Developing FOB-CTMQC for use in simulating charge transport in organic semiconductors

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I, Matt Ellis, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the work.

Abstract

Charge transfer in organic molecular systems are difficult to simulate due to (fast?) non-adiabatic transitions between Born-Oppenheimer energy surfaces. A range of techniques have been designed to overcome this, such as the Surface Hopping and Ehrenfest methods. However, they tend to suffer from unphysical overcoherence issues. In this report, I present an implementation of a fragment-orbital based coupled-trajectory mixed quantum-classical algorithm (FOB-CTMQC), which is designed for simulating charge transport in systems of tens to hundreds of organic molecules. This method uses an in-house analytical overlap method (AOM) within the framework of coupled-trajectory mixed quantum-classical (CTMQC) molecular dynamics. CTMQC enables the correct calculation of decoherence due to 2 new terms containing a quantity named the Quantum Momentum. While the AOM method allows the simulation of large systems, due to the method's analytic formulation of the off-diagonal elements of the Hamiltonian in terms of the overlap between singly occupied molecular orbitals. E.g. $H_{kl} = CS_{kl}$, where H_{kl} are the off-diagonal elements of the Hamiltonian, C is a constant of proportion and S_{kl} are the off-diagonal overlap elements. For many organic semiconductors we can assume pi-conjugation. Meaning only 1 optimized Slater p-orbital is needed for the calculation of the overlap.

Contents

Chapter 1

Introduction

1.1 Organic Semiconductors

Conductive polymers were first discovered in 1977 by Shirakawa et al [1, 2] for which they were awarded the Nobel prize in Chemistry. Recently these materials have become ubiquitous in many technologies, such as in organic solar cells[3], organic field-effect transistors (OFET) [4] and organic light-emitting diodes (OLED) [5]. While the other two technologies lag behind their inorganic counterparts, uptake of OLED screens is becoming increasingly popular especially in the smartphone and television market due to their flexibility, better colour reprsentation and lower energy consumption than conventional backlit LCD displays. In fact IHS markit's OLED market tracker predicts OLED to be the dominant technology in smartphone screens by 2020 [6] [1]. OLEDs have also found uses in lighting with their efficiency rivalling that of fluorescent tubes [7, 8]. Although, industry has made large strides in fabricating and using these materials the exact nature of the charge transport is still poorly understood. Conventional hopping and band theories break down in the regime of partial delocalisation of the charge carriers and atomistic simulations are required for a realistic picture.

Typically charge carrier mobilities in 'good' organic semiconductors (OSCs) fall between 1-10 cm^2 V^{-1}s^{-1} [9]. This is just beyond the range of hopping model

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[1]This is an online citation -Not sure whether I have cited correctly

validity ($\sim 1 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$) and below that of band theory ($> 50 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$). In this intermediate regime the charge carriers are typically not completely delocalised at the valence band edges (band regime) or localised to a single site/molecule (hopping regime) but delocalised over a few molecules. Without current analytic approaches being valid in this regime many computational approaches have been developed to investigate the underlying charge transport mechanisms [10].

Band theory paragraph...

Hopping theories assume the charge carrier is localised on one site and can hop from site to site in a series of discrete hops [10]. There are various underlying mechanisms for this. For example, the presence of the charge carrier at a site can alter the nuclear geometry. The distorted nuclear geometry can make it harder for the charge carrier to move onto the next site, creating a metastable state and trapping the charge carrier. The deformation in the nuclear geometry is called a small polaron.

Need a better connecting paragraph... Aim of the rest of this section is to lead on to the Born-Oppenhiemer approx

Polaronic hopping theories have been used to relative success and one of the key tools used in visualising this process (assuming harmonic response) are the Marcus Parabolas. These show how the free energy and reaction coordinates change after a charge transfer i.e. from initial to final diabatic states. The term 'diabatic state' isn't well defined and can refer to different things in different formulations. In this work a diabatic state can be imagined as the charge carrier localised on a single molecule. This is discussed later in more detail in 1.3
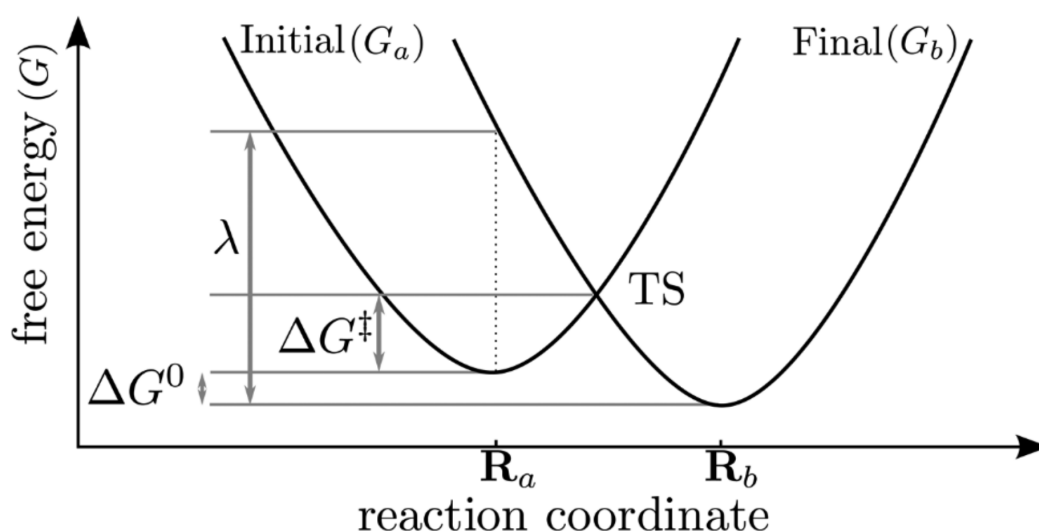
Figure 1.1: Marcus parabolas depicting the relationship between the free energy in the
system and the reaction coordinate at 0 electronic coupling. This figure was
taken from Oberhofer et al [10]

Figure 1.1 above defines various important quantities for calculating the mobility
in materials displaying hopping-like transport. The initial parabola describes the
change in free energy with respect to the reaction coordinate for the initial state,
for example when the charge is located on site 1. The final parabola describes the
change in free energy when the charge is located on site 2 e.g. when the charge has
relocated to site 2. The transition state (TS) is a point where the energies of the
initial and final states are the same. This degenerate point is the only point at which
the charge can move from the initial to final state as other points would result in a
non-zero jump in energy between the 2 parabolas. The diabatic activation energy
$\Delta G^{\ddagger}$ defines the energy required to get to this transition state from the minima of
the initial parabola. The driving force ΔG^0 is the difference in minima of the 2
parabolas, the reorganisation energy λ defines the energy required to change the
reaction coordinate from the final state minima to the initial state minima without
changing electronic state.

Figure 1.1 can change when there is a non-zero electronic coupling (H_{ab}) between
diabatic states. This parameter increases the chance of moving between the initial

and final diabatic states by lowering the diabatic activation energy i.e. the energy required to transition from state 1 to 2. This is visualised in figure 1.2 In figure 1.2
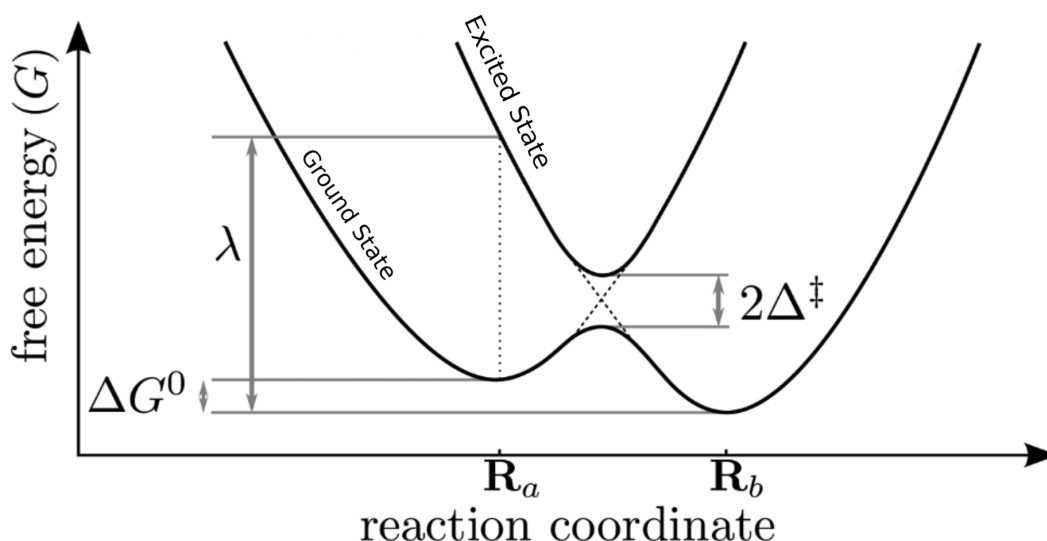

Figure 1.2: Graph depicting the change in free energy for a change in reaction coordinate for non-zero electronic coupling. Adapted from [10]

above the diabatic activation energy has be lowered to $\Delta G^\dagger = \Delta G^\ddagger - \Delta^\ddagger$ making it easier for charge carriers to transition between diabatic states. In our formalism this means it is easier for charge carriers to move between sites i.e. delocalise. We see also that instead of being described totally by 2 parabolas there are 2 new adiabatic potential energy surfaces arising -the ground and excited state. The amount that these new potential energy surfaces diverge from the diabatic wells is dependent on an adiabaticity factor which is proportional to the ratio between the electronic coupling, H_{ab}, and the re-organisation energy, λ. This has been discussed in detail in multiple papers [10–13] .

As a rule of thumb systems with couplings larger than $\frac{3\lambda}{8}$ cannot be properly treated with hopping theories [13] as strongly localised charge carrier states do not exist. Beyond this regime (i.e. when $H_{ab} > \frac{3}{8}\lambda$) hopping between the new adiabatic potential energy surfaces (PES) becomes much less likely and the system can be treated adiabatically. This means evolution occurs on just one PES and the Born-Oppenhiemer approximation is valid.

1.2   Atomisitc Simulations of Nonadiabatic Processes

All treat nuclei classically, all treat electrons QM'cally, way we construct the Hamiltonian and the back reaction via PES are different. Explain surface hopping and Ehrenfest.

In simulating processes involving electronic transfers a key approximation used in conventional molecular dynamics (MD) breaks down. That is the Born-Oppenheimer or adiabatic approximation [14]. This approximation relies on the fact that nuclei are more massive than electrons and are approximately stationary with respect to electron movement (need ref). This results in nuclear evolution that is governed by a single, adiabatic, potential energy surface. However, in many interesting processes, such as electron transfer, non-radiative decay and photochemical processes, electronic transitions between adiabatic potential energy surfaces occur (need ref). Simulating these processes requires non-adiabatic molecular dynamics (NAMD) techniques to be developed to correctly capture dynamical properties.

There have been many techniques proposed for use in NAMD such as the quantum classical Louiville equation (need ref), multiple spawning (need ref) or nonadiabatic Bohmian dynamics (need ref) [2] . However, two of the most popular are trajectory surface hopping (need ref) and mean-field approaches (need ref). This is probably due to their relative simplicity to implement (need ref), efficiency for large systems (need ref) and proven efficacy in a wide variety of

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[2]See first Frederica paper

situations (need ref). In both of these approaches one treats the nuclear subsystem classically and the electronic one quantum mechanically. The electronic evolution is determined by the time-dependent Schrödinger equation, normally expanded as a linear combination of adiabatic or diabatic states. The Hamiltonian in this varies with nuclear position, coupling nuclear motion to electronic transitions. However, the nuclear evolution is slightly different in each technique. In surface hopping, the nuclei are propagated along a single purely adiabatic surface. Which one depends on a series of sudden, stochastic 'hops' between surfaces -controlled by a hopping probability. This is calculated slightly differently for different flavours of surface hopping. Alternatively, in the mean-field approach the nuclei are propagated along a population-weighted average of the adiabatic states. Both methods have their advantages and disadvantages. However, in their original form, they both suffer from a well documented over-coherence of the nuclear and electronic subsytems (need ref). A novel technique has been derived to deal with this named coupled-trajectory mixed-quantum classical (CTMQC) molecular dynamics (need ref). CTMQC has been derived from the exact factorisation of the molecular wavefunction (need ref) and is the semi-classical limit.

1.3   FOB Formalism

Way we construct the Hamiltonian i.e. forcefield for diagonals and overlap for off-diagonals

1.4   CTMQC

The exact factorisation of the molecular wavefuntion involves re-writing it in terms of a nuclear and electronic component. Where the electronic term is parametrically dependent on the nuclear one. This is shown below in eq (1.1) where χ is the

nuclear wavefunction and Φ is the electronic one:

$$\Psi(\mathbf{R},\mathbf{r},t) = \Phi_{\mathbf{R}}(\mathbf{r},t)\chi(\mathbf{R},t) \tag{1.1}$$

The nuclear and electronic wavefunctions then obey separate, but coupled, equations for spatial and temporal evolution. This representation has proven to be useful in furthering understanding through exact solutions of small toy-model systems (need ref [3]) as well for creating a first-principles semi-classical limit of the Schrödinger equation. In this report I will focus on the latter and give some early results of an implementation of a highly efficient FOB-CTMQC algorithm designed for simulating systems of tens to hundreds of molecules -accounting correctly for decoherence.

The equations for the evolution of the electronic and nuclear wavefunctions in the exact factorisation (need ref) are given below:

$$i\hbar\delta_t\Phi_{\mathbf{R}}(\mathbf{r},t) \quad = \left(\hat{H}_{BO} + \hat{U}_{en}\left[\Phi_{\mathbf{R}},\chi\right] - \varepsilon(\mathbf{R},t)\right)\Phi_{\mathbf{R}}(\mathbf{r},t) \tag{1.2}$$

$$i\hbar\delta_t\chi(\mathbf{R},t) \quad = \left(\sum_{\nu=1}^{N_n} \frac{[-i\hbar\nabla_\nu + \mathbf{A}_\nu(\mathbf{R},t)]^2}{2M_\nu} + \varepsilon(\mathbf{R},t)\right)\chi(\mathbf{R},t) \tag{1.3}$$

In the above equations $\Phi_{\mathbf{R}}$ is the electronic which is parametrically dependent on the nuclear positions, $\mathbf{R}$ as well as being explcitly dependent on electronic positions, $\mathbf{r}$ and time, t. χ is the nuclear wavefunction. $\hat{H}_{BO}$ is the Born-Oppenheimer Hamiltonian containing the electronic kinetic energy operator, and interactions between the nuclei and electrons as well as nuclear and electronic self-interactions. The M_ν is the mass of nucleus, ν. The $\mathbf{A}_\nu$ is a time-dependent vector potential and ε is a time-dependent scalar potential. Finally the $\hat{U}_{en}$ is an operator coupling the nuclear and electronic wavefunctions. In Agostini, 16 (need ref) it was shown after applying five approximations, which are justified for many cases [4], we can get the semi-classical limit of the exact factorisation equations.

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[3]see deconstruction paper

[4]Will need to remember what these are, and how they are justified!

- Brief introduction to NAMD.

  - ~~Why isn't normal MD good enough?~~

  - ~~What sort of processes need NAMD to simulate them?~~

  - Characteristics of NAMD -Trivial Crossings, avoided crossings.

  - Give current standard methods and their advantages/disadvantages

- Briefly explain the AOM method.

  - How it works - The analytic off-diagonal elements of hamiltonian (Spencer -both)

  - What the alternatives are (Gajdos paper)

  - Why this is preferable (Gajdos)

  - What are the limitations

- Explain CTMQC

  - Intro -It was derived from exact factorisation (maybe put derivation in appendix)

  - Give the equations. -Ehrenfest + QM term

  - How does it compare to other techniques -decoherence, first principles

  - Why combine it with FOB-CTMQC? -Expensive DFT etc...

  - What sort of systems will I be looking at? Charge transfer in organic semiconductors -1D and 2D systems

Then Results

Chapter 2

My First Content Chapter

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Chapter 3

My Second Content Chapter

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Chapter 4

General Conclusions

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Appendix A

An Appendix About Stuff

(stuff)

Appendix B

Another Appendix About Things

(things)

Appendix C

Colophon

This is a description of the tools you used to make your thesis. It helps people make future documents, reminds you, and looks good.

(example) This document was set in the Times Roman typeface using LaTeX and BibTeX, composed with a text editor.

Bibliography

[1] C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, and Alan G. MacDiarmid. Electrical Conductivity in Doped Polyacetylene. *Physical Review Letters*, 39(17):1098–1101, October 1977.

[2] Hideki Shirakawa, Edwin J. Louis, Alan G. MacDiarmid, Chwan K. Chiang, and Alan J. Heeger. Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH)x. *J. Chem. Soc., Chem. Commun.*, 0(16):578–580, Jan 1977.

[3] Bernard Kippelen and Jean-Luc Brédas. Organic photovoltaics. *Energy Environ. Sci.*, 2(3):251–261, 2009.

[4] M. J. Małachowski and J. Żmija. Organic field-effect transistors. *Opto-Electron. Rev.*, 18(2):121–136, Jun 2010.

[5] N. Thejo Kalyani and S. J. Dhoble. Organic light emitting diodes: Energy saving lighting technology—A review. *Renewable Sustainable Energy Rev.*, 16(5):2696–2723, Jun 2012.

[6] OLED Display Market Tracker - Q2 2018 - IHS Technology, Nov 2018. [Online; accessed 23. Nov. 2018].

[7] Sebastian Reineke, Frank Lindner, Gregor Schwartz, Nico Seidler, Karsten Walzer, Björn Lüssem, and Karl Leo. White organic light-emitting diodes with fluorescent tube efficiency. *Nature*, 459(7244):234, May 2009.

[8] Kazuki Kato, Toshihiko Iwasaki, and Takatoshi Tsujimura. Over 130 lm/w

all-phosphorescent white oleds for next-generation lighting. *Journal of Photopolymer Science and Technology*, 28:335–340, 10 2015.

[9] I. Yavuz. Dichotomy between the band and hopping transport in organic crystals: insights from experiments. *Physical Chemistry Chemical Physics*, 19(38):25819–25828, 2017.

[10] Harald Oberhofer, Karsten Reuter, and Jochen Blumberger. Charge Transport in Molecular Materials: An Assessment of Computational Methods. *Chem. Rev.*, 117(15):10319–10357, August 2017.

[11] J. Spencer, F. Gajdos, and J. Blumberger. FOB-SH: Fragment orbital-based surface hopping for charge carrier transport in organic and biological molecules and materials. *The Journal of Chemical Physics*, 145(6):064102, August 2016.

[12] Jacob Spencer, Laura Scalfi, Antoine Carof, and Jochen Blumberger. Confronting surface hopping molecular dynamics with Marcus theory for a molecular donor–acceptor system. *Faraday Discussions*, 195:215–236, 2016.

[13] Fruzsina Gajdos, Harald Oberhofer, Michel Dupuis, and Jochen Blumberger. On the Inapplicability of Electron-Hopping Models for the Organic Semiconductor Phenyl-C61-butyric Acid Methyl Ester (PCBM). *J. Phys. Chem. Lett.*, 4(6):1012–1017, Mar 2013.

[14] John C. Tully. Nonadiabatic Dynamics. pages 34–71.