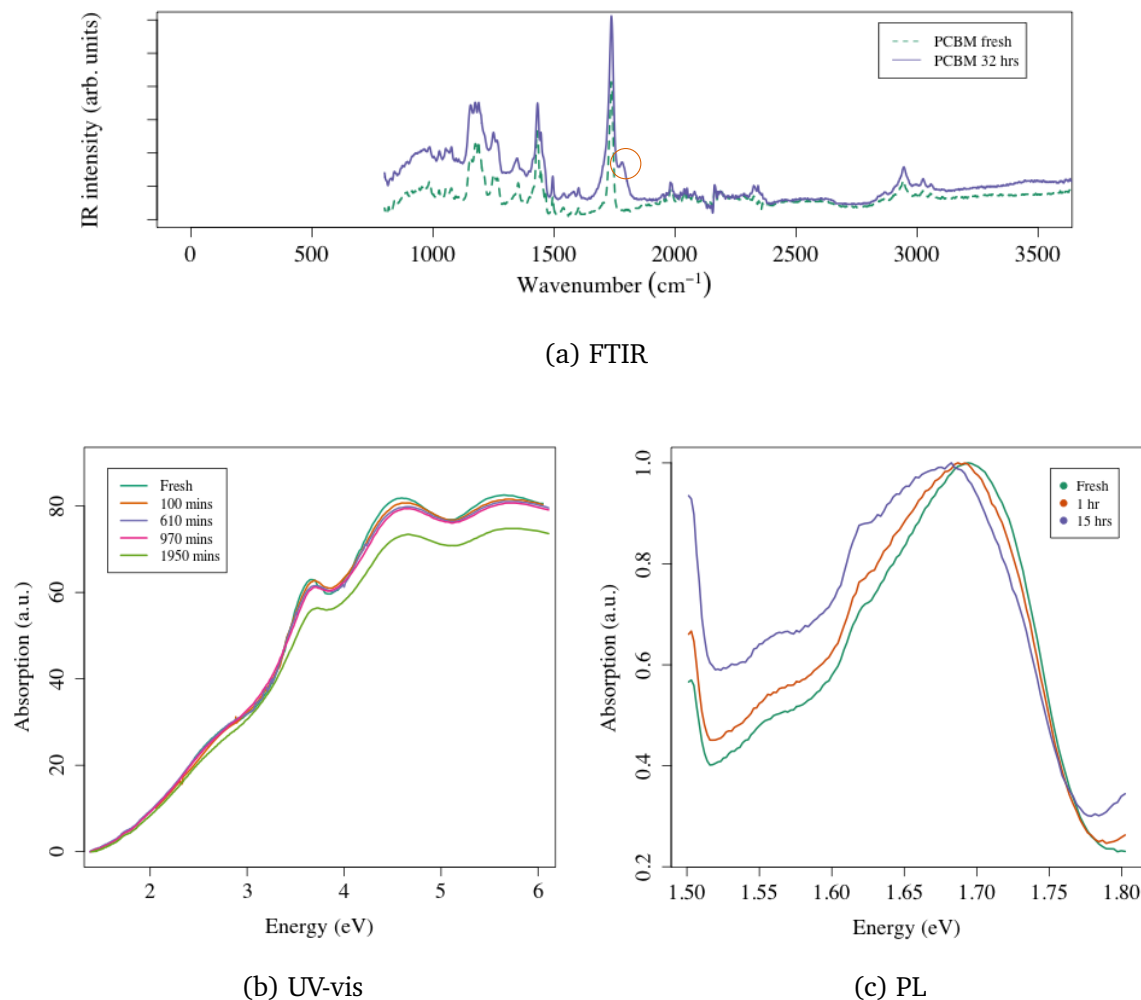


Figure 5.2: Experimental measurements by Emily Speller on PCBM before and after it was exposed to air and water.

5.3 Modelling and simulations

We performed simulations on PCBM without defects, as well as with epoxide, diol and carbonyl defects in different positions on the C60 cage. These were electronic structure calculations on the PCBM molecule, as well as a PCBM with different numbers of epoxide, diol and carbonyl defects. Since the position of the defects was not known, we performed calculations with the defects across every possible 6-6 carbon-carbon bond to obtain the total energy of the molecule. The total energy is a proxy for the likelihood of a particular defect forming, assuming that defect formation is thermodynamically (rather than kinetically) limited.

We performed a vibrational calculation to obtain the IR spectra of PCBM, along with PCBM containing one of each of the defects considered. For this, we calculated the spectrum for the most thermodynamically stable isomer of each defect type, identified from the total energy as above. In

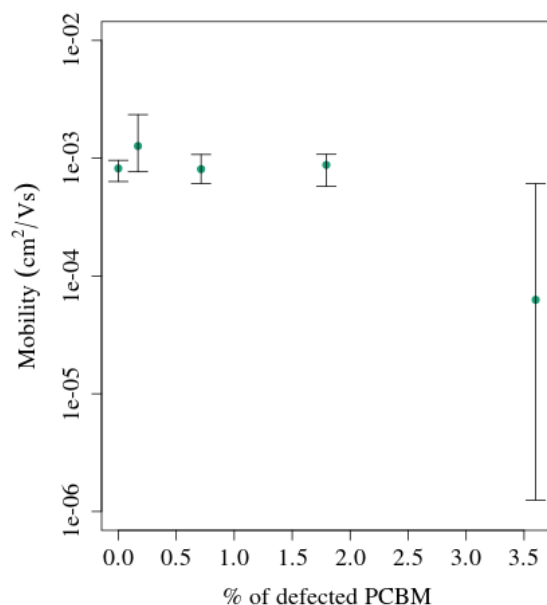


Figure 5.3: SCLC derived results from Jason Rohr on PCBM before and after it was exposed to air and water, showing electron “band” mobilities. The error bars indicate the maximum and minimum derived mobilities.

addition, we performed time-dependent density functional theory (TD-DFT) calculations to obtain excited state information. This was used to calculate the UV-visible absorption and photoluminescence (PL) spectra. As with the vibrational calculation, these were performed on the most thermodynamically stable isomer of each defect type.

These calculations allowed us to isolate the spectroscopic features of PCBM with different defects, and therefore suggest what the likely defects are, by comparing to experimental results from films containing oxidised PCBM. Next, we investigated the effect of different defects on the properties of the material, specifically the mobility. For this, we used structures obtained from coarse-grained molecular dynamics and transfer integrals that had been previously obtained (details in section 6.3.1 of chapter 6). We calculated the mobility in these assemblies with the Marcus equation, introducing "defects" into them by altering the LUMO levels which enter the Marcus equation via the energy difference term. We used a master equation approach to obtain a mobility from this set of rates. We compared the mobility with different proportions of epoxide, diol and carbonyl defects, based on the Boltzmann average LUMO level for these defects. We also investigated the effect of the trap depth on the mobility.

Here, we detail the simulation techniques and summarise the results to compare to experimental findings.

5.4 Electronic structure: HOMO and LUMO levels

We calculated the HOMO and LUMO levels of PCBM with epoxide, diol and carbonyl defects in different positions in every possible position across each 6-6 carbon bond, as well as with no defects.

First, we optimised the structure with the B3LYP functional and 6-31g* basis set. From this calculation, we obtained the total energy of the structure, which we used to find a Boltzmann average of the HOMO or LUMO values calculated with the defects in different positions. The Boltzmann average is defined as follows:

$$\langle A \rangle = \frac{\sum_i A_i e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}}, \quad (5.1)$$

where A_i is the HOMO or LUMO energy of the particular structure, and E_i is its total energy. It is assumed in this treatment that, for each defect group, different isomers occur in proportion to their thermodynamic probability. It should be noted here that performing these simulations on a single molecule in vacuum could bias which configurations are most thermodynamically stable, as interactions with other molecules in the bulk are not taken into account.

5.4.1 Methods

We used three different methods to calculate the HOMO and LUMO levels; they are detailed below.

- **Kohn-Sham orbitals**

Performing a single point energy calculation and taking the highest occupied Kohn-Sham orbital for the HOMO, and the first virtual Kohn-Sham orbital for the LUMO. In molecular systems, the Kohn-Sham HOMO has been shown to be a good estimate for the ionisation energy (Koopman's theorem [8]), but the LUMO with this method is not a good approximation for the electron affinity.

- **Delta-SCF method**

Performing total energy calculations for an N electron system, along with $N - 1$ and $N + 1$ electron systems. The difference between each of these compared to the N electron system

is the total energy upon adding (or removing) an electron, and is therefore the Electron Affinity or LUMO (Ionisation Energy or HOMO).

- **Kohn-Sham HOMO and TD-DFT for LUMO**

Taking the Kohn-Sham energy for the HOMO and adding the first excitation energy as calculated from TD-DFT for the LUMO.

5.4.2 Results

The results presented here are using the delta-SCF method. Although the absolute values of HOMO or LUMO levels vary, the difference in energy levels on adding a defect does not vary much between different methods. Appendix A.1 contains the average data for all of the methods as a comparison.

Figure 5.4 shows the range of HOMO and LUMO levels for each defect type in different positions on the cage compared to undefected PCBM. For every defect type, the LUMO is lowered, suggesting that all defects result in electron traps. This could negatively effect the mobility in devices that are degraded.

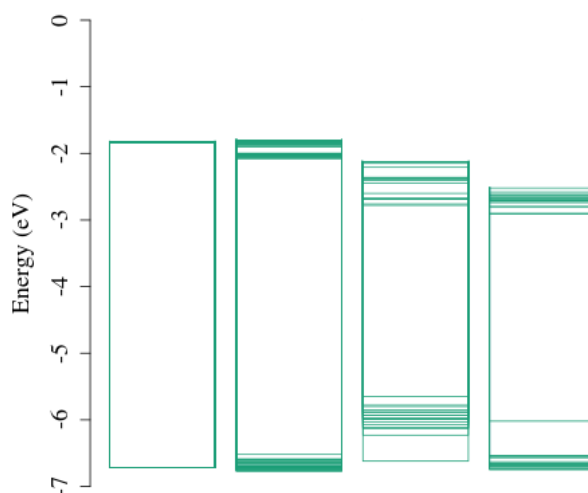


Figure 5.4: The HOMO and LUMO levels as calculated with the delta-SCF method for PCBM containing epoxide, diol and carbonyl defects in multiple positions on the cage.

5.5 IR spectra

The IR spectra were simulated with a vibrational calculation in *Gaussian* [9]. The defected structures with the lowest total energy were chosen for the simulation.

5.5.1 Vibrational calculation

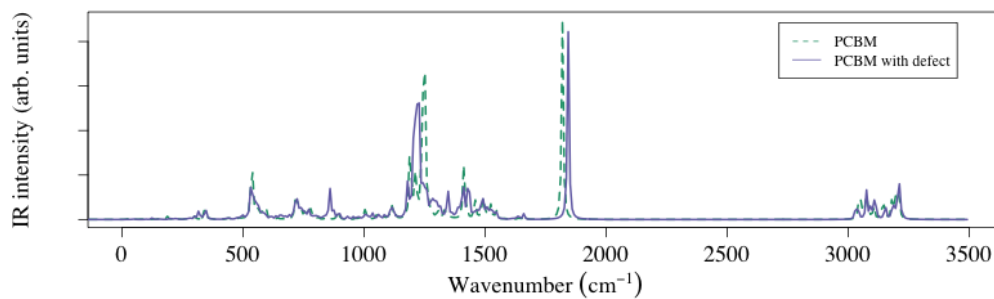
We first optimised the structures at the B3LYP level of theory with the 6-31g* basis set. We then applied a single point vibrational calculation (using the Gaussian keyword ‘freq’) to optimised structures at the same level of theory and using the same basis set. The calculation outputs the normal mode frequencies and corresponding reduced masses, force constants, IR intensities and Raman intensities.

The full details of the procedure used by *Gaussian* to obtain the normal mode frequencies, reduced masses, force constants and IR intensities are given in appendix A.2.

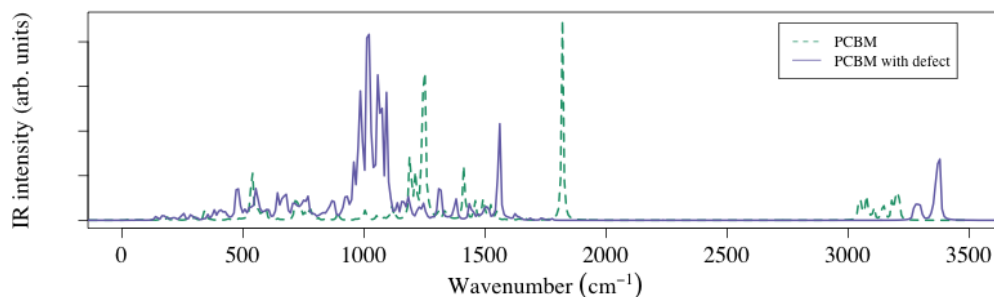
5.5.2 Results

The IR spectrum of PCBM, along with those of the most thermodynamically stable isomers of PCBM with epoxide, diol and carbonyl defects is given in Figure 5.5. We compared these IR spectra to the experimental IR spectra obtained by our collaborators in an attempt to determine the type of defects that formed in the degraded PCBM films.

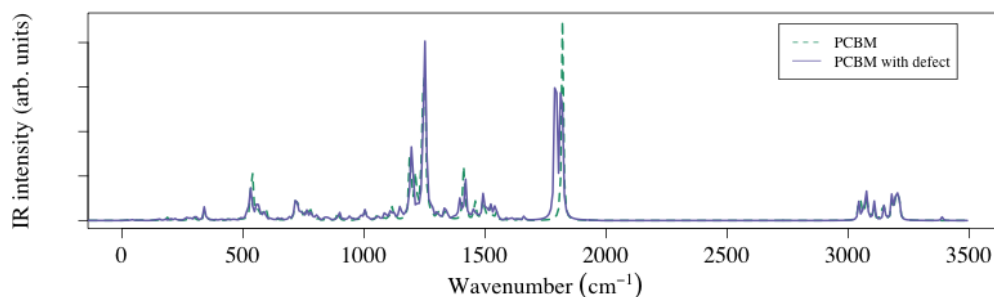
The epoxide defect corresponds to the small peak at $\approx 900\text{ cm}^{-1}$ in Figure 5.5a. The peaks associated with an alcohol group can be seen in the diol spectrum: these are the O-H stretch at $\approx 3500\text{ cm}^{-1}$ and the C-O stretch at $\approx 1000\text{ cm}^{-1}$. In experiments, the most visible defect was the carbonyl defect, which corresponds to a peak at $\approx 1780\text{ cm}^{-1}$. This can be seen in Figure 5.5c, alongside another peak very close to this due to the carbonyl that exists in the PCBM sidechain. From the experimental FTIR spectra, there appears to be no evidence of diol or epoxide defects. However, these peaks could be small in relation to larger peaks so much harder to detect. In particular, the peak associated with the epoxide defect is very small so is likely to be hard to detect in experiments.



(a) Epoxide defect



(b) Diol defect



(c) Carbonyl defect

Figure 5.5: IR spectra of PCBM with (a) epoxide, (b) diol and (c) carbonyl defects, in comparison with the IR spectrum of pristine PCBM in each case.

5.6 UV-vis and PL spectra

We calculated the excited state spectrum of PCBM along with PCBM containing epoxide, diol and carbonyl effects with time-dependent DFT (TD-DFT) calculations. From the transition energies and oscillator strengths of these, we calculated the UV-vis absorption and PL spectra.

5.6.1 TD-DFT

TD-DFT simulations were performed to obtain information about the excited states. This was then used to calculate the UV-vis absorbance and photoluminescence (PL) spectra. The TD-DFT calculation was done at the B3LYP level of theory with the 6-31g* basis set, with the number of transitions chosen to be 100.

The oscillator strengths, f_i , of all of the transitions between the chosen excited states and their corresponding wavelengths are outputted from the simulation, and these are used to calculate spectrum of the decadic extinction coefficient ε_d . This spectrum is the UV-vis spectrum and is defined as:

$$\varepsilon_d(E) = \frac{n}{\sigma} \sum_{i=1}^n (f_i D(E, E_i)), \quad (5.2)$$

where ε_d is given in $\text{L mol}^{-1} \text{cm}^{-1}$, n is the number of transitions, σ is the standard deviation of the energies (taken as 0.4 eV), E_i is the energy corresponding to the electronic excitation of interest, and $D(E, E_i)$ is a lineshape function.

Taking the lineshape function to be a Gaussian of width σ :

$$D(E, E_i) = \exp \left[- \left(\frac{E - E_i}{\sigma} \right)^2 \right]. \quad (5.3)$$

To approximate the PL spectra we use the principle of detailed balance to relate emission to absorption via the Roosbroeck-Shockley equation [10]. The PL spectra is then proportional to the UV vis absorption spectrum, weighted by E^2 and a Boltzmann factor:

$$\varepsilon(E) = \frac{n}{\sigma} \sum_{i=1}^n \left(f_i D(E, E_i) E_i^2 \exp \left(- \frac{E_i}{kT} \right) \right). \quad (5.4)$$

Note that this treatment of absorption and PL neglects the role of vibronic states.

5.6.2 Results

The PL spectrum shows red-shifting with increasing oxidation of PCBM, as was seen in the experimental PL with greater exposure time. This is consistent with the formation of electron traps. It should be noted that since these simulations were performed on a single molecule in vacuum, where vibronic structure is neglected, we would not expect to show quantitatively the same red shift as experiments performed on films.

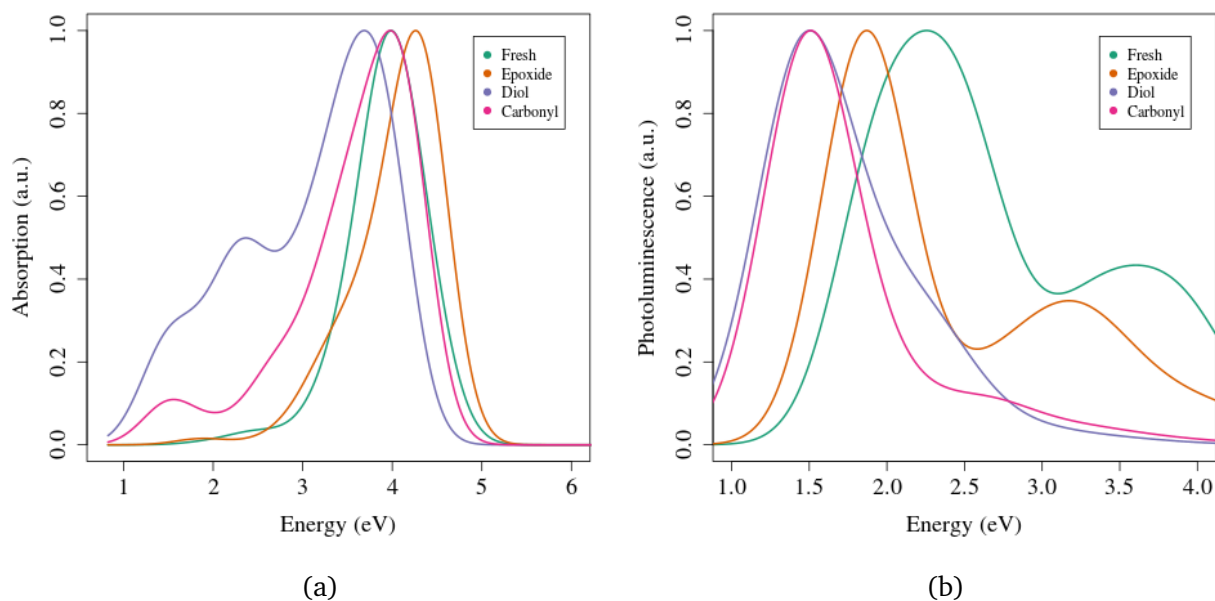


Figure 5.6: Normalised (a) UV-vis and (b) PL spectra of PCBM, along with PCBM with epoxide, diol and carbonyl defects.

5.7 Mobility

In Chapter 6, we investigate the spatial extent of charge states in PCBM and other fullerene adducts. These results suggest that in a system with no energetic disorder, it is likely that charge states would be delocalised over multiple PCBM molecules and a Marcus hopping model (section 2.6.2) would not be valid. However, the effect of defects is to deepen the LUMO energies, which effectively introduces some energetic disorder. The result of this would be charges being trapped and further localisation. Therefore, for this study on defects in PCBM, we assume that the PCBM molecules are weakly coupled and Marcus theory is valid. This gives us one limit of the mobility in terms of the rates of escaping traps.

We assume that the only difference between a PCBM molecule and a PCBM molecule containing

a defect is the LUMO energy, which depends on the type of defect. We assume the transfer integrals are isotropic, depending only on distance with a separation-dependent exponential, $J = J_0 \exp(-\beta d)$, referring to work by Steiner *et al.* [11]. This approximation is not necessarily appropriate for transfer integrals between different molecules, and we introduce a method to tackle this in chapter 7.

5.7.1 Method

We use coarse-grained molecular dynamics generated assemblies of 1000 PCBM molecules as the initial structures. This is based on work by Steiner *et al.* and more detail of the method used to generate these assemblies is given in section 6.3.1. These give us the separations (d) between each molecule with every other, and therefore the electronic couplings between all molecules. We calculate the reorganisation energy of PCBM with the 4-point method and assume it is the same for pristine and defected PCBM.

Initially, we set all of the on-site energies to the LUMO energy of PCBM (-3.7 eV). We then reduce the on-site energy of a random selection of a proportion of these molecules by an amount determined by the defect. We take the change in LUMO energy from our earlier calculations of LUMO energy for a PCBM molecule with a defect, and choose the value it is reduced by for a specific defect from a Boltzmann distribution from the complete set of calculated values.

We then apply a field of 10000 V cm^{-1} via the $\Delta E_{ij} = \varepsilon_i - \varepsilon_j - q\vec{F} \cdot \vec{r}_{ij}$ term in the Marcus equation as in section 4.3.3, and get a matrix of rates. We use the Master equation approach to get a mobility from these rates (section 3.5). We apply the field at 10 degree intervals in each of the 3 orthogonal planes to get an average field dependent mobility.

5.7.2 Results

The average field dependent mobility versus the proportion of different defect types is given in Figure 5.7a. It shows the significant effect of defects that result in a large change in the LUMO energy of a PCBM molecule. SCLC experimental measurements suggested that mobility doesn't decrease much with up to 2% defected PCBM, but could fall by up to three orders of magnitude with 3.6% defected PCBM (Figure 5.3). The large range of SCLC mobilities with this fraction of defected PCBM reflects the film irregularities resulting from defected PCBM being introduced into the pure PCBM.

We also investigated the mobility with the trap depth of only one defect (Figure 5.7b). It shows a sharp fall off at trap depths greater than 0.2 eV. However, it should be noted that the nature of the Master equation approach means that the effect of single defects is exaggerated, due to the fact that it will be sampled many times as the sum is over all sites with every other.

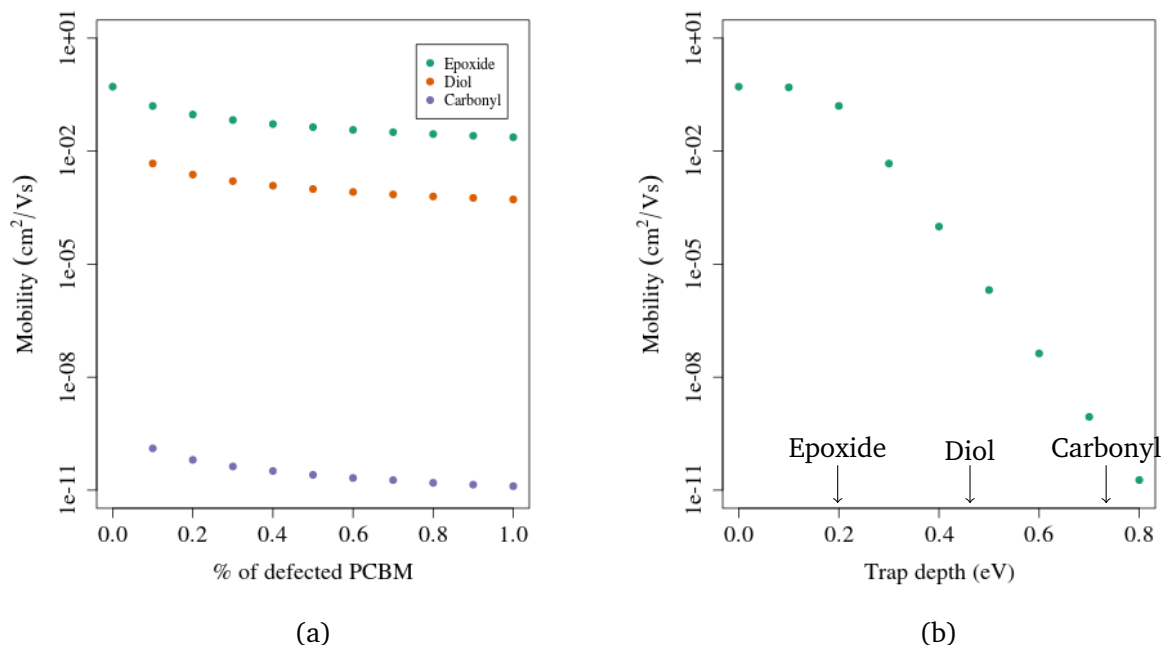


Figure 5.7: (a) Mobility versus proportion of defected PCBM for epoxide, diol and carbonyl defects. (b) Mobility versus trap depth for one defect (0.1%), with the Boltzmann average difference in LUMO for each defect indicated.

5.8 Conclusions

We performed simulations to complement experimental work to determine the types of defect that can form in PCBM, as well as the potential effects on optical properties of devices. We simulated PCBM along with PCBM containing epoxide, diol and carbonyl defects. based on an oxidation mechanism proposed by Xiao *et al.* [7].

We showed that all defect types tended to lower the LUMO level. This would create electron traps that could affect the mobility of the device, with carbonyl defects having a larger effect than diol and epoxide defects. The experimental UV-vis and PL spectra were red-shifted which is also consistent with the existence of electron traps. Our simulated UV-vis and PL spectra showed PCBM with defects red-shifting the spectra compared to PCBM with no defects, and with the carbonyl

and diol defects causing a larger shift than epoxide defects.

Our simulated IR spectra showed where peaks associated with addition epoxide and carbonyl defects would form. The experimental FTIR spectra showed a peak associated with a carbonyl defect (in addition to the carbonyl group in the PCBM sidechain). Although there was no peak visible for an epoxide defect, XPS measurements in the paper indicated that these were present. Our simulated spectra showed that the peak associated with an epoxide is small compared to that associated with a carbonyl so the FTIR may not have had the sensitivity to detect this. The likely oxidation mechanism would suggest that a mixture of epoxide, diol and carbonyl defects would be present in PCBM films after exposure to light and oxygen.

We investigated the effect of having defected PCBM molecules on the mobility of the films. SCLC measurements suggested a decrease in mobility of up to three orders of magnitude with 3.6% defected PCBM. Our simulations on coarse-grained assemblies of PCBM molecules with LUMO levels corresponding to PCBM with different defects suggest that even <1% of defected PCBM decreases the mobility by orders of magnitude, with the mobility falling exponentially with trap depth. However, as noted previously, the master equation approach used to calculate the mobility would tend to overestimate the effect of individual defected molecules.

Our results show that PCBM exposed to light and oxygen can be oxidised with epoxide and carbonyl defects forming in PCBM molecules. The result is electron traps forming, which would tend negatively affect the mobility in the defected films.

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6

Polaron states in organic systems

We develop a method to model polaron formation in organic semiconductors. Our model is based on treating each site separately as being surrounded by a continuous dielectric, and allowing its energy to be perturbed by the electron density on that site. We show how it can be applied to large, disordered assemblies of fullerene molecules to find the density of states and spatial extent of charge states. We explore this polaron formation as well as the effects of energetic disorder and electronic coupling disorder in assemblies of fullerene adducts. We show that the lowest energy states in C60 and PCBM are not localised to single molecules when there is no energetic disorder, and as such a Marcus hopping model would not be valid in this case.

6.1 Introduction

The word polaron comes from **polar** lattice and **electron**, because a polaron is a quasi-particle including these two components. When an excess charge carrier is in a material, the surrounding molecules will tend to distort in a way that lowers the energy of the electron (or hole). A potential well is formed. The electron along with the distorted surroundings is the polaron, and modelling this is important for understanding the charge states in the system [1]. We aim to model polarons in disordered organic semiconductors in a computationally efficient way, considering the specific

chemical structure, bulk packing features and different types of disorder.

Previously, polarons in OSCs have been modelled with a Holstein-Peierls model for the interaction between electrons and phonons [2], or with an SSH Hamiltonian for a 1D chain [3]. Polarons have also been modelled in PCBM with constrained density functional theory (CDFT) and Langevin Molecular Dynamics [4]. In disordered systems, they have been modelled with a modified Marcus rate equation [5]. However, these methods can be computationally expensive and limited to smaller system sizes.

In section 2.5, we outlined polaron theory. In this chapter, we introduce our polaron model and illustrate it in a simple 1D system. We then show how it can be applied to relatively large assemblies (1000+ molecules) of disordered molecular organic semiconductors (fullerene molecules). We present results for the density of states and spatial extent of charge states for different levels of disorder and polaron formation in these assemblies.

6.2 Polaron model

We develop a model of polaron formation within a tight-binding framework. The excess electron is described with a tight-binding Hamiltonian in the basis of the molecular orbitals (LUMOs) of the molecules. Similarly, an excess hole would be described by a Hamiltonian in the basis of the HOMOs.

The molecular-basis tight-binding Hamiltonian is given by:

$$\hat{H}_{TB} = \begin{pmatrix} \epsilon_1 & J_{1,2} & \cdots & \cdots & J_{1,N} \\ J_{2,1} & \epsilon_2 & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & J_{N-1,N} \\ J_{N,1} & \cdots & \cdots & J_{N,N-1} & \epsilon_N \end{pmatrix} \quad (6.1)$$

where ϵ_i is the energy of the i^{th} site and $J_{i,j}$ is the electronic coupling (transfer integral) between the i^{th} and j^{th} sites. These site energies and transfer integrals contain all chemical and packing

information about the modelled system. We solve $\hat{H}\psi = E\psi$ to obtain the eigenvalues E that form the density of states (DOS) for the system, and the eigenvectors ψ_n , where $|\psi_n|^2$ gives the occupation of the n^{th} state in the charge localised diabatic basis of the sites.

We calculate the inverse participation ratio (IPR) for the n^{th} state, defined by $IPR^{(n)} = 1/\sum_i |\psi_i^{(n)}|^4$. This varies from 1 for an electron localised to one site, to N for an electron density delocalised over all N sites. The tight-binding Hamiltonian allows us to also explore energetic (diagonal) and electronic coupling (off-diagonal) disorder. We can choose how to parametrise the matrix elements.

In our polaron model, we treat each site as being surrounded by a continuous dielectric and allow its site energy to deepen in response to electron density. We solve the tight-binding Hamiltonian to obtain the occupation of each site with $|\psi|^2$, and deepen the energy of each site in proportion to the electron density of each site. We repeat this process until convergence of the energy (i.e. when the energy does not change more than some small value, δE). The proportionality constant is W_p , the depth of the potential well for a fully localised polaron. This fully localised polaron is on the order of a lattice constant so we calculate W_p with small polaron theory (see section 2.5). We also note that the kinetic energy term present in the large polaron model is not required since it is already included within the tight-binding Hamiltonian via the off-diagonal elements. The self-consistent process is illustrated in Figure 6.1.

The polaron formation energy W_p in the small polaron formulation is given by

$$W_p = -\frac{q^2}{8\pi\epsilon_0 r_p} \left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon_{stat}} \right), \quad (6.2)$$

where ϵ_0 is the vacuum permittivity, ϵ_{opt} is the optical dielectric constant, ϵ_{stat} is the static dielectric constant, q is the charge on an electron, and r_p is the radius of the polaron. In our model, since the polaron is treated in segments per site, r_p is given by the radius of the molecule.

The following assumptions were made in constructing this model:

- Each site is treated independently as a point charge in a hollow sphere of radius r_p , in a continuum dielectric.
- Correlations between multiple sites (mediated by the polarisation field) are ignored.

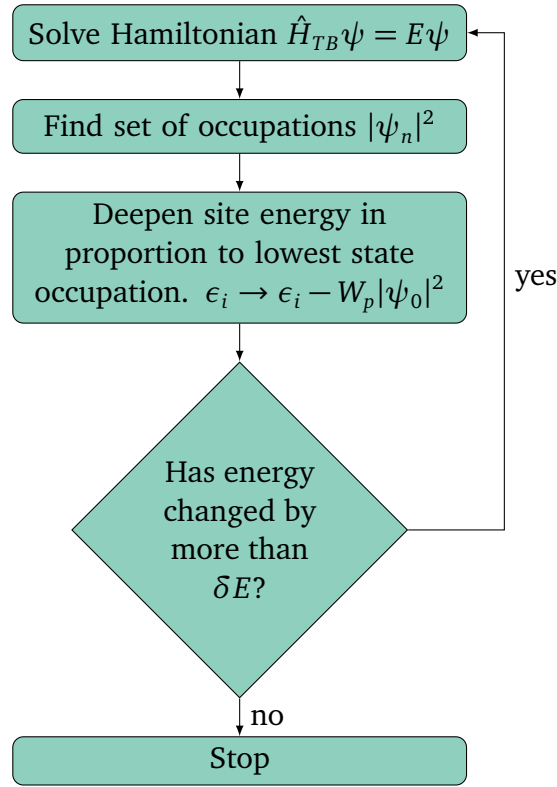


Figure 6.1: Flowchart showing method for including self-consistent polaron formation in TB code.

- A tight-binding model of the electronic structure is used, so there is no electron-electron correlation.
- The electron density is solved for self-consistently. This assumes that the charge is localised for a long period of time (i.e. the kinetic energy of the polaron wavepacket is low enough).

6.2.1 Polarons on a 1D chain

To illustrate this method, we consider a simple one-dimensional 100 unit chain of sites of energy E_0 , each coupled to their nearest neighbours with an electronic coupling of J_0 . Figure 6.2(a) shows the occupation (solid line) and energy (dashed line) of each site in this one-dimensional chain, after a given number of iterations through the algorithm. Figure (b) shows the density of states for the system before and after polaron formation, with the low energy localised state circled. The DOS have the familiar form for a 1D system and the Van Hove singularities can be seen [6].

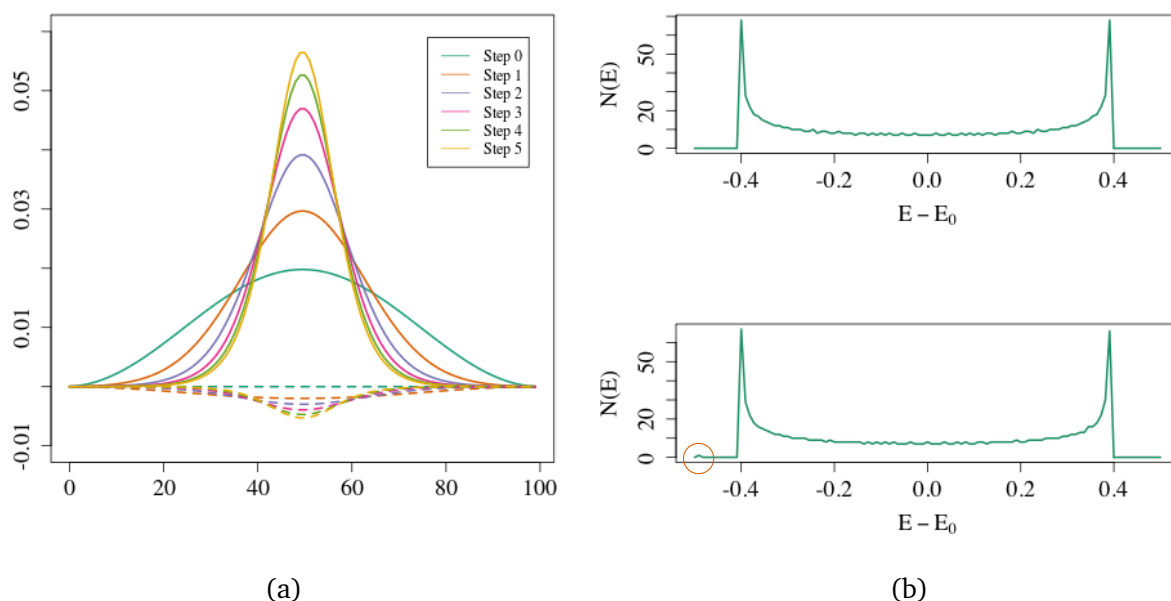


Figure 6.2: Tight-binding polaron method applied to a 1D system for a simple case. (a) The occupation (solid line) and energy (dashed line) of each site after a given number of iterations through the self-consistent algorithm. (b) The density of states (DOS) for the system with (bottom) and without (top) polaron formation.

6.3 Application to fullerene assemblies

We now apply our methods to fullerene assemblies: C60, PCBM ([6,6]- phenyl- C61- butyric acid methyl ester), along with its known and hypothetical higher adducts (bis-, tris-, tetrakis-, pentakis- and hexakis-PCBM). Fullerenes are disordered molecular semiconductors that are important for applications such as organic photovoltaics (OPVs). They are a convenient system to study since the transfer integrals (J_{ij}) between molecules can be well approximated by assuming an isotropic radial dependence of J_{ij} [7]. Populating the tight-binding Hamiltonian is straightforward, by pair separation of molecules in the assemblies. The tight-binding model allows us to empirically explore energetic (diagonal) disorder, while the different adducts allow us to explore configurational (off-diagonal) disorder.

C60 and PCBM are well-studied in terms of their charge transport characteristics. Although a Marcus hopping model is often used to model charge transport in OSCs, it is not necessarily valid for C60 and PCBM. Cheung and Troisi (2010) [8] used molecular dynamics combined with quantum chemical calculations and tight-binding to study the morphology and charge localisation. They found that the weak coupling approximation was not valid for assemblies of PCBM molecules. Gajdos *et al.* (2013) [9] used density functional theory (DFT) to calculate parameters for charge

transport and found that in crystalline C60 and PCBM the Marcus picture of one electron hopping between weakly-coupled sites does not apply because charges would likely be delocalised over several sites. Neither of these approaches take polaron formation or energetic disorder into account.

In this chapter, we build on previous work to generate fullerene assemblies using coarse-grained molecular dynamics [7]. We describe an excess electron in the system with a tight-binding Hamiltonian in the basis of the molecular orbitals (LUMOs, since we are interested in electron transport). We infer transfer integrals assuming isotropic spatial dependence of J , fitted from explicit calculation of the transfer integral at increasing separation. We solve this Hamiltonian to obtain the eigenvalues (E), which form a density of states (DOS), and eigenvectors ψ , where $|\psi|^2$ gives the occupations in the basis of the sites. We calculate the IPR as a metric of the spatial extent of the charge states.

We model polarons in this system within the tight-binding framework by treating the surroundings of each site as a continuous dielectric and deepening the site energy in proportion to the amount of electron density of the site. We do this self-consistently until convergence of the energy. This gives a set of polaron states of the system.

The energy of polaron formation - that is the depth of the well - depends on both ionic and electronic contributions. In a continuum model, these are included via the static and optical dielectric constants of the molecule (see equation 6.2). Here, we calculate the static and optical dielectric constants with electronic structure methods and find the depth of the potential well formed.

We explore both the density of states (DOS) and spatial extent of charge states in C60 and fullerene multiadducts. For C60, PCBM and bis-PCBM we also calculate their static and optical dielectric constants to investigate the effect of polaron formation on the system, and the nature of the polaron state.

6.3.1 Methodology

Fullerene assemblies from coarse-grained molecular dynamics

We use the coarse-grained force-field developed by Steiner *et al.* (2014) [7]. This is based on the force-field for C60 developed by Girifalco (2000) [10]. Steiner *et al.* investigated PCBM, along with bis- and tris-PCBM. Changing the side groups varies the LUMO level and so affects the V_{OC} of a photovoltaic device. We extend the investigation to tetrakis-, pentakis- and hexakis-PCBM. Including structures with additional side chains allows us to further investigate the effect of configurational disorder, including the effect on the Anderson transition.

The force-field models the C60 cage as a pseudo-atom and side chains as additional pseudo-atoms. The pseudo-atoms interact via a Lennard-Jones potential. The interaction energy for the C60 cage is directly from the Girifalco potential, and the side chains are assumed to have that interaction energy scaled by their mass. The bond between the C60 cage and the side chain is assumed to be stiff, leaving two free parameters: the minimum distance between a side chain and another molecule, and the C60- side chain bond length. In the work by Steiner *et al.*, these parameters were determined by a comparison of radial distribution functions of atomistic and coarse-grained simulations.

There are many potential positions for side chains when there is more than one, so different isomers exist. We assumed 6 possible positions for a side chain: top, bottom, left, right, front and back, shown in Figure 6.3. There are other possibilities, but we chose these to avoid steric hindrance of the side chains. In the cases of multiple isomers, we chose for detailed attention the isomer with sidechains closer to each other. Single point energy calculations on optimised multi-adduct structures showed that these were always the lowest energy configurations.

We simulate assemblies of $N = 1000$ coarse-grained molecules using the *Gromacs* molecular dynamics package [11] [12]. First, sparsely packed unit cells are energy minimised with a steepest descent algorithm, then equilibrated with NVT and NPT simulations, using a timestep of 5 fs and 200,000 steps (an equilibration of 1ns). Next, we use a process of ‘simulated annealing’ to generate multiple uncorrelated assemblies for each adduct. This involves heating the assemblies up to 1500K and cooling to 300K in successive 1ns cycles. We use the same 5 fs timestep and have 20,000,000 steps, which results in 100 simulated annealing cycles. Snapshots extracted at 300K give 100 uncorrelated assemblies of 1000 molecules for each adduct.

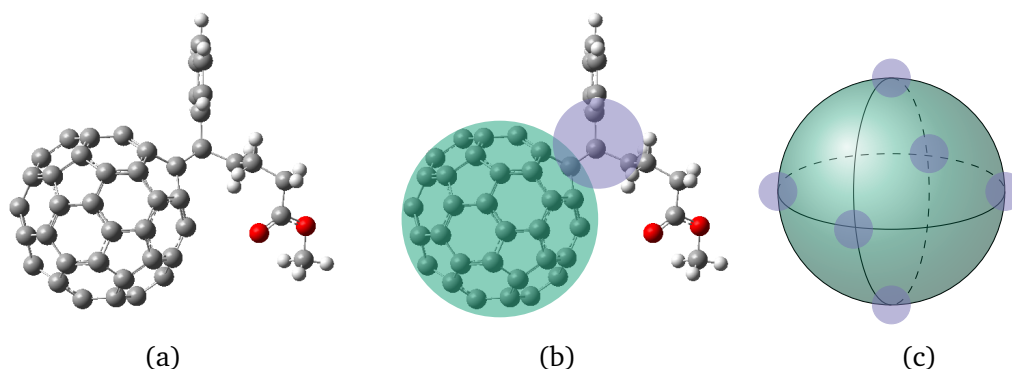


Figure 6.3: (a) PCBM molecule; (b) The two beads used to coarse-grain the PCBM superimposed on the molecular structure; (c) Possible sites for side chains for coarse-grained fullerene multiadducts.

Example snapshots at 300K for each adduct are shown in Figure 6.4. It can be seen that C₆₀ has crystalline ordering, and the coordination numbers in Table 6.1 indicate that this is a face centred cubic (fcc) configuration. Our value of 11.96 for C₆₀ is close to the expected value of 12, which comes from the fact that the molecules form an fcc lattice [13].

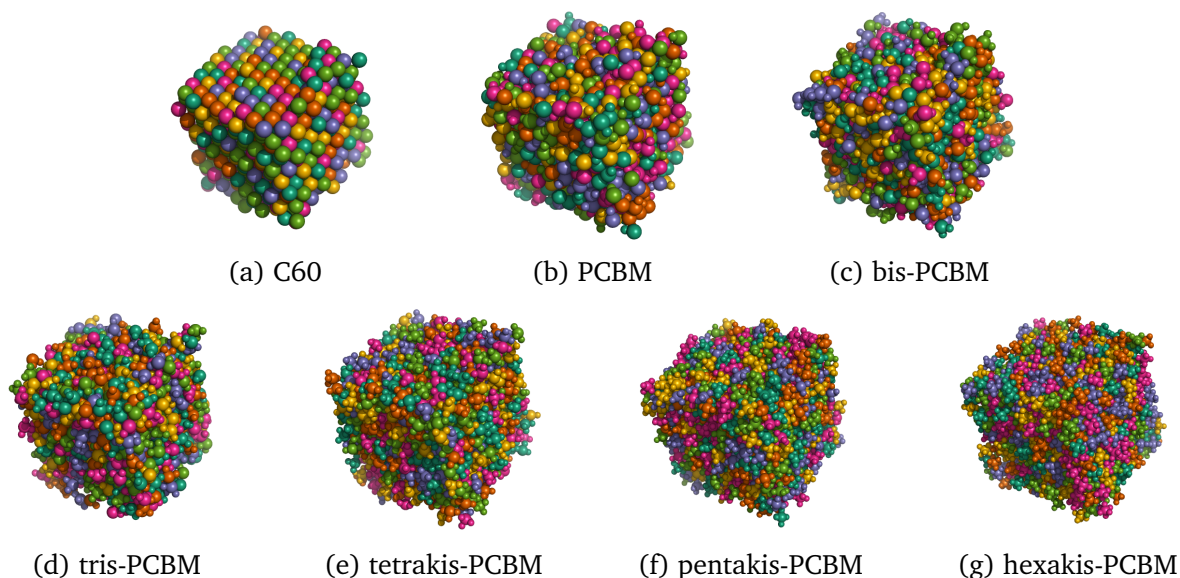


Figure 6.4: Example snapshots at 300K of assemblies of 1000 molecules for each adduct from coarse-grained molecular dynamics

Tight-binding model

As in section 3.3.3, the tight-binding Hamiltonian used to describe an excess electron in a system is defined by:

$$\hat{H}_{TB} = \sum_m \epsilon_m a_m^\dagger a_m + \sum_{m \neq n} J_{mn} a_m^\dagger a_n, \quad (6.3)$$

Table 6.1: Coordination numbers for C60 and each fullerene adduct.

Adduct	Coordination number
C60	11.96
PCBM	8.09
bis-PCBM	5.59
tris-PCBM	4.69
tetrakis-PCBM	2.59
pentakis-PCBM	2.57
hexakis-PCBM	2.13

where a_m^+ and a_m are the creation and annihilation operators, respectively, for a charge carrier on molecular site m , ϵ_m is the charge carrier site energy, and J_{mn} is the electronic coupling (transfer integral) between sites m and n . This tight-binding Hamiltonian is in the basis of molecular orbitals rather than atomic orbitals, and has one molecular orbital per site.

For the fullerene assemblies, we are interested in electron transport, so the site energies are taken as the LUMOs of the molecules. This uses the one-electron approximation, i.e. the diabatic states are associated with localised orthogonal monomer orbitals. These are calculated with a single point energy hybrid DFT calculation to get the Kohn-Sham HOMO energy, which is added to the energy of the first excited state calculated with TD-DFT to obtain the LUMO energy, as in section 5.4. In our tight-binding model, each molecule has a single non-degenerate LUMO. Degeneracy of LUMO energies and closest unoccupied orbitals in a single molecule is not considered.

Since fullerenes can be assumed to have isotropic coupling, the transfer integrals (J_{ij}) are approximated with a separation-dependent exponential, $J_{ij} = J_0 \exp(-\beta d_{ij})$, where d_{ij} is the separation between sites i and j [7]. The two parameters β and J_0 were fitted from projective method [14] hybrid DFT calculations on fullerene molecules as a function of separation by Steiner *et al.*. This fit allows a computationally efficient way to calculate the transfer integrals with only structural (molecule position) information required. Periodic boundary conditions are applied to the locations of molecules using the minimum image convention.

Solving the Hamiltonian $\hat{H}\psi = E\psi$ yields a set of energy eigenvalues (E), which form the density of states (DOS) in the one-orbital basis, as well as the electronic density in this basis with $|\psi|^2$ and the IPR.

Anderson localisation

Anderson localisation (section 2.4.1) is the process by which disorder induces localisation of charge states.

We explore energetic disorder in these systems by spreading the site energies (diagonal elements of the tight-binding Hamiltonian) with a Gaussian distribution of width σ , as is assumed in the Gaussian disorder model (GDM) outlined in section 2.4. We vary this parameter and observe the effect on the density of states and spatial extent of the charge states. Off-diagonal disorder, i.e. disorder in the electronic couplings, is explored by considering multiple adducts. Additional sidechains on the C60 cage induce configurational disorder in the assemblies, and therefore in the electronic couplings, which in their parameterised form depend only on separation of molecules.

Percolation threshold

A simple view of charge localised (non-conducting) assemblies is one in which the transfer integral must exceed a critical value in order to conduct. We calculate the percolation threshold in each of the adducts by examining the connectivity through the transfer integrals (J) with different cut-offs for J . For a site we find how many sites it is connected to within the cutoff, then find how many sites these are connected to, and continue until all sites in the cluster have been found. This identifies the number of molecules that are in a cluster coupled by some J . We do this for every cluster and then plot the maximum cluster size versus J_{cutoff} . The point at which this diverges is the percolation threshold. Figure 6.5 illustrates this process.

A related metric is the coordination number, since our electronic couplings only depend on the separation of molecules. This is the number of molecules within a distance cut-off, usually chosen to include the nearest neighbour peak in the radial distribution function. We find the coordination number for each adduct, using a Gromacs tool [11] [12] up to a distance of $1nm$, which is the lattice constant in the C60 crystal.

Polaron formation

We apply the self-consistent polaron model to the fullerene assemblies within the tight-binding framework of section 6.3.1. As outlined in section 6.2, we solve the tight-binding Hamiltonian to get the occupation of each site and deepen each site energy in proportion to this, repeating the process self-consistently until the energy converges.

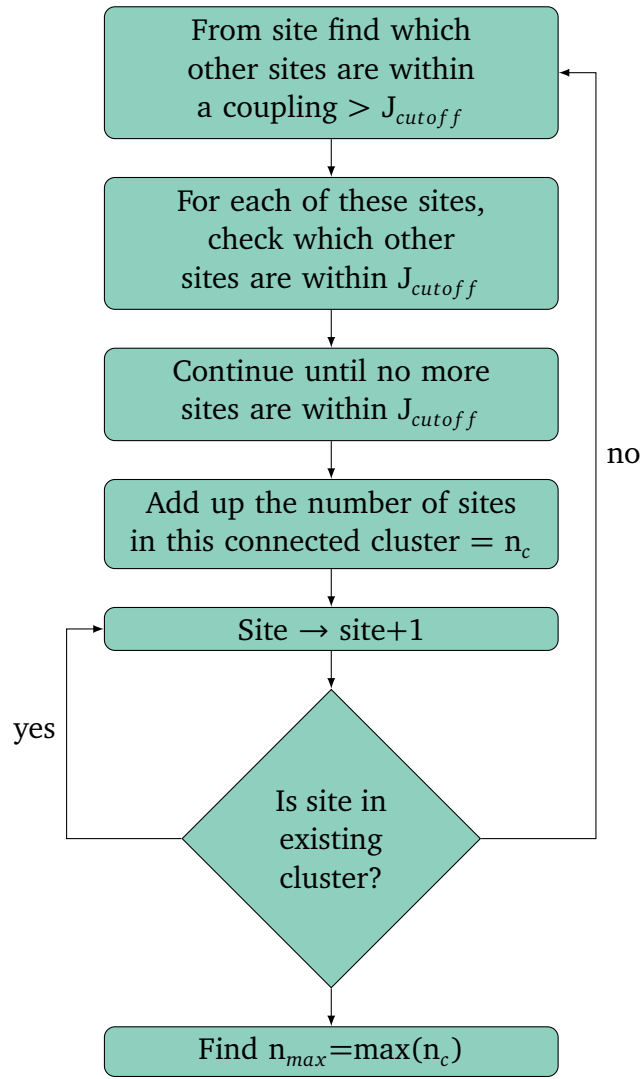


Figure 6.5: Flowchart showing method for calculating percolation threshold. Procedure is undertaken for different values of J_{cutoff} and the max cluster size is plotted against J_{cutoff}

To calculate the amount by which the site energies are perturbed by, we consider a polaron of charge $1q$ completely localised to a single site and calculate the depth of this potential well (W_p), treating the surroundings as a continuous dielectric. We then scale this value by the proportion of the electron density that is on each site, and deepen the site energy by this amount. This means that we are treating each part of the polaron independently, i.e. there is no correlation in the polarisation.

Now, we consider the proportionality constant W_p , which is the polaron formation energy or the depth of the potential well. The underlying theory of polarons is discussed in section 2.5. For our model, we do not need to consider the kinetic energy of the electron as a result of localisation (as in the large polaron), since this is already included in the tight-binding model

through the off-diagonal elements of the Hamiltonian. From a continuum approximation, the polaron localisation energy for a small polaron also given in equation 6.2 is

$$W_p = -\frac{e^2}{8\pi\epsilon_0 r_p} \left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon_{stat}} \right), \quad (6.4)$$

where r_p is the polaron radius, ϵ_{stat} is the static dielectric constant and ϵ_{opt} is the optical dielectric constant.

We treat the assembly around each site as a continuous dielectric, and consider the polaron in parts as it relates to each molecule. Assuming the electron is completely localised to one molecule, and therefore choosing an appropriate value of $r_p = 10 \text{ \AA}$, we calculate the polaron localisation energy for a polaron of this size. The other parameters required are the optical and static dielectric constants, ϵ_{opt} and ϵ_{stat} .

Calculation of ϵ_{opt}

The microscopic origin of the static and optical dielectric constants is outlined in section 2.3. In order to calculate the optical dielectric constant, we use the fact that it relates to the change in the macroscopic polarisation, $\mathbf{P}$, due to an electric field $\mathbf{E}$ with

$$\epsilon_{ij}^{opt} = \delta_{ij} + \frac{4\pi}{\epsilon_0} \frac{\partial P_i}{\partial E_j}. \quad (6.5)$$

We calculate it with Density Functional Perturbation Theory (DFPT) using the VASP plane wave electronic structure simulation package [15] [16]. The method is based on original work by Baroni and Resta (1986) [17], which is detailed in appendix A.3 [18].

Calculation of ϵ_{stat}

The static dielectric constant can also be obtained with DFPT, but it is a very computationally expensive process. Therefore, we obtain it with the Lorentz oscillator model outlined in section 2.3. This means we are directly considering the normal modes of the molecules that physically result in polaron formation. This gives the static dielectric constant as

$$\epsilon_{stat} = \epsilon_{opt} + \sum_j \frac{f_j \omega_p^2}{\omega_{0j}^2}, \quad (6.6)$$

where f_j is the oscillator strength of the j^{th} mode, ω_0 is the resonance frequency of that mode, and ω_p is the plasma frequency defined by

$$\omega_p = \sqrt{\frac{Ne^2}{\epsilon_0 m_e}}, \quad (6.7)$$

where N is the density of oscillators, e is the charge on an electron, ϵ_0 is the vacuum permittivity and m_e is the reduced mass. The sum is over all infrared active modes, since these are the modes that are associated with a change in dipole moment, and therefore an interaction with electrons. To evaluate this quantity, we must calculate the frequency and oscillator strengths of the vibrational modes of the molecule, which we do with *Gaussian* [19].

We first optimise the molecule at the B3LYP level of theory with the 6-31g* basis set. We then run a single point ‘freq’ calculation on the optimised molecule at the same level of theory with the same basis set. This yields the frequency and absorption intensity of each of the IR active modes. To convert the IR absorption intensity to an oscillator strength, we first express the oscillator strength in terms of the absorption cross-section:

$$f = \frac{2}{3} \frac{m_e \epsilon_0 n c}{4 \pi q^2 \hbar} \int \sigma_a d(\hbar \omega) \quad (6.8)$$

where n is the refractive index, c is the speed of light, q is the charge of an electron, ϵ_0 is the permittivity of free space, and m_e is the reduced mass. To get a result which we can directly relate to the *Gaussian* output, we substitute for the decadic extinction coefficient, $\epsilon_d = \log_{10} e \frac{N_A}{1000} \sigma_a$,

$$f = \frac{1}{6\pi} \frac{m_e e^2 n c}{e^2 \hbar} \frac{1000}{N_A \log_{10} e} \int \epsilon_d d(\hbar \omega). \quad (6.9)$$

Writing this in terms of the wavenumber, $\tilde{\nu}$, by using the relation $\hbar \omega = \hbar 2 \pi c \tilde{\nu}$, gives

$$f = \frac{1}{3} \frac{m_e \epsilon_0 n c^2}{e^2} \frac{1000}{N_A \log_{10} e} \int \epsilon_d d \tilde{\nu}. \quad (6.10)$$

Now, substituting this into the numerator of equation 6.6 and simplifying, gives

$$f_j \omega_p^2 = \frac{1000c^2}{3N_A \log_{10} e} N \int \epsilon_{d,j} d\tilde{\nu}, \quad (6.11)$$

where the subscript j references the decadic extinction coefficient corresponding to a particular mode. Finally, the static dielectric constant is given by

$$\epsilon_{stat} = \epsilon_{opt} + \frac{1000c^2}{3N_A \log_{10} e} N \sum_j \frac{\int \epsilon_{d,j} d\tilde{\nu}}{\omega_{0j}^2}. \quad (6.12)$$

The integral over the decadic extinction coefficient is directly proportional to the IR intensity that is outputted from the *Gaussian* ‘freq’ calculation. The IR intensity from *Gaussian* (I_{IR}) is in units of km mol^{-1} and is based on napierian absorbance. To get the intensity in the correct units for the integral of the decadic extinction coefficient ($\mathcal{A} = \int \epsilon_d d\tilde{\nu}$), which is based on linear absorbance, we do $\mathcal{A} = \frac{100}{\ln 10} I_{IR}$.

6.3.2 Results

We populate the tight-binding Hamiltonian off-diagonal elements based on a transfer integral that decays exponentially with distance, setting the parameters as $J_0 = 10$ eV and $\beta = 0.6 \text{ \AA}^{-1}$. We populate the diagonal elements with -3.7 eV, which is the LUMO energy of PCBM. When investigated energetic disorder, we sample the LUMO as a Gaussian random variable, varying σ between 0 and 100 meV .

Density of states (DOS)

We obtain the density of states for each fullerene adduct, first assuming no energetic disorder and then with energetic disorder. When there is no energetic disorder (Figure 6.6), there is a clear trend of a narrowing DOS with increasing number of sidechains. Additional sidechains increase the separation between molecule centres, and therefore decreasing the electronic coupling. Lower electronic coupling leads to a narrowing of the density of states (smaller bandwidth) as it reduces the number of accessible states.

The low energy region of the DOS (see section 2.4.3) is most important for charge transport. The states at the low energy end of the DOS can act as trap states, inhibiting mobility.

The symmetry of these DOS is interesting, since as the number of sidechains increases it becomes more symmetric. This could be due to the fact that more correlations in the lower adducts results in more higher energy states being accessible, which are not accessible in the higher adducts.

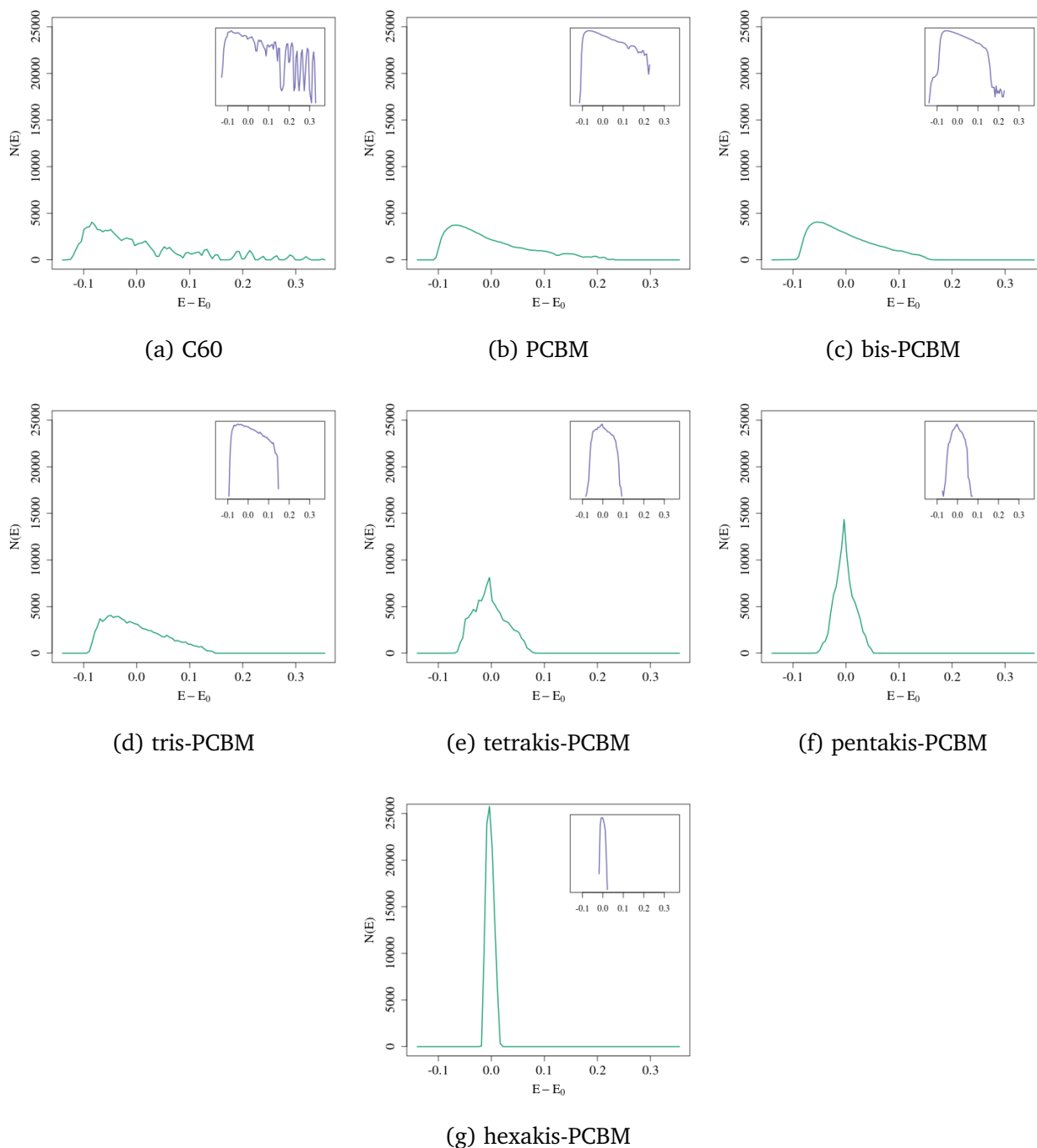


Figure 6.6: Density of states in one-orbital basis for each fullerene adduct, where E_0 is the LUMO of the adduct. The inset is the logarithm of the DOS.

The result of including energetic disorder by spreading the site energies about a Gaussian of different widths σ is given in Figure 6.7. Increasing energetic disorder increases the spread of the DOS, as expected. The extent of the tail increases with increasing energetic disorder, suggesting

that the number of potential trap states is also increasing. However, integration over this region is needed to determine this.

The extent of energetic disorder in fullerenes has been explored by other authors. Tummala *et al.* [20] reported on expected values of static and dynamic disorder in C60 and PCBM based on molecular dynamics and DFT simulations. They found the static disorder σ to be 50 meV for amorphous C60, and 0 eV for crystalline C60. For amorphous PCBM, they found $\sigma = 110$ meV and for crystalline PCBM they found $\sigma = 60$ meV. Frost *et al.* [21] reported on expected values of energetic disorder in bis-PCBM and tris-PCBM based on DFT calculations of the different isomers. They found the average values of σ for bis- and tris-PCBM to be 56 meV and 121 meV respectively.

Inverse Participation Ratio (IPR)

The IPR (see section 6.2) is a metric of the number of sites the charge density is delocalised over. The $\text{IPR}=1$ when the charge is localised to one site, and the $\text{IPR}=N$ when a charge is delocalised over N sites. Figure 6.8 gives the IPR for the first 10 states for each adduct. For C60, PCBM, bis-PCBM and tris-PCBM, the higher energy states have more delocalised charges, although the range is large particularly for C60. In the case of tetrakis-, pentakis- and hexakis-PCBM, the 10 lowest energy charge states are all localised to a few molecules.

Overall, the trend with increasing sidechains is towards a smaller average IPR for the first 10 charge states. However, hexakis-PCBM has larger charge states than pentakis- and tetrakis-PCBM. This is likely due to the high symmetry of hexakis-PCBM in our model that assumes spherically symmetric sidechains at up to 6 different positions on the central C60 sphere (see Figure 6.3), i.e. it starts behaving as an approximately spherical molecule.

Percolation threshold

The percolation threshold is a measure of the connectivity of the assemblies; a higher threshold means the system is more connected since we find how many molecules are within that value of the coupling to find each cluster. We take the value of the threshold as the point in Figure 6.9a at which the reciprocal of the percolating cluster size diverges from zero.

The values are plotted in Figure 6.9b. They show connectivity decreasing as the number of sidechains increases as we would expect due to the higher adducts having more weakly coupled clusters. The coordination number for each adduct is also given in Figure 6.9b. Both decrease

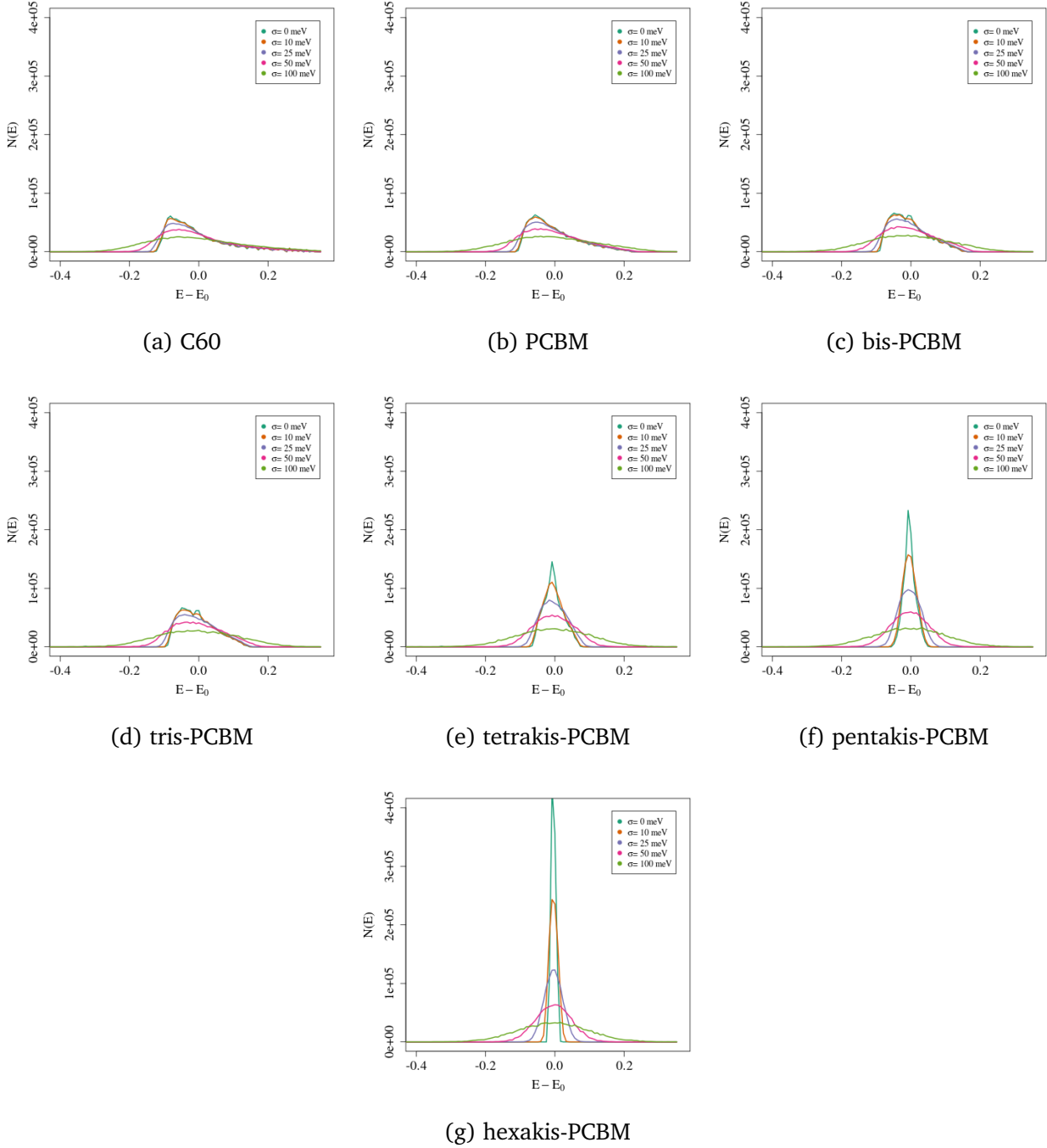


Figure 6.7: Density of states with different values of energetic disorder σ in one-orbital basis for each fullerene adduct, where E_0 is the LUMO of the adduct.

with additional sidechains since the C_{60} molecules cannot get as close to each other.

Calculation of parameters

We calculated the optical dielectric constant for C60 and mono-PCBM using the finite field method described above, since crystal structures have been reported for these molecules. There are no available crystal structures for bis-PCBM so we used published ellipsometry measurements [22] to obtain an equivalent value. For the higher adducts, we have no measurements or available crystal

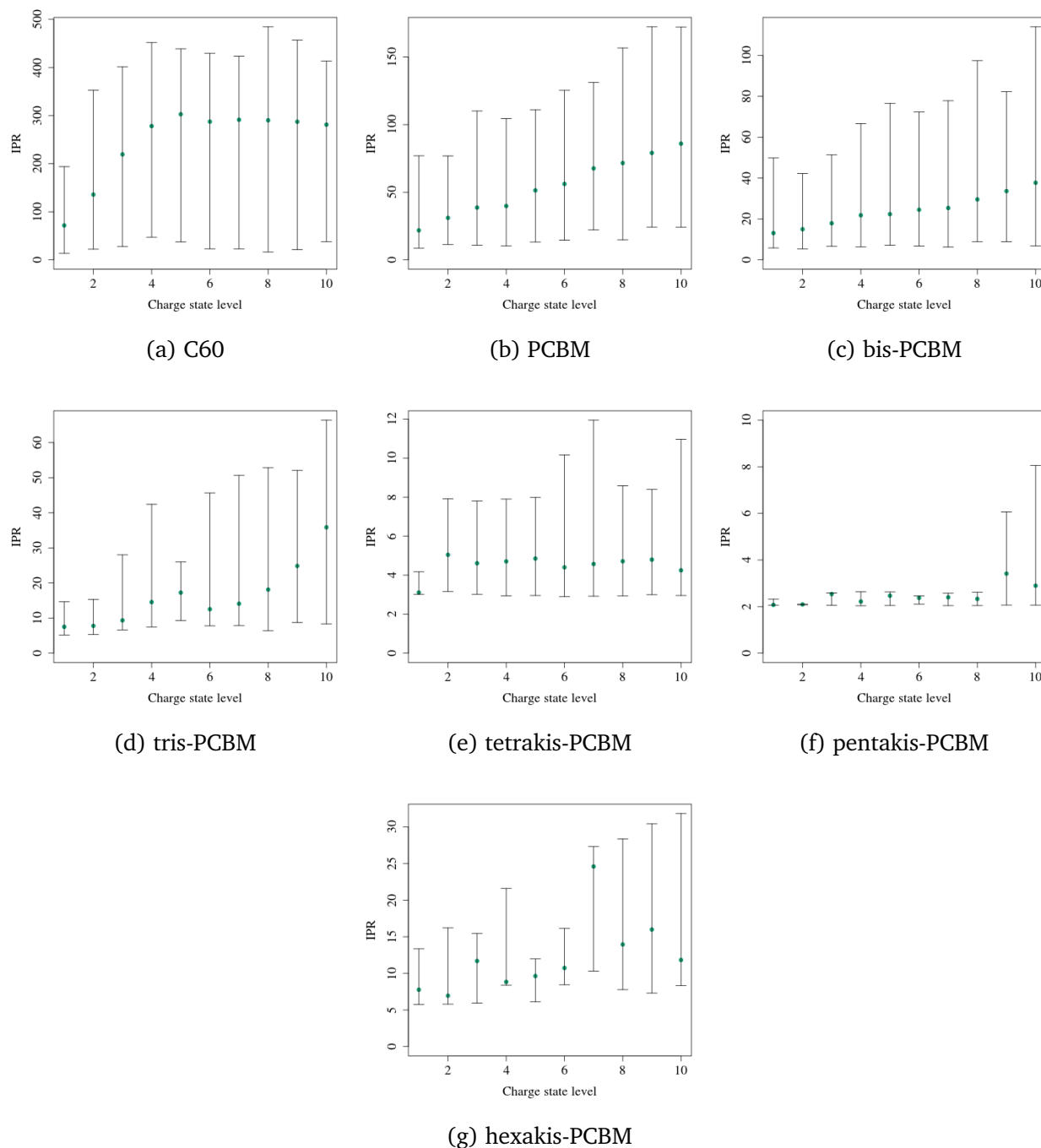


Figure 6.8: IPR for the first 10 states for each adduct. The error bars indicate the highest and lowest values from the set of 100 uncorrelated assemblies, the point shows the average.

structures. For the static dielectric constant we used the Lorentz oscillator approach described above for each of them.

As is clear from equation 6.12, the optical dielectric constant goes into the calculation of the static one, so this calculation alone can only access the difference between the two with no knowledge of the optical one.

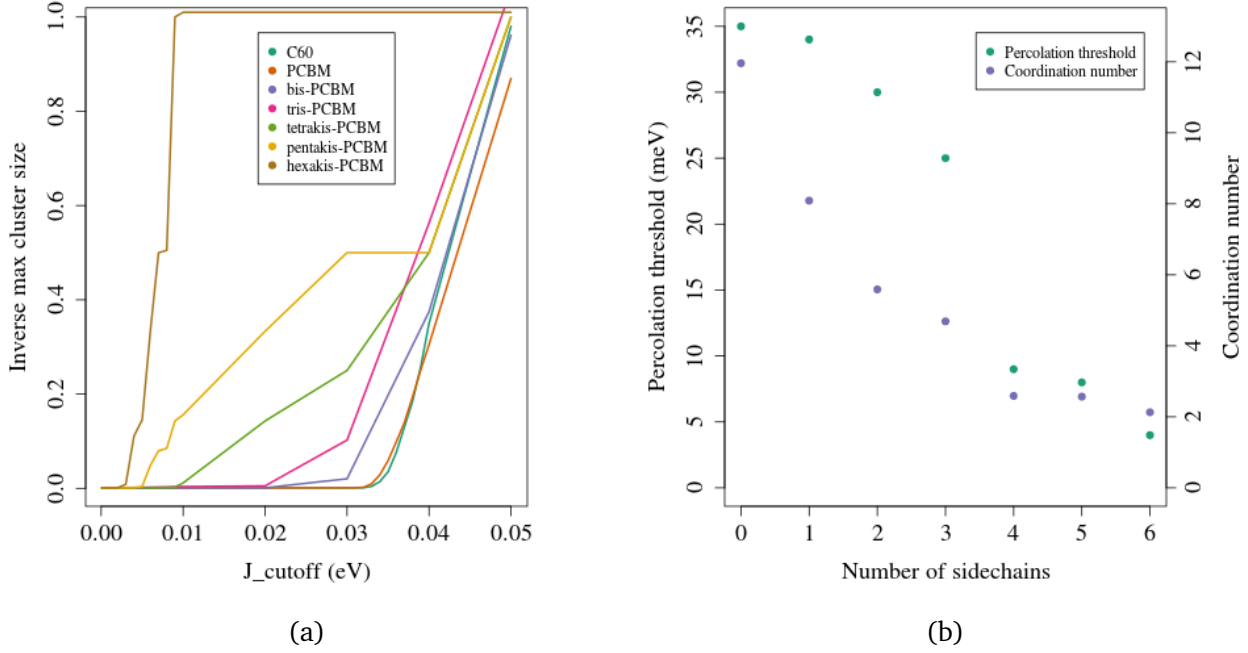


Figure 6.9: (a) Inverse maximum cluster size versus the cutoff in electronic couplings for each adduct. The percolation threshold is the point at which there is a sharp change from ≈ 0 . (b) The coordination number and extracted percolation threshold for each adduct

A summary of the calculated parameters is given in Table 6.2. The difference between the static and optical dielectric constants increases with $\text{C60} < \text{mono-PCBM} < \text{bis-PCBM}$, and this relates to the polarisability of the molecule, so the trend is sensible. The optical dielectric constant seems to decrease with increasing molecular volume, which is also as we would expect from the volumetric density of π electrons in each of these.

Table 6.2: Parameters calculated for polaron formation energy for C60, PCBM and bis-PCBM. Published experimental values for C60 and PCBM are given below our calculated values. W_p is calculated with our calculated values of the optical and static dielectric constants.

	C60	PCBM	bis-PCBM
ϵ_{opt} (calc)	4.83	4.00	–
ϵ_{opt} (exp)	4.0 [23]	3.38 [22]	3.31 [22]
ϵ_{stat} (calc)	4.93	5.08	6.59
ϵ_{stat} (exp)	4.4 [24]	3.9 [25]	–
W_p (eV)	0.006	0.077	0.165

This analysis yields a value for the polaron formation energy W_p as in Table 6.2, which we use in our tight-binding model to calculate the polaron. We have calculated the value of the static dielectric constant with two additional functionals - the results are in appendix A.4. There is not a large difference in the final value of W_p when a different functional has been used to calculate

ϵ_{stat} .

DOS and IPR with polaron formation

Using the parameters calculated above, we applied the polaron formation model described in section 6.3.1 to C60, PCBM and bis-PCBM. Looking at the density of states for each (Figure 6.10), it can be seen that when the lowest state energy is less than the low energy tail, it forms a distinct polaron state.

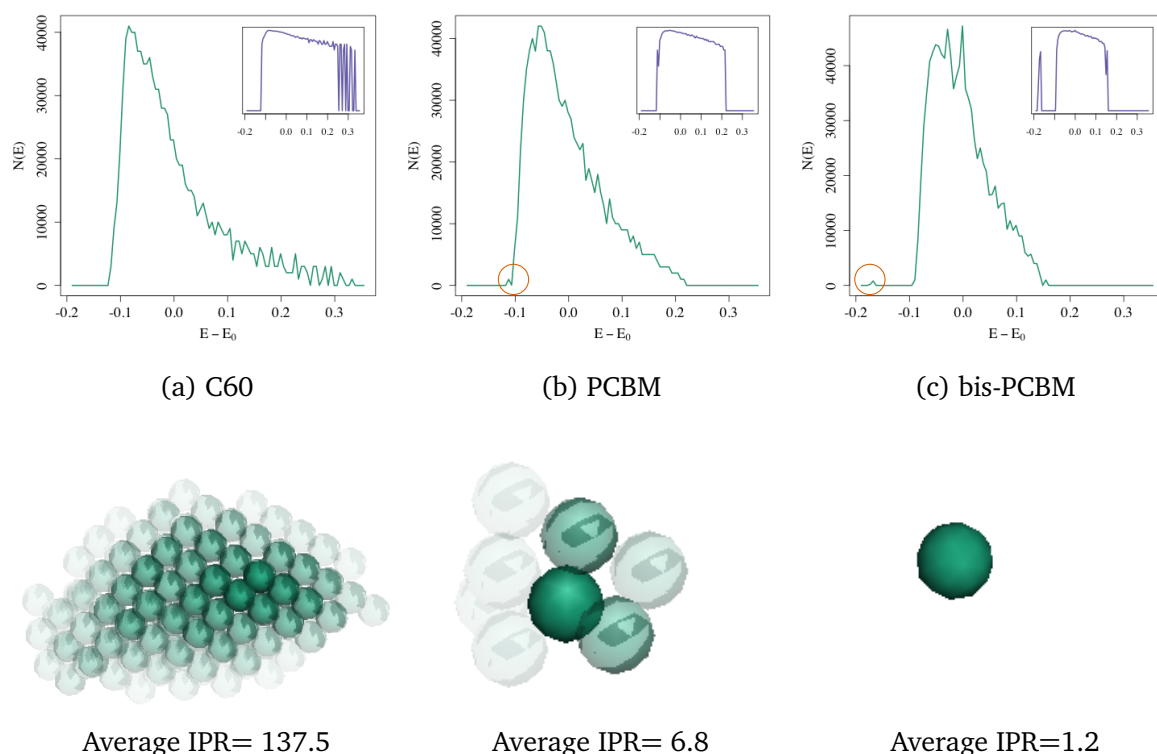


Figure 6.10: (a)-(c) The DOS with polaron for the fullerene adduct, with a representation of the size of the lowest charge state for the fullerene adduct below. The low energy states in the DOS are circled.

Varying energetic disorder and polaron formation energy

We explored the effect of the parameters σ and W_p in our model, in terms of their effect on delocalisation of the charge, through the IPR. We first varied σ between 0.001 and 0.1 eV for each adduct and calculated the average IPR, shown in Figure 6.11a. As expected, the IPR decreases with increasing energetic disorder, due to Anderson localisation. The higher adducts are more configurationally disordered due to the additional sidechains, so already have more localised charges from the same process. Adducts with multiple sidechains are likely to have increased energetic disorder due to the different isomers that can exist, but energetic disorder can also be

induced by polarisation effects and chemical defects in real assemblies.

Figure 6.11b shows the IPR with increasing energy of polaron formation, W_p . The effect of this increase is greater with the higher adducts, showing that charge states that are already somewhat localised can be more easily localised to approximately a single molecule. For the higher adducts (hexakis-, pentakis-, tetrakis- PCBM), there is a critical point where the IPR falls to ≈ 1 . Charge localised on one molecule is a necessary but not sufficient condition to treat charge transport in the system with a Marcus hopping model. From the calculations of W_p above, the trend so far shows an increasing energy of polaron formation with increasing sidechains, indicating that the higher adducts form more strongly localised polarons, i.e. are likely to have higher values of W_p . This means that with no energetic disorder, the adducts up to tris-PCBM probably cannot be treated with a Marcus hopping model.

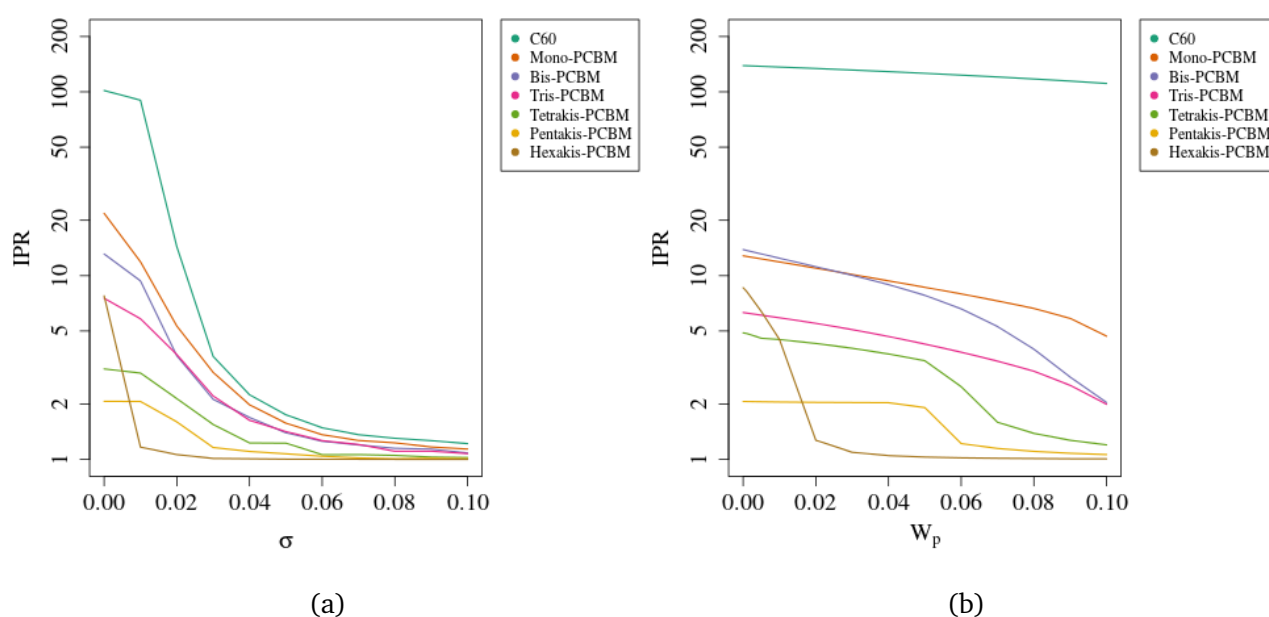


Figure 6.11: Change in inverse participation ratio (IPR) with (a) increasing energetic disorder σ and (b) increasing energy of polaron formation, W_p .

We also looked at combining energetic disorder and polaron formation in the model and have plotted a 2D histogram for the IPR for each adduct in Figure 6.12. The darkest green means that the $IPR \approx 1$, so it can clearly be seen that with small contributions of polaron formation and energetic disorder the higher adducts are localised to one molecule. For the lower adducts the picture is more complicated, but the plots show the interplay between energetic disorder and polaron formation, in that additional energetic disorder means a lower value of W_p is needed to

localise the charge to one molecule. The plots indicate that for the higher adducts a hopping model is valid, since the charge is localised to one site with very small amounts of energetic disorder (which would be larger in the higher adducts due to different isomers) and polaron formation.

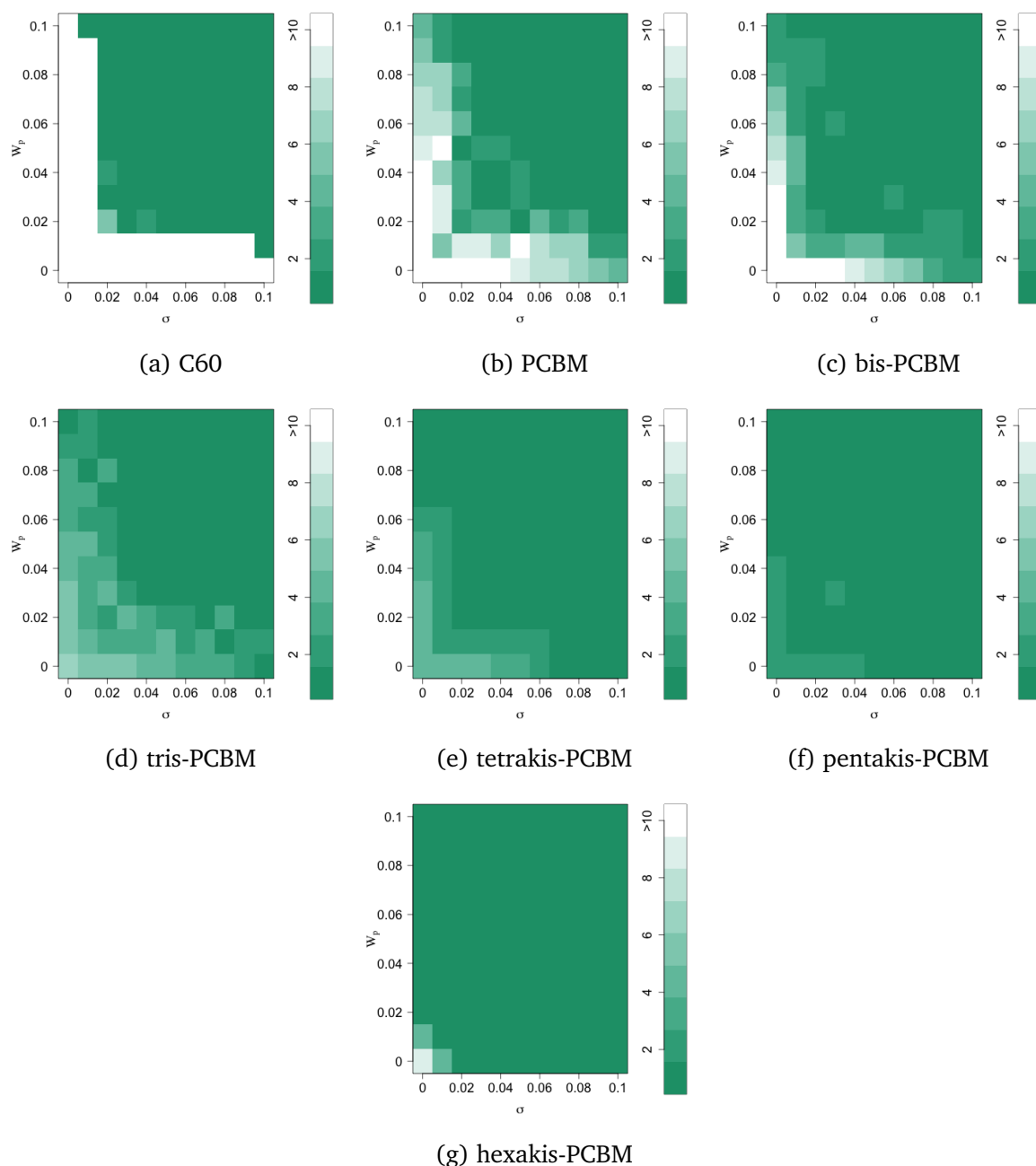


Figure 6.12: IPR for the first 10 states for each adduct. The error bars indicate the highest and lowest values from the set of 100 uncorrelated assemblies, the point shows the average.

6.4 Conclusions

We have developed a tight-binding approach to model polarons in organic semiconductors. The model allows us to treat large assemblies of molecules with relatively low computational cost. It is based on describing an excess electron in a system with a tight-binding Hamiltonian in the basis of the molecular orbitals of the sites, and allowing site energies to respond self-consistently to electron density within a continuum approximation.

Our model has allowed us to explore both energetic disorder and polaron formation in fullerene assemblies with up to six side chains. Both energetic disorder and polaron formation tend to localise the charge. The spatial extent depends on configurational disorder, which is determined in turn by the number of sidechains. The density of states are spread out by energetic disorder, resulting in a low energy "tail" that could trap charges. This is an important concern for both modelling and understanding charge transport in these materials.

We explored the effect of polaron formation in the fullerene systems by calculating the polaron formation energy, via calculations of the static and optical dielectric constants. We calculated the static and optical dielectric constants in three of the systems: C60, mono- and bis-PCBM, for which crystal structures and/or experimental parameters exist. We used a finite field approach to obtain the optical dielectric constants for C60 and mono-PCBM, since crystal structures are available for these materials. For bis-PCBM, we used reported ellipsometry measurements to obtain an equivalent parameter. For the static dielectric constant, we used a Lorentz oscillator approach, summing over the harmonic vibrational modes, to find it along with the dielectric spectrum. The difference between the static and optical dielectric constants, which related to the polarisability of the molecule, increases from $C60 < \text{mono-PCBM} < \text{bis-PCBM}$. This makes sense given the additional flexible sidechains.

We found that the polaron formation energy increases from $C60 < \text{mono-PCBM} < \text{bis-PCBM}$. More strongly localised polarons are formed in bis-PCBM compared to mono-PCBM and C60. Electron transport in the most technologically relevant adduct, i.e. mono-PCBM, is unlikely to be well modelled with Marcus theory where charge hops between sites if there is low energetic disorder. More work is required to build an appropriate model of charge transport in these systems, considering polaron formation.

We explored how different amounts of energetic disorder and different strengths of polaron formation influence each of the adducts, in terms of localisation of the charge through the IPR. Energetic disorder appears to have a greater impact of the localisation of the charge for equivalent magnitudes of these values. However, the amount of energetic disorder present in assemblies would likely vary with the specific adduct. We also explored how polaron formation and disorder both act to localise a charge. We showed that the higher adducts are completely localised for relatively small values of energetic disorder and polaron formation. For the more technologically relevant adducts (C60 and mono-PCBM), the charges are not localised unless there are large amounts of energetic disorder or polaron formation. This again suggests that Marcus theory is unlikely to be valid for these systems.

By finding the spatial extent of polaron states, we have started the process to understanding the nature of charge transport in these systems, and laid the groundwork for building a model based on the propagation of polaron states. Here, we show results for our model applied to assemblies of fullerene adducts, but this model of polaron states could be applied to many different systems of organic semiconductors where a tight-binding Hamiltonian can be constructed.

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7

Counterpoise method for calculating transfer integrals

We further develop a method for calculating transfer integrals in a wide variety of systems, which uses ghost atoms of the other molecule in calculations of each individual molecule. This ensures all calculations are performed in the same basis set. We show how this method is useful for calculating intramolecular transfer integrals, as well as transfer integrals between unlike molecules (such as between a donor and acceptor or dopant and host). We compare it to our previous method for performing these calculations and show that it can be applied to these systems where our previous method either cannot be applied, or would give errors.

7.1 Introduction

The transfer integrals (or electronic couplings) between molecules are an important parameter for understanding the nature of charge states and charge transport in a system. The relationship between structure and charge transport properties can be understood by considering the electronic Hamiltonian in a tight-binding approximation (see section 3.3.3)

$$\hat{H}_{TB} = \sum_m \epsilon_m a_m^\dagger a_m + \sum_{m \neq n} J_{mn} a_m^\dagger a_n, \quad (7.1)$$

where $a_m^\dagger$ and a_m are the creation and annihilation operators, respectively, for a charge carrier on molecular site m , $\epsilon_m = \langle \psi_m | \hat{H}_{TB} | \psi_m \rangle$ is the charge carrier site energy, and $J_{mn} = \langle \psi_m | \hat{H}_{TB} | \psi_n \rangle$ is the transfer integral (electronic coupling) between sites m and n [1]. Both of these parameters depend on the intramolecular and intermolecular geometric degrees of freedom [2].

Transfer integrals that are large in comparison to the reorganisation energy, $J \gg \lambda$, indicate that the charges will be delocalised and in an ordered system charge transport will be band-like. When they are small compared to the reorganisation energy, $J \ll \lambda$, this indicates that the transport will be via thermally-assisted hops, where the rate of hopping is proportional to $|J|^2$ (see section 2.6.2).

In section 3.4.2, the projective method for calculating transfer integrals was outlined. For charge transfer between two similar molecules, single point energy calculations (for donor A , acceptor B and pair AB) are performed in two different basis sets. This introduces a not insignificant basis set superposition error (BSSE) associated with the calculation. In the case of charge transfer between different molecules three different basis sets are used, increasing this error further.

Here, we define the "counterpoise method" as a projection-based method with a counterpoise correction to address the BSSE, originally developed by Baumeier *et al.* [3] (and referred to as DIPRO). They applied it to assemblies of Alq_3 molecules and concluded that the additional computational time required when using the counterpoise correction was not worth the improvement in accuracy. However, this conclusion was based on calculating transfer integrals between pairs in large assemblies of like molecules.

In this chapter, we show how the counterpoise method can be applied to strongly coupled (and covalently bonded) sites, i.e. for intramolecular charge transfer, as well as where there are different chemical structures for the donor and acceptor molecules.

7.2 Motivation

We require a method that is both accurate and computationally efficient, as well as being transparent, straightforward to implement, and applicable to a range of cases. We would like to be able to calculate transfer integrals between like and unlike molecules, as well as both inter- and intra-molecular transfer integrals.

Both the projective and counterpoise methods are transparent and straightforward to implement. However, the BSSE associated with the projective method increases when calculating transfer integrals between unlike molecules (since the three calculations are performed in three different basis sets) and it cannot be used for intramolecular transfer integrals (since the method does not allow for molecular orbitals from unrestricted calculations). Therefore, here we show how an alternative to the projective method that minimises the BSSE, which we call the counterpoise method, is used to calculate transfer integrals for a range of systems: (i) two like molecules; (ii) intramolecular charge transfer between monomers; (iii) two unlike molecules, for charge transfer between donor and acceptor, and between dopant and host.

We use *Gaussian* software to obtain the molecular orbitals, atomic orbital overlaps and energies in the counterpoise basis set. We then used the Python programming language (Python Software Foundation, <https://www.python.org/>) with the cclib library [4] for the calculation. The cclib library can also parse output files from the ADF, DALTON, Firefly, GAMESS, Jaguar, Molpro, NWChem, ORCA, Psi and Q-Chem computational chemistry packages (<https://cclib.github.io/index.html>). In each of these packages it is possible to specify ghost atoms to perform the calculation in the counterpoise basis set. Only in the case of DALTON, Psi and Q-Chem it is not (yet) possible to obtain the atomic orbital overlaps that are required for the calculation. Therefore, the Python code developed to implement the counterpoise method can be applied to the output files of any of the other computational chemistry packages listed.

Here we describe the theory and implementation of the counterpoise method, before benchmarking it and applying it to a number of systems.

7.3 Counterpoise method

The counterpoise method was developed by Baumeier *et al.* [3]. It addresses the BSSE issue of the projective method by using “ghost atoms” of the second molecule in the calculations on single molecules, which ensures all calculations are done in the same basis set. A ghost atom has the same basis functions and integration grid points associated with a normal atom, but no nuclear charge or electrons, and this requires a counterpoise calculation.

The method entails projecting the non-orthogonalised orbitals of molecule A (and molecule B) onto the orbitals of the pair, molecule AB , giving $\tilde{\phi}^{(A)}$ and $\tilde{\phi}^{(B)}$. The J matrix is then computed with $\langle \tilde{\phi}^{(A)} | E | \tilde{\phi}^{(B)} \rangle$, where E is a diagonal matrix containing the eigenvalues of the pair. Finally, this is orthogonalised, using the overlaps and energies of the individual molecules.

7.3.1 Theory

The theory of the method is outlined here [3]. From equation 3.42 above, the transfer integral is given by

$$J^{AB} = \frac{j_{AB} - \frac{1}{2}(\epsilon_A + \epsilon_B)S_{AB}}{1 - S_{AB}^2}, \quad (7.2)$$

where

$$j_{AB} = \langle \phi_A | \hat{H} | \phi_B \rangle. \quad (7.3)$$

To obtain j_{AB} , direct numerical integration is extremely computationally inefficient. However, because the set of molecular orbitals of the dimer ψ_j form a complete orthonormal system they are eigenfunctions of the pair Hamiltonian, which means that the unity operator can be written as [3]

$$\mathbf{1} = \sum_i |\psi_i\rangle \langle \psi_i|, \quad (7.4)$$

Inserting two unity operators into equation 7.3 ,

$$j_{AB} = \langle \phi_A | \sum_i |\psi_i\rangle \langle \psi_i| \hat{H} | \sum_j |\psi_j\rangle \langle \psi_j| \phi_B \rangle \quad (7.5)$$

$$= \sum_i \sum_j \langle \phi_A | \psi_i \rangle \langle \psi_i | \hat{H} | \psi_j \rangle \langle \psi_j | \phi_B \rangle. \quad (7.6)$$

In the basis of the dimer eigenfunctions, H is diagonal and $\langle \psi_i | \hat{H} | \psi_j \rangle = \epsilon_{i,j}$ is a diagonal matrix containing the molecular orbital energies of the pair. $\langle \phi_A | \psi_i \rangle$ and $\langle \psi_j | \phi_B \rangle$ are the projections of the individual molecule orbitals $\phi^{(A)}$ and $\phi^{(B)}$ onto the orbitals of the pair ψ_i and ψ_j respectively. Because each of these is calculated with a counterpoise calculation, the size of their basis sets is the same as each other and the pair basis set.

In the counterpoise basis set, the molecular orbitals can be expanded with a common basis set defined by the atomic orbitals of A and B φ ,

$$|\phi^{(A,B)}\rangle = \sum_{\alpha} c_{\alpha}^{(A,B)} |\varphi_{\alpha}\rangle, \quad (7.7)$$

$$|\psi_i\rangle = \sum_{\alpha} c_{\alpha}^{AB} |\varphi_{\alpha}\rangle. \quad (7.8)$$

Using a counterpoise basis set, the projections $\tilde{\phi}^{(A,B)} = \langle \phi^{(A,B)} | \psi_i \rangle$ are

$$\tilde{\phi}^{(A,B)} = \sum_{\alpha} c_{\alpha}^{(A,B)} \langle \varphi_{\alpha} | \sum_{\beta} c_{\beta}^{AB} |\varphi_{\beta}\rangle \quad (7.9)$$

$$= \sum_{\alpha} \sum_{\beta} c_{\alpha}^{(A,B)} c_{\beta}^{AB} \langle \varphi_{\alpha} | \varphi_{\beta} \rangle \quad (7.10)$$

$$= \sum_{\alpha} \sum_{\beta} c_{\alpha}^{(A,B)} S_{\alpha\beta} c_{\beta}^{AB} \quad (7.11)$$

where $S_{i,j}$ is the overlap matrix of the i^{th} and j^{th} atomic orbitals.

The matrix in the orthogonal basis set of the molecular orbitals of the pair is simply a diagonal matrix with energies corresponding to molecular orbital energies. Therefore the non-orthogonalised

transfer integral between the i^{th} molecular orbital of molecule A and the j^{th} molecular orbitals of molecule B is

$$j_{ij}^{AB} = \tilde{\phi}_{i,l}^{(A)} \epsilon_{l,k} (\tilde{\phi}_{j,k}^{(B)})^T, \quad (7.12)$$

where $\epsilon_{l,k} = \langle \psi_k | \hat{H} | \psi_l \rangle$ is a diagonal matrix containing the orbital energies of the pair.

Finally, to get the transfer integral, it is orthogonalised with a symmetric Lowdin transformation as before

$$J^{AB} = \frac{j^{AB} - \frac{1}{2}(e_A + e_B)S_{AB}}{1 - S_{AB}^2}, \quad (7.13)$$

where $S_{ij}^{AB} = \tilde{\phi}_i^{(A)} \tilde{\phi}_j^{(B)}$, $e_A = \tilde{\phi}_{i,l}^{(A)} \epsilon_{l,k} (\tilde{\phi}_{j,k}^{(A)})^T$ and $e_B = \tilde{\phi}_{i,l}^{(B)} \epsilon_{l,k} (\tilde{\phi}_{j,k}^{(B)})^T$.

7.3.2 Implementation

For an intermolecular transfer integral, molecules A and B are optimised at the B3LYP level of theory with the 6-31g* basis set, and molecule AB is made by putting the two optimised molecules together. For an intramolecular transfer integral between segments A and B of the same molecule, the dimer, AB , is optimised in the same way, and the individual molecule segments A and B are obtained by splitting AB into its conjugated segments.

Three single point calculations are run in *Gaussian* [5] to obtain the molecular orbitals, atomic orbital overlaps and energies, with molecule A with ghost atoms of molecule B , molecule B with ghost atoms of molecule A , and molecules A and B together. These calculations are performed at the B3LYP level of theory with the 6-31g* basis set. The keyword `IOP(6/7=3)` is specified for the calculations on the individual molecules to ensure all molecular orbitals are printed and the keyword `IOP(3/33=1)` is specified to ensure the orbital overlaps are printed for the calculation on AB . These are required for the next stage of the calculation.

The calculation of the transfer integrals from the molecular orbitals, atomic orbital overlaps and energies is then performed in Python with the `cclib` library [4]. The calculation is different depending on whether an inter- or intra-molecular transfer integral is required, and this is specified.

It should be noted that the choice of functional does affect the value of the transfer integral: Sutton *et al.* [6] found that the value increases linearly with the proportion of Hartree-Fock exchange in the functional. We are primarily calculating the transfer integrals to use in the Marcus equation to get a mobility, and as such the comparison between systems is more important than the absolute values, hence we take care to use a consistent method and functional.

7.4 Results

Initially, we applied the method to simple systems, where both the projective method (section 3.4.2) and the energy splitting in dimer method (ESID, section 3.4.2), would be expected to give accurate values, in order to validate the method. The molecules were first optimised at the B3LYP level of theory with the 6-31g* basis set. The single point energy calculations were then performed with the same level of theory and basis set, and the values of the transfer integrals were calculated with each of the three methods.

7.4.1 Test case: Ethene

For the simplest case, we calculated the transfer integral between two cofacial ethene molecules with increasing separation. We get very good agreement with the projective and energy splitting in dimer methods for this case, see Figure 7.1.

Now we take a case where we would expect the ESID method to fail, i.e. non symmetric molecule positions. We rotate one molecule about the y-axis (illustrated in Figure 7.1f), which means each molecule is differently polarised, causing the ESID method to fail. We get good agreement between the projective and counterpoise methods, and also good agreement with Valeev *et al.* (2006) [7] who use a related method. The projective method gives slightly higher values than the counterpoise methods, especially at closer distances, which could be associated with the basis set superposition error (BSSE).

7.4.2 Test case: Cofacial Benzene

We calculated the transfer integral versus cofacial distance for two benzene molecules, similar to the first case for ethene above. Because benzene has doubly degenerate HOMO and LUMO levels, the transfer integrals required from the J matrix to find the HOMO-HOMO and LUMO-LUMO

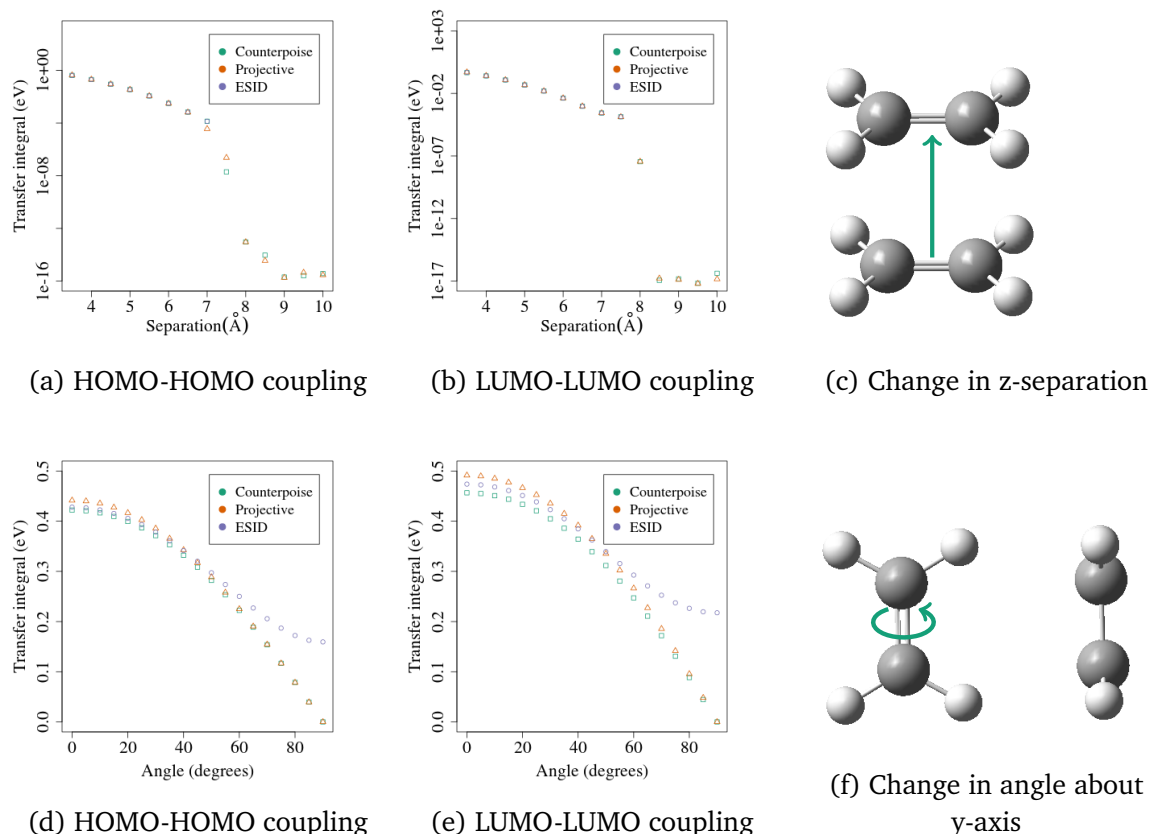


Figure 7.1: (a)-(c) Transfer integral for (a) HOMO-HOMO and (b) LUMO-LUMO versus separation for two co-facial ethene molecules, shown in (c), from the counterpoise, projective and energy splitting in dimer (ESID) methods. All three methods are approximately identical. (d)-(f) Transfer integral for (d) HOMO-HOMO and (e) LUMO-LUMO versus change in angle about the y-axis for one ethene molecule relative to the other, shown in (f), from counterpoise, projective and ESID methods.

coupling are slightly modified compared to the non-degenerate case. We use the method of Newton [8] and take the root mean squared of each of the couplings associated with degenerate orbitals in all combinations (either HOMO or LUMO). For example, where there is a doubly degenerate HOMO level, we take the root mean squared of the HOMO - HOMO coupling, HOMO - HOMO-1 coupling, HOMO-1 - HOMO coupling and HOMO-1 - HOMO-1 coupling.

The energy splitting in dimer method is not straightforward when there are degenerate orbitals involved, so we have just calculated the transfer integrals with the projective and counterpoise methods. There is good agreement between the two methods, with the projective method giving slightly higher values for some separations as before.

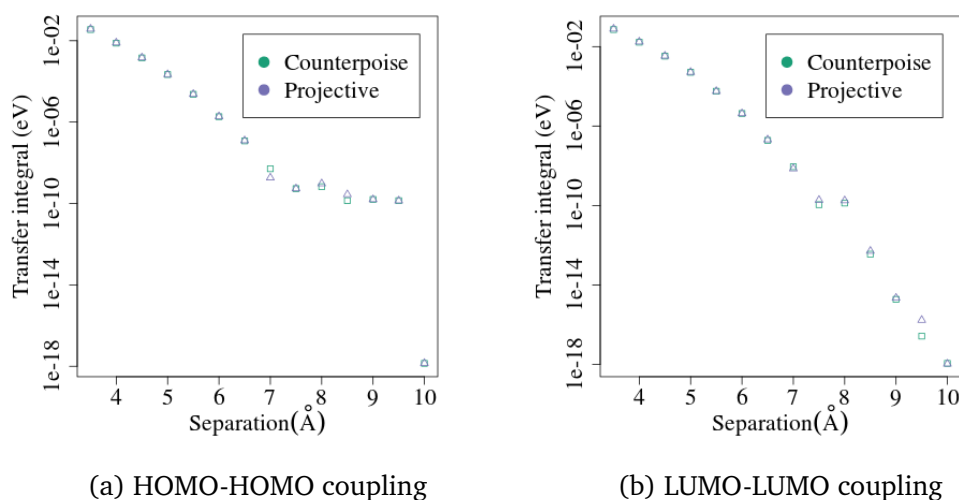


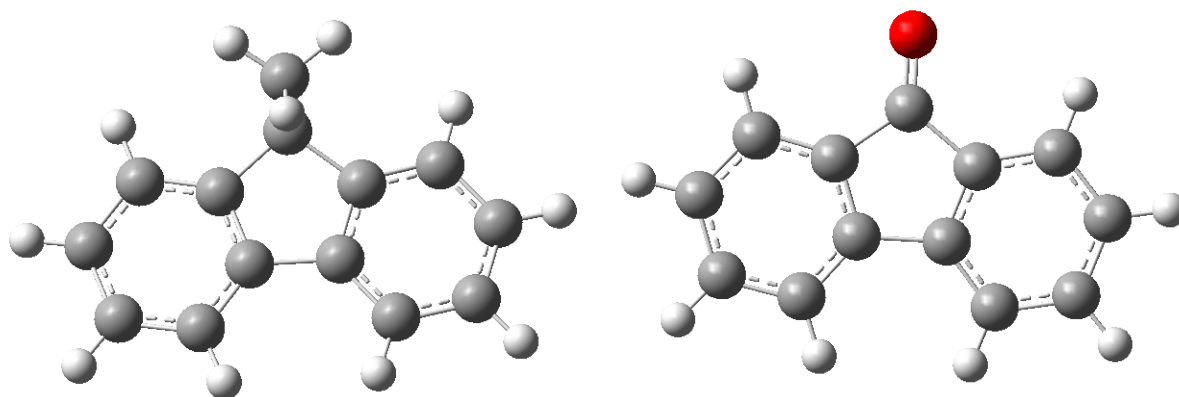
Figure 7.2: Transfer integral for (a) HOMO-HOMO and (b) LUMO-LUMO of two co-facial benzene molecules versus separation, using the counterpoise and projective methods

7.4.3 Test case: Oligofluorene, with and without keto defect

Moving on to transfer integrals between different molecules, to inform studies of charge transfer at interfaces and between a dopant and host, we first looked at oligomeric models of the polymer poly-9,9-dioctylfluorene (PFO). PFO can exist with a keto defect, where the pair of alkyl groups are replaced by a carbonyl (see Figure 7.6). We looked at the transfer integral calculated with the different methods between like and unlike molecules in this group, summarised in Table 7.1.

The results show good agreement between the counterpoise, projective and ESID methods for the HOMO-HOMO and LUMO-LUMO transfer integrals between like molecules. In the case of the transfer integrals between fluorene monomers with and without keto defects, the ESID method would be expected to fail, since symmetry has been broken. The values we get are larger by an order of magnitude compared to the case with no defect and this would not make physical sense. Now, looking at the results from the projective and counterpoise calculations alongside the molecular orbitals (visualised in Figure 7.4). Both the HOMO-HOMO and LUMO-LUMO transfer integrals are smaller when calculated with the projective method compared to the counterpoise method. Looking at the orbitals, the LUMO-LUMO transfer integral for the unlike pair would be expected to be less than either of the like pairs. The HOMO-HOMO transfer integral would be expected to be similar compared to that between like molecules, which is what we find.

Now we have validated the model for some simple cases, we apply it to molecule systems that are relevant for OSC applications.



(a) Monomer of fluorene, no defect

(b) Monomer of fluorene, with a keto defect

Figure 7.3: Structure of PFO, with and without a keto defect.

Table 7.1: Transfer integrals, HOMO-HOMO (LUMO-LUMO) coupling, for a fluorene monomer and fluorene monomer with a keto defect (called a fluorenone), calculated with three different methods.

	ESID (eV)	Projective (eV)	Counterpoise (eV)
Fluorene monomer - Fluorene monomer	0.0287 (0.0401)	0.0273 (0.0379)	0.0267 (0.0372)
Fluorene monomer - Fluorenone monomer	0.244 (0.607)	0.0251 (0.00819)	0.0372 (0.0101)
Fluorenone monomer - Fluorenone monomer	0.0263 (0.0276)	0.0259 (0.0272)	0.0258 (0.0271)

7.4.4 Intramolecular electron transfer

Charge transport along polymer chains can be understood through looking at the intramonomer charge transfer, but for this intramonomer transfer integrals must be known. We can use the counterpoise method for this by treating the two segments as the monomers of a dimer, each with one unpaired electron to form the bond. This requires unrestricted calculations for the individual molecules, which yields a set of ‘alpha’ and ‘beta’ molecular orbitals, where alpha and beta refer to spin up and spin down electrons respectively.

In an unrestricted calculation, the HOMO and LUMO levels needed to select the relevant transfer integral from the J matrix are also complicated by degeneracies in the alpha and beta molecular

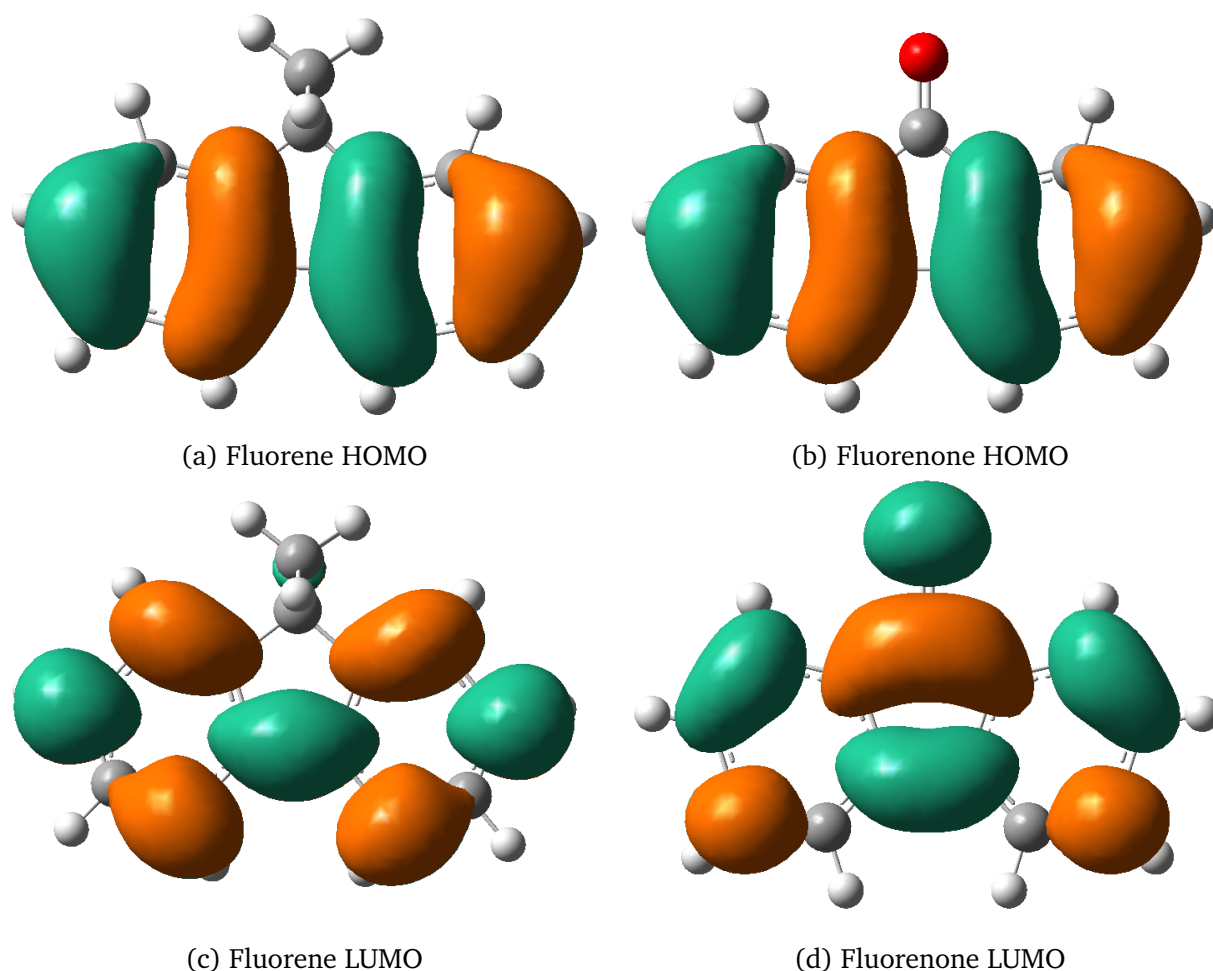


Figure 7.4: HOMO and LUMO levels of fluorene and fluorenone.

orbitals, e.g. the alpha-HOMO level may be quasi degenerate with the beta-HOMO level. We treat degeneracies in the same way as outlined above for benzene (section 7.4.2), i.e. take the root mean squared of all combinations of degenerate orbital couplings.

Intramolecular transfer integrals are often approximated with $J = J_0 |\cos(\theta)|$. To calculate the value of J_0 for either HOMO-HOMO or LUMO-LUMO coupling, a tight-binding approximation can be used, where a tridiagonal Hamiltonian has the HOMOs (or LUMOs) on the diagonals and J_0 on the off-diagonals. This can be solved analytically, for a perfectly ordered system, giving the eigenvalues as

$$E_k = E_0 \pm 2J_0 \cos(k\pi/(n+1)), \quad (7.14)$$

where E_k is the HOMO (or LUMO) of the oligomer containing k monomers, n is the total number of monomers, and E_0 is the HOMO (or LUMO) of the monomer. Therefore, by finding the HOMOs

(or LUMOs) of different length monomers, we can find J_0 by plotting the HOMO (or LUMO) versus number of monomers and fitting to this analytic solution. This provides a method with which to compare the counterpoise method for intramolecular transfer integrals.

Bithiophene, for P3HT

The calculated transfer integral for HOMO-HOMO and LUMO-LUMO coupling between monomers in a bithiophene dimer with dihedral angle is given in Figure 7.5. The Figure also shows the approximate coupling obtained by fitting the analytical form (equation 7.14) to oligomer length dependent HOMO or LUMO energies, where J_0 was calculated to be 0.82 eV and 1.0 eV for HOMO-HOMO and LUMO-LUMO coupling respectively. The results show that the $\cos(\theta)$ relationship is a good fit between the two methods, but the J_0 values have been both over and under-estimated with the tight-binding approximation compared to the counterpoise method.

Oligofluorene, for PFO

Figure 7.6 shows the intramolecular transfer integral with angle for a PFO dimer, along with the approximated fit. J_0 was calculated using the tight-binding approximation to be 0.38 eV and 0.39 eV for the HOMO-HOMO and LUMO-LUMO transfer integral respectively. Again, the $\cos(\theta)$ relationship proves to be a good approximation, but the J_0 values are under-estimated for the transfer integrals for the tight-binding approach compared to the counterpoise method.

Charge transport along polymer chains tends to be much faster than between chains (intermolecular). Therefore, the limiting step for charge transport in conjugated polymers is the intermolecular charge transfer. This is supported by comparing the J values for intramolecular charge transfer in fluorene in Table 7.1 with the values for intramolecular charge transfer in Figure 7.6.

7.4.5 Interfacial electron transfer: donor and acceptor

In organic photovoltaics, the charge transfer at the interface is the mechanism by which charges separate, and is therefore an important step for understanding the processes in OPVs. We can use the counterpoise method to find the transfer integral for this step in order to find the rate of this transfer. In OPVs, the electron in a donor is excited from the HOMO to the LUMO, and transferred to the LUMO of the acceptor.

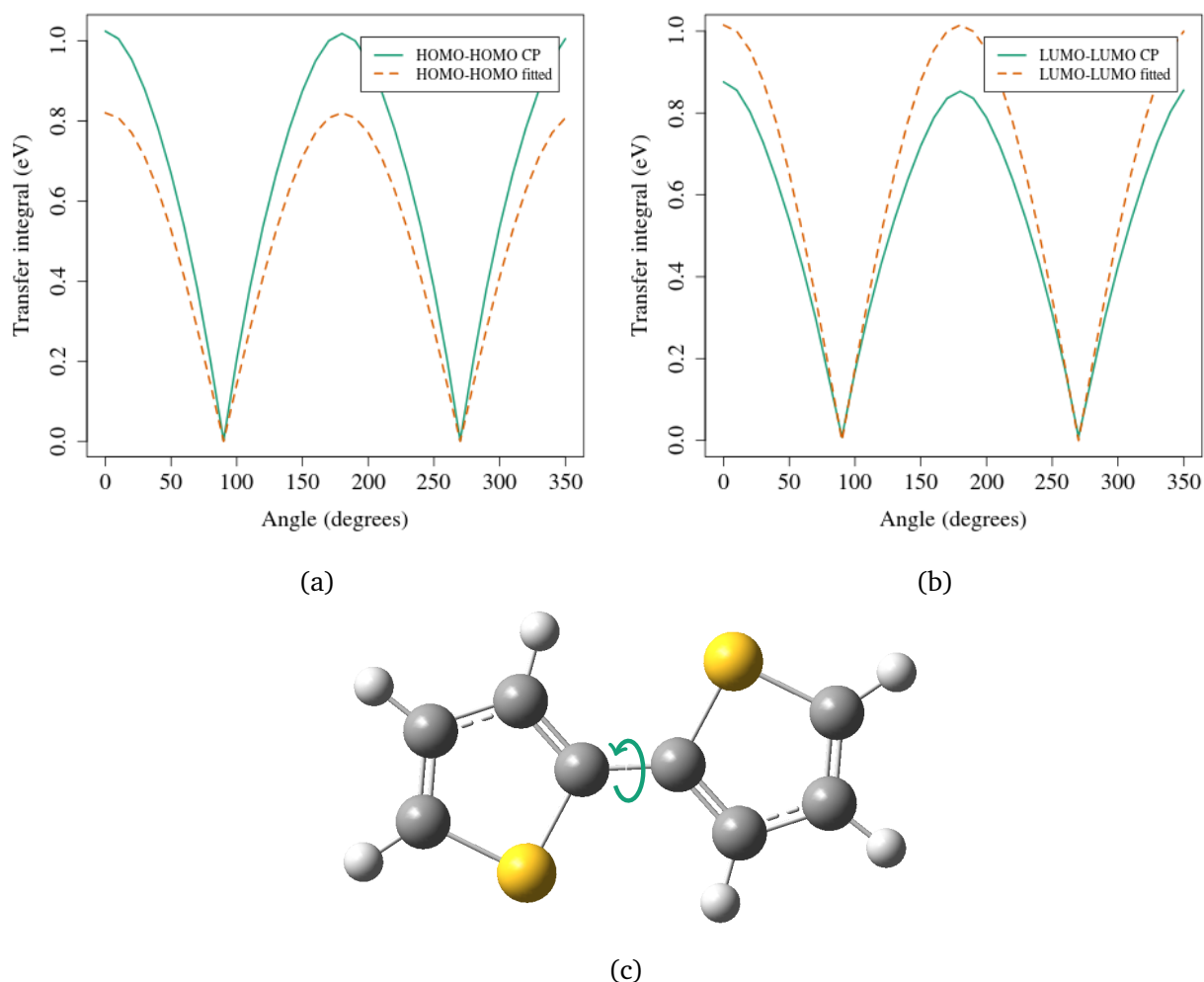


Figure 7.5: (a) HOMO- HOMO and (b) LUMO-LUMO transfer integrals versus dihedral angle for a bithiophene molecule, where the angle of interest is shown in (b). ‘CP’ means that it has been calculated with the counterpoise method and ‘fitted’ means it has been fitted to $J_0 \cos(\theta)$ with J_0 calculated as outlined above.

Figure 7.7 shows the processes that can happen between the energy levels in donor and acceptor molecules. We are interested in the electron transfer and recombination processes, and their relative rates. We can estimate these based on the transfer integrals associated with each of these processes, i.e. the $\text{LUMO}_D\text{-LUMO}_A$ transfer integral and the $\text{LUMO}_A\text{-HOMO}_D$ transfer integrals. Here D and A refer to the donor and acceptor respectively.

Next, we investigated the effect of these different transfer integrals on the rates of each of the processes using the Marcus-Levich-Jortner (M-L-J) equation. The M-L-J equation is similar to the Marcus equation used to calculate the rate of hopping between sites, but it includes additional terms to take into account the effect of quantum vibrational modes [9] [10]. The rate of charge hopping from site i to site j is given by

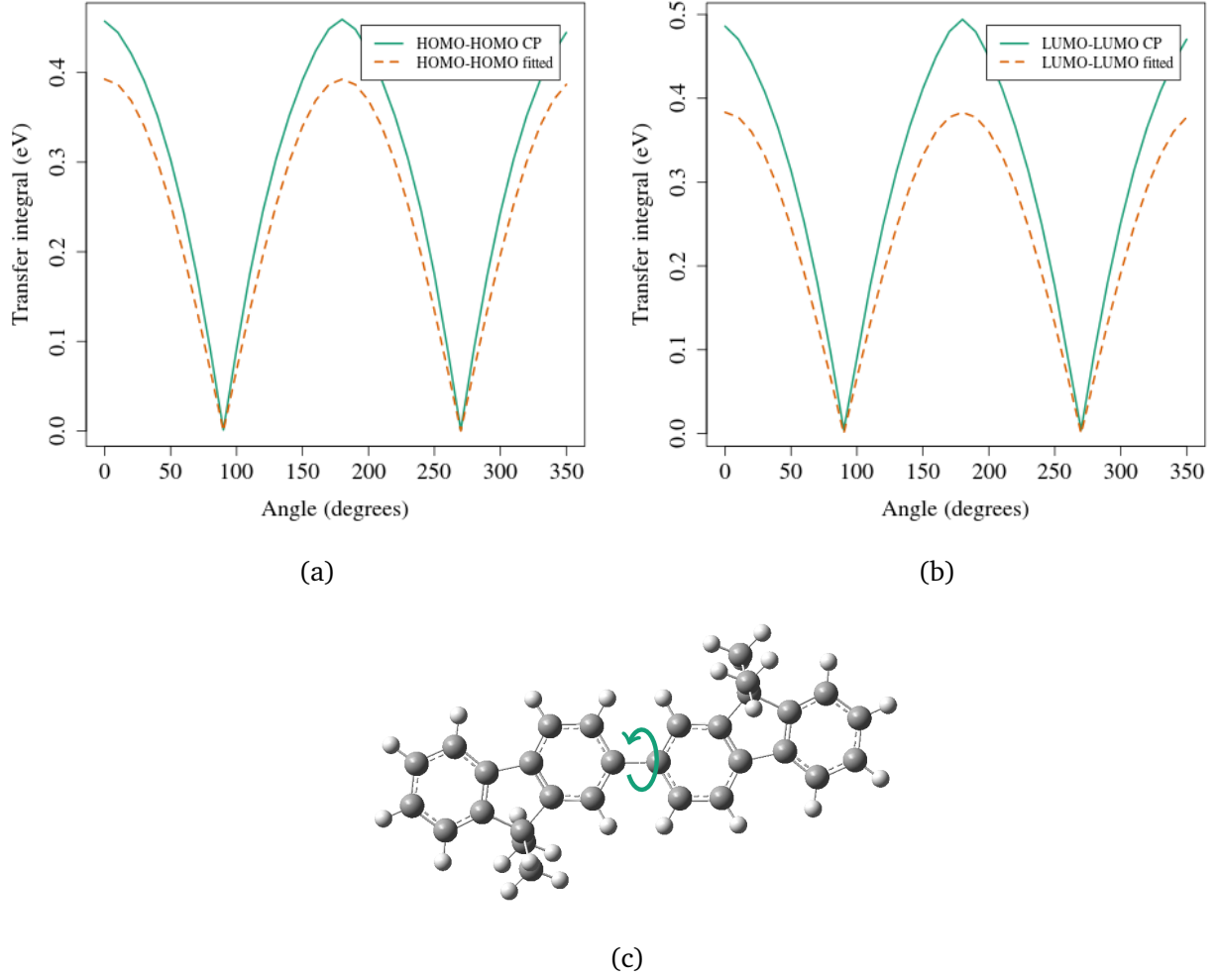


Figure 7.6: (a) HOMO- HOMO and (b) LUMO-LUMO transfer integrals versus dihedral angle for a PFO dimer molecule, where the angle of interest is shown in (b). ‘CP’ means that it has been calculated with the counterpoise method and ‘fitted’ means it has been approximated to $J_0 \cos(\theta)$ with J_0 fitted from HOMO or LUMO levels varying oligomer length as outlined above.

$$\Gamma_{ij}^{MLJ} = \frac{2\pi}{\hbar} |J_{ij}|^2 \frac{1}{\sqrt{4\pi\lambda_{outer}k_B T}} \sum_{\nu} \exp(-S_{eff}) \frac{S_{eff}^{\nu}}{\nu!} \exp\left(-\frac{(\lambda_{outer} + \nu\hbar\omega_{eff} + \Delta G_{ij})^2}{4\pi\lambda_{outer}k_B T}\right), \quad (7.15)$$

where J_{ij} is the transfer integral between site i and j , ΔG_{ij} is the Gibbs free energy difference between the initial and final states, λ_{outer} is the outer sphere reorganisation energy, S_{eff} is an effective Huang-Rhys factor, ω_{eff} is the frequency of one effective mode, k_B is the Boltzmann constant, T is the temperature, and the summation ν runs over all vibrational modes. The effective Huang-Rhs factor is defined as

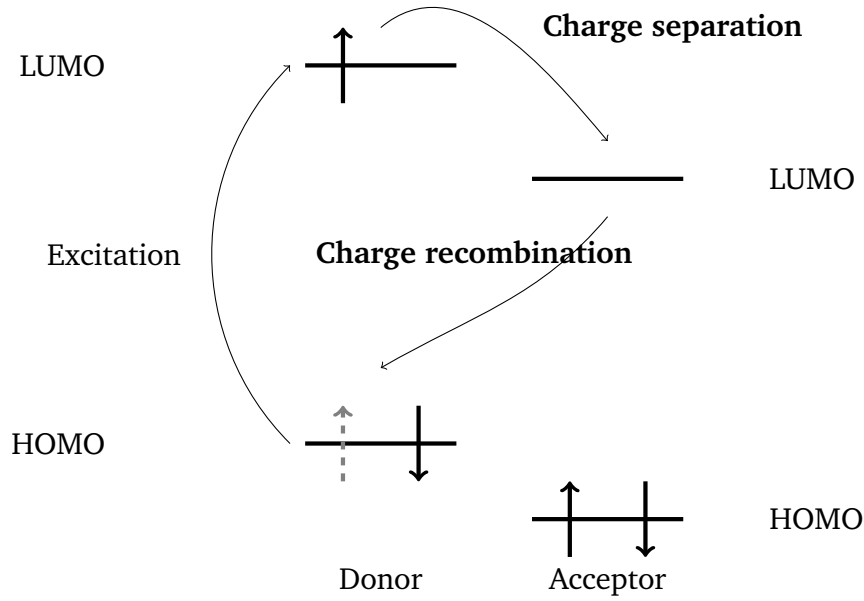


Figure 7.7: Donor and acceptor energy levels in an OPV active layer. We are interested in the relative rates of the electron transfer (charge separation) and charge recombination processes.

$$S_{eff} = \sum_i \frac{S_i \hbar \omega_i}{\omega_{eff}}, \quad (7.16)$$

where S_i is the Huang-Rhys factor of the i^{th} vibronic mode, of frequency ω_i .

This approach was used by Liu and Troisi [11] to calculate the absolute rates of charge separation and charge recombination between P3HT and PCBM.

We calculated the energy difference term (ΔG_{ij}) by subtracting the donor LUMO from the acceptor LUMO for charge separation, and subtracted the acceptor LUMO from the donor HOMO for charge recombination. We calculated these in vacuum with *Gaussian* [5] with the B3LYP functional and the 6-31g* basis set. We used the Kohn-Sham HOMO and obtained the first excited state energy with TD-DFT (specifying nstates=6) [12] which we added to the HOMO to obtain the LUMO.

Here we look at a common donor and acceptor system used in OPVs: P3HT and PCBM.

P3HT and PCBM

We calculated the transfer integral between donor and acceptor, P3HT and PCBM, which are popular materials used in the active layer of OPV. Here, we use oligothiophene in place of P3HT,

leaving off the sidechains, to simplify the calculation and reduce computational cost. We are primarily interested in the magnitude of the transfer integral, since it is squared in the rate expression. However, as stated in section 3.4.2, it should be noted that a negative sign indicates that a positive combination of the molecular orbitals of the individual molecules results in the lowest energy molecular orbital of the pair (and vice versa for a positive sign). The most interesting transfer integrals are the $\text{LUMO}_D\text{-LUMO}_A$ which corresponds to electron transfer between the donor and acceptor (charge separation), and the $\text{LUMO}_A\text{-HOMO}_D$ which corresponds to charge recombination.

We investigated the trend of transfer integral with length of the oligothiophene, where the configuration of the two molecules and results are shown in Figure 7.8. The results for the $\text{LUMO}_D\text{-LUMO}_A$ transfer integral and the $\text{LUMO}_A\text{-HOMO}_D$ transfer integral are in table 7.2. The length of the oligomer does not have a significant effect on the $\text{LUMO}_D\text{-LUMO}_A$ or $\text{LUMO}_A\text{-HOMO}_D$ transfer integrals. We find the transfer integrals for charge separation to be approximately four times larger compared to those for charge recombination. These relate to the rates of these processes, but do not tell the whole story.

To calculate the rates, we used the M-L-J equation (equation 7.15) with the same λ_{outer} as Liu and Troisi (0.11 eV); they found that varying this between reasonable values does not affect the rate much. In appendix A.5), we have explored the effect of increasing λ_{outer} relative to the magnitude ΔG , since this affects which regime the system is in: normal Marcus regime, activationless regime, or inverted Marcus regime.

We also used the values calculated by Liu and Troisi for $S_{eff} = 1.37$ and $\hbar\omega_{eff} = 0.186\text{eV}$. The results for the rates of charge separation and recombination are given in Figure 7.9. These results show that the rate of charge separation (k_{CS}) is one to two orders of magnitude greater than the rate of charge recombination (k_{CR}), which is reasonable given experimental observations that give $10^{11} < k_{CS} < 10^{12}$ and $10^8 < k_{CR} < 10^{10}$ [13] [14] [15] [16]. These observations are for P3HT with PCBM so the most relevant comparison would be the dodecamer thiophene.

Our results are similar to those of Liu and Troisi, who found $k_{CS} \approx 10^{11}$ and $k_{CR} \approx 10^9$. This makes sense given that we explored a similar parameter space. They used similar transfer integrals corresponding to the rates of separation and recombination, whereas ours vary by approximately a factor of four. However, to obtain their transfer integrals, they averaged over multiple configurations

of the molecules, and our results are well within the values they averaged over. In addition, some of the configurations they explored also had a similar difference in the $\text{LUMO}_D\text{-LUMO}_A$ transfer integral and the $\text{LUMO}_A\text{-HOMO}_D$ transfer integral. This shows the sensitivity of the transfer integral to the exact configuration of the molecules in relation to each other.

Our results show a trend of increasing rate when the magnitude of $-\Delta G$ decreases, i.e. that more resonant energy levels result in higher rates. Liu and Troisi also find this when they vary the values for ΔG_{CS} and ΔG_{CR} , keeping the sum of these parameters constant. Experimentally, this is not what is usually observed, in that a larger $-\Delta G$ has been shown to result in faster rates [13] [17]. This difference could be due to a number of factors: (i) we are modelling a different regime: the relative magnitudes of λ_{outer} and ΔG define the Marcus regime a that is being observed and there is some uncertainty in the calculation of them, more details of this are given in appendix A.5; (ii) this is a simple bimolecular model in vacuum and in reality there will be other molecules that could influence kinetics; (iii) there are many states accessible that could be involved in the charge transfer process, but we only model one state from the donor and one state from the acceptor.

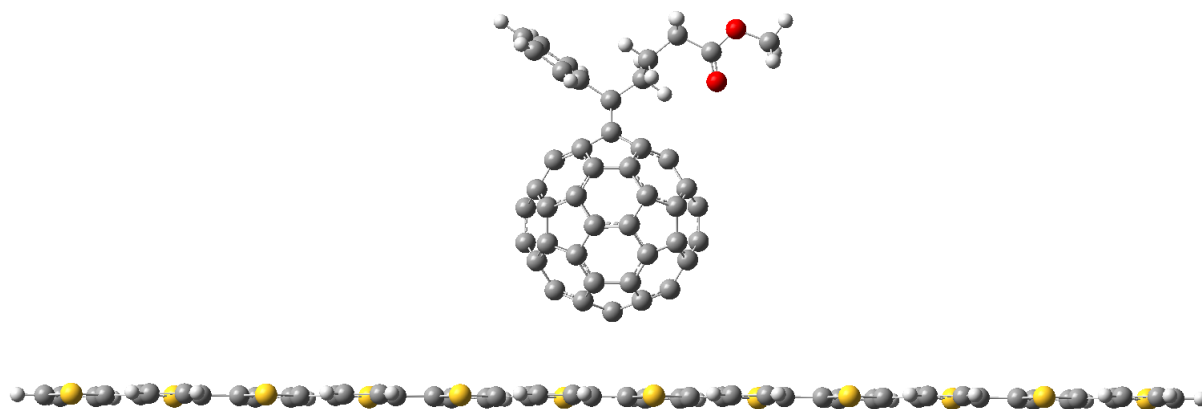


Figure 7.8: P3HT-PCBM configuration in simulation. The closest edge-to-edge distance is 3.5 Å.

In order to capture only the effect of the transfer integrals on the rate, we also calculated the transfer integrals between and dodecamer thiophene and PCBM, rotating the oligothiophene about its principle axis (Figure 7.10a). This means that both λ_{outer} and ΔG are kept constant. The transfer integrals are given in Table 7.3 and show that the maximum occurs at an angle of 30 degrees. The rates (Figure 7.10b) show a similar trend with the rates of charge separation and recombination peaking at an angle of 30 degrees. Since the central axis of the oligothiophene is kept at a constant distance from the PCBM molecule, this calculation suggests that 30 degrees is a

Table 7.2: The transfer integrals (eV) and change in energy between the initial and final states (eV) between PCBM and 3HT oligomers of different lengths.

Number of monomers	ΔG_{CS}	LUMO _D -LUMO _A	ΔG_{CR}	LUMO _A -HOMO _D
4	-1.51	-0.0314	-1.33	-7.6E-3
6	-1.21	-0.0304	-1.17	-7.9E-3
8	-1.06	0.0296	-1.09	-7.7E-3
10	-0.96	0.0297	-1.05	-7.5E-3
12	-0.93	0.0290	-1.06	-7.4E-4

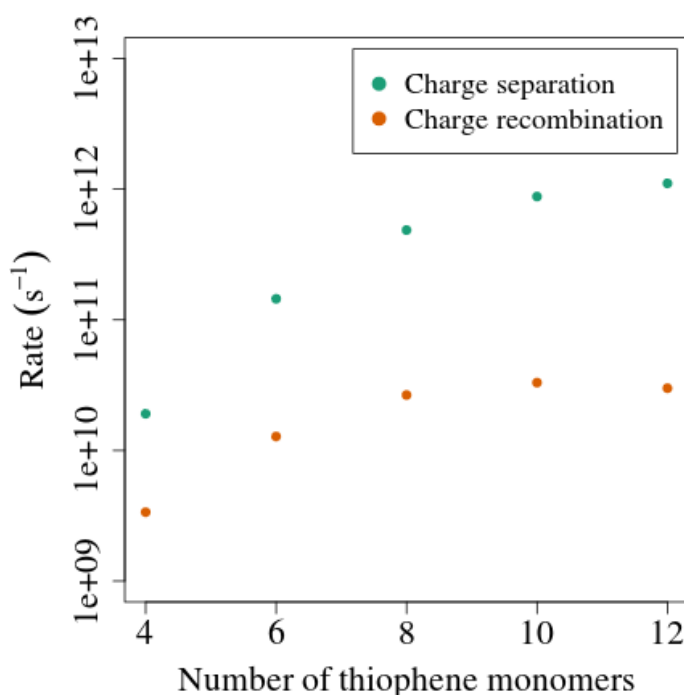


Figure 7.9: Rate of charge separation and charge recombination between PCBM and a thiophene oligomer.

balance between minimising the edge-to-edge separation and maximising the $\pi - \pi$ interactions. These would be expected to be maximised in the cofacial configuration, i.e. 90 degrees, whereas the edge-to-edge separation is minimised at 0 degrees.

The rate of charge transfer depends on the square of the transfer integral, so this is an important parameter determining the rate: the rate of charge separation varies by two orders of magnitude between the lowest and highest values for the oligothiophene rotation. The counterpoise method allows us to calculate this value, where the projective method fails. Attempting to calculate the same values with the projective method gives results that are unphysically large (> 1 eV).

Table 7.3: The transfer integrals for LUMO_D-LUMO_A and HOMO_D-LUMO_A between the oligothiophene and PCBM, where the angle of the oligothiophene is illustrated in Figure 7.10

Angle	LUMO _D -LUMO _A (eV)	HOMO _D -LUMO _A (eV)
0	-0.00294	0.000144
15	-0.00793	0.000459
30	-0.01288	0.000742
45	-0.01144	0.000732
60	0.00713	-0.00067
75	0.00297	-0.00050
90	0.00143	-0.00062

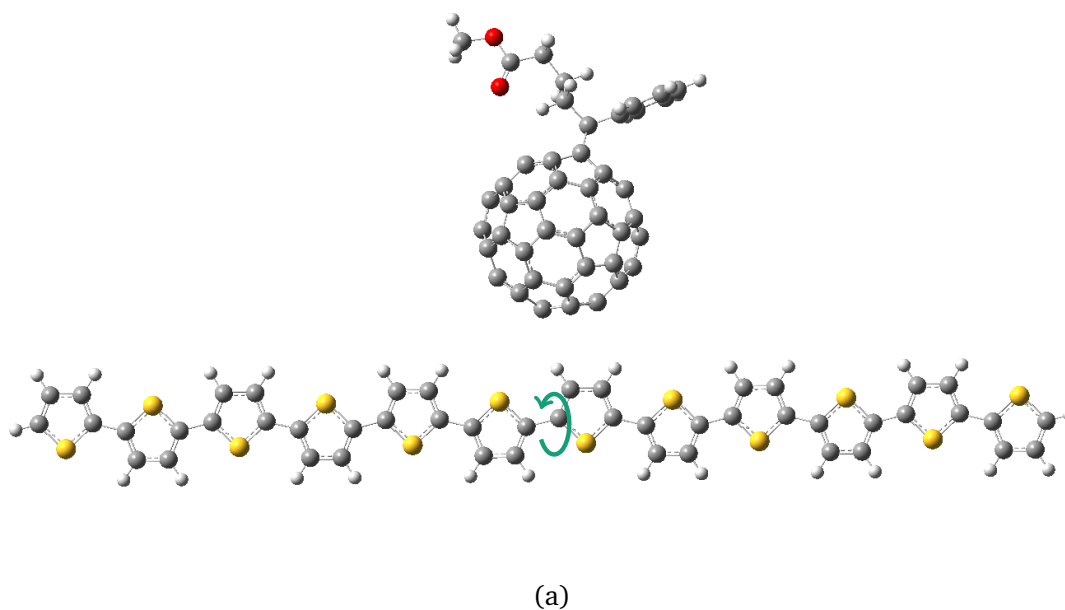
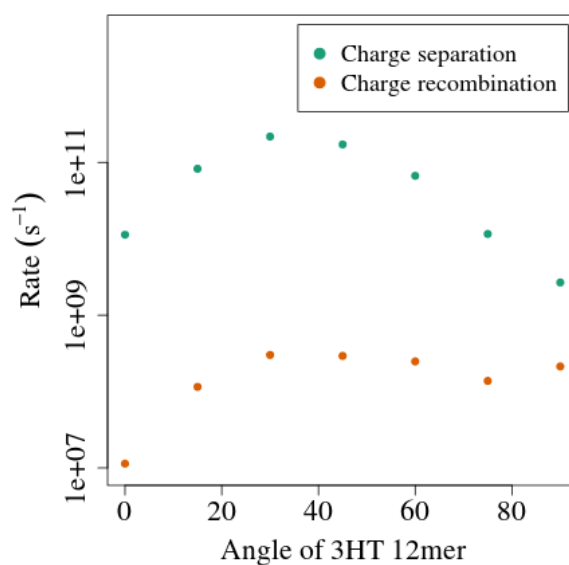
However, in this system where the donor and acceptor molecules are different, the biggest contribution to the rate from the M-L-J equation is in the exponential term, rather than the transfer integral. We explore the effect of the parameters in this exponent (λ_{outer} , ΔG and $\hbar\omega$) in appendix A.5, and show how they determine which Marcus regime is being explored.

7.4.6 Electron transfer between host and dopant

Doping in organic semiconductors to introduce additional charge carriers happens via intermolecular charge transfer between host and dopant molecules. This can take place via two different mechanisms: (i) integer charge transfer between a dopant and host; (ii) partial charge transfer where the frontier molecular orbitals between the host and dopant hybridise [18].

In p-type doping for integer charge transfer, the host is the electron donor and the dopant is the electron acceptor, while the opposite is the case in n-type doping [19]. A schematic of this process is shown in Figure 7.14 for n-type and p-type doping [20] [21]. For efficient integer charge transfer in a dopant-host system, the offset between the donor HOMO and the acceptor LUMO should be maximised. It has been suggested that integer charge transfer is more likely to occur in systems where the transfer integral between the dopant and host is weak [22].

In the case of p-type (n-type) partial charge transfer, frontier molecular orbital hybridisation of the host HOMO (LUMO) and dopant LUMO (HOMO) takes place, leading to the formation of a ground state charge transfer complex with a reduced energy gap between a doubly occupied bonding and an unoccupied antibonding hybrid orbital. This is illustrated in Figure 7.12. For



(b)

Figure 7.10: (a) P3HT-PCBM configuration in simulation. (b) Rate of charge separation and charge recombination with angle of dodecamer thiophene. 0 degrees (pictured) means that oligothiophene is perpendicular to the hexagonal PCBM face. At 90 degrees, the edge-to-edge distance is 5 Å.

efficient doping, the formation of the charge transfer complexes should be avoided, or at least the splitting of the hybrid orbitals should be minimised. It is the transfer integral that results in this splitting, so it should therefore be minimised [22].

In order to understand the type and efficiency of doping in OSC systems, we investigate the transfer integral between host and dopant HOMOs and LUMOs. For n-type doping, this is the

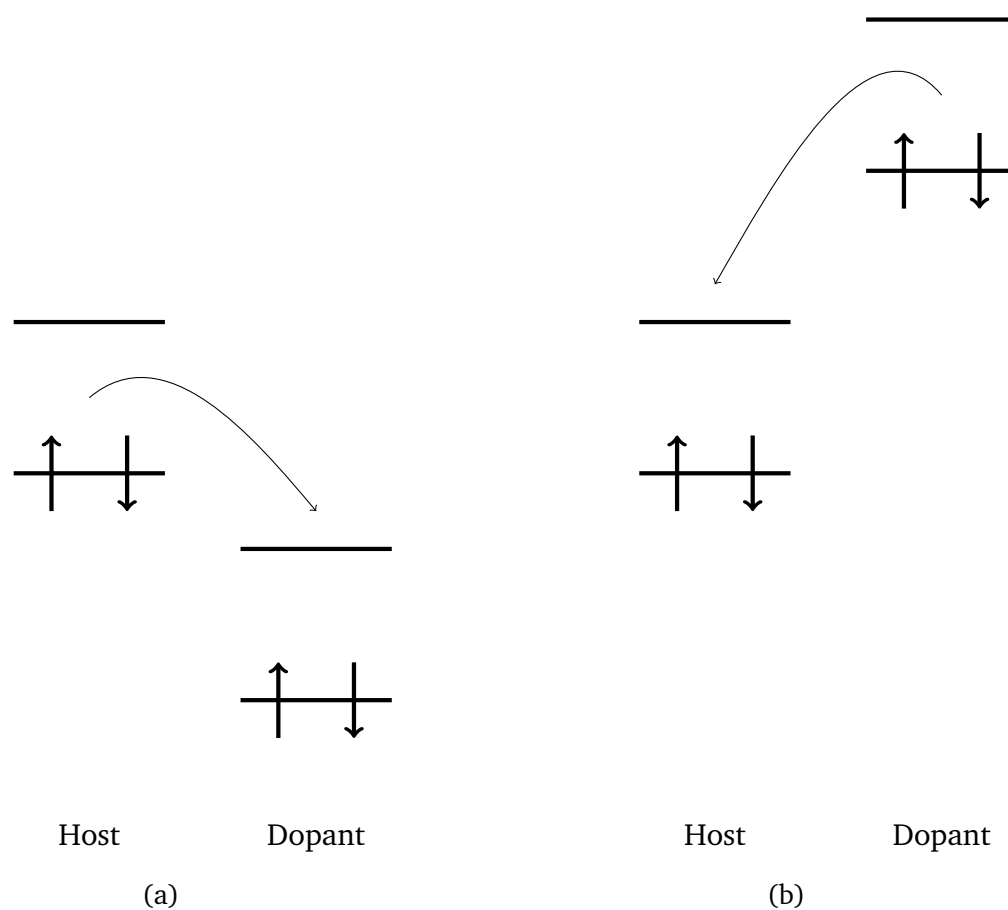


Figure 7.11: Dopant and host energy levels and mechanism for integer charge transfer (a) p-type doping and (b) n-type doping.

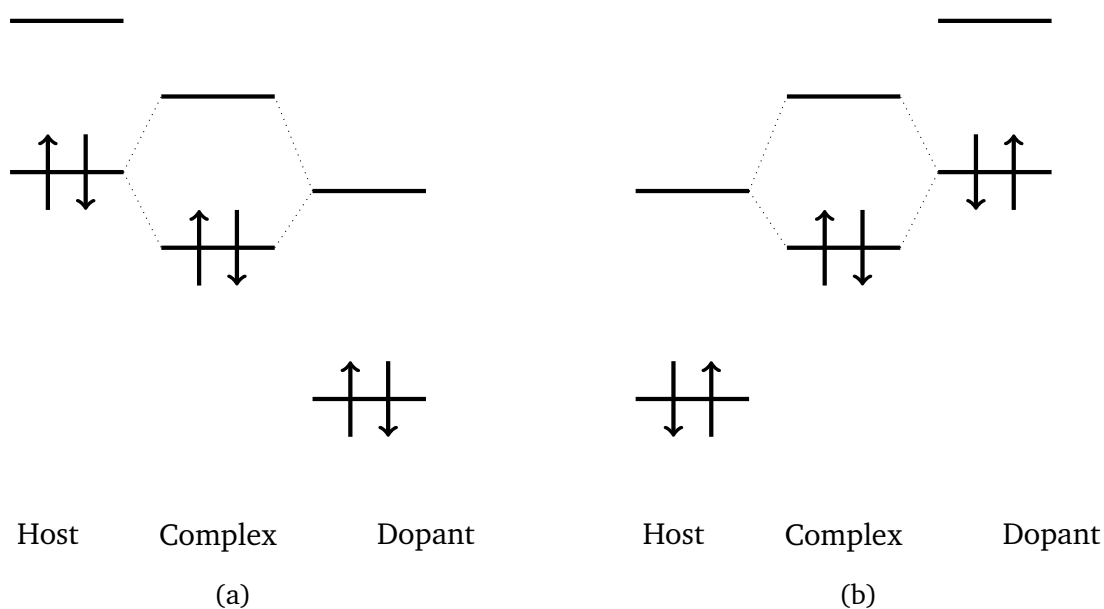


Figure 7.12: Dopant and host energy levels and mechanism for partial charge transfer for (a) p-type doping and (b) n-type doping.

HOMO of the dopant and the LUMO of the host, and in p-type doping this is the LUMO of the dopant and the HOMO of the host.

First we investigate a system where partial charge transfer has been observed and then one where integer charge transfer is observed. This is to benchmark the value of the transfer integral which makes partial transfer likely. Next, we investigate one p-type and one n-type dopant on ZnPc and its fluorinated derivatives.

Partial charge transfer (p type)

We calculated the transfer integral between the relevant molecular orbitals for an oliothiophene tetramer (4T), pentamer (5T) and hexamer (6T) with 2,3,5,6- tetrafluoro- 7,7,8,8- tetracyanoquino- dimethane (F4TCNQ), shown in Figure 7.13. This is a system where partial charge transfer has been observed via FTIR measurements by Mendez *et al.* [23]. For this calculation we position the molecules in a coplanar configuration, with a centre-to-centre separation of 3.5 Å.

The results for the HOMO_D - LUMO_A transfer integral are given in Table 7.4. These are large values according to the doping literature, which defines a large transfer integral as one that is greater than 0.4 eV [24] [19]. This supports the observation that partial charge transfer will take place in this system as a result of splitting of the complex energy levels [25]. Previous work to calculate the transfer integrals and amount of charge transferred for F4TCNQ and 4T, 5T and 6T by Zhu *et al.* [24] found the same trend in the transfer integrals. They also found that partial charge transfer took place in these systems and that the proportion of charge transferred increased with the number of thiophene monomers. This also means that a smaller transfer integral correlated with a greater proportion of charge transferred.

The HOMO and LUMO levels for each of these molecules is given in Table 7.5. It can be seen that both dopants have LUMO levels higher than the HOMO levels of the hosts, which would not be desirable for charge transfer (it should be the opposite way round). In general, for integer charge transfer it is desirable to maximise the offset between the HOMO of the donor and the LUMO of the acceptor.

Integer charge transfer (p type)

We calculated the transfer integral between the LUMO of F4TCNQ and the HOMO of ZnPc, which has integer charge transfer [21] [26]. The structures are shown in Figure 7.14. At a cofacial separation of 3.5 Å, we obtain the value for this transfer integral as 0.108 eV. This is less than the

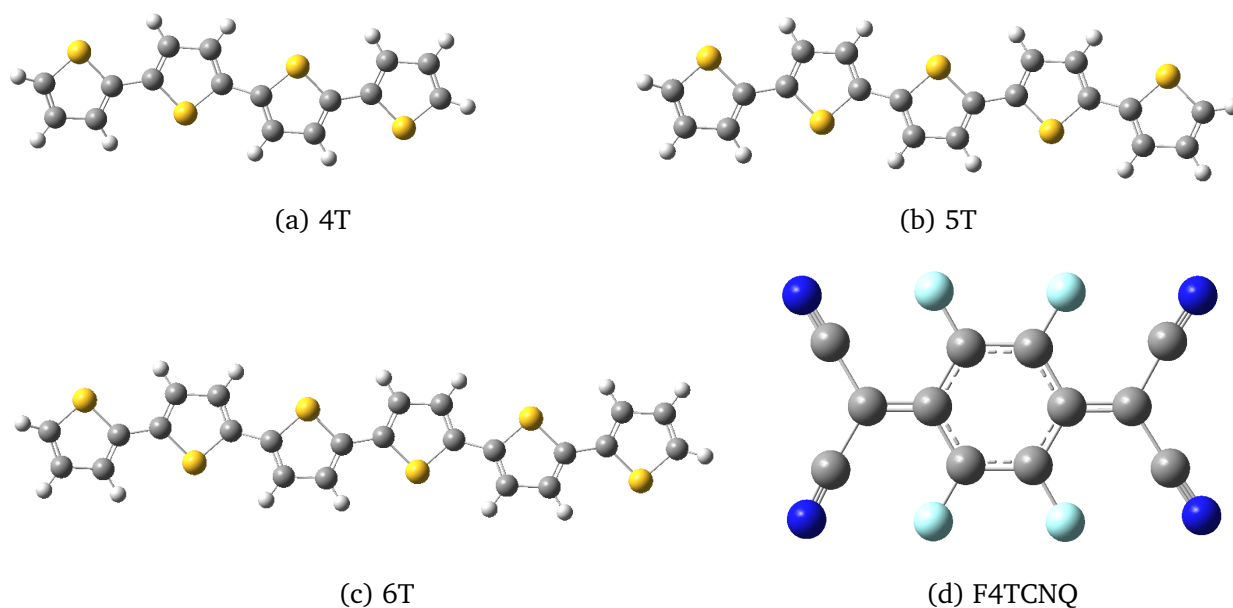


Figure 7.13: Chemical structures of the oligothiophene (a) tetramer, (b) pentamer and (c) hexamer, and (d) F4TCNQ. TCNQ is the same structure with hydrogens in place of fluorines.

Table 7.4: The transfer integral (eV) between the HOMO of the oligothiophene and the LUMO of the dopant molecule.

	F4TCNQ	TCNQ
4T	0.408	0.415
5T	-0.380	-0.378
6T	0.330	0.323

Table 7.5: The HOMO and LUMO levels for the molecules studied. The relevant levels are not in parenthesis.

Molecule	HOMO (eV)	LUMO (eV)
4T	-5.57	(-1.71)
5T	-5.50	(-1.83)
6T	-5.47	(-1.91)
F4TCNQ	(-7.68)	-5.19
TCNQ	(-7.39)	-4.74

values for 4T, 5T and 6T which the same dopant above, where partial charge transfer is observed.

The HOMO of ZnPc is -4.95 eV and the LUMO of F4TCNQ is at -5.19 eV. In this situation the HOMO of the donor is higher than the LUMO of the acceptor, which is desirable for integer charge transfer. These results correlate with the suggestion that partial charge transfer happens in systems where the transfer integral is large, and integer charge transfer happens in systems where the transfer

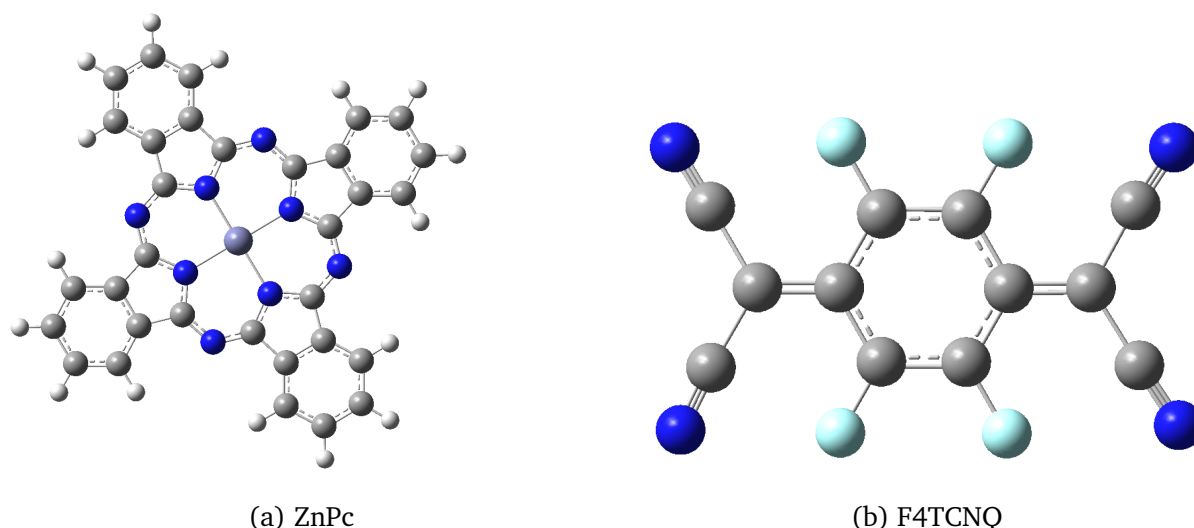


Figure 7.14: Chemical structures of (a) host ZnPc, and (b) dopant F4TCNQ.

integral is small and there is an offset between the donor HOMO and acceptor LUMO. Now, we explore ZnPc and its fluorinated derivatives ($F_x\text{ZnPc}$) with both n-type and p-type dopants.

P-type doping with $F_x\text{ZnPc}$

We investigated zinc phthalocyanine (ZnPc) and its fluorinated derivatives with p-type dopant hexafluorotetracyanonaphthoquinodimethane (F6TCNNQ), shown in Figure 7.15. Experiments have shown that both ZnPc and F4ZnPc can be doped by F6TCNNQ, but F8ZnPc and F16ZnPc cannot [27]. We calculated the transfer integral between the host HOMO and dopant LUMO in three different positions, since we know from experience that the relative orientation of the molecules can have a significant effect on the magnitude of transfer integral. It has been suggested that this should be minimised for efficient doping, and for integer charge transfer that the offset between the donor HOMO and acceptor LUMO should be maximised.

Figure 7.16 shows the three different positions of the dopant relative to the host molecule. A summary of the relevant transfer integrals calculated for each of these positions is given in Figure 7.17. There is not a large difference in transfer integrals between the different fluorinated derivatives for equivalent positions, although the trend is towards a decreasing transfer integral with increasing fluorination. These values are less than that of the system where partial transfer has been observed, but more information would be needed to determine what the mechanism is.

We also explore the offset between the donor HOMO and acceptor LUMO. Figure 7.19 shows the HOMO and LUMO levels of ZnPc and its fluorinated derivatives with those of F6TCNNQ. We

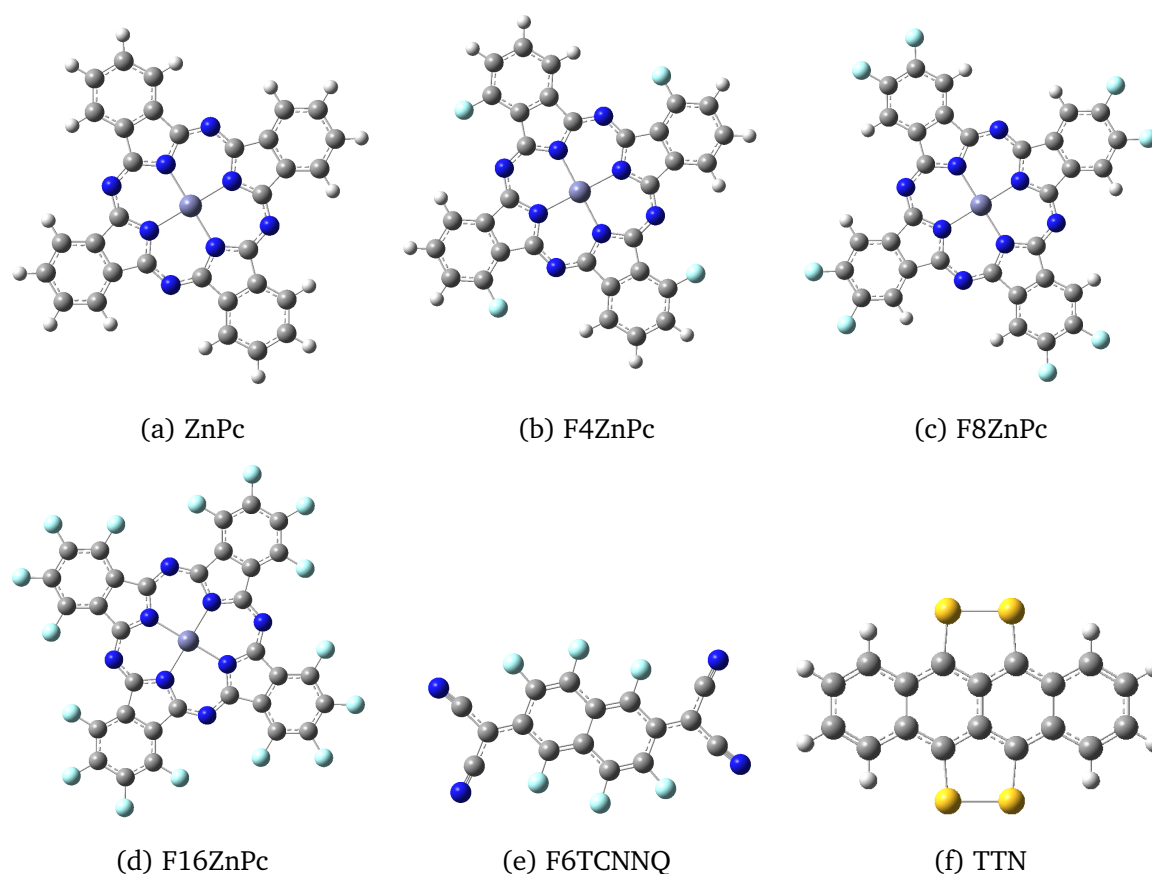


Figure 7.15: (a)-(d) Host molecules zinc phthalocyanine (ZnPc) and fluorinated derivatives. (e) p-type dopant and (f) n-type dopant.

calculated these with the hybrid DFT calculations and TD-DFT calculations as outlined in section 7.4.5 above. These results show that both ZnPc and F4ZnPc have a higher lying HOMO than the F6TCNNQ LUMO (see green dotted line), however F8ZnPc and F16ZnPc have a HOMO level lower than this.

N-type doping with F_x ZnPc

We investigated zinc phthalocyanine (ZnPc) and its fluorinated derivatives with n-type dopant tetrathianaphthalene (TTN), shown in Figure 7.18. Like with the p-type dopant, we calculated the transfer integral with the dopant and host in the same three different positions. Here, there is no clear trend of transfer integral with fluorination, but these transfer integrals are much smaller than those for the p-type dopant F6TCNNQ with the same hosts. Experimentally, F16ZnPc was shown to be doped by TTN in a UPS study [28], so it is clear the transfer integrals do not tell the whole story. However, these transfer do indicate that if charge transfer occurs, it will be integer charge transfer rather than partial charge transfer.

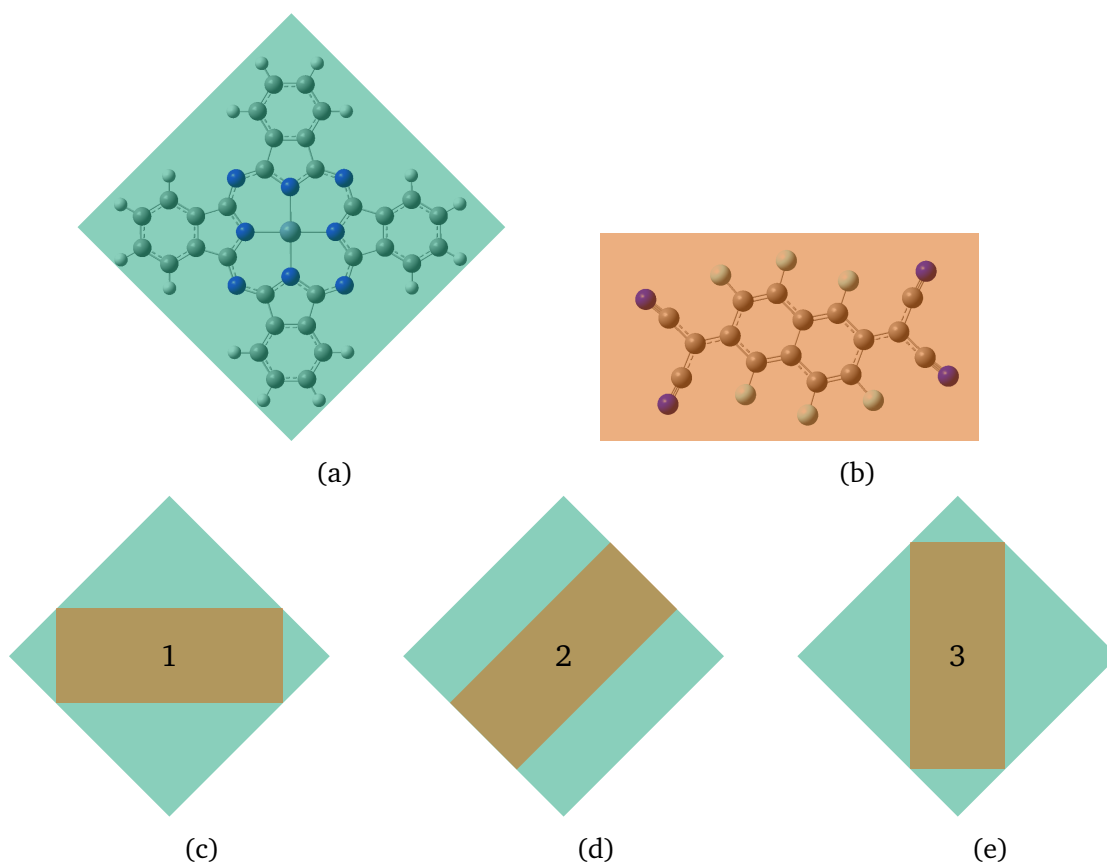


Figure 7.16: (c)-(e) The configurations of ZnPc (or fluorinated derivative) with dopant (F6TCNNQ or TTN), where (a) and (b) define the shapes showing positions.

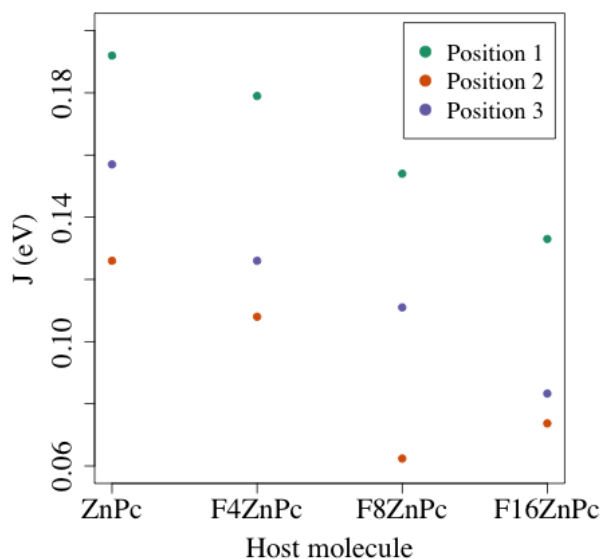


Figure 7.17: The transfer integral between the HOMO of the host (F_x ZnPc) and the LUMO of the dopant (F6TCNNQ) in the three different positions given in Figure 7.16.

To investigate further, we again look at the HOMO and LUMO levels of TTN with ZnPc and its fluorinated derivatives. Figure 7.19 shows the HOMO and LUMO levels of ZnPc and its fluorinated derivatives along with n-type dopant TTN and p-type dopant F6TCNNQ. Increasing fluorination

pushes down both the HOMO and LUMO levels of the ZnPc derivatives. The diagram shows that F16ZnPc is most likely to be doped by TTN, since there is closer alignment of the relevant HOMO and LUMO levels.

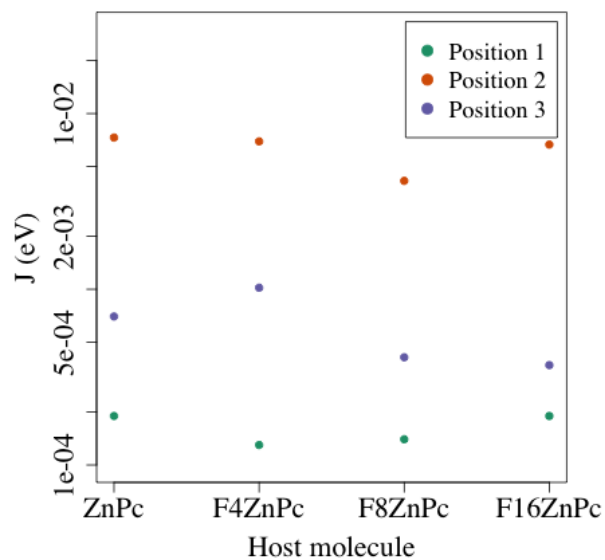


Figure 7.18: The transfer integral between the LUMO of the host (F_x ZnPc) and the HOMO of the dopant (TTN) in the three different positions given in Figure 7.16.

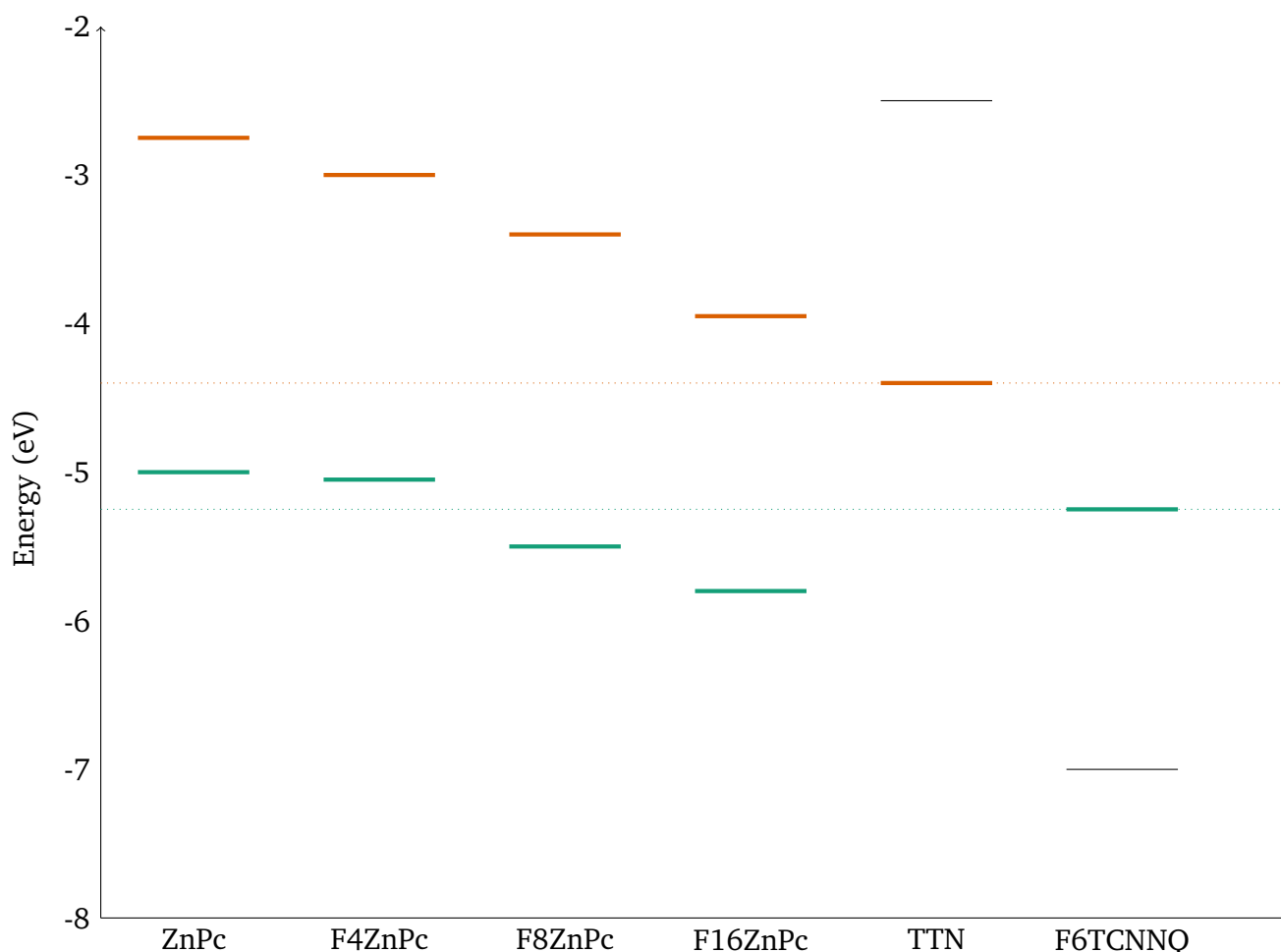


Figure 7.19: HOMO and LUMO levels for n-type dopant TTN, p-type dopant F6TCNNQ and ZnPc and its fluorinated derivatives. The green levels correspond to the HOMOs of the hosts and the LUMO of the p-type dopant (F6TCNNQ). The orange levels correspond to the HOMO of the n-type dopant (TTN) and the LUMOs of the hosts.

7.5 Conclusions

We have applied a method for calculating transfer integrals using a counterpoise basis set to pairs of unlike molecules, as well as intramolecular transfer integrals. Using ghost atoms of the other molecule in calculations on a single molecule ensures the basis set is the same for all calculations.

We validated the method with simple test systems and found good agreement with the energy splitting in dimer and projective methods, where they are valid. As noted earlier, it has previously been found that the choice of functional and basis set affects the magnitude of the transfer integral, so these should only be compared with calculations performed at the same level of theory with the same basis set.

For intramolecular transfer integrals, we showed that the $J_0 |\cos(\theta)|$ dependence is a good approximation.

However, the value of J_0 calculated from a tight-binding approximation may under- or overestimate the transfer integral compared to the counterpoise method.

We used this method to calculate donor and acceptor transfer integrals for P3HT and PCBM, using oligothiophene in place of P3HT. This gave us transfer integrals for charge separation and charge recombination processes, which were similar to those calculated by Liu and Troisi for the same system. We calculated the rates of these processes based on the Marcus-Levich-Jortner (M-L-J) equation. We calculated the energy difference term (ΔG_{ij}) by subtracting the donor LUMO from the acceptor LUMO for charge separation, and subtracted the acceptor LUMO from the donor HOMO for charge recombination.

We found that the relationship with the magnitude of $-\Delta G_{ij}$ did not match what is commonly found in experiments (although did follow what Liu and Troisi published). This could be due to the simple model system we were using to look at a complicated process, and that we did not include multiple states. We explored a system where the only parameter changing is the transfer integral but moving the molecules relative to each other. We found that the ΔG_{ij} term (relative to the external reorganisation energy, λ_{outer}) has the largest effect on the rate, and further explored the effect of these terms relative to each other in the appendix.

We applied the method to calculating transfer integrals between dopant and host systems, for both p-type and n-type dopants. This was to give insight into the exact doping mechanism and we were able to support the observation of partial charge transfer that had been observed experimentally in a *n*T/F4TCNQ system, and reproduced the trend in transfer integrals of previous work. We next calculated the transfer integral for a system where integer charge transport has been observed, and found that in this case the transfer integral was smaller.

We showed in the $F_x\text{ZnPc}$ systems that although the transfer integrals suggest integer charge transfer in the systems studied, they do not tell the whole story. The relevant HOMO and LUMO levels must also be taken into account. In future work, we will also look at the amount of charge transferred with DFT to see if this correlates with the magnitude of the transfer integral.

We have shown that this method can be extended to multiple systems relevant to OPV applications, and that using a counterpoise basis set enables this. In the case of intramolecular transfer integrals, the counterpoise basis set means that the calculation on the individual monomers can be performed

on the relevant fragments with an unrestricted calculation. For transfer integrals between unlike molecules, such as donor acceptor or dopant and host systems, the counterpoise basis set removes the basis set superposition error. In the donor acceptor system studied, the projective method gave unphysical values for the transfer integrals, showing that an alternative is required.

This method is therefore versatile and widely applicable, as well as being transparent and straightforward to implement. The molecular orbitals, atomic orbital overlaps and energies can be calculated with many different computational chemistry software packages (list in the introduction) and the method implemented in Python with the cclib library.

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8

Conclusions and Future Work

We have explored electronic states, charge transfer and charge transport in organic semiconducting materials, using established methods as well as developing our own.

In chapter 4, we used Marcus theory to calculate microscopic hopping rates between helicene molecules in a crystal. We calculated transfer integrals between a subset of the molecules and used the symmetry of the crystal structure to generate the complete set. We used this method to compare two different crystal structures of aza[6]helicene molecules (racemic and enantiopure), where experiments had shown that the hole mobility for the racemic form was two orders of magnitude greater than for the enantiopure form. Our results also showed that the hole mobility was greater for the racemic form, but the difference was less significant, which we attributed to other effects, such as polymorphism in the experimentally studied films.

Additionally, we applied the method to a set of 28 low energy crystal structures of [6]helicene molecules, to first see if we could find which macroscopic properties correlated with high electron or hole mobilities. None of the properties - energy, density or anisotropy - correlated strongly with high hole or electron mobility. However, we then investigated the correlation between particular packing motifs and mobility, and identified which substructures led to high electron or hole mobilities. This method of identifying high mobility substructures could be applied to

many different crystal structures, potentially paving the way for smart design of the structures for devices.

In chapter 5, we used simulations to complement experimental work to identify the types of defects that form in PCBM molecules. Our simulated PL spectra showed a red shift as did the experimentally measured PL spectra, which indicates the formation of traps. Our simulated IR spectra along with experimentally FTIR and XPS spectra indicated that both epoxide and carbonyl defects were forming in PCBM after exposure to light and oxygen. We also performed simulations to investigate the effect of these defects of device performance, since a red-shift in the PL would indicate that traps have formed. Simulations of the electron mobility in films containing a small percentage of defected material showed that this led to a significant reduction in the mobility, with the effect dependent on the size of the traps formed. Understanding how defects form and their effects is important for improving devices made with OSCs.

In chapter 6, we developed a model for polaron formation based on a tight-binding framework that could be applied to large, disordered assemblies. We illustrated it in the one-dimensional case and then applied it to assemblies of fullerene adducts. We used coarse-grained molecular dynamics generated assemblies of fullerene adducts and used a tight-binding model to explore configurational disorder, energetic disorder and polaron formation. We modelled polaron formation in this tight-binding model, treating the material as a continuous dielectric and allowing molecules to respond to the lattice through their site energies, self-consistently. We explored the relative contributions of configurational disorder, energetic disorder and polaron formation in localising the charge states.

This model could simply be applied to assemblies of other disordered systems with isotropic coupling between sites. In systems with anisotropic coupling between sites, populating the Hamiltonian would be more computationally expensive, but it is also possible. Next, we would like to propagate these polaron states in time. This would be done with the time-dependent Schrödinger equation, allowing the states to relax via a damping constant. The size of this constant would be determined by the relative time-scales involved: i.e. the competition between charge transport and charge relaxation.

We further developed a model for calculating transfer integrals between systems that are not accessible with the projective method used in the rest of the thesis in chapter 7. This includes

intramolecular transfer integrals and transfer integrals between unlike molecules. It is similar to the projective method, but by using ghost atoms of the other molecule in calculations on individual molecules, we ensure the basis set is the same for all calculations. We demonstrated the use of this method for intramolecular transfer integrals, transfer integrals between donor and acceptor molecules and transfer integrals between a dopant and host molecules. We calculated the rates associated with these transfer integrals for one of the donor-acceptor systems, and showed the importance of the energy difference term. More work could be applied to carefully calculating these other parameters. In future, it could also be applied to molecules for spin transport.



Appendix

A.1 HOMO and LUMO levels for defected PCBM by different methods

Table A.1 shows the Boltzmann average of the difference in the HOMO and LUMO levels for different defects compared to undefected PCBM for calculating them with the Kohn-Sham, delta-SCF and TD-DFT methods.

Table A.1: Boltzmann average of the difference in the HOMO and LUMO levels (in eV) for different defects compared to undefected PCBM for three methods of calculating them.

Defect type	Difference in HOMO (delta-SCF)	Difference in HOMO (Kohn-Sham)	Difference in LUMO (delta-SCF)	Difference in LUMO (Kohn-Sham)	Difference in LUMO (TD-DFT)
One epoxide	0.04	0.02	-0.10	-0.07	-0.05
Diol	0.77	0.60	-0.62	-0.60	-0.58
Two carbonyls	0.06	0.03	-0.88	-0.87	-0.87

A.2 Gaussian Vibrational Calculation

The procedure used by *Gaussian* [1] for a frequency calculation is as follows [2] [3]:

1. Set up the Hessian, then mass-weight and diagonalise

The Hessian matrix f holds the second order partial derivatives of the potential V with respect to displacement of the atoms in Cartesian coordinates

$$f_{ij} = \left(\frac{\partial^2 V}{\partial \xi_i \partial \xi_j} \right)_0 \quad (\text{A.1})$$

which is a $3N \times 3N$ matrix, where ξ_i and ξ_j are the displacements in Cartesian coordinates, taken at equilibrium positions.

The force constants are then converted to mass-weighted Cartesian coordinates (MWC).

$$f_{MWC,ij} = \frac{f_{ij}}{\sqrt{m_i m_j}} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 \quad (\text{A.2})$$

where $q_1 = \sqrt{m_1} \xi_1 = \sqrt{m_1} \Delta x_1$, $q_2 = \sqrt{m_1} \xi_2 = \sqrt{m_1} \Delta y_1$ and $q_3 = \sqrt{m_1} \xi_3 = \sqrt{m_1} \Delta z_1$.

This is then diagonalised, giving a set of $3N$ eigenvectors and eigenvalues. The roots of the eigenvalues are the fundamental frequencies, which are converted to cm^{-1} .

2. Determine the principal axes of inertia

Next, the centre of mass is translated to the origin, and the moments and products of inertia are determined. This is so the matrix that diagonalises the moment of inertia tensor can be found, which can be used to find the vectors corresponding to the rotations and translations. The centre of mass is found with:

$$R_{COM} = \frac{\sum_{\alpha} m_{\alpha} \mathbf{r}_{\alpha}}{\sum_{\alpha} m_{\alpha}}, \quad (\text{A.3})$$

with sums over atoms α . The origin is then shifted to the center of mass $r_{COM,\alpha} = r_{\alpha} - R_{COM}$.

The elements of the inertial tensor are then calculated. Diagonal elements are the moments of inertia and the off-diagonal elements are the products of inertia.

3. Generate coordinates in the rotating and translating frame

The aim is to generate the transformation D from mass weighted cartesian coordinates to a set of $3N$ coordinates where rotation and translation of the molecule are separated out, leaving $3N - 6$ or $3N - 5$ modes for vibrational analysis. The matrix is then normalised using the reciprocal square root of the scalar product. There should be three rotational and translational modes for atoms, five for linear molecules and six for others.

A Schmidt orthogonalisation is used to generate N_{vib} remaining vectors, which are orthogonal to the rotational and translational vectors. The result is a transformation matrix D which transforms from mass weighted cartesian coordinates q to internal coordinates $S = Dq$.

4. Transform the Hessian to internal coordinates and diagonalise

The mass weighted coordinates now need to be transformed to the new internal coordinates (INT). The transformation is done with:

$$f_{INT} = D^T f_{MWC} D \quad (\text{A.4})$$

The $N_{vib} \times N_{vib}$ submatrix of f_{INT} is diagonalised yielding N_{vib} eigenvalues $\lambda = 4\pi^2\nu^2$ and N_{vib} eigenvectors. The eigenvector matrix L and diagonal matrix with eigenvalues λ_i Λ are related by

$$L^T f_{INT} L = \Lambda \quad (\text{A.5})$$

5. Calculate the frequencies

The eigenvalues need to be converted to frequencies in units of cm^{-1} . Frequency ν is converted to wavenumber $\tilde{\nu}$, with $\nu = \tilde{\nu}c$, solving $\lambda^2 = 4\pi\tilde{\nu}^2c^2$,

$$\tilde{\nu}_i = \sqrt{\frac{\lambda_i}{4\pi^2c^2}}. \quad (\text{A.6})$$

6. Calculate reduced mass, force constants and cartesian displacements

Combining equations A.4 and A.5,

$$L^T D^T f_{MWC} D L = \Lambda = I_{MWC}^T f_{MWC} I_{MWC}, \quad (\text{A.7})$$

where $I = DL$ is the matrix needed to diagonalise f_{MWC}

Finally, the reduced masses, normal modes, frequencies, IR and Raman intensities are outputted.

A.3 Linear optical properties

The method used to calculate the optical dielectric tensor with VASP software was developed by Gajdos *et al* and based on the projector-augmented wave (PAW) methodology outlined in this paper [4].

Using density functional perturbation theory (DFPT), the first order change of the wavefunctions with respect to the wavevector $\mathbf{k}$ and band index n is determined by solving the linear Sternheimer equation

$$[H(\mathbf{k}) - \epsilon_{nk} S(\mathbf{k})] |\nabla_{\mathbf{k}} \tilde{u}_{nk}\rangle = -\frac{\partial [H(\mathbf{k}) - \epsilon_{nk} S(\mathbf{k})]}{\partial \mathbf{k}} |\tilde{u}_{nk}\rangle \quad (\text{A.8})$$

where $H(\mathbf{k})$ is the Hamiltonian for the cell periodic wavefunctions, $S(\mathbf{k})$ is the corresponding overlap operator, $|\tilde{u}_{nk}\rangle$ is the cell periodic part of the wavefunction, and ϵ_{nk} are the eigenenergies.

The dielectric tensor can be determined by calculating the first-order response of the wavefunctions $|\varphi_{nk}\rangle$ to an externally applied field. This involves solving

$$[H(\mathbf{k}) - \epsilon_{nk} S(\mathbf{k})] |\varphi_{nk}\rangle = -\Delta H_{SCF}(\mathbf{k}) |\tilde{u}_{nk}\rangle - |\hat{\mathbf{q}} \vec{\beta}_{nk}\rangle, \quad (\text{A.9})$$

where ΔH_{SCF} is the microscopic cell periodic change of the Hamiltonian resulting from the change of the wavefunctions (to first order) and $\vec{\beta}_{nk}$ is the polarisation vector. Local field effects are

included directly in the evaluation of the dielectric response. Equation A.9 must be solved for three directions $\hat{\mathbf{q}}$ that correspond to the principle axes of the dielectric tensor. The dielectric tensor is then given by

$$\epsilon_{opt}(\hat{\mathbf{q}}) = 1 - \frac{8\pi e^2}{\Omega} \sum_{i,k} 2w_k \langle \hat{\mathbf{q}} \vec{\beta}_{ik} | \varphi_{ik} \rangle, \quad (\text{A.10})$$

where w_k are the k-point weights and Ω is the volume of the cell.

A.4 Calculation of ϵ_{stat} with different functionals and basis sets

Here, we present the values of the static dielectric constant calculated for PCBM using different functionals and basis sets to explore the sensitivity of the value to the level of theory used.

Table A.2: Values of ϵ_{stat} and therefore W_p calculated for PCBM at different levels of theory. The cores hours required for the calculation on PCBM are also given for comparison.

Functional/Basis set	ϵ_{stat}	W_p (eV)	Core hours required (PCBM)
B3LYP/6-31g*	5.08	0.077	115.4
ω B97XD/6-31g*	5.87	0.11	145.9
CAM-B3LYP/6-31g*	5.26	0.086	135.9

A.5 Varying parameters in the Marcus-Levich-Jortner rate equation

We used the Marcus-Levich-Jortner (M-L-J) equation to calculate the rate of charge transfer between donor and acceptor molecules (oligothiophene and PCBM). The value of the parameters λ_{outer} , $\hbar\omega$ and ΔG has a large impact on the eventual rate and trends in the rate, and we explore the effect of them here.

In the M-L-J equation, the rate of charge hopping from site i to site j is given by

$$\Gamma_{ij}^{MLJ} = \frac{2\pi}{\hbar} |J_{ij}|^2 \frac{1}{\sqrt{4\pi\lambda_{outer}k_B T}} \sum_v \exp(-S_{eff}) \frac{S_{eff}^v}{v!} \exp\left(-\frac{(\lambda_{outer} + v\hbar\omega_{eff} + \Delta G_{ij})^2}{4\pi\lambda_{outer}k_B T}\right), \quad (\text{A.11})$$

where J_{ij} is the transfer integral between site i and j , ΔG_{ij} is the energy difference between these sites, λ_{outer} is the outer sphere reorganisation energy, S_{eff} is an effective Huang-Rhys factor, ω_{eff} is the frequency of one effective mode, k_B is the Boltzmann constant, T is the temperature, and the summation ν runs over all vibrational modes.

The maximum rate occurs when the final exponent is equal to zero. This will occur when an integer multiple of $\hbar\omega$ is equal to $\Delta G + \lambda_{outer}$. If $\hbar\omega$ is much less than $\Delta G + \lambda_{outer}$, then there are three situations to consider: (i) $\lambda_{outer} > \Delta G$, the normal Marcus regime; (ii) $\lambda_{outer} = \Delta G$, the activationless regime; and (iii) $\lambda_{outer} < \Delta G$, the inverted Marcus regime [5]. These three possibilities are illustrated in Figure A.1.

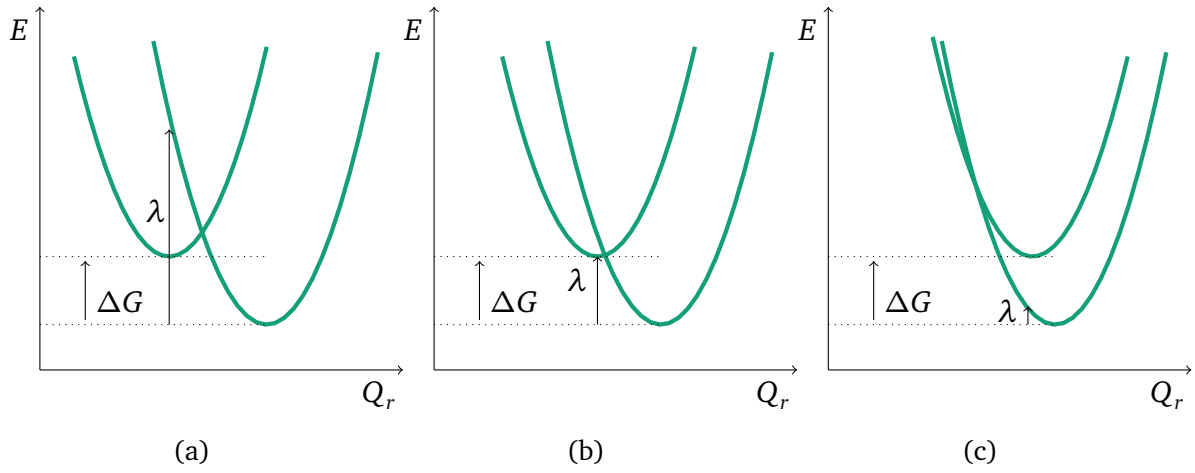


Figure A.1: Potential energy curves for reactants and products in the three different regimes: (a) Normal Marcus regime, $\lambda_{outer} > \Delta G$; (b) Activationless regime, $\lambda_{outer} = \Delta G$; (c) Inverted Marcus regime, $\lambda_{outer} < \Delta G$.

In the normal Marcus regime, the rate will be maximised where $-\Delta G = \lambda_{outer}$ and will decrease monotonically with the magnitude of ΔG . This means that increasing the “driving force” between the donor and acceptor molecules increases the rate. In the inverted Marcus regime, there will be a maximum rate at $-\Delta G = \lambda_{outer} + \hbar\omega$, but as the magnitude of ΔG becomes greater than this, the rate will decrease monotonically, meaning that a greater “driving force” does not result in a larger rate.

The values calculated for λ_{outer} , ΔG_{CS} and ΔG_{CR} by Liu and Troisi [6] suggest that this system is in the Marcus inverted regime. These values are difficult to quantify, so here we explore what the results would look like in the normal Marcus regime, i.e. where λ_{outer} is greater than the values for ΔG . The results for the different length thiophene oligomers with PCBM are given in

Figure A.2. The driving force decreases with increasing monomers for both charge separation and charge recombination (see table 7.2). For the charge separation, the rate decreases with decreasing driving force as would be expected in this regime. There is less of an effect for the charge recombination, but there is less difference between the driving forces in this case.

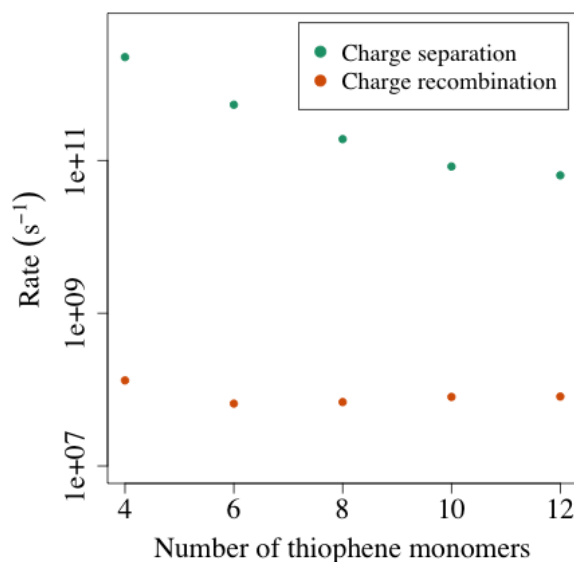


Figure A.2: Rate of charge separation and charge recombination for different lengths of thiophene oligomers.

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