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Murali Devi
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Theoretical Analysis of
Single Molecule Spectroscopy Lineshapes
of Conjugated Polymers

by

MURALI DEVI

A dissertation submitted to the Graduate Faculty in Physics
in partial fulfillment of the requirements for the degree of
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This manuscript has been read and accepted for the Graduate Faculty in Physics in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Abstract

Theoretical Analysis of Single Molecule Spectroscopy Lineshapes of Conjugated Polymers

by

Murali Devi

Adviser: Prof. Seogjoo Jang

Conjugated Polymers (CPs) exhibit a wide range of highly tunable optical properties. Quantitative and detailed understanding of the nature of excitons responsible for such a rich optical behavior has significant implications for better utilization of CPs for more efficient plastic solar cells and other novel optoelectronic devices. In general, samples of CPs are plagued with substantial inhomogeneous broadening due to various sources of disorder. Single molecule emission spectroscopy (SMES) offers a unique opportunity to investigate the energetics and dynamics of excitons and their interactions with phonon modes. The major subject of the present thesis is to analyze and understand room temperature SMES lineshapes for a particular CP, called poly(2,5-di-(2'-ethylhexyloxy)-1,4-phenylenevinylene)(DEH-PPV). A minimal quantum mechanical model of a two-level system coupled to a Brownian oscillator bath is utilized. The main objective is to identify the set of model parameters best fitting a SMES lineshape for each of about 200 samples of DEH-PPV, from which new insight into
the nature of exciton-bath coupling can be gained. This project also entails developing a reliable computational methodology for quantum mechanical modeling of spectral lineshapes in general. Well-known optimization techniques such as gradient descent, genetic algorithms, and heuristic searches have been tested, employing an $L^2$ measure between theoretical and experimental lineshapes for guiding the optimization. However, all of these tend to result in theoretical lineshapes qualitatively different from experimental ones. This is attributed to the ruggedness of the parameter space and inadequateness of the $L^2$ measure. On the other hand, when the dynamic reduction of the original parameter space to a 2-parameter space through feature searching and visualization of the search space paths using directed acyclic graphs (DAGs), the qualitative nature of the fitting improved significantly. For a more satisfactory fitting, it is shown that the inclusion of an additional energetic disorder is essential, representing the effect of quasi-static disorder accumulated during the SMES of each polymer. Various technical details, ambiguous issues, and implication of the present work are discussed.
Dedicated to

my mother Dr M M Devi,

my wife Dr H Lee,

and

my aunt Ms R P Devi.
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Chapter 1

Introduction

1.1 Motivation

Technology driven progress requires vast amounts of energy. The industrial revolution of the eighteen century revolved on the ease with which coal could be cheaply extracted and quickly burnt to drive steam engines that could manufacture goods, which in turn seeded and accelerated further mechanization, growth, and energy demand[1]. It is this access to cheap energy that has facilitated social and economic changes of modern western society.\(^1\)

The post industrial revolution period has stayed the course of this increasing energy usage, albeit augmented with other sources such as oil, natural gas, wind, hydropower, geothermal, biomass, nuclear, and solar. Consumer demand of better manufactured goods, population growth, the evolving modernization of second and third world countries, and continued economic growth has sustained this demand.\(^2\)

Even though there is consensus that fossil fuel as the predominant principal energy source

\(^1\)For instance, our egalitarian and other social concepts are derived on ultimately noting that during this industrialization period, machine manufactured goods were cheaper, quicker, and more exacting in measurement (albeit less crafted) than those which were hand produced that may have required indentured or forced labor. Servitude was a common and important staple of economic growth in most all cultures that have existed[94, 95] before the advent of manufactured goods of this industrialization period.

\(^2\)The Energy Information Administration Annual Energy Outlook 2015 Report [108] of the energy demands for the US alone states the Gross Domestic Product(GDP) will grow at 2 – 3% – 2.8% projected to 2040. While the International Monitary Fund’s World Economic Outlook Report of October 2015 estimate for World GDP growth till 2020 will be in the 3-5 % range[57]. Assuming a 2-5GDP will double within 15-30 years.
of our economy cannot be maintained due to its finite supply and its adverse effects on climate, alternative renewable energy sources are yet too costly to meet the expected demands in the next several decades.[108] Controlled nuclear fusion based technologies could ultimately meet our growing needs, but such devices are not expected to be used for several decades yet. Although fission based nuclear power stations are good alternatives to meet our energy needs, the stigma associated with their power after incidents like Chernobyl, Three Mile Island, and Fukushima Daiichi will sway little in public opinion in building more. However, the extreme consequences of continued carbon dioxide emission and global temperature rise may force public sentiment to use more nuclear energy.

Direct solar energy capture and electric conversion through photocells may offer a quick and intermediate stepping stone before other technologies can resume energy demands. However, photocell fabrication, efficiency, cost, consumer demand, and political hurdles from existing technologies have not been beneficial to the solar energy industry. Even if solar cells start being entrenched, the electrical storage of the energy produced during daylight hours for dusk and nighttime usage through batteries is still very expensive. Ultimately, it is consumer cost of ownership and maintenance that will put vigor in their usage. Government subsides would help in lowering this cost, but education of the consequences of climate change and a runaway green house effect has not yet reverberated though the general populace to overcome political entrenchment on holding to existing technologies. Nevertheless, this cost could be mitigated through the better understanding of these optoelectronic devices, which would lead to better fabrication and higher efficiencies.

The initial photovoltaic solar cells of the 1950’s consisted of a basic p-n junction comprised of a p-doped and n-doped mono-crystalline silicon semiconductor sandwiched between a transparent and regular conductor. The abundance and easy access of this expensive fabrication process of silicon made it viable in photovoltaic solar cells, even though it is
an indirect band gap semiconductor as compared to other crystalline compounds such as Gallium Arsenide. The so called second generation of thin film types of solar cells (using noncrystalline forms of either Polycrystalline Silicon, Cadmium Telluride, Copper-Indium-Gallium Selenide) were consequently introduced to lower the cost of energy production and manufacturing, but they lacked the efficiency of the larger crystalline silicon cells. The current generation of photovoltaic cells include dye-sensitized (Gratzel cells), quantum dot, Perovskite modified, and other organic solar cells. Though organic solar cells have the least efficiency and are the newest type, the possibility of inexpensive fabrication by chemical processes, simple physical deposition on large surfaces by spray painted with roll-to-roll manufacturing technologies at ambient temperatures, and organic molecular conformational flexibility are leading the push for their usage.

Similar to the Wannier-Mott exciton in band theory that describes crystalline photovoltaic p-n junction materials, a coulombically bound hole and electron pair is used to describe the initial photo absorption of energy in a conjugated polymer. As in the case of p-n junction type solid state light emitting diodes(LED), conjugated polymers have been used for energy efficient lighting and other optoelectronics. Unlike the inefficient incandescent light bulb which radiates a broadband black body spectrum which is principally invisible to the human eye, the photoluminescent properties of a narrow band florescence of conjugated polymers can be designed to work optimally within the visible range of the electromagnetic radiation. The luminescent properties of conjugated polymers do not change whether the initial energy transferred to the molecule is from an electronic closed circuit or from photo absorption. An understanding of this mechanism under which the initial excitation leads to exciton migration, charge separation, and florescence, may help the engineering of efficient devices based on conjugated organic molecules.

The demand for energy usage is growing. The diversion of the anthropogenic environment-
tal disaster of using fossil fuels will require technological progress in newer energy extraction and usage methods. Although solar cell energy capture may not be a final solution to our energy needs, it is the most promising for time realistic transition away from fossil fuels to a future with as yet uncertain and unknown technology. The mechanism by which conjugated polymers act like a semiconductor for use as both photovoltaic and luminescence may be part of the technology revolution needed for this transition.

1.2 Organic Conjugated Polymers

Heeger, MacDiarmid and Shirakowa received the Chemistry Nobel prize in 2000 for their ground breaking work in the 1970’s for the discovery of metal like conductivity behaviour in conjugated organic polymers[82]. Before their discovery, organic polymers were viewed as structural insulators whose properties such as the refractive index, translucence, density, tensile strength, elasticity, transporting of molecules, melting points, tacitity, and others could be controlled with fairly well understood synthetic and mechanical engineering processes [103, 50, 26]. Almost a decade passed, when in the late 1980’s, the electroluminescent properties of these conjugated polymers were first observed by Burroughs et al[58] in a polymer of p-phenylene vinylene(PPV). Since these seminal initial discoveries, these organic conjugated polymers have spawned a multi-billion dollar industry for uses in lighting[3], nano wires[2], photovoltaic cells[22, 102], electronic displays[38], molecular switches[106], chemical sensors [76, 4], and other optoelectronic devices[100]. It has been recognized that the optoelectronic properties of these macro molecules are associated with the π-conjugated double bonds and delocalization[34]. The detailed mechanism of how an initial exciton formed electronically or photonically, leads to subsequent polaron propagation, and possible florescence or phosphorescence[115] is not well known to the extent that better electronic devices can be engineered in a routine manner.
Common optical properties of conjugated polymers are attributed to the delocalization of the \( \pi \) molecular orbitals, and that the associated organic bandgap can be roughly related to the energy separation between Lowest Unoccupied Molecular Orbitals (LUMO) and the Highest Occupied Molecular Orbitals (HOMO). Although the quantum luminescent efficiency in organic light emitting diodes and the quantum efficiency of solar cells for organic conjugated polymers were both initially very low, recent improvements in both the efficiencies and their cost in production, as compared to their inorganic counterparts, make them feasible as practical optoelectronic devices. An understanding of the the mechanism of transport of the initial Frenkel type exciton\[37, 36\] along the back bone of the conjugated polymer would greatly improve the engineering of better optoelectronic devices. The absorption and fluorescence of single molecule spectroscopy of PPV has given us a deeper understanding of the physics associated with the initial exciton creation and subsequent exciton dynamics along the polymer backbone.

Although the tight binding type chromophoric model has been used to describe the transport of excitons along the conjugated back bone, there is still no consensus on the exact nature of what constitutes a chromophore. The underlying assumption that structural defects such as kinks, chemical defects, and sudden flips in planar segments\[117\] that could be used to define a chromophore has been questioned\[21\]. Nevertheless, it has been accepted from experimental and simulation studies that planarization of the ring moities of polymers in the excited state explains the narrowing of emission spectra as compared to the absorption lineshapes\[89, 70, 63\].

Although we do not know with certainty of what constitutes a chromaphore, several theoretical models have been used on the exciton transport mechanism along adjacent chromaphores of a conjugated polymer. Is such mobility phonon assisted coherent transport, or can it be thought of as simply hoping between adjacent chromaphores? Recent studies
have suggested that torsional dynamics may assist in the exciton transport for phenylene-vinylene conjugated polymers[13].

Single Molecule Spectroscopy(SMS) of individual molecules of conjugated polymer has offered the possibility of revealing processes occurring at the individual molecule level and may have important affects on the functioning of these devices[7, 118]. In the late nineteen eighties, the first single molecule spectroscopy was taken for pentacene in a host p-terphenyl crystal at liquid helium cryogenic temperatures[81, 84]. The first room temperature near field microscopy of a single molecules soon followed[11]. Far field Confocal microscopy was introduced by mid nineteen nineties[75].

Although cryogenic temperatures have produce higher signal to noise ratios in both absorption and emission spectra, room temperature studies of single molecules are important for understanding common reactions in biological systems and other conventional reactions that we are familiar with. Room temperature fluorescence observation of single molecule spectra of conjugated polymers are far more easier to contrast against a background signals than absorbance. Irrespective of the electronic or photonic excitation source, the wide band absorption and narrow band emission spectra of conjugated polymers means that a single molecule can be excited with an off-resonance excitation that will not overlap with the emission spectrum. So, it is more common and easier to see room temperature emission spectrum of single molecules, rather then absorption.

It has been observed that prolonged exposure of a conjugated polymers to a laser source causes photobleaching[16, 8, 42], intermittency[56, 73], spectral diffusion[79, 88] conformational fluctuations[88, 92], and photon antibunching[54, 107]. Consequently, long time emission spectra of conjugated polymers is convoluted with fluctuations of broad time scales.
Figure 1.1: Oligomer of poly(2,5-di-(2’-ethylhexyloxy)-1,4-phenylenevinylene)(DEH-PPV) where \( n \) is of order 11.

1.3 Thesis Overview

The understanding of conjugated polymers may lead to a major milestones in their usage in efficient energy capturing devices, electronic lighting, molecular switches, chemical sensors, other optoelectronic devices, and may greatly assist in the transitioning away from fossil fuel based energy sources. As electromagnetic radiation is our principal tool of investigation, simple modeling of the theoretical line shapes of single conjugated polymers is the first step in this undertaking.

This work utilizes a simple model of two electronic levels coupled to a bath of infinite number of harmonic oscillators in order to model the experimental room temperature single molecule spectroscopy of a short conjugated oligomer of poly(2,5-di-(2’-ethylhexyloxy)-1,4-phenylenevinylene)(DEH-PPV) (see Figure 1.1). The theoretical modeling may help in gaining insights into the various sources of disorder and dynamical mechanisms that can
cause fluctuations, relaxations, and localizations of the exciton. Excitons in conjugated polymers are not simple Frenkel excitons, as the localization of the such an exciton is related with the larger conjugation length found in the planarization of the excited singlet state in Phenylene-vinylene polymers.

In Chapter II, the two state electronic system coupled to a Brownian oscillator bath is introduced and justified as a minimal model to represent the observed experimental transitions. Chapter III discusses the experimental methodology in great detail for analysis of the experimental data and subsequent construction of the two novel search methods for the $L^2$ line shape fitting. As several numerical algorithms were used in the analysis, a further discussion is deferred to the Appendices where the methodologies are explained in more detail. Chapter IV provides the conclusion of this thesis.
Chapter 2

Theoretical Model: Two-level system coupled to a Brownian oscillator bath

In this chapter, we discuss the model of two-level electronic states coupled to a Brownian oscillator bath in order to describe the vibronic progression of the experimental single molecule emission spectrum of the conjugated oligomer poly(2,5-di-(2'-ethylhexyloxy)-1,4-phenylenevinylene)(DEH-PPV). We write the Hamiltonian for the model system, and show the line shape function for the the linear emission and absorption spectra within the Franck-Condon approximation and displaced oscillator model for the singlet ground and excited Adiabatic Born-Oppenheimer surfaces. We write down the effective spectral density associated with a spin system coupling to a single primary oscillator that then couples to the Ohmic bath. We also discuss, some aspects of the computer implementation of the line shape generations for the given spectral density.

2.1 Lineshape expressions for harmonic oscillator bath

We model a two level electronic system coupled to a Brownian oscillator as a displaced harmonic well representing the ground $S_0$ and excited $S_1$ surfaces(see Figure 2.1). The Brownian oscillator bath consists of a single harmonic oscillator that is linearly coupled to a thermalized bath (see Appendix for discussion of the Caldeira-Leggett Hamiltonian). In the
Figure 2.1: Model representation of Brownian oscillator coupled to a two level electronic system represented by $S_0$ and $S_1$ singlet surfaces. Each of vibronic black lines of each surface represent the levels of the Brownian oscillator that is itself coupled to the environment. The red vertical arrows represents the Franck-Condon transitions between the vibronic levels. The green diagonal transition lines represent relaxations into the ground vibronic levels of each singlet surface.
adiabatic limit within the Born-Oppenheimer approximation, our model Hamiltonian $H_m$ is given as

$$H_m = \epsilon_g |g\rangle \langle g| + \epsilon_e |e\rangle \langle e| + B |e\rangle \langle e| + H_b,$$ (2.1)

$$H_b = \sum_n \hbar w_n (b_n^+ b_n + \frac{1}{2}),$$ (2.2)

$$B = \sum_n g_n (b_n + b_n^+)$$ (2.3)

where $\epsilon_g$ and $\epsilon_e$ are the energies of the ground and excited states $S_0$ and $S_1$. The $H_b$ is the harmonic oscillator bath, and $B$ is the electronic-nuclear coupling (see Appendix on the Caldeira-Leggett Hamiltonian).

According to the Fermi Golden Rule, the absorption line shape is given by

$$I(w) = \int_{-\infty}^{\infty} dt \ e^{i(w-e/\bar{\hbar})t} \cdot \frac{1}{Z} Tr_b \left\{ e^{-i(H_b+B)t/\bar{\hbar}} e^{-\beta H_b} e^{iH_b t/\bar{\hbar}} \right\},$$ (2.4)

where $\epsilon = \epsilon_e - \epsilon_g$ and $Z = Tr_b\{e^{-\beta H_b}\}$. The emission line shape $E(w)$ is given by

$$E(w) = \int_{-\infty}^{\infty} dt \ e^{i(w-e/\bar{\hbar})t} \cdot \frac{1}{Z'} Tr_b \left\{ e^{-i(H_b+B)t/\bar{\hbar}} e^{-\beta H_b} e^{iH_b t/\bar{\hbar}} \right\},$$ (2.5)

where $Z' = Tr_b\{e^{-\beta(H_b+B)}\}$. In terms of the real and imaginary parts of the line shape function $\{G_r(t), G_i(t)\}$, the above lineshape functions are expressed as

$$I(w) = \int_{-\infty}^{\infty} e^{i(w-e/\bar{\hbar})t} e^{-G_r(t)} e^{-iG_i(t)} dt,$$ (2.6)

$$E(w) = \int_{-\infty}^{\infty} e^{i(w-e/\bar{\hbar}+2\lambda/\bar{\hbar})t} e^{-G_r(t)} e^{iG_i(t)} dt,$$ (2.7)

with

$$G_r(t) = \sum_n g_n^2 coth(\frac{\beta \hbar w_n}{2})(1 - \cos(w_n t))$$ (2.9)

$$G_i(t) = \sum_n g_n^2 (\sin(w_n t) - w_n t)$$ (2.10)
and $\lambda$ is the reorganization energy, defined as

$$\lambda = \sum_n \hbar w_n g_n^2. \quad (2.11)$$

Given the spectral density of the bath in terms of the couplings $g_n$ as

$$J(w) = \sum_n \delta(w - w_n) w_n^2 g_n^2, \quad (2.12)$$

we can rewrite the equations as

$$\lambda = \hbar \int_0^\infty \frac{J(w)}{w} dw \quad (2.13)$$
$$G_r(t) = \int_0^\infty \frac{J(w)}{w^2} \coth\left(\frac{\beta \hbar w_n}{2}\right) (1 - \cos(w_n t)) dw \quad (2.14)$$
$$G_i(t) = \int_0^\infty \frac{J(w)}{w^2} (\sin(w_n t) - w_n t) dw \quad (2.15)$$

The bath spectral density is assumed to be the following Brownian form[41]

$$J(w) = \frac{\eta \hbar w_b^4}{(w_b^2 - w^2)^2 + 4w^2 \gamma_b^2}, \quad (2.17)$$

where $\hbar w_b$ is the vibrational energy of the primary oscillator, which is expected to be close to the carbon-carbon double bond, $\eta$ represents the strength of the coupling, and $\gamma_b$ is the friction due to the other oscillators in the bath.

### 2.2 Aspects of Computer-Generated Lineshapes

Computational generation of line shapes involves integration with infinite boundaries. In the evaluation of the real and imaginary components of the line shape function, $G_r(t)$ and $G_i(t)$ which requires integration over $\omega$ in the range of $[0, \infty)$, we used the Runge-Kutta RK4 Method[19, 87] with a well bounded integration because the Brownian oscillation spectral...
Figure 2.2: (a) An example of the Brownian oscillator spectral density for $\eta = 0.29, \hbar \omega_b = 0.186eV, \gamma_b = 0.2\hbar \omega_b$. (b) The real part of the line shape function $G_r(t)$ corresponding to the spectral density in (a).
density function decays to zero asymptotically (see Figure 2.2(a)). As the real component of the line shape function $G_r(t)$ grows linearly (see Figure 2.2(b)), the convergence was assumed to be good enough for the final Fourier Transform of the integration from $(-\infty, +\infty)$ to be replaced with a Fast Fourier Transform (FFT) [87]. A full discussion of the Shannon Sampling Theorem [99] is given in the Appendix.
Chapter 3

Modeling Spectral Emission of DEHPPV

This chapter describes theoretical attempts to model and analyze the experimental Single Molecule Florescence Spectroscopy data taken for poly(2,5-di-(2'-ethylhexyloxy)-1,4-phenylenevinylene)(DEH-PPV). We first present the results of simple and generic approach, which turned out to be unsuccessful, and we then discuss more refined algorithms. The first of the algorithms demonstrates the invertibility of theoretical line shapes to find the model parameters using the least squared difference measure. The second algorithm demonstrates that a sufficiently convoluted line shapes can be produced by distinctly different model parameters.

3.1 Fourier Data Cleaning

The room temperature single molecule emission spectroscopy(SMES) data for DEH-PPV consisted of photon counts versus wavelengths, recorded at 1340 equally spaced wavelengths within the range of 310-882 nm. These correspond to 225 distinct SMES data sets available from different DEH-PPV polymer molecules. Each SMES data set contains reference photon count set at 310 nm. The first four raw experimental line shapes are shown in Figure 3.1.

After scaling with the reference signal, each line shape was linearly interpolated, so as
Figure 3.1: First 4 of 225 experimental DEHPPV line shapes
to construct the intensity versus the wavelength for any value within the range. The energy range in electronvolts corresponding to the wavelength range was then sampled with \(2^{11}\) equidistant points and the associated wavelength was evaluated and checked against the earlier linear interpolated spectrum to get a line shapes of intensity versus energy. The \(2^{11}\) data points were selected so as to match the input requirements to a Fast Fourier Transformation (FFT) used for noise cleaning as described below. Figure 3.2 shows the first four experimental line shapes interpolated into intensity versus energy graphs.

The baseline energy of each spectrum was adjusted by taking the average intensity between 2.7-3.7 eV and reducing all other values based on this mean. This range was selected to be above the continuous wave excitation laser set at 2.54 eV. Figure 3.3 contains the first four lines shapes that were base-lined.

The resulting 2048 sampled data sets were low pass filtered with a FFT\([24, 87, 14]\) to remove the top 2000 of the high frequency energy components which are assumed to be meaningless noise \((|f| > f_c \frac{24}{2048}\), where \(f_c\) is the Nyquist Sampling Frequency). This process amounts to first performing an inverse FFT into a time domain signal, and then multiplying by a rectangular function to cull the high frequency components. Figure 3.4 contains the inverse FFT signals of the first four experimental spectra before the application of a low pass window filter.

The low-pass filter amounts to setting all time array elements in the time signal outside the central \(48 = 2 \times 24\) elements to zero. Although we could have applied a Gaussian Convolution\([47]\) on the time data, it was simpler to apply a rectangular window filter which corresponds to a Sinc convolution in the frequency(energy) domain. After multiplication of the low-pass rectangular window filter, the signals were converted back to an energy domain with a forward FFT. Figure 3.5 shows the first four spectra of before and after FFT cleaning. These cleaned FFT spectra then served as the starting point of all the consequent
Figure 3.2: First 4 of 225 experimental DEHPPV line shapes of intensity versus energy
Figure 3.3: The first 4 of 225 experimental DEHPPV base lined spectra
Figure 3.4: The first 4 of 225 experimental DEHPPV after an inverse FFT.
Table 3.1: Statistics of 218 data sets of 225 which have double peaks with the high energy peak having a higher intensity

<table>
<thead>
<tr>
<th>Features</th>
<th>Avg</th>
<th>Std</th>
<th>Min</th>
<th>Max</th>
<th>Range</th>
</tr>
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<tr>
<td>$H_1$</td>
<td>$3.940 \times 10^{-3}$</td>
<td>$3.833 \times 10^{-4}$</td>
<td>$3.025 \times 10^{-3}$</td>
<td>$4.943 \times 10^{-3}$</td>
<td>$1.918 \times 10^{-3}$</td>
</tr>
<tr>
<td>$H_2$</td>
<td>$2.919 \times 10^{-3}$</td>
<td>$2.281 \times 10^{-4}$</td>
<td>$2.381 \times 10^{-3}$</td>
<td>$4.292 \times 10^{-3}$</td>
<td>$1.911 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\Delta$ (eV)</td>
<td>$1.569 \times 10^{-1}$</td>
<td>$1.369 \times 10^{-2}$</td>
<td>$9.469 \times 10^{-2}$</td>
<td>$1.818 \times 10^{-1}$</td>
<td>$8.711 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\frac{H_2}{H_1}$</td>
<td>$7.447 \times 10^{-1}$</td>
<td>$6.166 \times 10^{-2}$</td>
<td>$6.105 \times 10^{-1}$</td>
<td>$9.407 \times 10^{-1}$</td>
<td>$3.303 \times 10^{-1}$</td>
</tr>
<tr>
<td>$\lambda$ (eV)</td>
<td>$1.974 \times 10^{-1}$</td>
<td>$5.953 \times 10^{-2}$</td>
<td>$6.197 \times 10^{-2}$</td>
<td>$3.397 \times 10^{-1}$</td>
<td>$2.777 \times 10^{-1}$</td>
</tr>
<tr>
<td>$k$ ((eV)$^{-1}$)</td>
<td>$8.252 \times 10^{-1}$</td>
<td>$2.246 \times 10^{-1}$</td>
<td>$2.041 \times 10^{-1}$</td>
<td>$2.029$</td>
<td>$1.825$</td>
</tr>
<tr>
<td>$E_1$ (eV)</td>
<td>$2.343$</td>
<td>$5.953 \times 10^{-2}$</td>
<td>$2.201$</td>
<td>$2.479$</td>
<td>$2.777 \times 10^{-1}$</td>
</tr>
<tr>
<td>$E_2$ (eV)</td>
<td>$2.186$</td>
<td>$6.493 \times 10^{-2}$</td>
<td>$2.029$</td>
<td>$2.333$</td>
<td>$3.043 \times 10^{-1}$</td>
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<td>$\sigma_I$ (eV)</td>
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<td>$9.885 \times 10^{-3}$</td>
<td>$9.465 \times 10^{-2}$</td>
<td>$1.994 \times 10^{-1}$</td>
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<td>$\rho$ (eV)</td>
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<td>$2.020 \times 10^{-2}$</td>
<td>$1.313 \times 10^{-1}$</td>
<td>$1.111 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

3.2 Statistical Experimental Analysis

A gross statistical analysis was performed on the 225 experimentally FFT cleaned spectra which had at least two distinguishable double peaks where the higher energy peak had a stronger intensity then the lower energy peak (see Figure 3.6 ). Of the 225 line shape spectra, seven spectra were deemed to be outliers which either lacked distinguishable double peaks or did not have the higher energy peak being stronger than the lower energy peak. These seven outliers are shown in Figure 3.7. The remaining 218 spectra which did have double peaks and the intensity relationship were statistically analysed. Table 3.1 summarizes the results of these 218 spectra. The visualization of the meaning of the various statistical parameters are shown in Figure 3.6. The average energy distance between peaks is called $\Delta$, the height of the highest energy peak(right most peak) is $H_1$ with energy $E_1$, the height of the consequent lower energy peak is $H_2$ with energy $E_2$, the energy difference between the first peak below 2.5eV and the 488nm excitation laser is $\gamma$, and the exponential decay constant is $k$ supposing that $H_2 = H_1 e^{-k\Delta}$. The $\sigma_I$ variable is calculated as the standard deviation.
Figure 3.5: The first 4 of 225 experimental DEHPPV line shapes with original baselined spectra with the overlayed FFT cleaned data.
Figure 3.6: Legend of symbols in Table 3.1 using FFT cleaned data set 4.
Figure 3.7: The seven shapes skipped during the analysis due to the lack of two distinct principal peaks or not having the higher energy peak being more intense than the secondary.
of the unit area normalized line shape treated as a probability distribution function.\footnote{Assuming that the line shape function is unit normalized $\int_{-\infty}^{\infty} I(\nu) d\nu = 1$ and treated as a probability distribution on the random variable of energy, we can construct the standard deviation $\sigma_I$ as the square root of the variance $\sigma^2 = \int_{-\infty}^{\infty} I(\nu)(\nu - \bar{\nu})^2 d\nu$ where $\bar{\nu} = \int_{-\infty}^{\infty} I(\nu)\nu d\nu$.}

### 3.3 Lineshapes for the Brownian Oscillator Model

The effective spectral density due to a single vibrational mode coupled to an Ohmic harmonic oscillator bath is given as by the eq 2.17, where $\omega_b$ is the mode frequency, $\eta$ is the magnitude of the coupling of the primary oscillator, and $\gamma_b$ is the friction coefficient. Assuming this principal vibrational mode is the double carbon bond in the poly-phenylene vinlylene backbone of DEH-PPV to which the ground and excited Born-Oppenheimer electronic surfaces are coupled strongly, we can estimate the values of $\omega_b$ as the infrared spectroscopic vibrational mode of about 1400-1600 cm$^{-1}$. Using 1500 cm$^{-1}$ (0.186eV = $\hbar \omega_b$) as this mode, and applying the Fermi-Golden rule, we generated various homogenous absorption and emission line shapes in order to gain a qualitative understanding of the SMES lineshapes of DEH-PPV, which were taken by Zhonghua Yu’s group at $T=300K$.

Figure 3.8 demonstrates an example Brownian Oscillator spectral density and the calculated linear emission and absorption spectra. Changes in a single parameter while holding the other two parameters fixed are shown in Figures 3.9-3.11.

As the SMES lineshape should have some associated disorder, a convolution of a normalized Gaussian function scaled with various energies up to room temperature (25meV) was applied to the theory lineshapes. Figures 3.12 shows several examples of lineshapes convoluted with Gaussian distribution of disorder. In addition to the three parameters of specifying the Brownian oscillator bath, the width of the Gaussian convolution adds a fourth parameter to our theoretical model.

The principal qualitative feature of the the line shapes in the Brownian Oscillator Model,
Figure 3.8: Theory Brownian Oscillator spectral Density, emission, and absorption line shape for a parameter values of $\bar{\hbar}\omega_b = 0.186eV$, $\gamma_b = 0.25\omega_b$, and $\eta = 0.35$. 

(a) Brownian Oscillator Spectral Density

(b) Emission Spectrum

(c) Absorption Spectrum
Figure 3.9: Theory Brownian Oscillator spectral Density, emission, and absorption line shape for a parameter values of $\hbar\omega_b = 0.186\text{eV}$, and $\eta = 0.35$ with various $\gamma_b$ values.
Figure 3.10: Theory Brownian oscillator spectral density, emission, and absorption line shape for a parameter values of $\hbar \omega_b = 0.186\text{eV}$, and $\gamma_b = 0.25\omega_b$ with various $\eta$ values.
Figure 3.11: Theory Brownian oscillator spectral density, emission, and absorption line shape for a parameter values of $\eta = 0.35$, and $\gamma_b = 0.25\omega_b$ with various $\eta$ values.
Figure 3.12: Absorption and emission line shapes for parameter values of $\eta = 0.35$, $\hbar\omega_b = 0.186\text{eV}$, and $\gamma_b = 0.25\omega_b$ with various Gaussian disorders taken from 0-25 meV.
Figure 3.13: Line shape peak counts of $\eta$ vs $\gamma_s$ where $\hbar\gamma_s$ was scaled in energy units of $\hbar\omega_b$. In subfigure (a) Peaks that were below 5% the highest peak were excluded from the count. In subfigure (b) Peaks that were below 20% of the maximum peak were excluded. All graphs where sampled by 51x51 equidistant sample points in the interval $[0.1, 0.5] \times [0.1, 0.5]$ Note that the nonphysical kinked crossing lines in the boundary are due to our selection criterion for peak counts being a percentage of the max peak.
or in any highly resolved spectrum, is the number of peaks. To facilitate an understanding of the parameters of the model, a coarse count of the spectral peaks was performed across the parameter space. The three parameters \( \{\eta, \gamma_b, \omega_b\} \) were first reduced to two by noticing that energy units could be rescaled in terms of the energy of the vibrational mode \( E_b = \hbar \omega_b \).\(^2\) Figure 3.13 shows the count of the peaks in this reduced, scaled two parameter space. In order to remove negligible peaks, only peaks above the height of twenty percent of the highest peak were included in the count.

The peak to peak separation of consecutive spectral lines in the vibrational progression is expected to be close to that of the principal vibrational mode of the Brownian oscillator bath. Figure 3.14 does show a direct linear relationship between mode energy \( \hbar \omega_b \) and peak to peak distance \( \Delta \), albeit slightly dependent on the vibronic coupling \( \eta \) and the friction \( \gamma_b \).

Graphs of various parameters were generated to see correlations between the theory parameters and various features of the line shape. Figure 3.15 shows features which are positively related to known theory parameters. These positive correlations between parameters and features in the theory indicate that it is possible to construct a computer program that will take positively correlated features of some line shape and arrive at the theory parameter values. The abnormal curves generated for the graph of half-width at half-maximum (HWHF) vs \( \gamma \) were attributed to the loss of resolution in the calculation using the Fast Fourier Transform in generating theory line shapes.

\(^2\)In the scaled vibrational energy, the Spectral density reduces to
\[
J(\omega) = \frac{\eta \omega}{(\omega^2 - 1)^2 + 4\gamma^2 \omega^2}
\] (3.1)
Figure 3.14: The Peak to Peak energy distance $\Delta$ of the highest and second highest energy peaks were evaluated numerically from theory by generating line shapes for 101 equidistant values of $\hbar \omega_b$ taken from 100meV to 200meV. A linear regression was performed on the data and the $R^2$ coefficient of the fitted line was evaluated. a) $\eta = 0.10$, $\gamma = 0.10$, $R^2 = 0.999610$ 
b) $\eta = 0.35$, $\gamma = 0.10$, $R^2 = 0.999527$ 
c) $\eta = 0.10$, $\gamma = 0.25$, $R^2 = 0.999564$ 
d) $\eta = 0.35$, $\gamma = 0.25$, $R^2 = 0.999539$
Figure 3.15: Graphs show a positive slope in graphical features and known parameters with a fixed $\hbar\omega = 0.186\text{eV}$ a) Peaks height ratio of the second highest energy to the next lowest energy vs the $\gamma$ factor from theory. b) The offset of the highest energy peak from the area centered graph vs $\eta$ parameter from theory. c) The right half width half maximum(HWHM) of the highest energy peak(zero phonon line) vs $\gamma$. The abnormal values are attributed to the resolution of the FFT involved in calculating the line shape.
3.4 Theoretical Fitting of Experimental Lineshapes

The $L^2$ norm in the form of the least square deviation\(^3\) is often used to fit theoretical model line shapes to experimental data to ascertain the model parameters in nonlinear regression analysis\([32, 83, 60]\). Using the $L^2$ norm defined between a theory lineshape $L_{thry}(\omega)$ and experimental lineshape $L_{exp}(\omega)$ as

$$M = \left\{ \int_0^\infty |L_{thry}(\omega) - L_{exp}(\omega)|^2 d\omega \right\}^{\frac{1}{2}}, \quad (3.3)$$

we performed a gradient descent based extremization, various discrete parameter state space searches, a genetic algorithm based minimization, and ultimately a brute force uniform search of the parameter space that would optimize the Brownian oscillator spectral density model against the experimental data.\(^4\)

The optimization results of these procedures were scattered, and the converged values of the principal parameters seemed to depend on the trajectories through the parameter space. Consequently, to reduce the uncertainty in deciphering the causes of these various distinct convergence values in the parameter space from the experimental data, we reperformed the data analysis with these various algorithms using theoretically generated lines shapes with known search parameters. The results of these well known shapes also returned various distinct varied convergence values.

The multiple distinct convergence of the algorithms indicated that the search space is complicated and has multiple local minima, which trap the search trajectories. Although

\[^3\]The $L^n$ norm of a function $f : \mathbb{R} \rightarrow \mathbb{R}$ is defined as

$$|f|_n = \left\{ \int_{-\infty}^{\infty} |f(x)|^n \right\}^{\frac{1}{n}} dx \quad (3.2)$$

\[^4\]An expanded discussion is given in the appendix of the various algorithms used in our initial attempts to perform nonlinear regression analysis on the experimental data. We felt that the importance of the experimental search methodologies were not relevant to the final analysis for optimization so as to warrant their inclusion in our principal body of work, even though these calculations were extremely laborious, error prone to implement and test in programming.
more robust algorithms were discussed such as Metropolis, Simulated Annealing, Stochastic Hill Climbing, Swarm Searches, and Evolutionary Trees, it seemed more relevant to understand the search space further by graphical means rather than to expend blind attempts to use numerical algorithms without a clear criteria of convergence.

We performed a lattice point sampling of the parameters \((\eta, \gamma)\) in the region, while holding the value of \(\omega_b\) fixed. We then implemented the nearest neighbor search graph on the data to a target line shape. The nearest neighbor graph consists of taking every lattice point in the two parameter space of \((\eta, \gamma)\) and finding the nearest \(L^2\) norm distance to adjacent neighboring points. Figures 3.16 contains four various searches where the arrows for the directed graphs are generated by drawing the direction of a graph vertex to the lowest \(L^2\) neighbor with a lower \(L^2\) cost. Vertices on the graph which do not have any out-going edges are local minima where trajectories of paths would eventually collapse to. This explains the peculiar results of the minimal localization of the earlier mentioned algorithms.

To further understand these local minima, three dimensional plots were then generated (see Figures 3.17). Many of the local minimum including the global minimum in the graph lie within the main valley of the graph. Any purely Gradient Descent\(^5\) based Algorithm, started with an arbitrary point, will eventually reach some local minimum which is not necessarily the global minimum. By comparing various search surfaces, we noted that a Gradient Descent algorithm starting from a low value of \(\eta\) and high value of \(\gamma\) will eventually descend into the principal valley which contains the global minimum. This is very suggestive of an implementable numerical algorithm to reach at the best fit Brownian oscillator model line shape in some data analysis.

\(^5\)If \(x_i\) is a vector in some parameter space and \(f(x)\) is to be minimized, the next point in the iterative gradient descent optimization is arrived at with \(x_{i+1} = x_i - \alpha \frac{(\nabla f)(x_i)}{||\nabla f(x_i)||}\) \(\alpha\)\(\neq 0\) (\(\alpha\) is called the learning rate in Machine Learning).

36
Figure 3.16: $L^2$ minimum search graph of well known line shapes with $\hbar \omega_b = 0.186 eV$. The Green dots represent the target line shapes that the search graph attempts to find. a) $\eta = 0.2$ and $\gamma = 0.2 \hbar \omega_b$ b) $\eta = 0.2$ and $\gamma = 0.35 \hbar \omega_b$ c) $\eta = 0.35$ and $\gamma = 0.2 \hbar \omega_b$ d) $\eta = 0.35$ and $\gamma = 0.35 \hbar \omega_b$
Figure 3.17: $L^2$ search surface for $\eta = 0.2$ and $\gamma = 0.2\hbar\omega$. The global minimum lies within the principal valley in the graph. The side view of the surface shows the rugged nature of the valley floor. Although the jagged edges are due to the resolution of surface plot, they do indicated a rugged surface where numerical search algorithms based purely on gradient descent can get stuck in.
3.5 Brownian Oscillator Search Algorithm

As we mentioned earlier in section 3.4, our attempts to find the minimal $L^2$ fitness for parameter fitting of the Brownian Oscillator Line Shape Model were circumvented due to the collapse of trajectories into local minima in the parameter space. We also noted that the global minimum is found within the principal valley in the $L^2$ search space. Further more, through comparison of various other graphs, the minimal $L^2$ search trajectories that start with $\eta = 0.1$ and some $\gamma$ value will converge into one of the local minima in the principal valley. It was also mentioned that the $\bar{h}\omega_b$ is approximately the peak to peak distance between the primary and secondary energy peaks. We note that the principal valley in the $L^2$ search space seems to have a linear back backbone in the sense that all the containing extrema can be projected on to a line in the $\eta - \gamma$ plane.

With these pertinent ideas set down, a simplified algorithm to find the minimal $L^2$ spectral lines was constructed as follows:

1. Given a spectral line shape data, evaluate the peak to peak distance to find the $w_b$.

2. Perform several trajectories starting from the box boundary where $\eta = 0.1$ and perform a Gradient Descent Algorithm for that various fixed values of $\omega_b$, till extrema points have been reached.

3. As the collection of extrema points are in the principal valley of the $L^2$ search space, perform a regression analysis on the extrema points to arrive at a linear equation.

4. Perform a linear search along the regression line for the global minimum.

This algorithm can be iteratively corrected by adjusting the evaluated $\omega_b$ for the initial approximated line shape, and repeating the above steps to arrive at successively better approximations.
Figure 3.18: These four graphs show the linearity of the spine of the principal valley of the $L^2$ surface by performing 11 search trajectories with a simple step limited Gradient Descent Algorithm. As some trajectories may reach the same extrema points, there are fewer points than 11 in some of the figures (see sub figures b and c). The green dot represents the target ($\eta-\gamma$) parameters that this $L^2$ surface is generated for. All the lines shapes were generated for a fixed value of $\hbar \omega_b = 0.156eV$ and at 300K.
A very coarse gradient descent algorithm was implemented to test the procedure for finding the linear backbone of the principal valley of the $L^2$ search. Figure 3.18 represents the searches of four line shape with arbitrary extrema search starting from the edge boundary with $\eta = 0.1$. The regression analysis demonstrates the linearity of extrema points, and the approximate location of the global minimum of the $L^2$ search surface.

Figure 3.19 gives the result of a comparison of four theoretical line shapes that were fed into the above algorithm, and the returned calculated line shapes for a single iteration without a refined convergence (by adjusting $\omega_b$). Figure 3.20 gives the result of a comparison of four theoretical line shapes that were fed into the above algorithm, and the returned calculated line shapes for a two iterations without a refined convergence (by adjusting $\omega_b$).

Although we used a very coarse Gradient Descent for the detection of the spine of the principal valley and a large step size in the linear search along that spine, the stability of our numerical steps in converging to a near fit can be seen in Figure 3.21. Here, we performed ten iterations through the algorithmic steps of the worst looking graph (d) in Figure 3.19.

### 3.6 Algorithm Analysis of DEH-PPV

The algorithm described in Sect. 3.5 was applied to analyze the DEH-PPV experimental data. Although this algorithm made it possible to find the principal valley of the $L^2$ surface within a statistical $R^2$ approaching 1, the linear search for the minimum starting from the region of $\eta \in [0.1, 0.4]$ always ended up having $\eta = 0.4$. Extending the search range for $\eta$ always returned the maximum value in the search range. This indicated that the search algorithm favors the largest possible value of a $\eta$.

Similar non matching results were found in earlier attempts employing different algorithms.\(^6\) Figure 3.22 shows four results of $L^2$ fitness using a modified gradient descent based

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\(^6\)The appendix contains a discussion of the various algorithms used in $L^2$ fitness.
Figure 3.19: Each graph represents a single iteration of this sections algorithm for finding the extrema for four individual theory line shape generated curves with $\bar{h}\omega_b = 0.186\,\text{eV}$ and various $\eta$ and $\gamma$ values. The blue curves represent the data that the algorithm seeks to fit, while the red curves are the results of algorithm’s best fit with a single iteration of the steps. A gradient descent algorithm was performed starting with an $\eta = 0.1$ value to find the spine of the principal valley. The unitless three numbers in the legend are the values for $(\eta, \frac{\bar{h}\gamma}{\hbar\omega_b}, \bar{h}\omega_b)$ with $\bar{h}\omega_b$ given in eV.
Figure 3.20: These figures are generated with two iterations of our algorithm from those found in Figure 3.19.
Figure 3.21: The result of ten iterations of our algorithm with course step sizes in searches of the worst looking graph in Figure 3.19(d). The blue data curve is input to the algorithm, and the red curve is result of generating the theory line shape from the returned parameters from our algorithm. As both curves are near perfectly overlapped, the results look like a single curve.
Figure 3.22: Failed attempts to find the best fit using a modified Gradient Descent Algorithm to match experimental line shapes.
Figure 3.23: Results of a genetic algorithm using $L^2$ to fit the data of the first 4 experimental line shapes of room temperature DEHPPV spectral data.
algorithm which fail to reproduce the experimental feature of two major peaks. Figure 3.23 shows similar results based on a Genetic Algorithm using the $L^2$ fitness measure. As several methods returned ill fits to the experimental data, we concluded that the room temperature experimental data was not sufficient of a match to the theory line shapes without an energetic disorder using an $L^2$ norm.

Our conclusion that the $L^2$ norm being an insufficient match to the experimental data was reenforced by observing the graphs (see example Graph 3.24) of the various energy convolutions of theory of line shapes and evaluating the search surfaces. We concluded that the experimental data was too erratic from the side profiles for a good comparison against the spine of the principal valley of the $L^2$ search surface when the data has an intrinsic energy disorder.

Line narrowing of spectra as compared to that of absorption of conjugated polymers is well known and understood. As the length of time for each individual DEHPPV experimental data collection time was in seconds, and that hundreds of florescence transitions must have occurred to arrive at the final observed line shape, it occurred to us the possibility that only a single line shape distribution may be responsible for the observed data. From the central limit theorem, the sum of stochastic variables shifted in energy would eventually cause a Gaussian convolution of the data. To this end, we tested theory line shapes which are convoluted by a Gaussian energy function and performed a visual fit against the experimental data. The results were very promising; the first four line shapes shown in Figure 3.25. The earlier automated best fit searches of Figure 3.24 returned convolutions that were in order of the hand fitted values observed which supported the idea that convolution line shapes does match the experimental data.

---

7 The excited singlet $S_1$ Born-Oppenheimer potential energy surface causes a planarization of the Benzene rings which then causes fast coherent transport of the exciton along the conjugated backbone to an emission site.
Figure 3.24: Surface $L^2$ surface graphs for a 50meV with Gaussian disorder convolution search. Notice, the principal valley still stays intact, but the spine of the valley is too erratic from numerical errors to gauge the best fitness.
Figure 3.25: Programatic assisted visual fit of data by convolution of theory line shapes in comparison with the experimental data. The Four numbers above each graph represents the $\eta, \gamma$ factor, $\hbar\omega$ and convolution value. The $\hbar\omega$ and convolution values are in eV.
Table 3.2: Highest Peak Energy Statistics of the experimental DEH-PPV Emission line shapes.

<table>
<thead>
<tr>
<th>Avg</th>
<th>Std</th>
<th>Min</th>
<th>Max</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.342eV</td>
<td>0.061eV</td>
<td>2.202eV</td>
<td>2.480eV</td>
<td>0.278eV</td>
</tr>
</tbody>
</table>

Figure 3.26: Histogram of the count of peaks of the 225 of DEHPPV emission data.
Due to the high convolution in energy (50-60 meV) used for the visual matching of the experimental data, we performed an analysis of the amount of disorder of the peak energy of the individual line shapes (see Table 3.2). The high disorder of 61 meV in Table 3.2 supports the high convolution of 50-60 meV that was used in the visual fitting of the initial experimental line shapes, a few of which were seen in Figure 3.25. Figure 3.26 shows a histogram of the DEH-PPV emission peak data.

From this preliminary analysis, it occurred to us that it was possible to perform a best fit of the data using the observed standard deviation as an order of magnitude measure with which to find the convolution in the data. After performing several trial and error attempts to find the new four parameters of $\eta, \gamma, \omega$, and convolution, we noticed the following heuristic methodology of line shape fitting.

1. Generate an initial trial line shape for the experimental line shape, which has at least two peaks.

2. Adjust the $\omega$ by a convergence comparison$^8$ with the peak to peak distance feature.

3. We noticed that the amount of convolution applied to a line shape decreases the height separation between second lower energy peak with the local intervening minima between the two principal peaks. Like earlier, a convergence comparison by adjusting the convolution only can be performed to match the target line shape.

4. We noted that adjusting eta adjusts the height of the second peak directly. So, a convergence comparison can be used to adjust the correct height of the second peak.

5. Repeat the last three steps, till the line shapes match.

---

$^8$We use convergence comparison to mean the adjustment of some parameter and observing the generated output (in this case some feature). A positive correlation between the adjustment and feature, means that if our target feature value is greater than some feature value generated by some parameter, we increase the parameter. Or, if the the target feature value is smaller than the feature value generated by some parameter, we lower the parameter value. Mathematically, we mean that some feature $F = F(p)$ is a function of some parameter. If our function is analytic and has a good radius of convergence for $p$ and target value $F_0$. 

51
Figure 3.27: The height $h$ between the second lower energy peak and the intervening minima between the peaks changes based on the amount of convolution applied to the theoretical line shape. Increasing the convolution decreases $h$, while decreasing the convolution increases $h$. 
Although this new algorithm is not using an $L^2$ fit, the results were very accurate as was seen in the matching of the first four experimental line shapes (see Figure 3.28). Figure 3.28 fixed the value of $gamma = 0.08\hbar\omega$, while programmatically adjusting the other parameters using the above recent algorithm.

Selecting the various other fixed values of $\gamma$ also generated curves which are very close to that of the experimental data. Figures 3.29 for $\gamma = 0.06\hbar\omega$, Figures 3.30 are for $\gamma = 0.10\hbar\omega$, Figures 3.31 are for $\gamma = 0.12\hbar\omega$, and Figures 3.32 are for $\gamma = 0.20\hbar\omega$.

We did not perform an $L^2$ comparison between the data and the newly generated fitting, due to the goodness of the match. It is evident from the graphs that a numerical $L^2$ minimization would not be a good measure of fitness of the theoretical convoluted line shape due to the noisy errors in the edges as compared to the central two peaks and intervening trough (see Figures 3.33). One would expect that the central peaks are a better measure of fitness than the the edges. An $L^2$ difference measure would not give such relevance to the central peaks as compared to the edges, and so consequently it would be a poor indicator of fitness of a theory line shape. This unwarranted balance of fitting to the edges was also observed in earlier fitting algorithms.

We also did not perform a numerical $L^2$ fitting restricted to the half peak width of the center, as there was no little distinction between algorithmically generated theory line shapes to the experimental as compared to the much larger errors in the edges.

### 3.7 Ensemble Averaged Zero Phonon Line

As the absorption line was taken experimentally of DEHPPV, we calculated the Zero Phonon Line (ZPL) by assuming that the ensemble emission line shape would be representative of a full emission spectrum. Figure 3.34 holds the raw absorption and ensemble emission line shapes for DEHPPV. Each of the spectra was height normalized and overlayed to evaluate
Figure 3.28: Algorithmic Fitting with $\gamma = 0.08\hbar\omega_b$. The values of each factor of the four parameters are given above each subgraph. For instance, the first graph has parameters $\eta = 0.077$, $\gamma = 0.08\hbar\omega, \hbar\omega = 0.175eV$, and $conv = 0.055eV$. 
Figure 3.29: Algorithmic Fitting with $\gamma = 0.06\hbar\omega_b$. The values of each factor of the four parameters are given above each subgraph.
Figure 3.30: Algorithmic Fitting with $\gamma = 0.01\hbar\omega_b$. The values of each factor of the four parameters are given above each subgraph.
Figure 3.31: Algorithmic Fitting with $\gamma = 0.01 \hbar \omega_b$. The values of each factor of the four parameters are given above each subgraph.
Figure 3.32: Algorithmic Fitting with $\gamma = 0.01\hbar\omega_b$. The values of each factor of the four parameters are given above each subgraph.
Figure 3.33: These four graphs were generated from our feature fitting algorithm to the experimental data, and they illustrate the problem with an $L^2$ fitting. Both the theory and experimental fit well in the center peaks and trough through our algorithm, but the edges are fit less so. If our algorithm was using an $L^2$ fitting and not the feature fitting of the center peaks and intervening trough, there would be no discrimination between the edges and peaks. The $L^2$ would fit to the less relevant edges at a loss of discrimination to the central peaks and trough features. The top left graph is illustrated to show the locations of the edges, peaks, and trough.
Figure 3.34: The absorption spectrum and ensemble emission SMS line shape of DEHPPV.
Figure 3.35: The height normalized absorption and ensemble emission line shapes are overlaid over each other. The ZPL was found to be at 515.5\text{nm}(2.405\text{eV}).
the Zero Phonon Line (ZPL) in Figure 3.35.

Ideally, if our model is correct, and we are looking at the same curvature in both the excited and ground singlet surfaces, then the emission and absorption spectra would be mirror images of each other. The observed spectra are not perfect mirror images of each other. We assumed that slight disparity between the spectra was principally due to the absorption spectra being an ensemble of interacting molecules and not that of a collection of single molecules.
Chapter 4

Conclusion

We have demonstrated that perfect model lineshape can be inverted back to their model parameters using the least squared minimization. We have also shown that the large energetic disorder involved in the experimental lineshape can lead to multiple model parameters that all have similar $L^2$ minimization. We associated this minimization problem to the flattening of the bottom of the principal valley in the Brownian Oscillator $L^2$ search space.

We have also shown that the peak-to-peak distance between the vibronic peaks can be used with a simple bisection based algorithm to reduce the dimensionality of the $L^2$ search space by one in both the energetically disordered experimental lineshape and theoretical model lineshape. We further found that intervening trough of the first two peaks and the height of the second peak is an important feature that can be used to evaluate the underlying energetic disorder in the system.

We have demonstrated that Directed Acyclic Graphs of a two dimensional lattice sampled space can be useful in understanding parameter space search algorithms to find local and global minima. We used the graphs to understand why well known algorithms such as the Gradient Descent, Heuristic based, and the nonlinear Genetic Algorithm failed in reaching a global minimum in the $L^2$ manifold. This understanding led to construction of one of the two algorithms discussed in our work.
\( \gamma = 0.06h\omega \), \( \gamma = 0.08h\omega \), \( \gamma = 0.10h\omega \), \( \gamma = 0.12h\omega \), \( \gamma = 0.20h\omega \)

| \( \eta \) avg | 0.0605 | 0.0830 | 0.107 | 0.132 | 0.248 |
| \( \eta \) std | 0.00471 | 0.00653 | 0.00870 | 0.0103 | 0.0253 |
| \( \eta \) min | 0.0460 | 0.0630 | 0.0820 | 0.102 | 0.197 |
| \( \eta \) max | 0.0770 | 0.105 | 0.152 | 0.178 | 0.355 |
| \( \hbar\omega \) (eV) avg | 0.172 | 0.174 | 0.176 | 0.178 | 0.184 |
| \( \hbar\omega \) (eV) std | 0.00744 | 0.00737 | 0.00769 | 0.00773 | 0.00902 |
| \( \hbar\omega \) (eV) min | 0.142 | 0.0145 | 0.146 | 0.148 | 0.153 |
| \( \hbar\omega \) (eV) max | 0.202 | 0.0204 | 0.206 | 0.209 | 0.219 |
| conv avg(eV) | 0.0554 | 0.0537 | 0.0514 | 0.0493 | 0.0371 |
| conv std(eV) | 0.00500 | 0.00515 | 0.00575 | 0.00591 | 0.00980 |
| conv min(eV) | 0.0390 | 0.0370 | 0.0170 | 0.0200 | 0.0100 |
| conv max(eV) | 0.0690 | 0.0690 | 0.0660 | 0.0660 | 0.0600 |

Table 4.1: Algorithm generated parameters \( \omega, \eta \), and convolution for various \( \gamma \) values for emission spectra. The resulting statistics of various parameters are shown in each column.

Figure 4.1: Graphs of the theory reorganization energy where \( \hbar\omega_b = 0.186eV, \frac{\gamma}{\hbar\omega_b} \in [0.06, 0.20] \). The \( \eta \) value is dependent on \( \frac{\gamma}{\hbar\omega_b} + \Delta \). The graphs \( \Delta \) are given as -0.2(red), -0.1(green), 0.0(yellow), 0.1(blue), and 0.2(black).
For future studies, we have included Figure 4.1 to show how the reorganizational energy changes with shifts in the differences between the vibronic coupling $\eta$ and the scaled friction $\frac{\gamma_b}{\hbar\omega_b}$ shifted relative to each other. This amounts to a shift in the linear spine of principal valley of our $L^2$ search space.

In conclusion, we have shown that the experimental line shapes have high energetic disorder which causes multiple parameters to converge to the same line shape. Our second algorithm demonstrates that fixing one of the two parameters of $\gamma_b$ or $\eta$ makes all the remaining parameters converge. Table 4.1 shows the statistics of the found parameters of the BO model including the found energetic disorder for various selected values of $\gamma_b$ across the experimental emission spectra. The data provided in Table 4.1 provide important insights into the effective exciton-bath coupling and their fluctuations within the minimal two state bath model.
Appendix A

Mathematical Background

A.1 Open Quantum Systems

The Unitary evolution of any Quantum System $|\Psi(t)\rangle$ driven by a Hamiltonian $H(t)$ is well-defined using the unitary operator $U(t, t_0)$ which takes the system from an initial time $t_0$ to another at $t$.

\[ |\Psi(t)\rangle = U(t, t_0) |\Psi(t_0)\rangle \]  
(A.1)

\[ i\hbar \frac{dU(t, t_0)}{dt} = H(t)U(t, t_0) \]  
(A.2)

If the Hamiltonian is time independent, it is well known that the Quantum System like the classical version of Poincare[39] will have a recurrence time[15, 96], where the state vector at $t_0 + T$ is arbitrarily close to its initial value at a $t_0 : |\Psi(t_0 + T)\rangle = |\Psi(t_0)\rangle$. The canonical view of the lack of obvious visibility of this recurrence in real quantum systems is attributed to the exponential growth of this time with the number of degrees of freedom of the system, and the lack of decoupling of such a system to its environmental bath. A quantum system can never be separated from the universe that it is part of, and consequently, our idealized evolution of a quantum state of a system by an unitary propagation has to be modified to include the state of the environment. As the evolution of a small system may through environmental
interactions switch between various quantum states during its temporal evolution, a single state vector cannot describe the evolution of the system alone. Although the full evolution of a quantum system including its environment does still evolve with a unitary evolution as given in the above equations of motion, the quantum system itself does not necessarily follow such an evolution. The density matrix formulism that describes an ensemble collection of quantum states is more appropriate to describe this non unitary evolution.

The density matrices $\rho$ of either the idealized environmentally decoupled quantum system or the full quantum system with its surrounding environment can be in theory evolved using the Liouville-von Neumann Equation\[97, 18\] $i\hbar \frac{d\rho}{dt} = [H, \rho]$. As we are attempting to describe a full evolution of an environmentally coupled quantum system, we have to use in some way the Quantum Liouville-von Neumann Equation that includes the infinitely large degrees of freedom of the environment. As it is not possible to fully describe such an environment completely, we have to suffice to use approximations.

If the environment has reached a thermal equilibrium, we expect that the energy states of such have reached a maximum uncertainty and follow a Boltzmann Energy distribution (sees Appendix). As a consequence of the environmental canonical density matrix and Hamiltonian being diagonal in the energy basis, their is no temporal evolution of the environmental density matrix as is directly seen in the commutator of the Quantum Liouville-von Neumann Equation being zero. Although, in truth, the environmental fluctuations are nontrivial, non-static, and defined only stochastically, we can still describe such an environment with the Canonical Density Matrix assuming the the environment is much larger and highly entropic as compared to the system of interest. We expect all systems that are coupled to such an environment to also reach this same thermal equilibrium, with the eventual display of a canonical diagonal form of the density matrix in the energy basis.

An Open Quantum System consists of a small system of interest coupled to a larger
environment. The system evolves to reach the thermal equilibrium of the environment that it lies within. The diagonal population terms in the density matrix of the system in the energy basis will eventually evolve to reach the same statistical Boltzmann energy distributions as that of the environment at some given temperature. If a coupling exists between the states within the system beyond the environmental coupling, there will be an evolution of the population terms beyond that of the environmental dissipation. The eventual thermalization of a system is intricately dependent on the internal system couplings between states and the external couplings to the environment.

The Quantum Master Equation approach to Open Quantum Systems is to describe the evolution of the density matrix of the open quantum system excluding the degrees of the environmental reservoir that it is still in contact with. The Quantum Master equations are the first order integrodifferential equations that are arrived at using various approximations of taking the full Liouville-von Neumann Equation of the system and bath and integrating out the degrees of freedom of the environment.\(^1\) The various Quantum Master Equations look like a standard Liouville-von Neumann equation with an added dissipative term to include the effects of the environmental dissipation

\[
i\hbar \frac{d\rho_s}{dt} = [H, \rho_s] + \text{(dissipative correction)} \quad (A.4)
\]

As a system evolves and dissipates into the environment, one should rightly expect that the environment may reflect some of this loss back into the system at some retarded time. This non-Markovian behavior is demonstrated in an integro differential equation with a memory kernel to describe this retardation, and the arrived at equation are called the Time nonlocal Quantum Master Equations. A Markovian Quantum Master equation (or Time non-}

\(^1\) The reduced density matrix of the system \(\rho_s\) is constructed by integrating out the bath degrees of freedom of the full system and bath density matrix \(\rho\) using the partial trace operation

\[
\rho_s = \text{Tr}_b\{\rho\}
\]
covolutionless Quantum Master Equation) can be arrived at, if one can somehow remove the memory kernel, so as to have a dissipative part that only consists of the current time.

In the following sections, we derive the various Quantum Master Equations while discussing their various approximations, confines, and numerical simulations.

A.2 Wiener-Khintchine Theorem

In this section, we discuss the Weiner-Khintchine Theorem (WKT) that can be used to describe the spectral density of wide sense stationary stochastic processes. In our work, we use the theorem indirectly using spectral densities to describe an open system interactions with a thermalized bath as well as to describe the bath itself. Although, the theorem is applicable to any $L^2$ normed signal, our intent is to look at Ergodic Wide Sense Stationary Stochastic processes where temporal averages are the same as ensemble averages.\(^2\)

The Wiener-Khintchine Theorem[111, 62] associates the power spectral density with the Fourier transform of the auto correlation function of a wide sense stationary stochastic process.\(^3\) The theorem attempts to describe a wide sense stochastic processes by the fixed frequency components of the random temporal fluctuations. This is very useful in Quantum Open System modeling where we would like to describe the thermalized bath that a Quantum

\(^2\)The ensemble average and temporal average are given as

\[
<s(t)> = \int_{s=-\infty}^{\infty} s f(s,t) dt
\]

(A.5)

\[
<s(t)>_t = \frac{1}{2T} \int_{t=T}^{T} s(t) dt,
\]

(A.6)

The function $f(s,t)$ is the probability density of the random variable $s(t)$. The variable $T$ is the measurement time of the signal, which should be very large.

\(^3\)A single one dimensional stationary stochastic process $X(t)$ is one where the joint probability density function is translationally time invariant under displacement:

\[
f(x_1, t_1; x_2, t_2; ...) = f(x_1, t_1 + \tau; x_2, t_2 + \tau; ...),
\]

(A.7)

for any real $\tau$. A wide sense stationary process is one where translational time invariance is for only the lowest joint probability distribution of two positions: $f(x_1, t_1; x_2, t_2) = f(x_1, t_1 + \tau; x_2, t_2 + \tau)$. This implies that the joint probability of any two positions in the stochastic process is only dependent on the temporal difference: $f(x_1, x_2, \tau) = f(x_1, 0; x_2, \tau)$. Consequently, expectation averages of functions of two positions are completely dependent on the relative temporal measurements of the two points.
System Couples to by the bath’s motional frequency components. We have to treat the bath signals as a Stochastic Process, as the Poincare recurrence time of even a small system will far exceed the time measurement of any experimental signal.

The Weiner-Khintchine Theorem starts by construction of some wide sense stochastic signal \( y(t) \) which is constructible from a Fourier transformed signal \( \gamma(w) \). This is always possible in the sense that any experimentally measured signal must be a well bound and have a finite measurement time.

\[
y(t) = \frac{1}{\sqrt{2\pi}} \int_{w=-\infty}^{\infty} \gamma(w)e^{jwt} \, dw \quad (A.8)
\]

As the signal is well bound in time, the \( L^2 \) norm of the signal in both time and frequency are the same.\(^4\) As the signal \( y(t) \) is real, it can be seen that \( \gamma(w)^* = \gamma(-w) \). The temporal correlation function of the signal can be defined as

\[
C(\tau) = \int_{t=-\infty}^{\infty} y(t + \tau)y(t) \, dt. \quad (A.10)
\]

This correlation function must exist due to the same prior reasoning of well bound and finite time measurements of experimental signals. Construct, a new function \( g(t) = y(-t) \), so as to rewrite the integral in terms of a convolution function.

\[
C(\tau) = \int_{t=-\infty}^{\infty} g(-\tau - t)y(t) \, dt = \sqrt{2\pi}(g*y)(-\tau). \quad (A.11)
\]

We have used * to represent the convolution of the \( g \) and \( y \) (see footnote concerning the integral transformations\(^5\)). Taking the Fourier Transform of both sides gives us a relation

\[
|y|^2 = \int_{t=-\infty}^{\infty} y(t)^2 \, dt = \int_{w=-\infty}^{\infty} |\gamma(w)|^2 \, dw. \quad (A.9)
\]

This is a statement of Parseval’s Theorem\(^5\) which is simply proven by direct substitution of the Fourier Transform.

\(^4\)The \( L^2 \) norm of the signal is given as

\[
|y|^2 = \int_{t=-\infty}^{\infty} y(t)^2 \, dt = \int_{w=-\infty}^{\infty} |\gamma(w)|^2 \, dw.
\]

\(^5\)We define the Fourier and convolution operations with the following equations scaled with the appropriate
between the frequency components.

\[ C(w) = \mathcal{F}(C(\tau)) = \frac{1}{\sqrt{2\pi}} \int_{\tau=-\infty}^{+\infty} e^{i\omega \tau} C(\tau) d\tau \]  
\[ = \sqrt{2\pi} \mathcal{F}(g(-\tau)) \mathcal{F}(y(-\tau)) \]  
\[ = \sqrt{2\pi} \mathcal{F}(g(\tau)) \mathcal{F}(y(-\tau)) = \sqrt{2\pi} \gamma(w) \gamma(-w) \]  
\[ = \sqrt{2\pi} \gamma(w) \gamma(w)^* = \sqrt{2\pi} |\gamma(w)|^2 \]  
\[ = \sqrt{2\pi} \gamma(w) \gamma(w)^* = \sqrt{2\pi} |\gamma(w)|^2 \]  

(A.15)

The power spectral density \( J(w) \) of a wide sense stationary stochastic process is real, non negative, and even \( J(w) = J(-w) \).

\[ J(w) = \frac{1}{2\pi} \int_{t=-\infty}^{+\infty} e^{i\omega t} C(t) dt \]  

(A.19)

\section{A.3 Sampling Theorem}

The Sampling Theorem states that a signal whose spectral components are band limited can be reconstructed by finding a finite equidistant samplings of the original signal. Goodman\[45\] proves this theorem for a two dimensional problem. We demonstrate the proof for a much simpler one dimensional case. But, the analysis can easily be extended to two or more dimensions.

Goodman’s proof for the Sampling Theorem requires several ideas. The first is that the every signal can be uniquely transfered into a Fourier transformed one. Or simply, there is factors.

\[ m(w) = \mathcal{F}(m(t)) = \frac{1}{\sqrt{2\pi}} \int_{t=-\infty}^{\infty} e^{i\omega t} m(t) dt \]  
\[ (m * n)(t) = \frac{1}{\sqrt{2\pi}} \int_{t'=\infty}^{\infty} m(t-t') n(t') dt' \]  
\[ \mathcal{F}((m * n)(t)) = \mathcal{F}(m(t)) \mathcal{F}(n(t)) \]  

(A.12)

(A.13)

(A.14)

Here, the Fourier conjugate pair functions are simply denoted in parenthesis with \( w \) or \( t \).
a bijective mapping between the signal and the Fourier transformed signal. So, the Fourier transformed signal can be inverse transformed back to the original signal without ambiguity.

The Fourier Transform and its inverse are given as the following two equations.

\[
\mathcal{F}(F(w)) = f(t) = \int_{\infty}^{\infty} F(w)e^{2\pi i wt} \, dw
\]  

(A.20)

\[
\mathcal{F}^{-1}(f(t)) = F(w) = \int_{\infty}^{\infty} f(t)e^{-2\pi i wt} \, dt
\]  

(A.21)

The function \( F(w) \) is called the spectrum of the signal \( f(t) \). Our selection of the factor \( 2\pi i \) in the exponent is so that we do not have to worry about \( \pi \) factors when we multiply Fourier transformed products. With this factor, the inverse Fourier Transform is similar with the forward transform but with a minus in the exponential and change in integration variable.

A band limited signal \( f(t) \) means that the spectrum \( F(w) = 0 \) for all \( |w| > B \). Goodman constructs a sampled signal of the original \( f(t) \) using a comb function. The most important equation for the sampling theorem is that the Fourier transform of the Dirac Comb function is also a Dirac Comb function.

\[
\mathcal{F}(\text{Comb}(w, A)) = \mathcal{F}\left\{ \sum_{n=-\infty}^{\infty} \delta(w - nA) \right\}
\]  

(A.22)

\[
= \frac{1}{A} \sum_{n=-\infty}^{\infty} \delta(t - \frac{n}{A})
\]  

(A.23)

\[
= \frac{1}{A} \text{Comb}(t, \frac{1}{A})
\]  

(A.24)

We also need the definition of the convolution \( f(t) \) and \( g(t) \) denoted by \((f, g)\) for the sampling theorem proof.
\[ (f,g) = \int_{-\infty}^{\infty} f(x)g(y-x)dx \] (A.25)

We note that the Fourier transform of a convolution of two functions is the product of the Fourier of the functions.

\[ \mathcal{F}(f(w), g(w)) = \mathcal{F} \int_x f(x)g(w-x) \] (A.26)

\[ = \int_{x,w} f(x)g(w-x)e^{2\pi i wt} \] (A.27)

\[ = \int_{x,w} f(x)g(w-x)e^{2\pi i (w-x)t}e^{2\pi i xt} \] (A.28)

\[ = \int_x e^{2\pi i xt}f(x)\int_w g(w-x)e^{2\pi i (w-x)t} \] (A.29)

\[ = \int_x e^{2\pi i xt}f(x)\int_{w-x} g(w-x)e^{2\pi i (w-x)t} \] (A.30)

\[ = \int_x e^{2\pi i xt}f(x)\int_u g(u)e^{2\pi i ut} \] (A.31)

\[ = \int_x e^{2\pi i xt}f(x)\mathcal{F}(g(w)) \] (A.32)

\[ = \mathcal{F}(g(w))\int_x e^{2\pi i xt}f(x) \] (A.33)

\[ \mathcal{F}(f,g) = \mathcal{F}(f)\mathcal{F}(g) \] (A.34)

By similar analysis, we can demonstrate the same is true for the inverse Fourier transform.

\[ \mathcal{F}^{-1}(f,g) = \mathcal{F}^{-1}(f)\mathcal{F}^{-1}(g) \] (A.35)

The sampling theorem proof first assumes that a function \( f(t) \) has a spectrum of \( F(w) \) which is zero when \( |w| > B \). We then construct a sampling function \( f_s(t) \) based on the function \( f(t) \).
\[ f_s(t) = Comb(t, A)f(t) \]  

(A.36)

The comb function acts to filter out all the points outside the set

\[ \{ \ldots f(t - 3A), f(t - 2A), f(t - A), f(t), f(t + A), f(t + 2A), \ldots \} \].  

(A.37)

In a sense, we have thrown out all the points outside the delta functions spaced apart by \( A \). The Fourier transform is then applied on the sampling function \( f_s(t) \). But, the Fourier transform of the sampling function is nothing more then the convolution of the Fourier Transformed Comb function and the Fourier transformed \( f(t) \).

\[ F^{-1}\{f_s(t)\} = F_s(w) \]  

(A.38)

\[ = F^{-1}\{Comb(t, A) f(t)\} \]  

(A.39)

\[ = (F^{-1}\{Comb(t, A)\}, F^{-1}\{f(t)\}) \]  

(A.40)

\[ = (\frac{1}{A}Comb(w, \frac{1}{A}), F(w)) \]  

(A.41)

\[ F^{-1}\{f_s(t)\} = \frac{1}{A}(Comb(w, \frac{1}{A}), F(w)) = F_s(w) \]  

(A.42)

The convolution of the comb function with the spectrum \( F(w) \) will cause the spectrum to reappear periodically at \( \frac{1}{A} \) in the \( w \) space. If the \( F(w) \) functions do not overlap by a judicious selection of \( A \), then we can construct the original function \( f(s) \) by limiting the Sampled Spectrum \( F_s(w) \) to only a region to only permit the \( F(w) \) to exist. We then Fourier transform the \( F(w) \) back to \( f(t) \) to reconstruct the original signal.

In essence, we are saying that we can take a sampled function \( f_s(t) \) and reconstruct the original signal \( f(t) \) using the following procedure.
• Convert sampled function $f_s(t)$ with samplings of T distance apart into it Fourier sampled spectrum $F_s(w)$. We are assuming that the band the spectrum $F(w)$ of the original signal is band limited ($F(w) = 0$ when $|w| <= B$).

• If $F_s(w)$ has non overlapping band limited $F(w)$ signals, we can then filter out only a single $F(w)$ from the $F_s(w)$.

• Fourier transform the filtered $F_s(w)$ back into the original signal $f(t)$.

Our sampling displacement of T means that the the Fourier Transformed sample signal will repeat at a distance apart of $\frac{1}{T}$. Our band limited assumption for the original signal is that the spectrum must be $|w| \leq B$. The width for which the spectrum of the original signal is then $2B$. For no overlapping in the sampled spectrum signal, we must have $\frac{1}{T} \geq 2B$. That is to say that we must sample faster then then twice highest spectral frequency to reconstruct the original signal.

We should also note that if we sample the original signal less then the proscribed rate greater then the band width, we will have introduce correlation errors in the reconstructed signal because of the overlap of adjacent spectrum regions.

### A.4 Caldeira-Leggett Hamiltonian

The following account of the Caldeira-Leggett Hamiltonian is a summary of well known results[20, 110, 18]. We discuss this model as it relates to the specialized case when the system is composed of a harmonic oscillator that is bi linearly coupled to an environment comprising thermalized harmonic oscillators. The quantum mechanical system position correlation function for this Brownian oscillator is used in our line shape expression.

All quantum systems are open. The full quantum evolution of a small portion of the universe, which we will call the open system, cannot be separated from the rest of the
We can simplify the evolution of the open system, by assuming a thermalized universe, called the bath, and a simplified interaction between the degrees of freedom of the open system and degrees of freedom the bath. Our endeavor is to describe the open system drive towards thermalization and decoherence.

The Caldeira-Leggett Hamiltonian consists of a bilinear coupling $H_{sb}(q, q_a)$ between an open system $H_s(p, q)$ with an environmental bath comprised of many harmonic oscillators $H(p, p_a, q_a)$. 

\[ H = H_s(p, q) + H_b(p_a, q_a) + H_{sb} \]  

(A.43) 

\[ H = \frac{p^2}{2m} + V(q) + \sum_a \left\{ \frac{p_a^2}{2m_a} + \frac{m_a w_a^2}{2} (q_a - \frac{D_n q}{m_n w_n^2})^2 \right\} \]  

(A.44) 

In the classical solution using the Hamiltonian equations of motion, the minimal energy is arrived at when all the $q_a = \frac{D_n q}{m_n w_n^2} = 0$. When all the bath oscillators are relaxed at $q_a = 0$, the system coordinate $q = 0$ and the energy becomes kinetic energy terms and $V(0)$. If $V(0)$ is a minimal potential energy of the system, the relaxed bath oscillators will not translationally effect the motion of the system.

When the Hamiltonian is treated in the quantum mechanical case with the conjugate variable pairs have commutation relations $([q, p] = i\hbar, [q_a, p_a] = i\hbar)$ and, when viewed in the Heisenberg picture with time dependent operators, the minimal expectation value of energy (using the Ehrenfest Theorem) corresponds to $\langle q_a \rangle = q_a = \frac{D_n(q)}{m_n w_n^2}$ and the same translational invariance of the system is observed as in the classical system.

If the Hamiltonian is not written in the above form, and is written with all independent bath oscillators and system addended with a single coupling term $q \sum_a C_a q_a$, then when the bath has relaxed coordinates ($q_a = 0$ classically and $\langle q_a \rangle = 0$ quantum mechanically), an artificial quadratics potential in $q^2$ called the counter term will affect the motion of the
In this form, the Caldeira-Leggett Hamiltonian can be converted into the classical and quantum mechanical Langevin equations:

\[ m \ddot{q} + \int_{t'=0}^{t} K(t-t')\dot{q}(t')dt' + \frac{\partial V(q)}{q} = F(t). \]  

(A.45)

The Generalized Langevin equation kernel \( K(t) \) represents an inclusion of memory effects of the velocity on the system in the past. \( F(t) \) is a stochastic force acting on the system. The Langevin equation models a time invariant and retarded response of a system to outside forces represented by the stochastic force \( F(t) \).

Solving the equations of motions classically for the Caldeira-Leggett Hamiltonian, we arrive at the coupled equations of motion of the system and the bath.

\[ m \ddot{q} = -\frac{\partial V(q)}{q} + \sum_a c_a q_a \]  

(A.46)

\[ m_a \ddot{q}_a = -m_a w_a^2 q_a + c_a q \]  

(A.47)

The integral solution of \( q_a \) using Leplace transforms is given as,

\[ q_a = q_{ao} \cos(w_a t) + \frac{\dot{q}_{ao}}{w_a} \sin(w_a t) + \frac{c_a}{m_a w_a} \int_{t'=0}^{t} q(t-t') \sin(w_a t') dt', \]  

(A.48)

where we have selected \( q_{ao} \) and \( \dot{q}_{ao} \) as the initial coordinate and velocity values of a harmonic oscillator.

Back substitution of this equation into the system evolution, we get a closed form solution of the open system in terms of the couplings \( c_a \), initial bath positions \( q_{ao} \), and initial bath velocities \( \dot{q}_{ao} \).
\[
m\ddot{q} + \frac{\partial V(q)}{\partial q} - \sum_a \left\{ c_a q_o \cos(w_a t) + \frac{c_a \dot{q}_o}{w_a} \sin(w_a t) \right\} = 
\]
\[
= \sum_a \frac{c_a^2}{m_a w_a} \int_{t'=0}^t q(t - t') \sin(w_a t') dt' 
\]
\[
= \sum_a \frac{c_a^2}{m_a w_a} \left\{ \frac{1}{w_a} (q(t) - q_o \cos(w_a t)) - \frac{1}{w_a} \int_{t'=0}^t \dot{q}(t - t') \cos(w t') dt' \right\} 
\]
\[
= \sum_a \frac{c_a^2}{m_a w_a^2} q - \sum_a \frac{c_a^2}{m_a w_a^2} \int_{t'=0}^t \dot{q}(t - t') \cos(w_a t') dt' 
- \sum_a \frac{c_a^2}{m_a w_a^2} q_o \cos(w_a t) 
\]
\[
(A.49) 
\]
\[
(A.50) 
\]
\[
(A.51) 
\]

Rearranging these terms, we get a general form of the solution of the open system.
\[ m\ddot{q} + \frac{\partial(V(q) - \frac{1}{2}Rq^2)}{\partial q} + \int_{t'=0}^{t} \gamma(t')\dot{q}(t - t')dt' \]

\[ = \sum_{a} \left[ A_{a}\cos(w_{a}t) + B_{a}\sin(w_{a}t) \right] \quad (A.52) \]

\[ = \sum_{a} M_{a}\cos(w_{a}t + \theta_{a}) \quad (A.53) \]

\[ R = \sum_{a} \frac{c_{a}^{2}}{m_{a}w_{a}^{2}} \quad (A.54) \]

\[ A_{a} = c_{a}q_{ao} - q_{o}\frac{c_{a}^{2}}{m_{a}w_{a}^{2}} \quad (A.55) \]

\[ B_{a} = \frac{c_{a}\dot{q}_{ao}}{w_{a}} \quad (A.56) \]

\[ M_{a} = \sqrt{A_{a}^{2} + B_{a}^{2}} \quad (A.57) \]

\[ \tan \theta_{a} = \frac{B_{a}}{A_{a}} \quad (A.58) \]

\[ \gamma(t') = \sum_{a} \frac{c_{a}^{2}}{m_{a}w_{a}^{2}}\cos(w_{a}t') \quad (A.59) \]

The derives the Classical Generalized Langevin Equation where the right hand side represents a stochastic bath force and the integral kernel \( \gamma(t) \) represents the memory effects of the particles velocity. If the integral memory kernel is an a delta function within the interval time, then the dissipative force represented by that integral is proportional to the instantaneous velocity and can be identified as an Ohmic density of coupled Bath oscillators.

The general solutions of a simple Harmonic Oscillator with a Hamiltonian of

\[ H = \frac{p^{2}}{2m} + \frac{mw^{2}}{2}x^{2} \quad (A.60) \]
is given as

\( x(t) = x_0 \cos(wt) + \frac{\dot{x}_0}{w} \sin(wt) \)  \hspace{1cm} (A.61)

\( = A_0 \cos(wt + \theta) \)  \hspace{1cm} (A.62)

\( = \sqrt{\frac{2E_0}{mw^2}} \cos(wt + \theta) \)  \hspace{1cm} (A.63)

\( A_0 = \sqrt{x_0^2 + \left(\frac{x_0}{w}\right)^2} \)  \hspace{1cm} (A.64)

\( E_0 = \frac{m}{2} A_0^2 w^2 \)  \hspace{1cm} (A.65)

The correlation function for the classical harmonic oscillator is given as

\[ C(t) = \lim_{T \to \infty} \frac{1}{T} \int_{-T}^{T} x(t' + t)x(t')dt' \]  \hspace{1cm} (A.66)

\[ = \frac{E_0}{mw^2} \cos(wt) \]  \hspace{1cm} (A.67)

The Generalized Quantum Langevin Equation\([35]\) can be constructed by taking the time independent Caldeira-Leggett Hamiltonian and using the operator equations of motion

\[ i\hbar \frac{dA(t)}{dt} = [A(t), H] \]  \hspace{1cm} (A.68)

, where we have assumed \( A(t) \) is an implicit operator function of time. Using the commutations rules([q, p] = \( i\hbar \), [qa, pa] = \( i\hbar \)) and the position and momentum operators in time, we can construct second order in time equations of motion of the bath and system position operators:
\[
\frac{i\hbar}{dt} dp(t) = [p, H] = -i\hbar \left[ \frac{\partial V(q)}{\partial q} + \sum_i D_i q_i \right] \quad (A.69)
\]

\[
\frac{i\hbar}{dt} dq(t) = [q, H] = i\hbar \frac{p}{m} \quad (A.70)
\]

\[
\frac{i\hbar}{dt} dp_a(t) = [p_a, H] = -i\hbar \left[ m_a w_a q_a + D_a q \right] \quad (A.71)
\]

\[
\frac{i\hbar}{dt} dq_a(t) = [q_a, H] = i\hbar \frac{p_a}{m_a} \quad (A.72)
\]

These equations are exactly the same derivation as the classical equations of motion of second order in time, with the exception that \( x(t), x_a(t) \) are Heisenberg time dependent operators. Using the Laplace transformation, we can arrive at the same integral solution of each of the bath position operator \( x_a \). Back substitution of \( x_a \) back into \( x \) gives the Quantum Langevin equation as from the earlier classical version. The real problem with the Quantum Langevin equation is in the derivation of the correlation function \( C(t) \), where the position operators \( x(t) \) at two distinct times do not necessarily commute. Although lacking in this temporal computation, the Generalized Quantum Langevin equation is very instructive in understanding some aspects of Quantum Evolution in classical terms.

### A.5 Quantum Correlation Functions

We use quantum temporal correlation functions to define the characteristics of the coupling of the Caldeira-Leggette type system to a thermalized oscillator bath as well as to describe the stochastic properties of that bath. These time correlation function can be used with linear response theory to describe relaxation of slightly perturbed equilibrium systems\[119\]. The two point quantum time correlation function of any two observables \( \{A, B\} \) on some
system with Hamiltonian $H$ that is coupled to a thermalized bath is

$$C(t_1, t_2) = \langle A(t_1)B(t_2) \rangle = Tr\{A(t_1)B(t_2)e^{\frac{-H}{k_B T}}\}/Tr\{e^{\frac{-H}{k_B T}}\} \quad (A.73)$$

$$= Tr\{e^{-\frac{H}{k_B T}} Ae^{\frac{H}{k_B T}} e^{-\frac{H}{k_B T}} Be^{\frac{H}{k_B T}} e^{\frac{-H}{k_B T}}\}/Tr\{e^{\frac{-H}{k_B T}}\} \quad (A.74)$$

where the observables time dependence is defined in the Heisenberg picture. We have assumed that both observables and Hamiltonian are time independent in the Schrödinger picture. The circular properties of the trace operator means that the two time correlation function $C(t_1, t_2) = C(t_1 + \tau, t_2 + \tau)$ is time translationally shift invariant. So, a single time $t = t_1 - t_2$ could be used to redefine the two point time correlation function to a single one time function

$$C(t) = C(t, 0) = \langle A(t)B \rangle \quad (A.75)$$

This quantum correlation function has the symmetry property $C(t) = C(-t)^*$. The thermalized quantum harmonic oscillator with Hamiltonian

$$H = \frac{p^2}{2m} + \frac{mw^2x^2}{2} = \hbar \omega (a^+a + \frac{1}{2}) = \hbar \omega (N + \frac{1}{2}) \quad (A.84)$$

We intermix between the creation and annihilation operators with the following equations

$$H = A^2x^2 + B^2p^2 = \hbar \omega (a^+a + \frac{1}{2}) \quad (A.76)$$

$$a = \frac{Ax + iBp}{\sqrt{2\hbar AB}} \quad (A.77)$$

$$w = 2AB \quad (A.78)$$

$$a(t) = ae^{-i\omega t} \quad (A.79)$$

$$x = \frac{a\sqrt{2AB}\hbar + a^+\sqrt{2AB}\hbar}{2A} \quad (A.80)$$

$$a\left|n\right> = \sqrt{n}\left|n - 1\right> \quad (A.81)$$

$$a^+\left|n\right> = \sqrt{n+1}\left|n + 1\right> \quad (A.82)$$

$$Tr\{F\} = \sum_n \langle n | F | n \rangle \quad (A.83)$$

, where $A$ and $B$ are real numbers and $a(t)$ is the lowering operator in the Heisenberg picture.
can be described with a position correlation function

\[ C_x(t) = \langle x(t) x(0) \rangle \]  \hspace{1cm} (A.85)

\[ = \frac{1}{2m\hbar^2} \left\langle \left( a e^{-i\omega t} \sqrt{\hbar}w + a^+ e^{+i\omega t} \sqrt{\hbar}w \right) \left( a \sqrt{\hbar}w + a^+ \sqrt{\hbar}w \right) \right\rangle \]  \hspace{1cm} (A.86)

\[ = \frac{\hbar}{2m\hbar^2} \left\langle Ne^{i\omega t} + (N + 1)(e^{-i\omega t}) \right\rangle \]  \hspace{1cm} (A.87)

\[ = \frac{\hbar}{2m\hbar^2} \sum_{n=0}^{\infty} \langle n | (Ne^{i\omega t} + (N + 1)e^{-i\omega t}) e^{-\hbar w(N + \frac{1}{2}) \frac{k_B T}{\hbar^2}} | n \rangle \]  \hspace{1cm} (A.88)

\[ = \frac{\hbar}{2m\hbar^2} \coth\left( \frac{\hbar w}{2k_B T} \right) \cos(\omega t) - i\sin(\omega t). \]  \hspace{1cm} (A.89)

In the high temperature limit, the \( \coth\left( \frac{\hbar w}{2k_B T} \right) \rightarrow \frac{2k_B T}{\hbar w} \) (see footnote\(^7\)), and the auto position correlation function becomes

\[ C_x(t) = \langle x(t) x(0) \rangle = \frac{k_B T}{m\hbar^2} \cos(\omega t) - i\sin(\omega t), \]  \hspace{1cm} (A.91)

where the imaginary portion of the correlation function becomes trivial in magnitude to the real portion.

The classical time correlation functions between two observable can also be defined similarly as the quantum version. The classical system evolves observables under the Hamiltonian formulation of mechanics as

\[ \frac{dA(p, q)}{dt} = \sum_i \frac{\partial A}{\partial q_i} \dot{q}_i + \sum_i \frac{\partial A}{\partial p_i} \dot{p}_i = \sum_i \frac{\partial A}{\partial q_i} \frac{\partial H}{\partial p_i} - \sum_i \frac{\partial A}{\partial p_i} \frac{\partial H}{\partial q_i} \]  \hspace{1cm} (A.92)

\[ = \{A, H\} = i\mathcal{L}A \]  \hspace{1cm} (A.93)

where we have used the Poison brackets \( \{f, g\} = \sum_i \frac{\partial f}{\partial q_i} \frac{\partial g}{\partial p_i} - \sum_i \frac{\partial f}{\partial p_i} \frac{\partial g}{\partial q_i} \) and the Liouville propagator \( i\mathcal{L} = \sum_i \sum_i \frac{\partial H}{\partial p_i} \frac{\partial}{\partial q_i} - \sum_i \frac{\partial H}{\partial q_i} \frac{\partial}{\partial p_i}. \) The evolution is then given formally as

\[ A(t) = e^{it\mathcal{L}} A(0). \]  \hspace{1cm} (A.94)

\(^7\)When \( x \rightarrow 0, \)

\[ \coth(x) = \frac{e^x + e^{-x}}{e^x - e^{-x}} = \frac{2 + x^2 + \ldots}{2x + 2x^3/3! + \ldots} \approx \frac{1}{x}. \]  \hspace{1cm} (A.90)
We can define the two time correlation function \( C(t_1, t_2) \) of the observable \( A \) as

\[
C_h(t_1, t_2) = \lim_{T \to \infty} \frac{1}{T} \int_{t=0}^{T} A(t + t_1)B(t + t_2)dt
\]  \hspace{1cm} (A.95)

Although the Hamiltonian equations of mechanics is a very general formulation, we use the Hamiltonian to mean energy so as to perform statistical averaging of this correlation function over all energy ensemble members. The full classical correlation function can then be given as

\[
C(t_1, t_2) = \int_E C_h(t_1, t_2)e^{-\frac{E}{k_B T}}dE.
\]  \hspace{1cm} (A.96)

Like the Quantum Correlation Function, we can construct the single point time correlation function assuming that the expectation averages are translationally invariant in time.

\[
C_{cl}(t) = \int_E C_h(t, 0)e^{-\frac{E}{k_B T}}dE
\]  \hspace{1cm} (A.97)

The classical position correlation function \( <x(t)x(0)> \) for the Harmonic Oscillator can be evaluated by first evaluating the time dependent position \( x(t) \).

\[
x(t) = x_o\cos(wt) + \frac{\dot{x}_o\sin(wt)}{w} = \sqrt{x_o^2 + \left(\frac{\dot{x}_o}{w}\right)^2}\cos(wt + \phi)
\]  \hspace{1cm} (A.98)

The \( \phi \) is a phase relating the initial velocity \( \dot{x}_o \) and initial position \( x_o \) that will disappear when evaluating the correlation function. The temporal correlation function is then

\[
C_h(t) = \lim_{T \to \infty} \frac{1}{T} \int_{t'=0}^{T} x(t + t')x(t' + 0)dt'
\]  \hspace{1cm} (A.99)

\[
= \frac{1}{2} \left(x_o^2 + \left(\frac{\dot{x}_o}{w}\right)^2\right)\cos(wt)
\]  \hspace{1cm} (A.100)

The energy of the system given the initial position and velocity is

\[
E = \frac{m\omega^2}{2} \left(x_o^2 + \left(\frac{\dot{x}_o}{w}\right)^2\right).
\]  \hspace{1cm} (A.101)
Hence the time correlation of a single system of the energy ensemble is given as
\[ C_h(t) = \frac{E}{mw^2} \cos(wt) \]  
(A.102)

The ensemble correlation function is then
\[ C_{cl}(t) = \int_{E=0}^{\infty} \frac{E}{mw^2} \cos(wt) e^{-\frac{E}{k_BT}} dE = \frac{k_B T}{mw^2} \cos(wt) \]  
(A.103)

This is exactly the same correlation function that we arrived at in the high temperature limit of the quantum correlation function.

### A.6 Fermi Golden Rule

The Fermi Golden Rule\(^{[31]}\) gives the transition rate of finding a system in an final energy eigen state starting from an initial energy eigen state under a short time perturbation where the system is coupled to a continuum of states. The unitary propagator in time dependent perturbation theory is given in the following where the Hamiltonian is written \( H = H_o + W_t(t) \) with \( W_t(t) \) is time dependent perturbation.

\[
U(t, t_0) = e^{\frac{H_o}{\hbar} (t-t_0)} + \frac{1}{(i\hbar)} \int_{t'=t_0}^{t} e^{\frac{H_o}{\hbar} (t-t')} W_t(t') e^{\frac{H_o}{\hbar} (t'-t_0)} dt' \\
+ \frac{1}{(i\hbar)^2} \int_{t'=t_0}^{t} \int_{t''=t_0}^{t'} e^{\frac{H_o}{\hbar} (t-t')} W_t(t') e^{\frac{H_o}{\hbar} (t'-t'')} W_t(t'') e^{\frac{H_o}{\hbar} (t''-t_0)} dt'' dt' \\
+ \frac{1}{(i\hbar)^3} \int_{t'=t_0}^{t} \int_{t''=t_0}^{t'} \int_{t'''=t_0}^{t''} e^{\frac{H_o}{\hbar} (t-t')} W_t(t') e^{\frac{H_o}{\hbar} (t'-t'')} W_t(t'') e^{\frac{H_o}{\hbar} (t''-t''')} W_t(t''') e^{\frac{H_o}{\hbar} (t'''-t_0)} dt''' dt'' dt' \\
+ ... 
\]  
(A.104)

Approximating the propagator only to first order perturbation and assuming that the initial state \( |a\rangle \), final state \( |b\rangle \), and \( t_0 = 0 \), the quantum amplitude of the final state to the initial
state is then

\[ A(t) = \langle b \left| e^{i\frac{\mathcal{H}}{\hbar}t} + \frac{1}{i\hbar} \int_{t'=0}^{t} e^{i\frac{\mathcal{H}}{\hbar}(t-t')} W_t(t') e^{i\frac{\mathcal{H}}{\hbar}(t')} dt' \right| a \rangle \quad , \quad b \neq a \quad (A.105) \]

\[ = \frac{1}{i\hbar} \langle b \left| \int_{t'=0}^{t} e^{i\frac{\mathcal{H}}{\hbar}(t-t')} W_t(t') e^{i\frac{\mathcal{H}}{\hbar}(t')} dt' \right| a \rangle \quad (A.106) \]

\[ = \frac{1}{i\hbar} \int_{t'=0}^{t} e^{\frac{E_b}{\hbar}(t-t')} \langle b \left| W_t(t') \right| a \rangle e^{\frac{E_a}{\hbar}(t')} dt' \quad (A.107) \]

\[ = \frac{1}{i\hbar} e^{\frac{+E_b t}{\hbar}} \int_{t'=0}^{t} \langle b \left| W_t(t') \right| a \rangle e^{\frac{E_a-E_b}{\hbar} t'} dt' \quad (A.108) \]

Squaring the amplitude gives us the probability of finding the system in state \(|b\rangle\) with an initial state\(|a\rangle\).

\[ P_{ab}(t) = \frac{1}{\hbar^2} \left| \int_{t'=0}^{t} \langle b \left| W_t(t') \right| a \rangle e^{\frac{i(E_a-E_b) t'}{\hbar}} dt' \right|^2 \quad (A.109) \]

\[ R_{ab}(t) = \frac{dP_{ab}(dt)}{t} \quad (A.110) \]

We are specifically interested in the interaction of molecules due to electromagnetic disturbances. Visible light with wavelengths of 450nm-780nm far exceeds the size of the chromophoric absorption and emission unit that we are interested in. As such, we treat the molecular-electromagnetic interaction as weak in the classical field approximation without field quantization[27]. We also will assume that the interaction can be treated within the point dipole approximation. Consequently, The electromagnetic perturbation of a system with a fixed dipole will have a general form of the as \( W(t) = -\vec{p} \cdot \vec{E} = D' \cos(\omega t) \) dipole moment \( \vec{p} \) and electric field \( \vec{E} \). Take the term \( \langle b \left| W_t(t') \right| a \rangle = D' \cos(\omega t') \).

\[ A_{ab}(t) = \frac{D}{i\hbar} e^{\frac{E_p t}{\hbar}} \int_{t'=0}^{t} (e^{i\omega t'} + e^{-i\omega t'}) e^{\frac{i(E_a-E_b)}{\hbar} t'} dt' \quad , \quad \omega_0 = \frac{E_a - E_b}{i\hbar} \quad (A.111) \]

\[ = \frac{D}{i\hbar} e^{\frac{E_p t}{\hbar}} e^{\frac{i(-\omega +\omega_0) t}{2}} \left\{ \frac{\sin(\frac{-\omega +\omega_0) t}{2})}{w-\omega_0} \right\} + \frac{-w-\omega_0}{w-\omega_0} \quad (A.112) \]
We did not expand the second term completely, as we will neglect it within the Rotating Wave Approximation\cite{23, 78, 69} which assumes that the high order oscillations are not important.

\begin{align*}
A_{ab}(t) &= \frac{D}{i\hbar} e^{\frac{E_b t}{\hbar}} e^{\frac{w - w_0}{2} t} \left\{ \frac{\sin\left(\frac{w - w_0}{2} t\right)}{w - w_0} \right\} \\
P_{ab}(t) &= \frac{D^2}{\hbar^2} \left\{ \frac{\sin\left(\frac{w - w_0}{2} t\right)}{w - w_0} \right\}^2
\end{align*}
\text{(A.113)}
\text{(A.114)}

This probability refers to the probability of transition from $|a\rangle$ to state $|b\rangle$. Integration over a continuum of states $|b\rangle$ will show the probability of the system to be not in state $|a\rangle$. As we are switching to a continuum, we expect that there is a density of states $\rho = \frac{dn}{dE}$ in the vicinity of the state $|b\rangle$.

\begin{align*}
P_a(t) &= \sum_b P_{ab}(t) = \int_b P_{ab} dn = \int_E P_{ab} \rho(E) dE \\
&= \int_{\bar{w}=-\infty}^{\bar{w}=\infty} \frac{D^2}{\hbar^2} \left\{ \frac{\sin\left(\frac{w - w_0}{2} t\right)}{w - w_0} \right\}^2 \rho(w) d\bar{w} \\
&= \frac{D^2 \rho(w_o)}{\hbar} \int_{\bar{w}=-\infty}^{\bar{w}=\infty} \left\{ \frac{\sin\left(\frac{w - w_0}{2} t\right)}{w - w_0} \right\}^2 d\bar{w} \\
&= \frac{D^2 \rho(w_o)}{\hbar} \left( \frac{t}{2} \right)^2 \int_{\bar{w}=-\infty}^{\bar{w}=\infty} \left\{ \frac{\sin\left(\frac{w - w_0}{2} t\right)}{(w - w_0) t^2} \right\}^2 d\bar{w} \\
&= \frac{D^2 \rho(w_o)}{\hbar} \frac{t}{2\pi} \\
&= \frac{D^2 \rho(w_o)}{2\hbar} (2\pi)
\end{align*}
\text{(A.115)}
\text{(A.116)}
\text{(A.117)}
\text{(A.118)}
\text{(A.119)}

The last integral is the integration of a sinc squared function that is centered at $w_o$. Consequently, the rate change of probability of the system evolving from $|a\rangle$ is a constant through time.

\begin{align*}
R &= \frac{dP_a(t)}{dt} = \frac{\pi D^2 \rho(w_o)}{2\hbar}
\end{align*}
\text{(A.120)}

This is the Fermi-Golden Rule of a system weakly perturbed by a periodic disturbance.
A.7 Quantum Master Equation

Quantum Master Equations are the derived equations of motion of the reduced density matrix of a system coupled to a larger number of degree environment based on the Liouville-von Neumann Equation [97, 18]. The Liouville-von Neumann Equation for the coupled system is given by.

\[ i\hbar \frac{\partial \rho(t)}{\partial t} = [H, \rho], \quad H = H_s + H_b + H_{sb} = H_s \otimes 1 + 1 \otimes H_b + H_{sb}, \quad \rho = \rho_s \otimes \rho_b + \rho_{sb} \]  

(A.121)

Here, the full Hamiltonian $H$ is expanded as a tensor product of the system and environment degrees of freedom. The system Hamiltonian is given as $H_s$ and represented as a tensor product $H_s \otimes 1$ in the full system and bath basis. Similarly, the environment bath Hamiltonian in the $H_b$ bath basis and $1 \otimes H_b$ int the system basis. The density matrix $\rho$ is decomposed into the density matrix consisting of the separate evolution of the individual density matrices of the system $\rho_s$, the bath $\rho_b$, and the non separable entangled portion $\rho_{sb}$. The Bath Trace Operator is the projection operator which takes densities in the Hilbert product space $\mathcal{H}_s \otimes \mathcal{H}_b$ into the Hilbert space of only the system $\mathcal{H}_s$. Assuming that $\{|j_a \rangle_b\}$ is a basis set, the Bath Trace Operator can be constructed as

\[ Tr_b(\rho) = \sum_a |j_a \rangle_b \rho |j_a \rangle_b = \sum_a \left\{ 1 \otimes |j_a \rangle_b \right\} \rho \left\{ 1 \otimes |j_a \rangle_b \right\}, \quad \rho \in \mathcal{H}_s \otimes \mathcal{H}_b. \]

(A.122)

With the above definition, we can arrive at the following rules.

\[ Tr_b\left\{ \rho_s \otimes \rho_b \right\} = \rho_s \ Tr(\rho_b), \quad , \rho_s \otimes \rho_b \in \mathcal{H}_s \otimes \mathcal{H}_b \]  

(A.123)

\[ Tr_b\left\{ \rho_1 + \rho_2 \right\} = Tr_b\left\{ \rho_1 \right\} + Tr_b\left\{ \rho_2 \right\}, \quad , \rho_1, \rho_2 \in \mathcal{H}_s \otimes \mathcal{H}_b \]  

(A.124)
The Quantum Master Equation consisting of the reduced density matrix must abide by the general rules of all density matrices of being Hermitian, having Semi-positivity, and being Normalized. The evolution of the reduced density matrix is construable as

\[ \rho_s(t) = \text{Tr}_b \left\{ U(t, t_o) \rho(t_o) U(t, t_o)^+ \right\} = V(t, t_o) \rho_s(t_0) \]  

(A.125)

where \( V(t_1, t_2) \) is a dynamical map that preserves these properties. The Lindblad-Gorini-Kossakowski-Sudarshan Quantum Master Equation\[18\] is a mathematical, rigorous, general Markovian form using the one parameter dynamical semi-group map \( V(t) \). Lindblad\[74\] proved that this most general form maintains all three above properties. The alternative construction of a Quantum Master Equations are the microscope derivations\[18\] using appropriate Hamiltonians to understand the underlying structure of the total system. Microscope derivations of the Quantum Master equation may not fully keep positivity or normalization. It would be ideal to construct Lindblad form from the Microscopic derivation to hold the prior properties during the evolution of the density reduced density matrix.

### A.7.1 Chapman-Kolmogorov Equation

The Markov condition for a Stochastic Process\[85\] is given by the conditional probability density

\[ f(x_1, t_1|x_2, t_2; x_3, t_3, ...) = f(x_1, t_1|x_2, t_2). \quad t_1 \geq t_2 \geq t_3 \geq ... \]  

(A.126)

This is to say that the probability of an event occurring at position \( x_1 \) at time \( t_1 \) is determined fully on only the last position \( x_2 \) at time \( t_2 \). It is not determined by the prior history of events at positions in prior times.

We can construct the Chapman-Kolmogorov Equation simply using the definition of conditional probability and marginalization.
\( f(x_1, t_1 | x_3, t_3) = \frac{f(x_1, t_1; x_3, t_3)}{f(x_3, t_3)} \) \( t_1 \geq t_3 \) \hspace{1cm} (A.127)

\[ = \int_{x_2} \frac{f(x_1, t_1; x_2, t_2; x_3, t_3)}{f(x_3, t_3)} \, dx_2 \quad t_1 \geq t_2 \geq t_3 \] \hspace{1cm} (A.128)

\[ = \int_{x_2} \frac{f(x_1, t_1; x_2, t_2; x_3, t_3)}{f(x_2, t_2; x_3, t_3)} \frac{f(x_2, t_2; x_3, t_3)}{f(x_3, t_3)} \, dx_2 \] \hspace{1cm} (A.129)

\[ = \int_{x_2} f(x_1, t_1 | x_2, t_2) f(x_2, t_2 | x_3, t_3) \, dx_2 \quad t_1 \geq t_2 \geq t_3 \] \hspace{1cm} (A.130)

### A.7.2 Master Equation

For stationary processes, the conditional probability density is determined by the time difference between the events.

\[ f(x_1, t_1 | x_3, t_3) = f_\tau(x_1 | x_3) \quad , \tau = t_1 - t_2 \] \hspace{1cm} (A.131)

The Chapman-Kolmogorov Equation can then be written for stationary Markov processes as

\[ f_{\tau_1 + \tau_2}(x_1 | x_3) = \int_{x_2} f_{\tau_1}(x_1 | x_2) f_{\tau_2}(x_2 | x_3) \, dx_2 \] \hspace{1cm} (A.132)

Construction the of the partial derivative with respect to time is done with the difference between the next two equations over the \( \Delta t \rightarrow 0. \)

\[ f_{\Delta t + \tau}(x_1 | x_3) = \int_{x_2} f_{\Delta t}(x_1 | x_2) f_t(x_2 | x_3) \, dx_2 \] \hspace{1cm} (A.133)

\[ f_{0 + \tau}(x_1 | x_3) = \int_{x_2} f_0(x_1 | x_2) f_t(x_2 | x_3) \, dx_2 = \int_{x_2} \delta(x_1 - x_2) f_t(x_2 | x_3) \, dx_2 \] \hspace{1cm} (A.134)
The partial derivative of the conditional density of the Stationary Markovian process is the Master Equation.

\[
\frac{\partial f_t(x_1|x_3)}{\partial t} = \int_{x_2} \frac{f_{\Delta t}(x_1|x_2) - \delta(x_1 - x_2)}{\Delta t} f_t(x_2|x_3) dx_2, \quad \Delta t \to 0 \tag{A.135}
\]

\[
= \int_{x_2} \frac{\partial f_t(x_1|x_2)}{\partial t} \bigg|_0 f_t(x_2|x_3) dx_2 \tag{A.136}
\]

\[
= \int_{x_2} G(x_1, x_2) f_t(x_2|x_3) dx_2 \tag{A.137}
\]

A.7.3 Redfield Quantum Master Equation

The Redfield Equation\cite{90} is a second order regular time perturbation quantum master equation which does not hold positivity\cite{104}. The description is given by

\[
H = H_s + H_b + H_{sb} = H_s \otimes 1 + 1 \otimes H_b + H_{sb} \tag{A.138}
\]

\[
\rho = \rho_s \otimes \rho_b + \rho_{sb} \tag{A.139}
\]

\[
\rho(0) = \rho_s(0) \otimes \rho_b(0) \tag{A.140}
\]

The weak coupling approximation is the assumption that the $H_{sb}$ is a perturbation on $H_s + H_b = H_s \otimes 1 + 1 \otimes H_b$. The interaction Hamiltonian in the interaction picture is then given by

\[
H_i(t) = e^{-\frac{(H_s + H_b)t}{\hbar}} H_{sb} e^{\frac{(H_s + H_b)t}{\hbar}}. \tag{A.141}
\]

The density matrix in the interaction picture is
\[ \rho_i(t) = e^{-\frac{(H_s+H_b)t}{\hbar}} \rho(0) e^{\frac{(H_s+H_b)t}{\hbar}} \]  
(A.142)

\[ i\hbar \frac{\partial \rho(t)_i}{\partial t} = [H_i, \rho_i] \]  
(A.143)

\[ \rho_i(t) = \rho_i(0) + \frac{1}{i\hbar} \int_{s=0}^{t} [H_i(s), \rho_i(s)] ds \]  
(A.144)

\[ = \rho_i(0) + \frac{1}{i\hbar} \int_{s=0}^{t} [H_i(s), \rho(0)] ds + \frac{1}{i\hbar} \int_{u=0}^{s} [H_i(u), \rho_i(u)] du ds \]  
(A.145)

\[ = \rho_i(0) + \frac{1}{i\hbar} \int_{s=0}^{t} [H_i(s), \rho_i(0)] ds \]

\[ + \frac{1}{(i\hbar)^2} \int_{s=0}^{t} \int_{u=0}^{s} [H_i(s), [H_i(u), \rho_i(u)]] duds \]  
(A.146)

Taking the time derivative and bath trace, we arrive at

\[ \frac{\partial \rho(t)_i}{\partial t} = \frac{1}{i\hbar} [H_i(t), \rho_i(0)] + \frac{1}{(i\hbar)^2} \int_{u=0}^{t} [H_i(t), [H_i(u), \rho_i(u)] du \]  
(A.147)

\[ \frac{\partial \rho(t)_s}{\partial t} = \frac{1}{i\hbar} Tr_b[H_i(t), \rho_i(0)] + \frac{1}{(i\hbar)^2} \int_{u=0}^{t} Tr_b[H_i(t), [H_i(u), \rho_i(u)]] du \]  
(A.148)

We can reduce \( Tr_b[H_i(t), \rho_i(0)] \). We will assume that the \( H_{sb} = \sum_a \lambda_a S_a B_a \)

\[ Tr_b[H_i(t), \rho_i(0)] = Tr_b[e^{-\frac{(H_s+H_b)t}{\hbar}} H_{sb} e^{\frac{(H_s+H_b)t}{\hbar}}, \rho_s(0) \otimes \rho_b(0)] \]  
(A.149)

\[ = Tr_b[e^{-\frac{(H_s+H_b)t}{\hbar}} H_{sb} e^{\frac{(H_s+H_b)t}{\hbar}}, \rho_s(0) \otimes \rho_b(0)] \]  
(A.150)

\[ = Tr_b[e^{-\frac{H_{st}}{i\hbar}} H_{sb} e^{\frac{H_{st}}{i\hbar}}, \rho_s(0) \otimes \rho_b(0)] \]  
(A.151)

\[ = Tr_b[e^{-\frac{H_{st}}{i\hbar}} (\sum_{a} \lambda_a S_a B_a) e^{\frac{H_{st}}{i\hbar}}, \rho_s(0) \otimes \rho_b(0)] \]  
(A.152)

\[ = [e^{-\frac{H_{st}}{i\hbar}} (\sum_{a} \gamma_a S_a) e^{\frac{H_{st}}{i\hbar}}, \rho_s(0)] \]  
(A.153)

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The first assumption in the Redfield Equation is that this bath trace over the initial system density operator is zero. We are saying that the initial density distribution is uncorrelated with the evolution of the System operators.

This leads to a simpler equation of motions of the reduced density matrix as

\[
\frac{\partial \rho_s(t)}{\partial t} = \frac{1}{(i\hbar)^2} \int_{u=0}^{t} Tr_b[H_i(t), [H_i(u), \rho(u)]] du. \tag{A.154}
\]

The second approximation in the Redfield Master Equation is that of the Born approximation where the evolution of the density matrix has no entangled states between the bath and system.

\[
\rho = \rho_s \otimes \rho_b + \rho_{sb}, \quad \rho_{sb} = 0 \tag{A.155}
\]

We now have the equation

\[
\frac{\partial \rho_s(t)}{\partial t} = \frac{1}{(i\hbar)^2} \int_{u=0}^{t} Tr_b[H_i(t), [H_i(u), \rho_s(u) \otimes \rho_b]] du. \tag{A.156}
\]

The Markov property requires that the differential evolution does not depend on the history. It is only dependent on the current local time. We also require that the bath reservoir does not vary in time.

\[
\frac{\partial \rho_s(t)}{\partial t} = \frac{1}{(i\hbar)^2} \int_{u=0}^{t} Tr_b[H_i(t), [H_i(u), \rho_s(t) \otimes \rho_b]] du \tag{A.157}
\]

\[
= \frac{1}{(i\hbar)^2} \int_{v=0}^{t} Tr_b[H_i(t), [H_i(t-v), \rho_s(t-v) \otimes \rho_b]] dv. \tag{A.158}
\]

\[
\approx \frac{1}{(i\hbar)^2} \int_{v=0}^{\infty} Tr_b[H_i(t), [H_i(t-v), \rho_s(t) \otimes \rho_b]] dv. \tag{A.159}
\]

\[
\approx \frac{1}{(i\hbar)^2} \int_{v=0}^{\infty} Tr_b[H_i(t), [H_i(t-v), \rho_s(t) \otimes \rho_b]] dv. \tag{A.160}
\]

This is the Redfield Markovian Quantum Master Equation.
A.8 Cumulant Expansion

The following synopsis is of modern probability theory as needed to understand moment and cumulant generating functions.

Modern probability theory[64, 85] starts with concept of an experiment that generates certain outcomes called the state space Ω. Subsets of these outcome state space Ω with certain properties are then called a sigma field(σ(Ω)). These members in the sigma field F are then assigned a probability measure. The map of σ(Ω) into another set X is called the random variable (M : σ(Ω) → X). The probability measure of a subset in X is defined as the probability measure of the union of all members of the sigma algebra σ(Ω) that are contained in that subset of X.\(^9\)

We will put our attention to the case where X is the Real field, and the definition of a restrictive differentiable probability density function \(f_M\) can be defined.\(^11\)

The \(n\)-th moment of a probability distribution M (random variable map assumed on the

\(^8\)A sigma field σ(Ω) defined on the outcome state space Ω with the following properties.
1. \(Ω \in σ(Ω)\) and \(\{\} \in σ(Ω)\)
2. \(∀w \in σ(Ω) \implies \bar{w} \in σ(Ω)\). The \(\bar{w}\) is defined as the complement with respect to \(Ω\).
3. \(∀u_i \in σ(Ω) \implies ∪_i u_i \in σ(Ω)\) The infinite union of members is also a member.
4. \(u, v \in σ(Ω) \implies u \cap v \in σ(Ω)\) The finite intersection of members is a member.

\(^9\)A measure \(P\) on the sigma field \(F(Ω)\) members have the properties
1. \(∀w \in σ(Ω), P(w) ≥ 0\)
2. \(P(\{\}) = 0\)
3. \(∀u \in sigma(Ω)\) with a measure \(P(w), P(\bar{w}) = 1 – P(w)\).
4. \(∀u, v \in σ(Ω), u \cap v = \{\} \implies P(u \cup v) = P(u) + P(v)\)

\(^10\)In the special case that range X of the random variable map M has a total order such as \(\mathcal{R}\), abbreviated notation such as \(a > M > b\) can be used to identify all the sigma field members that have values between a and b. So too, a differential element dX can be well defined as the probability measure associated with the differential dX. Integrals such as \(\int G(X) dX\) are understood as the generalized Reimann-Stieltjes integration.

\(^11\)The probability density \(f_M\) of the random variable map \(M : σ(Σ) \rightarrow \mathcal{R}\) is defined as the probability measure of the differential element dx. So, in terms of the cumulative measure \(P(x) = \{M ≤ x\}\), the density is \(f_M(x) = \frac{dP(x)}{dx}\) (We will assume that the probability density function is differentiable).
Real numbers) is

\[ \langle x^n \rangle = \int_{-\infty}^{+\infty} x^n f_M(x) \, dx, \]  

(A.161)

where \( f_M(x) \) is the probability distribution\(^{12}\) of the random variable map \( M : \sigma(\Omega) \rightarrow X \). The characteristic moment generating function associated with the distribution \( M \) is the Fourier transform if the probability distribution function.

\[ C_M(it) = \langle e^{itx} \rangle = \int_{-\infty}^{+\infty} e^{itx} f_M(x) \, dx \]  

(A.162)

The characteristic moment generating function always exists for a differentiable distribution function that is absolutely convergent.\(^{13}\) The \( n \)-th order moment \( \mu_n \) can be calculated by using the \( n \)-th derivative of the characteristic function at \( t=0 \).

\[ \mu_n = \langle x^n \rangle = \left. \frac{\partial^n}{\partial (it)^n} C_M(it) \right|_{t=0} \]  

(A.163)

\[ = \left[ \frac{\partial^n}{\partial (it)^n} \int_{-\infty}^{+\infty} e^{itx} f_M(x) \, dx \right]_{t=0} \]  

(A.164)

The cumulant generating function \( K(t) \) is defined as

\[ K(t) = \ln \langle e^{tx} \rangle = \sum_{n=0}^{\infty} \frac{K_n t^n}{n!} \]  

(A.165)

\[ , \text{ where } K_n \text{ is the } n \text{-th order cumulant of the the distribution } M. \]

\[ K_n = \left. \frac{\partial^n K(t)}{\partial t^n} \right|_{t=0} \]  

(A.166)

The first several \( n \)-th order cumulant expanded in terms of moments are found in the following following table.

\(^{12}\)We will sometimes drop the \( M \), when it is understood that the density is associated with the random variable map \( M \). Hence, \( f_M(x) = f(x) \).

\(^{13}\)\( |C_M(it)| = |\int_{-\infty}^{+\infty} e^{itx} f_M(x) \, dx| \leq \int_{-\infty}^{+\infty} |e^{itx} f_M(x)| \, dx = \int_{-\infty}^{+\infty} |f_M(x)| \, dx \)
<table>
<thead>
<tr>
<th>Cumulant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_0$</td>
<td>0</td>
</tr>
<tr>
<td>$K_1$</td>
<td>$\mu_1$</td>
</tr>
<tr>
<td>$K_2$</td>
<td>$\mu_2 - \mu_1^2$</td>
</tr>
<tr>
<td>$K_3$</td>
<td>$\mu_3 - 3\mu_2\mu_1 + 2\mu_1^3$</td>
</tr>
</tbody>
</table>

Distinct distributions generate distinct cumulants and moments.\(^{14}\)

For simulation studies, one needs to be able to generate various distributions on the computer.

\[^{14}\]

\[
\langle e^{ikx} \rangle_x = \langle e^{iky} \rangle_y \Rightarrow \int_{-\infty}^{+\infty} e^{ikx} f_x(x) dx = \int_{-\infty}^{+\infty} e^{iky} f_y(y) dy \quad (A.167)
\]

\[
\Rightarrow f_x(x) = f_y(y). \quad (A.168)
\]

\[
\ln\langle e^{kx} \rangle_x = \ln\langle e^{ky} \rangle_y \Rightarrow \int_{-\infty}^{+\infty} e^{kx} f_x(x) dx = \int_{-\infty}^{+\infty} e^{ky} f_y(y) dy \quad (A.169)
\]

\[
\Rightarrow f_x(x) = f_y(y). \quad (A.170)
\]
Appendix B

Computational Aspects

B.1 Random Number Generation

Quantum mechanical simulations require computer generated random numbers for synthesizing realizations of stochastic processes that conform to some distribution. We discuss, the Inverse Probability Integral Transform(IPIT) applied to an exponential random number generator and its application in the Box-Muller algorithm for normal distributions.

The simplest numerical random number generation for some arbitrary distribution is the Inverse Probability Integral Transform(IPIT)[29, 85]. It is based on the construction of the probability distribution function(PDF) of some random variable which is a function of another random variable, and the use of an existing uniform random number generator.¹

Assume that \( Y = G(X) \), where \( X \) is a real random variable with PDF \( f_X \). The calculation for the PDF \( f_Y \) follows² as

\[
1. As computers systems are deterministic, there can never be a truly random number generation algorithm. The pseudo random numbers generated computationally are trajectories of numerical sequences from some computation that has a long period. The algorithm is called an Pseudorandom Number Generator(PRNG). The most common algorithm is the Linear Congruential Generator(LCG) is the simple and fast using integer operations of addition, multiplication, and modular arithmetic. It consists of the using the sequence \( r_{i+1} = (Ar_i + B)modN \) where the sequence \( < r_i > \) are the pseudo random number generated, the integer constants A,B and N are large usually relative prime numbers. Like all PRNG algorithms, an initial seed is used to start the algorithm. For the LCG, the seed would be the initial \( r_0 \).

²Our derivation for evaluation of the PDF can be slightly modified, so that it looks more like the standard derivation using the Dirac \( \delta \) function.
\[ f_Y(y) = \frac{\partial}{\partial y} \int_{-\infty}^{y} f_Y(u)du = \frac{\partial}{\partial y} \int_{y \geq u} f_Y(u)du = \frac{\partial}{\partial y} \int_{y \geq G(x)} f_X(x)dx. \quad (B.4) \]

In the special case where \( G(x) \) is the Cumulative Distribution Function (CDF) of the \( Y \), \( F_Y^{-1}(x) \) and \( X \) is the unit uniform distribution,

\[ f_Y(y) = \frac{\partial}{\partial y} \int_{y \geq F_Y^{-1}(x)} f_X(x)dx = \frac{\partial}{\partial y} \int_{F_Y(y) \geq (x)} f_X(x)dx = \frac{\partial}{\partial y} \int_{F_Y(y) \geq (x)} 1dx = f_Y(y) \quad (B.5) \]

The probability integral transform states that the evaluation of some random number generation with distribution \( f_Y(y) \) is given by, finding the CDF and inverting the CDF of the function and using a uniform unit random number generator. Although this procedure seems simple enough, it depends on the existence of the inverse CDF. If an inverse CDF does not exists, then an alternative construction is needed\[29\].

For instance, a simple example of a random generator for the PDF \( f(x) = e^{-x} \) where \( x \geq 0 \). The CDF is \( F(X) = 1 - e^{-x} \), and the inverse CDF is \( x = -\ln(1 - F(x)) \). So, the random number generator is given simple as an evaluation of \(-\ln(1 - U)\), where \( U \) is the uniform number generator. We implemented this exponential random number generator using an uniform random generator\(^3\) and a single realization of the random number generation is given in Figure B.1. The Probability Distribution Function (PDF) for the

\[ f_Y(y) = \frac{\partial}{\partial y} \int_{-\infty}^{y} f_Y(u)du = \frac{\partial}{\partial y} \int_{y \geq u} f_Y(u)du \]

\[ = \frac{\partial}{\partial y} \int_{y \geq G(x)} f_X(x)dx = \frac{\partial}{\partial y} \int_{x = -\infty}^{\infty} H(y - G(x))f_X(x)dx \]

\[ = \int_{x = -\infty}^{\infty} \delta(y - G(x))f_X(x)dx \quad (B.3) \]

We use \( H(x) \) as the Heaviside function.

\(^3\)We converted an uniform generator that produces numbers in the range \([0, 1)\) into C++ for our implementation from a Fortran Source code for a Pseudorandom Number Generator (PRNG) which was written by Joel Koplick, City College CUNY\[65\]. This converted Uniform Generator was used as input our other various random number generators such as the Exponential and Gaussian.
Figure B.1: A single realization of Exponential Random number generator with a Probability Distribution Function (PDF) of \( e^{-x} \) built using the Inverse Probability Integral Transform Method.
Figure B.2: A single realization of Exponential Random number generator with a Probability Distribution Function (PDF) of $e^{-x}$ built using the Inverse Probability Integral Transform Method.
realization of Figure B.1 was generated and overlayed with the expected exponential PDF $f_x(x) = e^{-x}$ in Figure B.2.

The random number generator we used in our work for a Gaussian Distribution was implemented the Box-Muller Method[17, 87, 6]. The implementation of the Box-Muller algorithm is still derived using an IPIT with a modified joint PDF in two dimensions. The PDF for a Gaussian distribution is given as

$$f_x(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}}. \quad (B.6)$$

As the direct IPIT cannot be applied to this PDF, as the integration produces a non elementary integral. The key idea is to convert the problem into a two dimensional joint probability distribution and convert it into a polar coordinates. Taking the product of two independent Gaussian distributions can be used to convert into a joint distribution

$$f_x(x)f_y(y) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}} \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{y^2}{2\sigma^2}}$$

$$= \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2+y^2}{2\sigma^2}} = f_{XY}(x, y) \quad (B.7)$$

Using a change of polar coordinates, equating the differential probability of the two spaces, we can arrive at the polar joint pdf $f_{r\theta}(r, \theta)$.

$$(x, y) = (r \cos(\theta), r \sin(\theta)) \quad (B.9)$$

$$f_{XY}(x, y) dx dy = f_{XY}(r \cos(\theta), r \sin(\theta)) \left| \frac{\partial(x, y)}{\partial(r, \theta)} \right| dr d\theta$$

$$= \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{r^2}{2\sigma^2}} r dr d\theta = f_{r\theta}(r, \theta) dr d\theta \quad (B.10)$$

$$f_{r\theta}(r, \theta) = \frac{r}{\sqrt{2\pi\sigma^2}} e^{-\frac{r^2}{2\sigma^2}} \quad (B.12)$$

Marginalizing the joint probability $f_{r\theta}(r, \theta)$, we arrive at the radial PDF which is amenable
to IPIT.

\[ f(r) = \int_{\theta=0}^{2\pi} f_{r\theta}(r, \theta) d\theta = \sqrt{\frac{2\pi}{\sigma^2}} r e^{-\frac{r^2}{2\sigma^2}} \] (B.13)

The process consists of using the IPIT algorithm and generating a random \( r \) under the radial pdf, and then generating random \( \theta \) from the uniform distribution in \([1, 2\pi)\). Converting \( r \) and \( \theta \) to \( x \) and \( y \) produces two random numbers which conform to a Gaussian distribution. A realization and distribution of the Gaussian Generator using the Box-Muller algorithm are shown in Figures B.3 and B.4.

The IPIT method was implemented to generate the PDF distribution given by \( f(w) = w e^{-w} \) where we demonstrate that the construction is always possible, albeit more computational, due to the non elementary inversion of the CDF. The implementation is described by the equations

\[
\begin{align*}
    f(w) &= \frac{w}{B^2} e^{-\frac{w}{B}}, \quad B \in \mathbb{R}^+ \\
    F(w) &= \int_{w=0}^{w} J_n(w) dw = 1 - e^{-\frac{w}{B}} \left( \frac{w}{B} + 1 \right), \quad F(0) = 0 \text{ and } F(\infty) = 1
\end{align*}
\] (B.14)

where we generalize the pdf with a positive constant \( B \). The inversion of the cumulative function \( F(w) \) is not algebraically solvable by elementary means. As the CDF is a positive function, we implemented a simple bisection algorithm to evaluate the procedures. Figures B.5 and B.6 shows realization of the number generation and the associated PDF generated.

We also implemented this specific PDF in the intent to demonstrate the feasibility of construction of random time series generation of a stochastic process using an Fast Fourier Transform Method[30] with a Power Spectral Density(PSD) of being Ohmic with an exponential cut off.

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Figure B.3: A single realization of Gaussian random number generator with a PDF of \( \frac{1}{\sqrt{2\pi}} e^{-x^2/2} \) built using the Box-Muller algorithm.
Figure B.4: The PDF distribution of the realization of $\frac{1}{\sqrt{2\pi} \sigma^2} e^{-x^2/(2\sigma^2)}$ with $\sigma = 1$ built using the Box-Muller Algorithm.
Figure B.5: A single realization of the pdf constructed from $f(w) = we^{-w}$. 
Figure B.6: The PDF distribution of the realizations of $f(w) = we^{-w}$. 

PDF

Generator
$we^{-w}$

ω Range

0 2 4 6 8 10
0 0.2 0.4 0.6

$\omega$ Range

PDF

$we^{-w}$
B.2 Gradient Descent Algorithm

The Gradient Descent Algorithm (GDA) is the simplest of the linear optimization algorithms [60, 105, 43] which can be used to find a local minimum of some scalar differentiable function $F$ of reals ($F : \mathbb{R}^n \rightarrow \mathbb{R}$). We denote the Gradient of the function $F$ by

$$\nabla F = \left( \frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}, \ldots, \frac{\partial}{\partial x_n} \right) F. \quad (B.16)$$

Holding the value of $F$ constant, the implicit generated function $F(x_1, x_2, \ldots, x_n) = c$ has a total differential expansion as

$$dF = \nabla F \cdot dr = 0, \quad (B.17)$$

where we have used the $\cdot$ represents the vector dot product. The differential position $dr = (dx_1, dx_2, \ldots, dx_n)$ is embedded in the surface within the infinitesimal approximation, and it is part of the tangent manifold of the constant surface $F$. Consequently, the $\nabla F$ is orthogonal to the implicit surface $F(x_1, x_2, \ldots, x_n) = c$. We also note that, if the differential position $dr$ is in the same direction as $\nabla F$, then the $dF$ increases the most. Hence, the $\nabla F$ is points in the maximal increasing scalar value of $F$ in $\mathbb{R}^n$. If the $\nabla F = 0$, then it is an extremum point which may or may not be an minimum. Expanding the differential $F$ to second order in the function $F$ at extremum points produces

$$dF = \nabla F \cdot dr + \frac{1}{2}(dr)^t H(F) dr + \ldots \quad (B.18)$$

, where we have used $H(F)$ as the Hessian matrix [5]

$$H(F) = \begin{bmatrix}
\frac{\partial^2 F}{\partial x_1 \partial x_1} & \frac{\partial^2 F}{\partial x_1 \partial x_2} & \ldots & \frac{\partial^2 F}{\partial x_1 \partial x_n} \\
\frac{\partial^2 F}{\partial x_2 \partial x_1} & \frac{\partial^2 F}{\partial x_2 \partial x_2} & \ldots & \frac{\partial^2 F}{\partial x_2 \partial x_n} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial^2 F}{\partial x_n \partial x_1} & \frac{\partial^2 F}{\partial x_n \partial x_2} & \ldots & \frac{\partial^2 F}{\partial x_n \partial x_n}
\end{bmatrix} \quad (B.19)$$
A positive determinant of the Hessian matrix at the extremum points implies that the point is a minimum, while a negative determinant implies a maximum. If the Hessian determinant is zero, then we need to expand to higher orders of the Taylor’s expansion of total differential $dF$.

The implementation of a GDA to find the lowest minimization value of $F$ is given as the following steps.

1. Start with an initial point $r_0$ in the space $\mathcal{R}^n$

2. Evaluate the next point with

$$r_{i+1} = r_i - \alpha_i \frac{\nabla F(r_i)}{|\nabla F(r_i)|}$$  \hspace{1cm} (B.20)

where $\alpha_i > 0$.

3. We stop when $|\nabla F(r_i)|$ reaches zero, or when $F(r_{i+1})$ is within some threshold of its prior value.

Mapping a parameter space of variables directly onto the space $\mathcal{R}^n$ is the simplest method of optimization, but such a mapping has been recognized to lead to slow convergence of GDA algorithms[49]. The methods of Rescaling and Unit Length Scaling are often used to map the parameter space to the space $\mathcal{R}^n$ which the scaler optimizing function is applied. The Rescaling method consists of taking each search parameter defined in some fixed range and linearly scaling into some interval such as $[0, 1]$. A Unit Scaling Method consists of taking a parameter space vector $(p_1, p_2, ..., p_q)$ and scaling the parameters by it $L^1$ norm.\footnote{The $L^1$ norm of a vector $(x_1, ..., x_q)$ is defined as $|x|_1 = \left( \sum_{i=1}^{q} x_i^1 \right)^{\frac{1}{1}}$.}

$$|x|_n = \left( \sum_{i=1}^{q} x_i^n \right)^{\frac{1}{n}} \hspace{1cm} (B.21)$$
We implemented several versions of the GDA to match various needs. As the parameters were well bound, many of our GDA implementations have used a linear rescaling of each parameter into the range \([-1, +1]\). As the gradient \( \nabla F \) may sometimes be difficult to evaluate algebraically, we have also used an implementation where the gradient is approximated with the component terms

\[
\frac{\partial F}{\partial x_i} \approx \frac{F(x_1, \ldots, x_i + \Delta, \ldots, x_n) - F(x_1, \ldots, x_i, \ldots, x_n)}{\Delta}
\] (B.22)

We selected \( \Delta \) to be much smaller then iterative steps in the position \( \mathbf{r}(x_1, \ldots, x_n) \). Within the rescaling definition of our domain, our optimization function \( F \) is a mapping now from \( F : [-1, +1]^n \rightarrow \mathbb{R} \). The \( \Delta \) and the \( \alpha_i \) in the rescaled implementation are independent of the optimization function \( F \), and consequently, the rescaled GDA implementation is problem domain independent. A restricted version of the GDA was used which performed iterative steps that stay within a ball radius of a threshold \( \epsilon > 0 \) where \( |\mathbf{r}_{i+1} - \mathbf{r}_i| \leq \epsilon \). In another implementation, a discrete version of the GDA was used where the search progresses by only moving to fixed lattice points of a sample search space (we discuss these lattice based methods more descriptively in subsequent sections of our work).

The usefulness of a GDA is demonstrated in Figure B.7 where best fit of a Brownian Oscillator Spectral Density \( J_{bo}(w) \) with known coefficients \((\eta_b, \omega_b, \gamma_b)\) with that of a Lorentzian Spectral Density \( J_l(w) \) with unknown parameters \((\eta_l, \omega_l, \gamma_l)\) defined with the following equations

\[
J_{bo}(w) = \frac{\eta_b \omega_b^4 w}{(w^2 - \omega_b^2)^2 + 4w^2 \gamma_b^2}
\] (B.23)

\[
J_l(w) = \frac{\eta_l \gamma_l}{(w - \omega_l)^2 + \gamma_l^2}.
\] (B.24)

The figure graphs represent selected iterations through a GDA as the Lorentzian curve is progressively fits the Brownian spectral density. The \( L^2 \) norm of the difference between
Figure B.7: The graphs a-d represent the progressive fit of GDA of the Lorentzian spectral density (Green) with unknown parameters ($\eta_l, \gamma_l, \omega_l$) to a known Brownian Oscillator spectral density (Red).
Figure B.8: The three parameters ($\eta_l, \gamma_l, \omega_l$) of the Lorentzian are scaled into [-1, +1] ranges. The leveling off of the parameters shows that the GDA is converging to an answer. Notice, that approximately around 140 iterations, the curves levels oscillate quickly. This indicates that the $\alpha$ should be refined to a smaller value as the GDA is oscillating in some basin around a minimum of the optimization function.
Brownian Oscillator & Known Parameters  
\( \eta_b = 0.25 \)  
\( \hbar \omega_b = 6.84 \times 10^{-3} \text{Ha} \)  
\( \gamma_b = 0.25 \hbar \omega_b \)  

Fitted Lorentzian & GDA arrived parameters  
\( \eta_l = 1.17483 \times 10^5 \)  
\( \gamma_l = 0.00161884 \)  
\( \hbar \omega_l = 6.64 \times 10^{-3} \text{Ha} \)  

| Table B.1: GDA Fitting Results of a Lorentzian Spectral Density to a Brownian Oscillator Spectral Density |

the curves was used for the optimization function. Figure B.8 shows the rescaled parameters into \([-1, +1]\) range to observe the convergence of the parameters. The leveling off of the rescaled parameter curves can be seen as an indication that the optimization is reaching completion. The fine fluctuations in the horizontal portions of the curves indicate that the \( \alpha \) should be refined to get better convergence. The GDA in these horizontal portions of the curve is oscillating in a basin of the local minimum of the optimization function. The results of the fitting are shown in Table B.1.

### B.3 Nearest Neighbor Graphs

The \( L^2 \) surface graphs for nearest adjacent neighbor have been very beneficial in recognizing problems in the optimization algorithms used in our work. Our problem consisted of minimizing the \( L^2 \) norm distance between the experimental and theory line shapes, so as to evaluate the best fit parameters in the model. If \( I_{\text{thry}}(\vec{p}, \omega) \) is the the theory line shape with \( \vec{p} \) being a vector of the parameter space in the model, and \( I_{\exp}(\omega) \) is the experimental data, we are attempting to minimize the \( L^2 \) norm \( M(\vec{p}) \) such that

\[
M(\vec{p}) = \left[ \int_{\omega=0}^{\infty} (I_{\text{thry}}(\vec{p}, \omega) - I_{\exp}(\omega))^2 \right]^\frac{1}{2} \tag{B.25}
\]

Our construction of the nearest neighbor graph consists of a sampling the parameter
space with set of uniform distant points \( \{ \vec{p}_i \} \). For instance, if our parameter space is three dimensional, a cubic lattice of points could be used. For each point, we generate a theory line shape \( I_{\text{thry}}(\vec{p}_i, \omega) \) and evaluate the \( L^2 \) norm \( M(\vec{p}_i) \). The full set of points and norms are collected as \( \{ \vec{p}_i, M(\vec{p}_i) \} \) and a directed graph \( G \) is constructed for every vertex point \( \vec{p}_i \) to the nearest immediate neighbor with the lowest norm and lower than that of the current vertex.

In an n-dimensional parameter space, each vertex has \( 2^n \) nearest neighbors, except at the boundaries. As the directed arrows(edges) are only drawn to the nearest lower neighboring vertex, the directed graph \( G \) is acyclic, and all points that have no outbound arrows are the local minima of the vertex set. All Gradient Descent based algorithms must approximately follow the flow of directed edges of the graph.\(^5\)

Although refinement of the the sampling vertex set \( \{ \vec{p}_i \} \) could be adjusted to increase the resolution, the graph \( G \) is to understand which algorithms would work or fail in the optimization search. Ideally, only a single local minimum should exists where all directed paths eventually end up at that single local minimum, which can be considered the global minimum of the bounded parameter space. If several minima points are found, then any simple gradient descent algorithm will eventually get trapped in one of the local minima without reaching the global minimum. A more elaborate algorithm such as Simulated Annealing, Genetic Algorithms, Monte Carlo sampling, Evolutionary Algorithms, and others should be used.

Once the directed acyclic graph \( G \) is generated, either visual inspection or coloring algorithms can be performed to understand possible search strategy. Figure B.9 shows an example \( L^2 \) search graph for the optimal search of some Gaussian Distribution with the most optimal Lorentzian distribution. The two dimensional \( L^2 \) surface is drawn in Figure B.9 to compare to the graph. When the parameter space is larger then two dimensions, a

\(^5\)This can be seen by increasing the vertex point sampling of the parameter space and noticing that any edge between two points must be the same direction as the negative of the n-dimensional gradient \( \nabla M(\vec{p}) \)
The $L^2$ graph for a search of the best fitting Lorentzian distribution for some known Gaussian distribution data. The parameters define the Lorentzian are its center and full width at half maximum (FWHM). The pink points represent the sampled vertices in the two-dimensional parameter space, while the blue arrows are the edges between the nearest neighbor with a lower $L^2$ norm. The green dots represent the optimal $L^2$ norm fit of the Lorentzian line shape. Notice that only a single global minimum exists, and that all paths starting from any parameter point will eventually converge to the global minimum. See Figure B.10 to see $L^2$ Surface.
Figure B.10: The $L^2$ surface for a search of the best fitting Lorentzian distribution for some known Gaussian distribution data. The parameters that define the Lorentzian are its center and full width at half maximum (FWHM). The black dot represents the optimal $L^2$ norm fit of the Lorentzian line shape. See Figure B.9 for the search graph.
simple linear search of the vertices to assure that only a single global maximum is still very helpful in deciding, whether an $L^2$ search strategy is beneficial. Other searches of Lorentzian and Gaussian mutual fits have similar graphs consisting of a single global minimum which is reachable from any of the point in the search graph. Consequently, fitting of these curves to each other is simple to implement.

### B.4 Lineshape Deconvolution

Our implementation of the algorithm for deconvolution of the spectral data consists of following analysis. Consider upper case symbols and lower case symbols to be the N-dimensional vectors of associated reciprocal Fourier Spaces such as frequency and time. As such, we define the Discrete Fourier Transform between symbols $(F, G)$ and $(f, g)$ as

\[
f_m = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} F_n e^{\frac{2\pi inm}{N}} \quad \text{(B.26)}
\]

\[
g_m = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} G_n e^{\frac{2\pi inm}{N}} \quad \text{(B.27)}
\]

where the subscript denotes the individual components of the perspective vectors. These two equation are further curtailed with the notation that

\[
f = \mathcal{F}(F) \quad \text{(B.28)}
\]

\[
g = \mathcal{F}(G) \quad \text{(B.29)}
\]

For periodicity constraints, we use the simplified notation $F_a = F_{a+N}$ for any index value $a$ for any symbol. With define the convolution, product, and fraction between $F$ and $G$ as
Using this notation, we state the problem as the following: A measured signal $M$ is thought to be a convolution of a true signal $S$ and a Gaussian distribution $G$. That is to say $M = S \ast G$. We know $G$ and $M$, and we are attempting to reconstruct the signal $S$. As the Gaussian signal tapers off to zero far from its center, a simple analysis of

$$\mathcal{F}(M) = \mathcal{F}(S \ast G) = \mathcal{F}(S)\mathcal{F}(G)$$

$$S = \mathcal{F}^{-1}\left(\frac{\mathcal{F}(M)}{\mathcal{F}(G)}\right)$$

cannot be used. Division by near zero values in the Gaussian $G$ far from the center will cause a divergence in the signal $S$. With this in mind, we performed the following analysis of Window limiting the Gaussian to four standard deviations. It was assumed that limiting the window size of the gaussian convolution function $G$ would remove the division by zero.

This deconvolution method was tested with Theory line shapes($S$) that were convolved with gaussian distributions($G$) to get various energy disordered line shapes($M$). The computational results of the cleaned expected original signal $S$ was so distorted that very little of the true line shape was evident in the output.

After a careful analysis of the code, a different methodology to understand the deconvolution failure in the above windowed gaussian method resolved that the failure was due the numerical precision. Instead of using a continuous Fourier transform to describe
the convolution, the analysis can be simplified to that of a discrete matrix transformation of \( M = GS \). Here the S is the input signal as a column matrix whose elements are the various amplitudes of the underlying fourier basis signals. The matrix G can now be thought of as a band diagonal matrix whose rows are gaussian distributions centered along that diagonal.

In principal, our deconvolution would mount to a simple inverse calculation of: \( S = G^{-1}M \).

Although the inverse of square matrices of dimension several thousand can be done, the numerical stability of the answer failed to give a correct answer.

One can recognize this as a problem when one is evaluating the determinant of G and noting that the dimensions of the matrix is of several thousand elements. The largest term within the theoretical sum of the \( N! \) product terms in calculating the determinant would be the product of the diagonal terms of G.\(^6\) In the special case when the convolution is so small (ie zero), G becomes an diagonal identity matrix. But, in our case, the needed necessary calculations mounted to a hundred or so non zero Gaussian distributed elements along every row in G centered along the diagonal. Even the simplist block diagonal product term in the determinant calculation exceeds the numerical precision of numbers in our computational system.

### B.5 Genetic Algorithms

A genetic algorithm is an heuristic optimizing algorithm based on the evolutionary principals of Darwinian adaptation in biology[66, 86, 33, 109, 43, 53]. Belonging to a larger class of evolutionary algorithms[Back1,Simon1], a genetic algorithm consists of populations of organisms represented by binary encoded chromosomal strings which are mated with each other to produce progressively fitter populations that approximate better optimiza-

\(^6\)Numerical Algorithms for matrix determinants never use \( N! \) term expansion. Matrix determinants calculations and inverses can be done with several methodologies such as Gauss-Jordan elimination, LU Factorization, Eigenvalue decomposition, and others. We use the term analysis only to understand the order of the communional error that we are getting in our calculations.
tion solutions to a problem. Invented by John Holland[53, 80] in the 1960s, genetic algorithms have been applied to numerous diverse scientific problems ranging from electronic circuit design[40, 114, 116], Chemical Kinetics[91], Molecular Recognition[112], RNA Structure Prediction[9], Neural Network Training[46], Seismic Waveform Inversion[93], Image Feature Extraction[12], and Spectra Analysis[77] to name a few.

The basic algorithm for a genetic algorithm consists of the following steps.

- Define a chromosomal bit representation that can be used to identify some possible solution in a problem parameter space. Further define, some fitness function that takes any chromosomal bit representation and arrives at some measure of the goodness of that chromosome for being a solution of the problem. Devise a mating strategy that takes two chromosomes and produces progeny called the mating operator. Further define a mutation mechanism operator that arbitrarily can take any chromosome and generate a new modified version.

- Initialize a fixed size population of randomly generated chromosomes in the solution parameter space.

- Using the fitness function, cull the population of the least fit members by a certain amount. If a member has been found that is either a solution or close enough to the solution of the problem, stop the algorithm.

- Apply the mating operator on the members of the remaining population after the cull to bring back the size to its original.

- Using an infrequent rate, apply the mutation operator on arbitrary members of the population. Repeat the last three steps again.
The original bit string representation of encoded chromosomes of a population member fit intuitively well with a biological DNA segment where a fixed sub bit strings represented various genes. Consequent mating of two chromosomes through a simple crossover cut and exchange at a random fixed distance in both bit binary strings produces offspring population members with exactly the same chromosome size and does not effect the bit start and end location of the various genes. Using an IEEE real precession representation[44] for genes is problematic in that that crossover with a random point in the chromosome cannot be done, as this will destroy the bit representation of the real number. Even if crossover could be aligned with the real number boundary points(called Naive Crossover[28]), the size of the space formed during mating will be just a subset of the existing set of real values in the total population. Consequently, this approach relies on the mutation operator to fully sample the parameter search space.

Various approaches exist for dealing with real valued chromosomes.[101, 51, 28] The Linear Crossover operator[113] was one of the earliest and simplist approaches in using real numbers in the chromosome for blending real valued genes across both parents. The linear crossover consists of taking the two parent real values \( \{r_1, r_2\} \) and generating three values \( \{c_1, c_2, c_3\} \) generated from

\[
c_1 = \frac{r_1}{2} + \frac{r_2}{2} \quad \text{(B.35)}
\]
\[
c_2 = \frac{3r_1}{2} - \frac{r_2}{2} \quad \text{(B.36)}
\]
\[
c_3 = -\frac{r_1}{2} + \frac{3r_2}{2}. \quad \text{(B.37)}
\]

The two best fit values of the chromosomes containing \( \{c_1, c_2, c_3\} \) are selected as the products of the mating.
B.6 Heuristic Search

The best unknown set of parameters in a theoretical spectral density that fits an experimental line shape is usually thought of as a search on some manifold which is assumed differentiable and where standard numerical iterative methods[60] such as Newtons[61], Gradient Descent[105] , and Conjugate Gradient[52] apply. Ideally, we would wish that traveling through the parameter space, we are bound to a single manifold where the rules of Calculus and the earlier mentioned iterative methods apply.7 But, these iterative methods will fail, if we are traveling through a parameter space where a step size between iterative points causes us to switch between two distinct unconnected regions of the line shape manifold.8 Instead of assuming this, we can reformulate the optimization problem into a discrete Heuristic Search of a bounded parameter space.

Our Best First Search Heuristic Algorithm[59] is based on a Bound and Branch[67] optimization for a state space search that guarantees that a solution will be found, although the amount of time required for such a search may not be small. Our implementation is that of the $B^*$ algorithm[10] where our space is partitioned into non overlapping interval regions and the search is always commenced on states that have the best lowest cost.

For some given parameters in the spectral density, we can generate a line shape based on the Brownian Oscillator Model, and the analysis of this arrived at shape, gives us a numerical evaluation the features $\{F_i\}$. As analytical inversion of solving parameters from features is

---

7Each set of parameters $\eta, \gamma, \omega_b$ in the Garg Spectral Density generates a single emission or absorption line shape using the mathematical construction of Brownian Oscillator Model which can be thought of as a differentiable manifold that takes points in $\mathbb{R}^3$ to surface line shapes in $\mathbb{R}^2$ of frequency $\nu$ vs intensity. Around a good neighborhood in the three dimensional parameter space, we expect that the line shapes to be somewhat similar, yet, it is possible as seen by the denominator in the Garg Spectral densities that various values in $\gamma$ and $\omega_b$ may produce singular spectral densities. Traversing through these singularities, will cause us to switch between two topologically distinct connected differentiable surfaces.

8An example of this is the function $f(x) = \frac{1}{x}$. Traveling along the x axis from negative to positive in small increments of $\Delta x$, we may inadvertently travel from the connected manifold in quadrant three to the another distinct connected manifold in quadrant one. Of course, ideally we would take smaller steps when approaching the singularity, but if our knowledge of the function is lacking such as to place restrictions in the step size, we may still falter and hop between manifolds.
yet unknown, we wish to apply some iterative algorithm that will converge on a solution. Our Heuristic algorithm consists of first selecting our cost function $C$ (see eq. B.38) as the $L^2$ norm of the difference between a set of experimental features($\{F'_i\}$) and theoretical features $\{F_i\}$ attained from a theoretical line shape of some specified parameter.

$$C = \left( \sum_i (F_i - F'_i)^2 \right)^{\frac{1}{2}} \tag{B.38}$$

Each experimental line shape generates an unique set of features that we would like to get the best fit parameter to. But, due to the unknown solvability of the inverse problem, we only suffice to take arbitrary values of parameters in a bounded region and evaluate those arrived at that are close to the experimental values. Doing this through a Random algorithm would be very inefficient and computationally time consuming. We optimize this procedure of finding the best parameters by selecting only those associated features which are positively correlated with the parameters. We do not expect the correlation to be a strictly linear one. We just want to assure that a positive change in some parameter, will cause a positive change in the feature, and conversely a negative change in the parameter will cause a negative change in the same feature. This positive correlation will assure us that in some bounded parameter region that we are interested in, the Cost function will oscillate towards a convergence when parameter points oscillate around their optimal value.

Although, this choice of feature selection is similar to iterative algorithms such as Gradient Descent, where your step size is adapted at each iteration, our search strategy is not based on a single trajectory path.

A general heuristic based Search comprises of a finding a path in a State Space where states that are closer to the expected answer are scrutinized more carefully than others. Our state representation that was used in our line shape search strategy consisted of a set of
P open intervals \((L_i, H_i)\) correspond to \(P\) features \(\{P_i\}\) and a Cost value of the line shape generated by taking the set of all the centers of the intervals.\(^9\) The state consisting of these intervals and cost represent our heuristic belief that the optimal value lies within that \(P\) dimensional open volume built by the cartesian product of the intervals \(\prod_{i=1}^{P}(L_i, H_i)\).

The Heuristic state space search requires an open candidate priority list of states that have not been visited and a closed list which holds states that have been already visited. The closed list is to assure that the algorithm will not fall into an endless cyclic search pattern in the state space. When a state is searched, for the best cost, the possible children states that are close to the given state are generated. Those children that are not in the closed list and are thus known to have been unvisited, are thrown into the open list where they will eventually be analysed in future. The current visited state is itself thrown into the closed list so that it will not be analysed further. The search continues by removing the state with the smallest cost in the open priority list, and repeating our earlier procedure of finding the nearest children. The open list is usually implemented as a Heap Data Structure\(^{98, 68, 55}\) where the heap property is to assure that the parent node has a lower or equal cost then its children. The insert and removal time complexity\(^{25}\) of the heap is of order \(\Theta(lg\ n)\)\(^{10}\) and it represents the most time efficient data structure for inserts, retrieval, and removal of priority ordered items. Although linear time searches are forced in the closed list barring extra information, one can still implement it using a hash table.

Our line shape Heuristic algorithm consists of taking the best current cost state from the closed list and generating child states. Our child states are arrived by evenly splitting each of

\(^{9}\)For instance, if \(P_1\) is associated with a single parameter interval \((0, 1)\) the center point 0.5. The features and consequent cost are then found for the line shape based on the given midpoint parameter.

\(^{10}\)\(\Theta(f)\) is the set of all functions \(g(n)\) that are bounded above and below by \(f(n)\): \(\Theta(f) = \{g : \mathcal{N} \rightarrow \mathbb{R}^+ | \exists A \in \mathbb{R}^+ \exists B \in \mathbb{R}^+ \exists N \in \mathcal{N} n > N \Rightarrow Af(n) \leq g(n) \leq Bf(n)\}\) where we have used \(\mathbb{R}\) to the set set of reals and \(\mathcal{N}\) to the set of Natural numbers . It is usual in Computer Science to use \(\lg\) is an abbreviation for \(\log_2\).
the intervals \((L_i, H_i)\) into the intervals \((L_i, \frac{L_i + H_i}{2})\) and \((\frac{L_i + H_i}{2}, H_i)\). With P parameters, each parent state would produce \(2^P\) states.\(^{11}\) Since, the children nodes are distinctly different from their parent nodes, the need for a closed list is not required. Representing our states as intervals also makes it easier to restrict searches to within a certain threshold of uncertainty. Any children that have interval sizes below the certain threshold can be thrown away and not placed into the open list for continual search.

This line shape heuristic search strategy and state space representation can still fully search the parameters domain for the best near optimal feature fit and not fall into an endless cyclic search. The heuristic search algorithm is not bound to any one single differentiable manifold like the Gradient Descent. Execution of the algorithm for a longer time will find better near optimal solutions.

**B.7 Numerov Method**

In this section, we discuss the Numerov Algorithm for evaluating the wave function for a one dimensional quantum system. We use the implementation to write a binary division algorithm that is able to evaluate the n-th Eigen function and Eigen values for some bounded potential using the nodal points of the wave function. We then demonstrate the functionality with simple bounded potentials, and we use it to evaluate Franck-Condon Factors where we assume that singlet \(S_0\) and \(S_1\) adiabatic potential energy surfaces are displaced.

The Numerov algorithm\(^{69}\) is used to numerically solve a differential equation of the form below, where \(g(x, y)\) is devoid of derivatives of \(y\).

\[
\frac{d^2 y}{dx^2} = g(x, y). \quad (B.39)
\]

\(^{11}\)For three parameters, we will get eight children. For four parameters, we get sixteen children.
The One dimensional Time Independent Schrödinger’s Equation below is of a similar form through minor rearrangement.

\[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + V(x) \psi(x) = E \psi(x)\]  \hspace{1cm} (B.40)

So as to solve Schrödinger’s equation numerically, we will specialize the Numerov equation to the following:

\[\frac{d^2}{dx^2} y = g(x)y.\]  \hspace{1cm} (B.41)

We assume that \(f(x)\) can be expanded in terms of \(x\) through a Taylor’s series.

\[f(x + a) = \frac{f(x)}{0!} + \frac{f'(x)}{1!} a + \frac{f''(x)}{2!} a^2 + \frac{f'''(x)}{3!} a^3 + \frac{f''''(x)}{4!} a^4 + \ldots\]  \hspace{1cm} (B.42)

\[f(x - a) = \frac{f(x)}{0!} - \frac{f'(x)}{1!} a + \frac{f''(x)}{2!} a^2 - \frac{f'''(x)}{3!} a^3 + \frac{f''''(x)}{4!} a^4 + \ldots\]  \hspace{1cm} (B.43)

Adding both Taylor’s series together with the consequent odd terms canceling, we get the sum:

\[f(x + a) + f(x - a) = 2 \frac{f(x)}{0!} + 2 \frac{f''(x)}{2!} a^2 + 2 \frac{f''''(x)}{4!} a^4 + \ldots (\beta) \ldots\]  \hspace{1cm} (B.44)

Numerov’s key transformation is noticing that this Taylor’s sum expansion is true for any smooth function, including the second derivative of \(f\).

\[f''(x + a) + f''(x - a) = 2 \frac{f''(x)}{0!} + 2 \frac{f'''(x)}{2!} a^2 + \ldots (\gamma) \ldots\]  \hspace{1cm} (B.45)
Although the regular Numerov’s derivation assumes that we drop off the higher order terms of $a^6$, we will leave these terms with dots(...) distinguished by $\beta$ and $\gamma$ so as to keep the exact solution for deeper analysis later. The symbol $\beta$ is understood to have terms of order $a^6$, while the symbol $\gamma$ is of order $a^4$. Solving for the fourth derivative of $f$ gives

$$f''(x + a) + f''(x - a) = 2\frac{f''(x)}{0!} + 2\frac{f''(x)}{2!}a^2 + \gamma \quad (B.46)$$

$$f''(x + a) + f''(x - a) - 2\frac{f''(x)}{0!} - \gamma = 2\frac{f''(x)}{2!}a^2 \quad (B.47)$$

We continue this derivation by multiplying by $2a^2$ and dividing by $4!$ so as to have a correspondence with the last term in the Taylor sum equation.

$$2a^2\frac{f''(x + a)}{4!} + 2a^2\frac{f''(x - a)}{4!} - 2(2)a^2\frac{f''(x)}{4!} - 2a^2\frac{\gamma}{4!} = 2\frac{f''(x)}{4!}a^4 \quad (B.48)$$

We substitute this equation for the $f'''(x)$ term into the original Taylor sum equation.

$$f(x + a) + f(x - a) = 2\frac{f(x)}{0!} + 2\frac{f''(x)}{2!}a^2 + 2\frac{f''(x)}{4!}a^4 + \beta \quad (B.49)$$

$$f(x + a) + f(x - a) - 2\frac{f(x)}{0!} - 2\frac{f''(x)}{2!}a^2 - \beta = +2\frac{f''(x)}{4!}a^4 \quad (B.50)$$

$$f(x + a) + f(x - a) - 2\frac{f(x)}{0!} - 2\frac{f''(x)}{2!}a^2 - \beta = 2a^2\frac{f''(x + a)}{4!} + 2a^2\frac{f''(x - a)}{4!}$$

$$- 2(2)a^2\frac{f''(x)}{4!} - 2a^2\frac{\gamma}{4!} \quad (B.51)$$

This key equation has no fourth derivatives in $f$. We will substitute out simplified Numerov equation for $\frac{d^2f(x)}{dx} = g(x)f(x)$ noting the correct argument values for $f$. 

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\[ f(x + a) + f(x - a) - 2f(x) \frac{g(x) f(x)}{2!} a^2 - \beta = 2a^2 g(x + a) f(x + a) \]
\[ + 2a^2 g(x - a) f(x - a) \]
\[ - 2(2)a^2 \frac{g(x) f(x)}{4!} - 2a^2 \frac{\gamma}{4!} \quad (B.52) \]

We solve for \( f(x + a) \).

\[ f(x + a) \left( 1 - 2a^2 \frac{g(x + a)}{4!} \right) = f(x) \left( \frac{2}{0!} + \frac{2}{2!} a^2 g(x) - \frac{2(2)}{4!} a^2 g(x) \right) \]
\[ + f(x - a) \left( -1 + \frac{2}{4!} a^2 g(x - a) \right) \]
\[ + \left( \beta + \frac{2}{4!} a^2 \gamma \right) \quad (B.53) \]

Notice that the last \( \beta \) and \( \gamma \) sum term or of order \( a^6 \). Assuming that \( a \) is sufficiently small, we can drop this term and get the final approximation for \( f(x+a) \). Given an initial value of \( f \) and \( g \) at \( x \) and \( x-a \). This is fundamentally Numerov’s Method when converted into a discrete values of \( x \) differing by \( a \).

The Numerov Approximation Equation can be discritized with initial values of \( x \) taken from the range \([A,B]\) with an interval size of \( a \). The values of \( x \) will be set such that \( x_n - x_{n-1} = a, x_0 = A, x_N = B, f_n = f(x_n), \) and \( g_n = g(x_n) \). With these substitution, we finally get the Numerov approximation.

\[ f_{n+1} \left( 1 - 2a^2 \frac{g_{n+1}}{4!} \right) = f_n \left( \frac{2}{0!} + \frac{2}{2!} a^2 g_n - \frac{2(2)}{4!} a^2 g_n \right) \]
\[ + f_{n-1} \left( -1 + \frac{2}{4!} a^2 g_{n-1} \right) \quad (B.54) \]
This recursive equation can be converted into an amenable form which can be represented on the computer. The form reduced with proper constants values can be found in Levine[69].

This discrete equation should be confirmed with known solutions for $g(x)$. Assume that $g(x) = 0$. The general solution of the differential equation $\frac{d^2 f(x)}{dx^2} = 0$ will be $f(x) = Ax + B$. If we take $f(0) = 0$ and $f(1) = 1$, we arrive at $f(x) = x$. Plugging these values into our Numerov difference equation, we arrive at the correct difference solution.

$$f_{n+1} = 2f_n - f_{n-1} \quad (B.55)$$

$$f_{n+1} - f_n = f_n - f_{n-1} \quad (B.56)$$

It should be noted that we would have arrived at the same equations when we considered $a \to 0$ in the Numerov recurrence equation.

After converting the Schröedinger’s Equation into we arrive at the equation:

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad (B.57)$$

$$\frac{2\psi(x)}{x} = \frac{2m}{\hbar^2} (V(x) - E)\psi(x) \quad (B.58)$$

$$\psi''(x) = G(x)\psi(x) \quad (B.59)$$

$$G(x) = \frac{2m}{\hbar^2} (V(x) - E) \quad (B.60)$$

Although, this equation is in a form which seems to be solvable by the Numerov method, we lack the Energy eigen value $E$, and initial two values to start off the numerical solution. It is the energy eigen values that is observed in electromagnetic spectrum that either confirm or rejects a possible potential $V(x)$ and consequent based model.
Our procedure for calculating the Energy Eigen values for the Time Independent Bounded One Dimensional Schröedinger’s Equation will consist of guessing the value and using the Numerov Method to build a numerical wave function $\psi(x)$ which compares our closeness to the final solution. The convergence of the energy eigen values require several background ideas.

We will first assume the bounding potential is given by $V(x)$ defined in the interval $[a, b]$. We will assume that the potential is too high to the left of $a$ and to the right of $b$ for the wave function to exist. As the wave function $\psi(x)$ is square integrable, it can only have a nominal value in a finite region to assure that $\int_{-\infty}^{\infty} \psi(x)^* \psi(x) dx$ is normalizable. Square integrable normalization means that $\lim_{x \to \infty} \psi(x) \to 0$ and $\lim_{x \to -\infty} \psi(x) \to 0$.

The Sturm-Liouville Theory[48] assures us that there is a minimal energy eigen value for proper potentials $V(x)$. Physically, this means that a quantum system cannot keep dropping to lower and lower energy levels, releasing in exorbitant amounts of energy to the physical universe. The wave function in the classical forbidden domains decays exponentially[71], and thus the wave function is negligible in regions far outside the $[a, b]$ interval. We will consider the limits of this region to mean that the wave function is approximately near zero.
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