
Determining the Mobility of Charge Carriers in Organic Semiconductors

MASTERS' THESIS

*Submitted in partial fulfillment of the requirements of
BITS F421T Thesis*

By

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- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
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Abstract

Master of Science

Determining the Mobility of Charge Carriers in Organic Semiconductors

by Pranay VENKATESH

The Thesis Abstract is written here (and usually kept to just this page). The page is kept centered vertically so can expand into the blank space above the title too...

Acknowledgements

The acknowledgements and the people to thank go here, don't forget to include your project advisor. . .

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Abbreviations

LAH List Abbreviations **Here**

Physical Constants

$$\text{Speed of Light } c = 2.997\,924\,58 \times 10^8 \text{ ms}^{-\text{S}} \text{ (exact)}$$

Dedicate this to someone, anyone.

Chapter 1

Introduction

1.1 Semiconductor Materials

1.2 Electronic Structure

The electronic structure is the solution of the quantum states of electrons in a given chemical system. Typically, this involves determining the energies and wavefunctions of the various states. This can be done by solving the Schrödinger equation for molecules.

1.3 Phonons

1.4 Path Integrals

Chapter 2

Organic Semiconductor Materials

2.1 Introduction

2.2 Rubrene

2.3 Y6

Chapter 3

Polarons

3.1 Introduction

3.2 Pekar's Polaron

3.3 Fröhlich Polaron

3.4 Holstein Polaron

Chapter 4

Path Integrals and Quantum Dynamics

4.1 Introduction

If we want to understand the electronic properties of materials, our limited understanding of analytically solvable quantum systems does not get us very far. There's only a limited number of systems with analytical solutions.

As in the case of classical mechanics, any realistic depiction of quantum systems would require understanding how the system couples with an environment, which influences it heavily. Open quantum system theory hence helps us with this problem since we can learn what happens to systems that interact with an environment and how that affects their dynamics. The easiest models of open quantum systems are called "system-bath" models where you have a (reasonably) solvable system coupled to a bath that represents the effects of an environment.

For studying electron-phonon systems, we need to construct models whereby we can understand what happens to the electrons when they interact with an ionic lattice as an environment. This chapter starts by covering the general theory of open quantum systems and the best ways to treat their evolution. We then move on to the path integral formulation and discuss how that helps us with the quantum dynamics of system-bath models. Once we have constructed these path integral equations, we move onto evaluating the path integrals using Monte Carlo simulations.

4.2 Dynamics of Open Quantum Systems

For isolated quantum systems, the dynamics can be described by the time-dependent Schrödinger equation (TDSE):

$$-i\hbar \frac{\partial}{\partial t} |\Psi(x, t)\rangle = \mathcal{H} |\Psi(x, t)\rangle \quad (4.1)$$

The average values of a time-dependent observable A is given by

$$A(t) = \langle \Psi(t) | \hat{A} | \Psi(t) \rangle \quad (4.2)$$

One of our objectives is to figure out how a quantum-mechanical system moves from an initial state t_0 to a final state. A convenient tool to describe the states of macroscopic systems that can be formed from a mixture of pure states $\{\Psi_\nu\}$ is the density operator \hat{W} , given by

$$\hat{W} = \sum_{\nu} w_{\nu} |\Psi_{\nu}\rangle \langle \Psi_{\nu}| \quad (4.3)$$

which is a summation over the projection operators onto the pure states with a probability weight of w_{ν} . Expectations for observables can now be determined by : $\langle \hat{A} \rangle = \text{Tr}\{\hat{W} \hat{A}\}$.

First let us try to construct an equation of motion for the density operator.

4.2.1 Liouville-von Neumann Equation

John von Neumann extended the classical Liouville equation for phase space trajectories to quantum statistics.

The time propagation of the wavefunctions in eq. 4.1 can be written as

$$|\Psi(t)\rangle = U(t, t_0) |\Psi(t_0)\rangle \quad (4.4)$$

where

$$U(t, t_0) = \exp\left(-\frac{i\mathcal{H}(t - t_0)}{\hbar}\right)$$

.

We can substitute eq 4.4 in in eq 4.3 to obtain a time-dependent equation for the density operator.

$$\hat{W}(t) = \sum_{\nu} w_{\nu} U(t, t_0) |\Psi(t_0)\rangle \langle \Psi(t_0)| U^{\dagger}(t, t_0) = \sum_{\nu} U(t, t_0) W(t_0) U^{\dagger}(t, t_0) \quad (4.5)$$

To derive a time-derivative equation, take a partial derivative on both sides with respect to t :

$$\frac{\partial}{\partial t} \hat{W}(t) = -\frac{i}{\hbar} (\mathcal{H} \hat{W} - \hat{W} \mathcal{H}) = -\frac{i}{\hbar} [\mathcal{H}, \hat{W}(t)] \quad (4.6)$$

Equation 4.6 is called the Liouville-von Neumann equation and is the simplest equation for the evolution of macroscopic quantum systems. For brevity we can use the notation of super-operator $\mathcal{L} = \frac{1}{\hbar} [H, (\cdot)]$ to get

$$\frac{\partial}{\partial t} \hat{W} = -i \mathcal{L} \hat{W}$$

4.2.2 System-Bath Models and The Reduced Density Matrix

For models where we have a system coupled to a bath, we will represent our Hamiltonian in the form :

$$\mathcal{H} = \mathcal{H}_S + \mathcal{H}_R + \mathcal{H}_{int} \quad (4.7)$$

Where \mathcal{H}_S is the Hamiltonian of the relevant system, represented only in terms of system coordinates $s = \{s_j\}$ and momenta $p = \{p_j\}$, \mathcal{H}_R is the Hamiltonian of the reservoir having coordinates $Z = \{Z_\xi\}$ and momenta $P = \{P_\xi\}$. \mathcal{H}_{int} is the linear coupling term of the system and the reservoir.

For harmonic baths, the reservoir Hamiltonian reads

$$\mathcal{H}_R = \sum_{\xi} \frac{P_{\xi}^2}{2M} + \frac{1}{2} M \omega_{\xi}^2$$

4.3 Path Integral Treatment of Open Quantum Systems

For a general Hamiltonian in cartesian co-ordinates

$$\mathcal{H} = \sum_j \frac{p_j^2}{2m_j} + V(x_1, \dots, x_n)$$

To propagate this system from an initial (t_0, x_0) to a final (t_f, x_f) , let us split the time scale t into N short time chunks $\Delta t \equiv \frac{t}{N}$. Now the time-evolution operator can be written as :

$$e^{-i\mathcal{H}t/\hbar} = e^{-i\mathcal{H}\Delta t/\hbar} \dots e^{-i\mathcal{H}\Delta t/\hbar} = \prod_{k=1}^N e^{-i\mathcal{H}(t_k - t_{k-1})/\hbar} \quad (4.8)$$

where $t_k = kt/N$.

Using

$$\int dx_k |\psi_k\rangle \langle \psi_k| = 1$$

between successive steps we get :

$$\langle x_f | e^{-i\mathcal{H}t/\hbar} | x_0 \rangle = \int dx_1 \dots \int dx_{N-1} \prod_{k=1}^N \langle x_k | e^{-i\mathcal{H}(t_k - t_{k-1})/\hbar} | x_{k-1} \rangle \quad (4.9)$$

This is an exact representation for any value of N . $x_f \equiv x_N$ is the final point in the propagation.

To evaluate this integral, we need an approximation to evaluate the short time propagator in a time-step Δt . If operators A and B do not commute, we cannot use the rule of exponential of a sum of operators equals the product of exponentials of the operators. The expansion of e^{A+B} developed by Suzuki and Trotter helps us alleviate this problem. They found that :

$$e^{\delta(A+B)} = e^{\delta A} e^{\delta B} + O(\delta^2) \quad (4.10)$$

The error term $O(\delta^2)$ vanishes when we take the limit of $\delta \rightarrow 0$.

As a guess way to split the Hamiltonian if we separate out the kinetic term \mathcal{T} and the potential term \mathcal{V} in the following way :

$$e^{-i\mathcal{H}\Delta t/\hbar} \approx e^{-i\mathcal{V}\Delta t/2\hbar} e^{-i\mathcal{T}\Delta t/\hbar} e^{-i\mathcal{V}\Delta t/2\hbar} \quad (4.11)$$

We can evaluate the kinetic part exactly to get :

$$\langle x_k | e^{-i\mathcal{H}\Delta t/\hbar} | x_{k-1} \rangle = \prod_{j=1}^n \left(\frac{m_j}{2\pi i \hbar \Delta t} \right)^{1/2} \exp \left(\frac{i}{\hbar} \frac{m_j}{2\Delta t} (x_{j,k} - x_{j,k-1})^2 \right) \quad (4.12)$$

Plugging this into the propagation expression we get :

$$\begin{aligned} \langle x_f | e^{-i\mathcal{H}t/\hbar} | x_0 \rangle &\approx \prod_{j=1}^n \left(\frac{m_j N}{2\pi i \hbar t} \right)^{1/2} \int d^n x_1 \dots \int d^n x_{N-1} \\ &\exp \left(\frac{i}{\hbar} \sum_{k=1}^N \left(\sum_{j=1}^n \frac{m_j N}{2t} (x_{j,k} - x_{j,k-1})^2 - \frac{t}{2N} [\mathcal{V}(x_k) + \mathcal{V}(x_{k-1})] \right) \right) \end{aligned} \quad (4.13)$$

This equation is the "primitive" discretized path integral expression. As we use more sophisticated methods to split the Hamiltonian we will get better discretized expressions to work with.

When we take the limit of $N \rightarrow \infty$, we get an equality.

4.4 Imaginary Time Path Integral Monte-Carlo

4.5 Real Time Path Integral Dynamics

One of the major issues with performing real-time path integral monte carlo simulations is the infamous sign problem.

To alleviate the sign problem, we employ a method developed by Makri and co-workers to develop equations that converge when attempting to numerically sample the integrals.

4.5.1 Quasi-Adiabatic Propagator Path Integral (QuAPI)

4.5.2 Quantum-Classical Path Integral (QCPI)

4.5.3 Evaluating the Real-Time Path Integrals

4.6 Analytic Continuation Method

4.7 Determining Observables

4.7.1 Mobility

4.7.2 Polaron Radius

4.7.3 Self-Energy

Chapter 5

Modelling Real Materials

5.1 Introduction

To model real materials

5.2 Electronic Structure Data

5.3 Phonon Modes

5.4 Coupling Constants

5.5 Constructing Reference Hamiltonians

5.6 Modelling Dynamics

Chapter 6

Results

6.1 Pentacene

In this example, we model the dynamics of the pentacene dimer and tetramer using the path integral non-adiabatic dynamics techniques as mentioned.

To study charge transfer processes in molecular aggregates, we use a one-dimensional nearest-neighbours (NN) Hamiltonian of the form [Borelli Ref]. :

$$\mathcal{H} = \sum_{n,m}^{N_e} \epsilon_{nm} |n\rangle \langle m| + \sum_{k=1}^F \frac{\omega_k}{2} (P_k^2 + Z_k^2) + \sum_{n,k}^{N_e, F} g_k^{(n)} Z_k |n\rangle \langle n| \quad (6.1)$$

Here ϵ_{nm} represents the members of a matrix of electronic energies and couplings. For the nearest-neighbour pentacene model we are considering we use a value of $\epsilon_{12} = 300cm^{-1}$. The "system" part of the Hamiltonian (\mathcal{H}_s) is described by the first term of electron couplings. The second term represents the energies of the vibrational modes, treated as harmonic in this case. The third term is the linear coupling between each electron and the vibrational mode at site k. The vibrational frequencies and linear coupling terms are determined by Density Functional Theory calculations [Borelli Hopping Ref].

The effects of the bath are taken into consideration by the spectral density. We model the interactions as an effective Debye spectral density with reorganization energy $\lambda = 100cm^{-1}$ and characteristic frequency $\gamma = 50cm^{-1}$.

Using calculations from the Quantum-Classical Path Integral method, we can see the propagation of the density matrix. We can use this data to obtain the populations of the various sites (diagonal elements) and the coherences between the sites (off-diagonal elements).

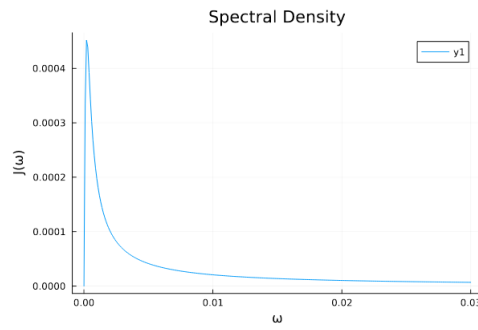
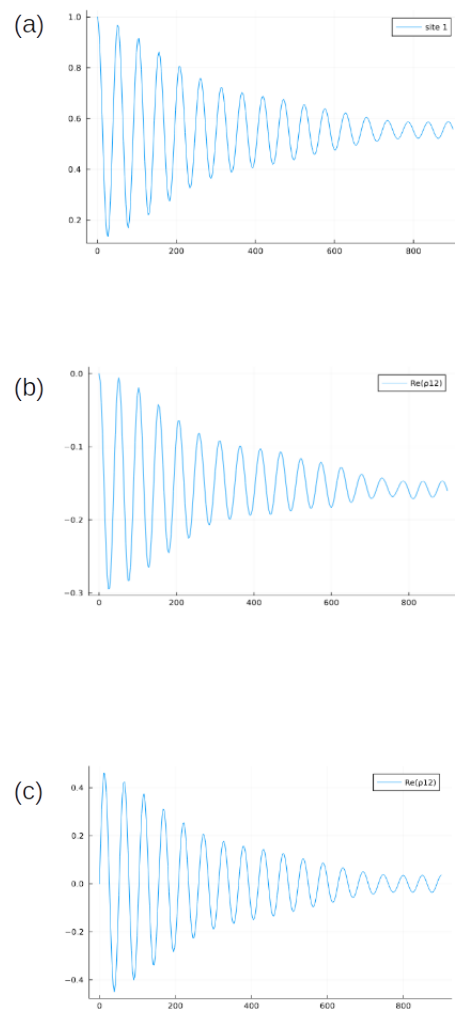


FIGURE 6.1: Debye Spectral Density for Pentacene

FIGURE 6.2: Density Matrix Elements of Pentacene dimer. (a) ρ_{11} population of site 1 (b) $Re(\rho_{12})$ Real part of coherence (c) $Im(\rho_{12})$ Imaginary part of coherence

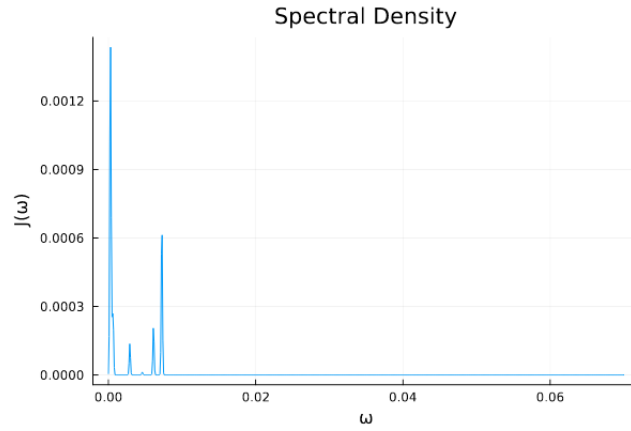


FIGURE 6.3: Spectral Density (with Gaussian broadening) for Rubrene

6.2 Rubrene

The effects of the bath are taken into consideration by the spectral density $J(\omega) = \sum_i g_i^2 \delta(\omega - \omega_i)$. We use a Gaussian line-shape broadening to model the spectral density $J(\omega)$.

Appendix A

Feynman Variational Approach to the Polaron Problem