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PROPAGATION OF ELECTRONIC EXCITATION ON A POLYMER CHAIN

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KOMIN KAEWPHALUK : PROPAGATION OF ELECTRONIC EXCITATION ON A POLYMER CHAIN. THESIS ADVISOR : ASSOC. PROF. WICHIT SRITRAKOOL, Ph.D. THESIS CO-ADVISOR : PROF. VIRULH SA-YAKANIT, F.D., 77 pp. ISBN 974-17-3743-2.

In this thesis, we study a model system of a linear polymer chain in terms of time-dependent Schrödinger equation in the tight-binding representation. We have shown that the continuous limit of a discrete model can be formulated in terms of Feynman's path integrals. We introduce randomness to the system and study in the case where the electronic excitation energy is distributed Gaussian randomly. The Feynman propagator leads to the density of states which is important to evaluate the spectral density function. We also obtain the spectral density function of electronic excitation of a polymer chain consisting of identical monomers in 3D system under the influence of lattice vibrations, the nearest neighbor intermolecular coupling and absence of internal vibrations.

In the low-energy range, we obtain the spectral density function as the asymmetric line shape. The width of the electronic excitation line shape is directly proportional to the fluctuations of the system. If the width is wide (narrow) then there is high (low) fluctuation.

Department Physics	Student's signature…………………………………………
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Chapter 1

Introduction

The optical line shapes of excitons in molecular crystals and aggregates are of interest in many research groups [1-12]. Exciton spectra can display either a set of distinct narrow lines, a set of relatively broad, merging lines or can consist only of a single broad line with a characteristic shape.

The structure of the spectrum is due to exciton interaction with internal molecular vibrations, lattice vibrations and to disorder in the system. In this thesis we evaluate the spectral density function of electronic excitation on linear polymer chains of identical monomers under the influence of lattice vibration. Nearest-neighbor intermolecular coupling and the absence of internal vibrations are assumed.

In this method, for convenience, we approach the model system in terms of the time-dependent Schrödinger equation in the tight-binding representation [13] and show that the continuous limit of this discrete model can be formulated in terms of the Feynman path integral [14] by using a coordinate space matrix element of the time evolution operator (Hamiltonian path integrals) [15].

We now introduce randomness into the system and study the case where the electronic excitation energy $\varepsilon^0(\vec{r})$ (diagonal disorder) is distributed in a Gaussian random fashion [18,19]. We assume an electronic excitation-lattice vibration coupling $\overrightarrow{g}[\vec{r}(\tau)]$ (off-diagonal disorder) and apply to the model of an electron moving in a random system [16]. In the Feymnan path integral approach we calculate the 2D density of state (DOS) in the presence of a disordered potential [17].

The spectral density function of the Schrödinger equation for a particle in a random potential is defined in Ref. (34) which we apply to a 3D system. In this thesis we calculate the spectral density function for the case $\vec{K}\cdot\vec{r} << 1(e^{\vec{K}\cdot\vec{r}} \approx 1$; dipole approximation) where $\vec{K}$ is the excitation wave vector. In the low-energy range ($\frac{E-E_0}{E_L} \rightarrow -\infty$, or, equivalently, $\nu \gg 1$), we consider the limiting value of ν and plot the optical density function $A(\nu)$, which is a function of the energy ν. For the case $\nu \gg 1$, we have $A(\nu) = \frac{2^{\frac{5}{2}}\nu^{\frac{9}{4}}}{E_L\xi'^2\sqrt{\pi}}\exp\left[-\frac{\nu^2}{2\xi'}\right]$ and obtain the asymmetric line shape. The width of the electronic excitation line shape is directly proportional to the fluctuations of the system. If the width is wide (narrow) then there is high (low) fluctuation .

The thesis is organized as follows. First we review the Feynman path integral approach to calculate the propagator of the exciton in Chapter 2. In Chapter 3, we review some important basic ideas about excitons on polymers and define the model system. In Chapter 4, we present an evaluation of the propagator for an electronic excitation moving on a polymer chain under the influence of a Gaussian distribution in 3D and apply our result to calculate the density of states and the spectral density functional. Discussion and Conclusion are presented in Chapter 5.

Chapter 2

Feynman's Path Integration

The application of the Feynman path integral method to the problem of polymer physics is given in details by Khandekar [20]. Before we present our calculation in next chapter, in this chapter we introduce the basic ideas of the Feynman path integral formulation of the propagator and present some applications for our work.

2.1 Feynman Propagator

According to Feynman's idea [21], when a particle moves from one point to another point there are an infinite number of possible paths. We can consider the particle as a point in classical mechanics. The principle of least action technique is used to determine a particular path from all possible paths.

If a particle moves under the restrictive condition from $\vec{x}\,(t_a) = \vec{x}_a$ at an initial time t_a and goes to $\vec{x}\,(t_b) = \vec{x}_b$ at a final time t_b, there are an infinite number of possible paths of interest. Each trajectory contributes to the total amplitude to go from $\vec{x}_a$ to $\vec{x}_b$. They contribute equal amounts to the total amplitude, but have different phases. The phase of the contribution from a given path is the action S for that path in units of action $\hbar$. The action S is defind by

$$S = \int_{t_a}^{t_b} L\left(\dot{\vec{x}}, \vec{x}, t\right) dt \ , \tag{2.1}$$

where L is the Lagrangian of the system. According to the principle of least action, the particular path $\vec{x}\,(t)$ which the particle travels in the area of interest, is such that S takes a minimum value. We can say that the value of S is unchanged if the path $\vec{x}\,(t)$ is "the classical path". In quantum mechanics one deals with probabilities, the probability of a particle for a path $\vec{x}\,(t)$ lying somewhere within the space time continuum is the absolute square of the probability amplitude. The probability amplitude is associated with the entire motion of the particle as a function of time, rather than simply with the position of the particle of a particular time. We now consider the path by which the particles move from a to b and we specify how each trajectory contributes to the probability amplitude $K\,(b,a)$. The amplitude $K\,(b,a)$ is the sum over all trajectories between the end points a and b of the contributions $\Phi\left[\vec{x}\,(t)\right]$

$$K\,(b,a) = \sum_{\text{over all path from a to b}} \Phi\left[\vec{x}\,(t)\right] \ , \tag{2.2}$$

where the contribution $\Phi\left[\vec{x}\,(t)\right]$ of a path depends on the classical action S in unit of $\hbar$.

$$\Phi\left[\vec{x}\left(t\right)\right]=\left(\text{conts}\right)\exp\left\{\frac{i}{\hbar}S\left[\vec{x}\left(t\right)\right]\right\}\ . \tag{2.3}$$

From Eq. (2.2) and Eq. (2.3), we obtain

$$K\left(b,a\right)=\sum_{\text{over all path from a to b}}\left(\text{conts}\right)\exp\left[\frac{i}{\hbar}S\left[\vec{x}\left(t\right)\right]\right]\ . \tag{2.4}$$

From the above equation, we cannot evaluate $K\left(b,a\right)$ directly because we have infinitely many paths contributing. Feynman [21] proposed another way to formulate the amplitude in Eq. (2.4) by dividing the time variable into steps of width $\varepsilon\to 0$. This gives us a set of time t_i spaced at a distance ε apart between the values t_a and t_b. At each time t_i we select some special $\vec{x}_i$ and construct a path by connecting all point. It is possible to define a sum over all paths in this manner by taking a multiple integral over all values of $\vec{x}_i$ for i between 1 and $n-1$, where

$$\left.\begin{array}{c} n\varepsilon=t_b-t_a \\ \varepsilon=t_i-t_{i-1} \\ t_0=t_a \\ t_n=t_b \\ x_0=x_a \\ x_n=x_b \end{array}\right\}. \tag{2.5}$$

From this method, Eq. (2.4) becomes

$$K\left(b,a\right)=\int\int...\int\left(\text{const.}\right)\exp\left[\frac{i}{\hbar}S\left[\vec{x}\left(t\right)\right]\right]d^3x_1d^3x_2...d^3x_{n-1}\ . \tag{2.6}$$

In order to proceed we take the limit $\varepsilon\to 0$ and find normalizing factor A^{-n} which depends on ε. This leads Eq. (2.6) to

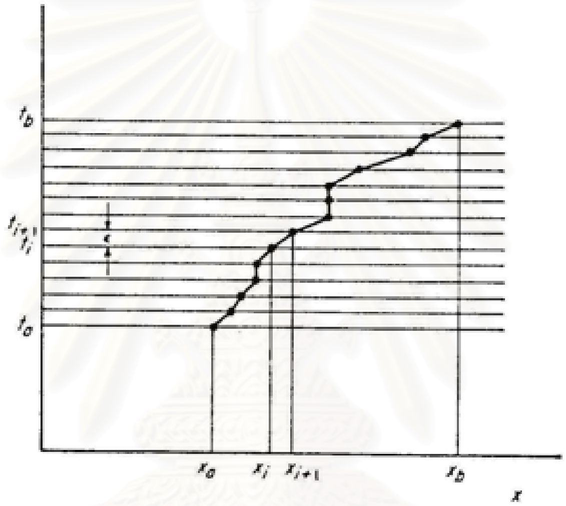

Figure 2.1: Diagram showing the sum over paths defined as a limit, in which at first the path is specified by giving only its coordinate x at a large number of specified times separated by very small interval ϵ. The path sum is then an integral over all these specific coordinates. Then to achieve the correct measure, the limit is taken as ϵ approaches zero[21].

$$K\left(b,a\right)\approx\lim_{\varepsilon\rightarrow 0}\frac{1}{A}\int\int...\int\exp\left[\frac{i}{\hbar}S\left[\vec{x}\left(t\right)\right]\right]\frac{d^{3}x_{1}}{A}\frac{d^{3}x_{2}}{A}...\frac{d^{3}x_{n-1}}{A}. \tag{2.7}$$

This is a path integral and the amplitude $K\left(b,a\right)$ is known as the Feynman propagator.

2.2 Propagator from Schrödinger's Equation

In this section we will show that the propagator can be derived directly from Schrödinger's equation [36]. In Quantum mechanics, the dynamical information of the system is contained in the wave function which is sometimes called the probability amplitude. Therefore, in Schrödinger's picture, the state vector is defined by

$$\left|\Psi\left(t\right)\right\rangle=\hat{U}\left(t,t'\right)\left|\Psi\left(t'\right)\right\rangle\ , \tag{2.8}$$

where $\hat{U}\left(t,t'\right)$ is the time development operator, given by

$$\hat{U}\left(t,t'\right)=\exp\left[-\frac{i}{\hbar}\hat{H}\left(t-t'\right)\right]\theta\left(t-t'\right)\ , \tag{2.9}$$

with $\hat{H}$ is the time-independent Hamiltonian operator and $\theta\left(t-t'\right)$ is the step function

$$\theta\left(t-t'\right)=\left\{\begin{array}{ll}1 & t>t'\\ 0 & t<t'\end{array}\right. . \tag{2.10}$$

The configuration of the wave function can be expressed in terms of the coordinate space projection of the state vector $\Psi(\vec{x},t) \equiv \langle \vec{x} \,| \Psi(t) \rangle$. So Eq. (2.8) becomes

$$\langle \vec{x} \,| \Psi(t) \rangle = \int_{-\infty}^{+\infty} d^3x' \ \left\langle \vec{x} \middle| \hat{U}(t,t') \middle| \vec{x}' \right\rangle \left\langle \vec{x} \middle| \Psi(t') \right\rangle \ , \tag{2.11}$$

where the complete set of coordinate states

$$\int_{-\infty}^{+\infty} d^3x' \left| \vec{x}' \right\rangle \left\langle \vec{x}' \right| = 1 \ , \tag{2.12}$$

has been introduced. Eq. (2.11) can be rewriten as

$$\langle \vec{x} \,| \Psi(t) \rangle = \int_{-\infty}^{+\infty} d^3x' K(\vec{x},t;\vec{x}',t') \left\langle \vec{x}' \middle| \Psi(t') \right\rangle \ , \tag{2.13}$$

where

$$K(\vec{x},t;\vec{x}',t') = \left\langle \vec{x} \middle| \hat{U}(t,t') \middle| \vec{x}' \right\rangle \quad . \tag{2.14}$$

This is the "propagator" as the probability amplitude of a particle to go from $\vec{x}'$ at time t' to $\vec{x}$ at time t. We now substitute Eq. (2.9) into Eq. (2.14) and obtain,

$$K(\vec{x},t;\vec{x}',t') = \left\langle \vec{x} \middle| \exp\left[-\frac{i}{\hbar} \hat{H}(t-t') \right] \middle| \vec{x}' \right\rangle . \tag{2.15}$$

Breaking the time interval $t - t'$ (assumed to be positive) into n discrete steps of size

$$\epsilon = \frac{t-t'}{n} \ , \tag{2.16}$$

we can write

$$
\begin{aligned}
K(\vec{x},t;\vec{x}^{\prime},t') &= \int_{-\infty}^{+\infty} d^3x_1...d^3x_{n-1}\,\langle\vec{x}_n|\exp\left(-\frac{i}{\hbar}\epsilon\hat{H}\right)|\vec{x}_{n-1}\rangle \\
&\quad \langle\vec{x}_{n-1}|\exp\left(-\frac{i}{\hbar}\epsilon\hat{H}\right)|\vec{x}_{n-2}\rangle\,...\,\langle\vec{x}_1|\exp\left(-\frac{i}{\hbar}\epsilon\hat{H}\right)|\vec{x}_0\rangle\,.
\end{aligned}
\tag{2.17}
$$

We now consider the Hamiltonian of the system in the position representation

$$
\hat{H} = \frac{\hat{p}^2}{2m} + V\left(\hat{x}\right)\ , \tag{2.18}
$$

where $\hat{p}$ is the momentum operator. Thus in the limit of large n, the time slices become infinitesimal

$$
\begin{aligned}
\left\langle\vec{x}_l\left|\exp\left[-\frac{i}{\hbar}\epsilon\hat{H}\left(t-t'\right)\right]\right|\vec{x}^{\prime}_{l-1}\right\rangle &= \left\langle\vec{x}_l\left|\exp\left[-\frac{i}{\hbar}\epsilon\left(\frac{\hat{p}^2}{2m}+V\left(\hat{x}\right)\right)\right]\right|\vec{x}^{\prime}_{l-1}\right\rangle \\
&\approx \exp\left(-\frac{i}{\hbar}\epsilon V\left(\vec{x}_l\right)\right)\times \\
&\quad \left\langle\vec{x}_l\left|\exp\left[-\frac{i}{\hbar}\epsilon\left(\frac{\hat{p}^2}{2m}\right)\right]\right|\vec{x}^{\prime}_{l-1}\right\rangle + \mathcal{O}\left(\epsilon^2\right).
\end{aligned}
\tag{2.19}
$$

Introducing a complete set of momentum states, we have

$$
\begin{aligned}
\left\langle\vec{x}_l\left|\exp\left[-\frac{i}{\hbar}\epsilon\left(\frac{\hat{p}^2}{2m}\right)\right]\right|\vec{x}^{\prime}_{l-1}\right\rangle &= \int_{-\infty}^{+\infty}\frac{d^3p}{\left(2\pi\hbar\right)^3}\exp\frac{i}{\hbar}\epsilon\overrightarrow{p}.\left(\vec{x}_l-\vec{x}_{l-1}\right) \\
&\quad \times\exp-\frac{i}{\hbar}\epsilon\left(\frac{\vec{p}^2}{2m}\right) \\
&= \sqrt[3]{\frac{m}{2\pi i\hbar\epsilon}}\exp\frac{i}{\hbar}\frac{m}{2\epsilon}\left(\vec{x}_l-\vec{x}_{l-1}\right)^2\ ,
\end{aligned}
\tag{2.20}
$$

and, taking the continuum limit, we find the path integral prescription

$$\begin{aligned} K(\vec{x},t;\vec{x}',t') &= \lim_{n\to\infty}\frac{1}{A}\int\int...\int\exp\left[\frac{i}{\hbar}\sum_{l-1}^{n-1}\frac{m}{2}\frac{\left(\vec{x}_l-\vec{x}_{l-1}\right)^2}{\epsilon}+\epsilon V\left(\vec{x}_l\right)\right] \\ &\quad \times\frac{d^3x_1}{A}\frac{d^3x_2}{A}...\frac{d^3x_{n-1}}{A}\ , \end{aligned} \tag{2.21}$$

where $\frac{1}{A}=\left(\frac{m}{2\pi i\hbar\epsilon}\right)^{\frac{3}{2}}$is the normalization factor . Or, in short,

$$K(\vec{x},t;\vec{x}',t')=\int\mathcal{D}\left[\vec{x}\left(t\right)\right]\exp\frac{i}{\hbar}S\left[\vec{x}\left(t\right)\right]\ , \tag{2.22}$$

where the notation is that the integral represents a sum over all paths $\vec{x}\left(t\right)$ connecting the initial and final space time point $\vec{x},t$ and $\vec{x}',t'$ respectively. For each path there is a weighting factor given by $\exp\left(\frac{i}{\hbar}S\right)$ where $S=\int_{t_1}^{t_2}dt\left(\frac{m}{2}\dot{\vec{x}}^2-V\left(\vec{x}\left(t\right)\right)\right)$ is the classical action associated with that path.

2.3 Path Integral for a Free Particle

We now calculate the propagator for a free particle with the Lagrangian for a free particle [21] given by

$$L\left(\dot{\vec{x}},\vec{x},t\right)=\frac{m}{2}\dot{\vec{x}}^2. \tag{2.23}$$

Thus Eq. (2.21)becomes

$$\begin{aligned} K(\vec{x},t;\vec{x}',t') &= \lim_{n\to\infty}\frac{1}{A}\int\int...\int\exp\left[\frac{i}{\hbar}\sum_{l-1}^{n-1}\frac{m}{2}\frac{\left(\vec{x}_l-\vec{x}_{l-1}\right)^2}{\epsilon}\right] \\ &\quad \times\frac{d^3x_1}{A}\frac{d^3x_2}{A}...\frac{d^3x_{n-1}}{A}. \end{aligned} \tag{2.24}$$

The integrations may be performed sequentially using the Gaussian integral

$$\int_{-\infty}^{+\infty} d^3x \exp\left[-a\vec{x}^2 + b\vec{x}\right] = \sqrt[3]{\frac{\pi}{a}} \exp\left[-\frac{b^2}{4a}\right]. \qquad (2.25)$$

First, we consider the integral of $\vec{x}_1$

$$\frac{1}{A}\int \exp\left\{\frac{i}{\hbar}\frac{m}{2\epsilon}\left[(\vec{x}_1-\vec{x}_0)^2+(\vec{x}_2-\vec{x}_1)^2\right]\right\}\frac{d^3x_1}{A}\ , \qquad (2.26)$$

we have

$$\begin{aligned} &\left(\frac{m}{2\pi i\hbar\epsilon}\right)^{\frac{3}{2}}\int_{-\infty}^{+\infty}\exp\left\{\frac{i}{\hbar}\frac{m}{2\epsilon}\left[(\vec{x}_1-\vec{x}_0)^2+(\vec{x}_2-\vec{x}_1)^2\right]\right\}d^3x_1 \\ =\ &\left(\frac{m}{2\pi i\hbar\,(2\epsilon)}\right)^{\frac{3}{2}}\exp\left\{\frac{i}{\hbar}\frac{m}{2.\,(2\epsilon)}\left[(\vec{x}_2-\vec{x}_0)^2\right]\right\}. \end{aligned} \qquad (2.27)$$

Second, we consider the integration of $\vec{x}_2$

$$\frac{1}{A}\int\int \exp\left\{\frac{i}{\hbar}\frac{m}{2\epsilon}\left[(\vec{x}_1-\vec{x}_0)^2+(\vec{x}_2-\vec{x}_1)^2+(\vec{x}_3-\vec{x}_2)^2\right]\right\}\frac{d^3x_1}{A}\frac{d^3x_2}{A}. \qquad (2.28)$$

Substituting the result from Eq. (2.27) into Eq. (2.28) and forming the integration of $\vec{x}_2$, we obtain

$$\left(\frac{m}{2\pi i\hbar\,(3\epsilon)}\right)^{\frac{3}{2}}\exp\left\{\frac{i}{\hbar}\frac{m}{2.\,(3\epsilon)}\left[(\vec{x}_3-\vec{x}_0)^2\right]\right\}. \qquad (2.29)$$

We integrate to $n-1$ steps, and obtain

$$K(\vec{x},t;\vec{x}^{'},t') = \left(\frac{m}{2\pi i\hbar\,(n\epsilon)}\right)^{\frac{3}{2}}\left\{\frac{i}{\hbar}\frac{m}{2.\,(n\epsilon)}\left[(\vec{x}_n-\vec{x}_0)^2\right]\right\}. \qquad (2.30)$$

Since $n\varepsilon = t-t^{'}$, $\vec{x}_n=\vec{x}$, and $\vec{x}_0=\vec{x}^{'}$, therefore

$$K(\vec{x},t;\vec{x}^{'},t') = \left(\frac{m}{2\pi i\hbar\,(t-t^{'})}\right)^{\frac{3}{2}}\left\{\frac{i}{\hbar}\frac{m}{2}\left[\frac{\left(\vec{x}-\vec{x}^{'}\right)^2}{t-t^{'}}\right]\right\}. \qquad (2.31)$$

2.4 The Quadratic Lagrangian

For the case of a free particle, we can carry out the direct integration. In other cases, the path is more difficult to work out. Therefore, we present a different way to solve this difficult problem. We now consider a quadratic Lagrangian[21], this corresponds to the case in which the action S contains the path $x(t)$ up to the second power, i.e.

$$L(\dot{x},x,t)=a(t)\dot{x}^2+b(t)\,x\cdot\dot{x}+c(t)\,x^2+d(t)\,\dot{x}+e(t)\,x+f(t)\ , \tag{2.32}$$

and the general form of the Feynman path integral

$$K(b,a)=\int_a^b\mathcal{D}\left[x(t)\right]\exp\frac{i}{\hbar}S\left[x(t)\right]\ , \tag{2.33}$$

is integral over all paths which go from (x_a,t_a) to (x_b,t_b) . Since we can determine the most important characteristics of the propagator. Let $x_{cl}(t)$ be the classical path between the specified end points. This is the path, which has an extremum for the action S. For this notation we have been using

$$S_{cl}\left[b,a\right]=S\left[x_{cl}(t)\right]. \tag{2.34}$$

For any path $x(t)$, we can express as the sum of the classical path, $x_{cl}(t)$, and a new variable $y(t)$. That is

$$x(t)=x_{cl}(t)+y(t). \tag{2.35}$$

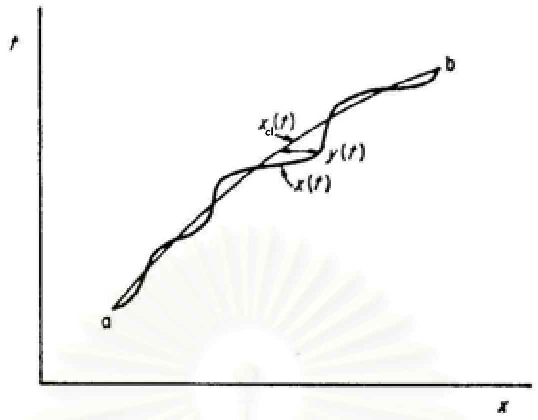

Figure 2.2: The difference between the classical path x_{cl} and some possible alternative path. The end point $y(t_a) = y(t_b) = 0$[21].

That is to say, instead of defining a point on the path by its distance $x(t)$ from an arbitrary coordinate axis, we measure instead the deviation $y(t)$ from the classical path as shown in Fig. (2.2)

At each t the variable $x(t)$ and $y(t)$ differ by the constant $x_{cl}(t)$. Therefore, clearly, $dx_i = dy_i$ for each specific point t_i in the subdivision of time. In general, we may say $\mathcal{D}[x(t)] = \mathcal{D}[y(t)]$. The integral for the action can be written as

$$S[x(t)] = S[x_{cl}(t) + y(t)] = \int_{t_a}^{t_b} dt \left[a(t)\left(\dot{x}_{cl}^2 + 2x_{cl}\dot{y} + \dot{y}^2\right) + ...\right]. \tag{2.36}$$

If all the terms, which do not involve y are collected, the resulting integral is just $S[x_{cl}(t)] = S_{cl}$. If all the terms, which contains y as a linear factor, are collected, the resulting integral vanishes. This could be proved by actually carrying out the integration, however, such a calculation is unnecessary, since we already know the result is true. The function x_{cl} is determined by this very requirement Eq. (2.34). That is x_{cl} is chosen so that there is no change in S, to first variation of path around x_{cl}. All that remains are the second order term in y. These can be easily picked out, so that we can write

$$S\left[x_{cl}\left(t\right)\right] = S_{cl}\left[b,a\right] + \int_{t_a}^{t_b} dt\left[a\left(t\right)\dot{y}^2 + b\left(t\right)y\cdot\dot{y} + c\left(t\right)y^2\right]. \tag{2.37}$$

From above equation, the classical path does not depend upon the integral over all paths. So we can separate the propagator to be

$$\begin{aligned} K\left(b,a\right) &= \exp\left\{\frac{i}{\hbar}S_{cl}\left[b,a\right]\right\} \\ &\quad \int_0^0 \mathcal{D}\left[y\right]\exp\left\{\frac{i}{\hbar}\int_{t_a}^{t_b} dt\left[a\left(t\right)\dot{y}^2 + b\left(t\right)y\cdot\dot{y} + c\left(t\right)y^2\right]\right\}. \end{aligned} \tag{2.38}$$

Since all paths y start from and return to the point $y = 0$, the integral over paths can be a function only of times at the end points. Thus the propagator can be written as

$$K\left(b,a\right) = F\left(T\right)\exp\left\{\frac{i}{\hbar}S_{cl}\left[b,a\right]\right\}\ , \tag{2.39}$$

where

$$F\left(T\right) = \int_0^0 \mathcal{D}\left[y\right]\exp\left\{\frac{i}{\hbar}\int_{t_a}^{t_b} dt\left[a\left(t\right)\dot{y}^2 + b\left(t\right)y\cdot\dot{y} + c\left(t\right)y^2\right]\right\}\ , \tag{2.40}$$

is the prefactor.

2.5 Path Integral for Forced Harmonic Oscillator

The example of a problem which can be solved exactly to obtain the propagator, is that of a one dimensional forced harmonic oscillator which is acted by an external time varying force $f(t)$. The corresponding Lagrangian [21] is

$$L(\dot{x}, x, t) = \frac{m}{2}\dot{x}^2 - \frac{m}{2}\omega^2 x^2 + f(t)\,x. \tag{2.41}$$

We will obtain the equation of motion by using the Euler-Lagrange equation for the Lagrangian

$$\frac{\partial L}{\partial x} - \frac{d}{dt}\frac{\partial L}{\partial \dot{x}} = 0\ , \tag{2.42}$$

thus we have

$$\ddot{x} + \omega^2 x - \frac{f(t)}{m} = 0. \tag{2.43}$$

From the action S, substituting Eq. (2.41) into Eq. (2.1) and using Eq. (2.43), we obtain

$$\begin{aligned} S &= \int_{t_1}^{t_2} L(\dot{x}, x, t)\,dt' \\ &= \frac{m}{2}\,x\dot{x}\Big|_{t_1}^{t_2} + \frac{1}{2}\int_{t_1}^{t_2} xf\left(t'\right)dt' \\ &= \frac{m}{2}\left[x(t_2)\,\dot{x}(t_2) - x(t_1)\,\dot{x}(t_1)\right] + \frac{1}{2}\int_{t_1}^{t_2} xf\left(t'\right)dt'. \end{aligned} \tag{2.44}$$

The solution of Eq. (2.43) is

$$x(t) = x_I(t) + x_H(t)\ \ , \tag{2.45}$$

where x_H and x_I are the homogeneous and inhomogeneous solutions respectiveiy. For the homogeneous case (x_H) and using Eq. (2.42), we have

$$\ddot{x} + \omega^2 x = 0 \ , \tag{2.46}$$

with solution

$$x_H = Ae^{i\omega t} + Be^{-i\omega t}. \tag{2.47}$$

For the Inhomogeneous case (x_I), we use the Green's function method, i.e.

$$\left(\frac{d^2}{dt^2} + \omega^2\right) G\left(t - t'\right) = \delta\left(t - t'\right) \ , \tag{2.48}$$

where

$$G\left(t - t'\right) = \int \frac{d\omega}{\sqrt{2\pi}} e^{i\omega(t-t')} G\left(\omega\right) \ , \tag{2.49}$$

and

$$\delta\left(t - t'\right) = \int \frac{d\omega}{\sqrt{2\pi}} e^{i\omega(t-t')}. \tag{2.50}$$

Substituting Eqs. (2.49) and (2.50) into (2.48), we obtain

$$G\left(t - t'\right) = -\theta\left(t - t'\right) \frac{e^{-i\omega(t-t')}}{2i\omega} - \theta\left(t - t'\right) \frac{e^{i\omega(t-t')}}{2i\omega}. \tag{2.51}$$

So, we can rewrite the solution of Eq. (2.45) to be

$$x\left(t\right) = Ae^{i\omega t} + Be^{-i\omega t} + \int_{t_1}^{t_2} dt' G\left(t - t'\right) \frac{f\left(t'\right)}{m} \ , \tag{2.52}$$

and we obtain

$$\begin{aligned} x\left(t\right) &= x_1\cos\omega\left(t-t_1\right)+\int_{t_1}^{t}dt'\frac{f\left(t'\right)}{m\omega}\sin\omega\left(t-t'\right) \\ &+\frac{x_2-x_1\cos\omega\left(t_2-t_1\right)-\int_{t_1}^{t_2}dt'\frac{f(t')}{m\omega}\sin\omega\left(t_2-t'\right)}{\sin\omega\left(t_2-t_1\right)}\sin\omega\left(t-t_2\right). \end{aligned} \tag{2.53}$$

Using Eq. (2.53) to find the derivative of x, and substituting into Eq. (2.44), we have

$$\begin{aligned} S\left[x\left(t\right)\right] &= \frac{m\omega}{2\sin\omega T}\left[\left(x_1^2+x_2^2\right)\cos\omega T+\frac{2x_1}{m\omega}\int_{t_1}^{t_2}dtf\left(t\right)\sin\omega\left(t_2-T\right)\right. \\ &\quad -x_1x_2+\frac{2x_2}{m\omega}\int_{t_1}^{t_2}dtf\left(t\right)\sin\omega\left(t-t_1\right) \\ &\quad \left.-\frac{2}{\left(m\omega\right)^2}\int_{t_1}^{t_2}dt\int_{t_1}^{t}dsf\left(t\right)f\left(s\right)\sin\omega\left(s-t_1\right)\sin\omega\left(t_2-t\right)\right] , \end{aligned} \tag{2.54}$$

and $T=t_2-t_1$, that is the classical action of a forced harmonic oscillator. From Eqs. (2.39) and (2.40), we see that, to complete the propagator we must find the prefactor $F(T)$, which is equivalent to a free harmonic oscillator. We have

$$F\left(T\right)=\int_0^0\mathcal{D}\left[\vec{y}\right]\exp\left[\frac{i}{\hbar}\int_0^T\left\{\frac{m}{2}\dot{y}^2-\frac{m}{2}\omega^2y^2\right\}\right] , \tag{2.55}$$

with the boundary condition $y\left(0\right)=y\left(T\right)=0$. By expressing $y\left(t\right)$ in the form of a Fourier series with a fundamental period of T,

$$y\left(t\right)=\sum_n a_n\sin\frac{n\pi t}{T} , \tag{2.56}$$

we can consider the paths as functions of the coefficients of a_n instead of functions of y for any value of t. This is a linear transformation whose Jacobian J is a constant and independent of ω, m and $\hbar$. However, we shall avoid the evaluation of J by collecting all factors which are independent of ω (including J) into a single constant factor. The integral for the action can be written in terms of the Fourier series of Eq. (2.56). Thus the kinetic-energy term becomes

$$\begin{aligned} \int_0^T \dot{y}^2 dt &= \sum_n \sum_m \frac{n\pi}{T} \frac{m\pi}{T} a_n a_m \int_0^T \cos\frac{n\pi t}{T} \cos\frac{m\pi t}{T} dt \\ &= \frac{T}{2} \sum_n \left(\frac{n\pi}{T}\right)^2 a_n^2 \ , \end{aligned} \tag{2.57}$$

and similarly the potential-energy term is

$$\int_0^T y^2 dt = \frac{T}{2} \sum_n a_n^2 \ , \tag{2.58}$$

with the assumption that the time T is divided into discrete steps of length ϵ, so that there are only a finite number N of coefficients a_n, the path integral becomes

$$F(T) \ = \ J \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} ... \int_{-\infty}^{+\infty} \exp\left\{ \frac{T}{2} \sum_{n=1}^{N} \frac{im}{2\hbar} \left[\left(\frac{n\pi}{T}\right)^2 - \omega^2 \right] a_n^2 \right\} \frac{da_1}{A} \frac{da_2}{A} ... \frac{da_N}{A}. \tag{2.59}$$

Since the exponent can be separated into factors, the integral over each coefficient a_n can be done separately. The result of one such integration is

$$\int_{-\infty}^{+\infty} \left\{ \exp \sum_{n=1}^{N} \frac{im}{2\hbar} \left[\left(\frac{n\pi}{T}\right)^2 - \omega^2 \right] \right\} a_n^2 \frac{da_n}{A} = \left(\frac{n^2\pi^2}{T^2} - \omega^2 \right)^{-\frac{1}{2}} . \tag{2.60}$$

Thus the path integral is proportional to

$$\prod_{n=1}^{N}\left(\frac{n^2\pi^2}{T^2}-\omega^2\right)^{-\frac{1}{2}}=\prod_{n=1}^{N}\left(\frac{n^2\pi^2}{T^2}\right)^{-\frac{1}{2}}\prod_{n=1}^{N}\left(1-\frac{\omega^2T^2}{n^2\pi^2}\right)^{-\frac{1}{2}}. \tag{2.61}$$

The first product does not depend on ω and combines with the Jacobian and other factors we have collected into a single constant. The second factor has the limit $[(\sin\omega T)/\omega T]^{-\frac{1}{2}}$ as $N\rightarrow\infty$, that is, as $\epsilon\rightarrow 0$. Thus

$$F(T)=C\left(\frac{\sin\omega T}{\omega T}\right)^{-\frac{1}{2}}, \tag{2.62}$$

where C is independent of ω. But for $\omega=0$ our integral is that for a free particle, for which we have already found that

$$F(T)=\left(\frac{m}{2\pi i\hbar T}\right)^{\frac{1}{2}}. \tag{2.63}$$

Hence for the harmonic oscillator we have

$$F(T)=\left(\frac{m\omega}{2\pi i\hbar\sin\omega T}\right)^{\frac{1}{2}}. \tag{2.64}$$

Substituting Eqs. (2.54) and (2.64) into (2.39) to obtain the complete solution.

Chapter 3

The Molecular Exciton for One Dimension

Many researchers are interested in the exciton problem and attempt to describe the optical properties of molecular aggregates [16]. The concept of the exciton was first introduced by Frenkel [27] and led to studies of the optical properties of solids and molecular aggregates [32]. In this chapter we introduce the basic idea of polymers, some important properties of the exciton and introduce also a model system.

3.1 Polymers

Molecular aggregates (polymer or crystals) are small agglomerations of molecules having one (chain), two (monolayer), or three spatial dimensions. In this thesis we are interested in the linear case. The molecular aggregate in one dimension, the polymer, is essentially a macromolecule consisting of many repeating units. These units are called monomers which are strongly bound by chemical forces.

3.2 The Molecular Exciton Spectra

In this section we introduce the exciton and discuss its properties. A superposition of states in which one monomer is excited electronically whilst the rest remain in their electronic ground states is called an “exciton”. The structure of the spectrum is due to exciton interaction with molecular vibrations and optical phonons. It splits the exciton band into a series of bands each corresponding to a specific vibration transition. Acoustical phonons which couple to the exciton yield the phonon side band, a broad and structureless feature accompanying the individual lines.

The exciton band (in the case of a single excitation) consists of N states, where N is the aggregate size, the number of molecules in the aggregate. The number N_{del} of molecules over which the exciton is delocalized is called delocalization length and usually ranges from a few to some ten molecules. One has to clearly distinguish between N_{del} and the aggregate size N which may be much larger ($10^4 - 10^6$molecules). Many excitons may be located on one aggregate and the delocalization length of the excitons on an aggregate depends on the coupling strength between the molecules and other factors like the presence of dynamic (phonons) and static (environmental inhomogeneities, kinks, ...) disorder.

The width of the exciton band is given by the coupling strength between the molecules in an aggregate and the exciton band usually extends over an energy region around the monomer transition energy. The transitions to different states in the exciton band are not all equally allowed, causing the appearance of bands in the absorption spectrum which are located within the exciton band, but much narrower than the exciton band itself. If the molecules in an aggregate are all identical and have equivalent positions, only one absorption band appears, resulting either from transitions to the bottom or the top edge of the exciton band.

3.3 Model System

In this thesis we consider a linear polymer chain consisting of a sum of n identical monomers in three dimensions. The exchange of electrons between the constituent monomers and nuclear interaction within a monomer (internal vibrations) are ignored. Different monomers, have (repulsive) nuclear interactions and electronic coulomb interaction. The monomers execute vibrations (lattice vibration) along the polymer chain. We assume that monomers have only a single excited electronic state. The model are shown in Fig. (3.1) and Fig. (3.2)

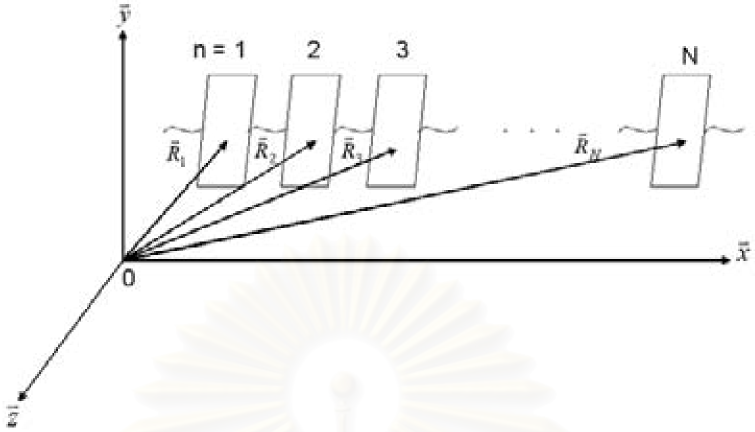

Fig. (3.1) Schematic representation of one dimensional linear chain of polymer which consists of a sum of n identical monomers. $\vec{R}_n$ is the position of the center of mass of n^{th} monomer.

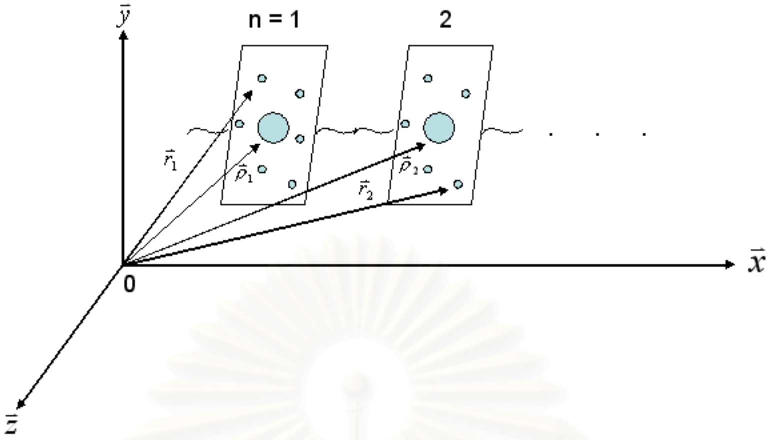

Fig. (3.2) Schematic representation of coordinates of internal electronic and nuclear degrees of freedom of the monomer molecules $\vec{r}$ and $\vec{\rho}$ respectively.

The present model is described by the polymer Hamiltonian as

$$\hat{H} = \sum_n \left[\hat{H}_n^{el}\left(\vec{r}_n\right) + \hat{H}_n^{N}\left(\vec{\rho}_n\right)\right] + \sum_{mn} \hat{V}_{mn}\left(\vec{r}_m, \vec{r}_n\right) + \sum_n \hat{K}_n\left(\vec{R}_n\right) + \sum_{mn} \hat{V}_{mn}^{N}\left(\vec{R}_m, \vec{R}_n\right), \tag{3.1}$$

where $\vec{R}_n$ is the position of the center of mass of the n^{th} monomer with summation over all monomers in the polymer chain. The internal electronic and nuclear coordinates of monomer molecules are $\vec{r}_n$, $\vec{\rho}_n$ respectively. The Hamiltonian $\hat{H}_n^{el}$ and $\hat{H}_n^{N}$ are the internal electronic and nuclear Hamiltonian of the n^{th} monomer. The Hamiltonian $\hat{K}_n$ describes the kinetic energy of the n^{th} monomer as a whole (lattice kinetic energy) and $\hat{V}_{mn}^{N}\left(\vec{R}_m, \vec{R}_n\right)$ describes the (repulsive) nuclear interactions of nuclei on different monomers. The nuclear interaction within a monomer is contained in $\hat{H}_n^{N}$. The totality of electronic coulomb interactions on different monomers is contained in $\hat{V}_{mn}\left(\vec{r}_m, \vec{r}_n\right)$. In the first approximation we neglect the internal vibrational Hamiltonian $\hat{H}_n^N\left(\vec{\rho}_n\right)$ and we can write the polymer Hamiltonian in terms of a sum over electronic and vibrational lattice Hamiltonian

$$\hat{H} = \hat{H}^{el} + \hat{H}^{N}, \tag{3.2}$$

where

$$\hat{H}^{el} = \sum_n \hat{H}_n^{el}\left(\vec{r}_n\right) + \sum_{mn} \hat{V}_{mn}\left(\vec{r}_m, \vec{r}_n\right), \tag{3.3}$$

and

$$\hat{H}^{N} = \sum_n \hat{K}_n\left(\vec{R}_n\right) + \sum_{mn} \hat{V}_{mn}^{N}\left(\vec{R}_m, \vec{R}_n\right). \tag{3.4}$$

Chapter 4

Path Integral Representation

The main concept of Feynman's path integral is the propagator which contains all information about the system. In this thesis, the propagator which leads to the density of states is important for understanding the spectral density function. The propagator is defined by the coordinate space matrix element of the time evolution operator. The propagator $G\left(\vec{r}_2, t_2; \vec{r}_1, t_1\right)$ represents the quantum mechanical transition amplitude for a particle at position $\vec{r}_1$ at time t_1 "propagates" to position $\vec{r}_2$ at time t_2. For more details on the concept of Feynman's path integral, the interested reader is referred to see the book of Feynman and Hibbs [21]. In this problem, we apply the method of Sa-yakanit [17, 22] to the exciton moving in a randomly distributed system. The introduced non-local harmonic trial action and the path integral of this action involves only a Gaussian integral and can be performed exactly [23].

4.1 Hamiltonian Equation

4.1.1 Time-Dependent Schrödinger Equation

The starting point of our calculation is the time-dependent Schrödinger equation of polymer state vector, and we look for a solution of

$$\left(\hat{H} - i\hbar\frac{\partial}{\partial t}\right)\left|\Psi(\vec{r},\vec{R},t)\right\rangle = 0 \ , \tag{4.1}$$

where $\left|\Psi\left(\vec{r} = \vec{r}_1, ..., \vec{r}_N \ ; \ \vec{R} = \vec{R}_1, ..., \vec{R}_N ; \ t\right)\right\rangle$ is dependent on the internal electronic and center of mass coordinates of N monomers. The electronic part describes the de-localization of the excitation and the state vector can be written in terms of the monomers state vector $|\pi_n(\vec{r})\rangle$ as

$$\left|\Psi(\vec{r},\vec{R},t)\right\rangle = \sum_n a_n\left(\vec{R},t\right)|\pi_n(\vec{r})\rangle \ . \tag{4.2}$$

There are n monomers excited electronically and all others in their ground states. It is required the normalization that

$$\left\langle\Psi(\vec{r},\vec{R},t)\middle|\Psi(\vec{r},\vec{R},t)\right\rangle = \sum_{m,n} a_m^* a_n \langle\pi_m|\,\pi_n\rangle = \sum_n |a_n|^2 = 1 \ , \tag{4.3}$$

since the $|\pi_n\rangle$ are orthonormal. In according of Eq. (3.2), we evaluate the matrix element of the Schrödinger operator, $\hat{H} - i\hbar\frac{\partial}{\partial t}$, by projecting the bra state $\langle\pi_m|$

on Eq. (4.1) from the left hand-side and the result is

$$\begin{aligned}\left\langle \pi_m \middle| \left(\hat{H} - i\hbar\frac{\partial}{\partial t}\right) \middle| \Psi \right\rangle &= \left\langle \pi_m \middle| \left(\hat{H}^{el} + \hat{H}^{N}\right) \sum_n a_n \left(\vec{R}, t\right) \middle| \pi_n \right\rangle \\ &\quad - \langle \pi_m | \, i\hbar\frac{\partial}{\partial t}\sum_n a_n \left(\vec{R}, t\right) |\pi_n\rangle \ ,\end{aligned} \tag{4.4}$$

where

$$\begin{aligned}\sum_n \langle \pi_m | \, \hat{H}^{el} \, |\pi_n\rangle \, a_n \left(\vec{R}, t\right) &= \sum_n \langle \pi_m | \, \hat{H}^{el}_n \left(\vec{r}_n\right) |\pi_n\rangle \, a_n \left(\vec{R}, t\right) \\ &\quad + \sum_{m,n} \langle \pi_m | \, \hat{V}_{mn} \left(\vec{r}_m, \vec{r}_n\right) |\pi_n\rangle \, a_n \left(\vec{R}, t\right) \\ &= \varepsilon_m a_m \left(\vec{R}, t\right) + \sum_{n \neq m} V_{mn} a_n \left(\vec{R}, t\right) .\end{aligned} \tag{4.5}$$

with ε_m is the molecular excitation of energy at site m and $V_{mn} \equiv \langle \pi_m | \, \hat{V}_{mn} \left(\vec{r}_m, \vec{r}_n\right) |\pi_n\rangle$ is the matrix element of interaction between monomers. Since $\langle \pi_m |$ does not depend on $\vec{R}$ coordinates and time, we can write

$$\sum_n \langle \pi_m | \, \hat{H}^{N} \, |\pi_n\rangle \, a_n \left(\vec{R}, t\right) = \hat{H}^{N} a_m \left(\vec{R}, t\right) , \tag{4.6}$$

and

$$\sum_n \langle \pi_m | \, i\hbar\frac{\partial}{\partial t} a_n \left(\vec{R}, t\right) |\pi_n\rangle = i\hbar\frac{\partial}{\partial t} a_m \left(\vec{R}, t\right) \tag{4.7}$$

From Eqs. (4.4), (4.5), (4.6) and (4.7), we can represent the system in terms of the time-dependent Schrödinger equation in the tight-binding representation

$$i\hbar\frac{\partial}{\partial t}a_m\left(\vec{R},t\right)=\varepsilon_m a_m\left(\vec{R},t\right)+\sum_{n\neq m}V_{mn}a_n\left(\vec{R},t\right)+\hat{H}^N a_m\left(\vec{R},t\right). \tag{4.8}$$

4.1.2 Adiabatic Approximation

In this thesis the effect of electronic excitation and interaction between monomers is due to the monomer molecular vibration (lattice vibration). From the previous subsection, we have obtained ε_m and V_{mn} which are scalar quanlities and depend on sites m and mn respectively. Hence, the site of each monomer can be labelled by using only the center of mass coordinates we have assumed no internal vibration in the previous section. Since in the adiabatic limit the lattice coordinates move slower than electronic coordinates. So we can expand ε_m and V_{mn} about the equilibrium $\vec{R}^0_m$ and $\vec{R}^0_n$ up to the first order. We then have

$$\varepsilon_m\left(\vec{R}_m\right)\approx\varepsilon_m\left(\vec{R}^0_m\right)+\vec{\zeta}_m\cdot\left(\vec{\nabla}_{R_m}\varepsilon_m\right)_{\vec{R}_m=\vec{R}^0_m}+\ \dots\ , \tag{4.9}$$

and

$$\begin{aligned}V_{mn}\left(\vec{R}_m,\vec{R}_n\right)\ &\approx\ V_{mn}\left(\vec{R}^0_m,\vec{R}^0_n\right)+\vec{\zeta}_m\cdot\left(\vec{\nabla}_{R_m}V_{mn}\right)_{\substack{\vec{R}_m=\vec{R}^0_m\\ \vec{R}_n=\vec{R}^0_n}}\\ &\quad+\vec{\zeta}_n\cdot\left(\vec{\nabla}_{R_n}V_{mn}\right)_{\substack{\vec{R}_m=\vec{R}^0_m\\ \vec{R}_n=\vec{R}^0_n}}+\dots\ ,\end{aligned} \tag{4.10}$$

where $\vec{\zeta}_m$ and $\vec{\zeta}_n$ are small displacement of each monomer at site m and n respectively. Let $\varepsilon_m\left(\vec{R}^0_m\right)=\varepsilon^0_m$ and $V_{mn}\left(\vec{R}^0_m,\vec{R}^0_n\right)=V^0_{mn}$. Then Eq. (4.8) becomes

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}a_m &\cong \varepsilon_m^0 a_m + \sum_{n\neq m} V_{mn}^0 a_n + \hat{H}^N a_m + \vec{\zeta}_m \cdot \left(\vec{\nabla}_{R_m}\varepsilon_m\right)_{\vec{R}_m=\vec{R}_m^0} a_m \\ &+ \sum_{n\neq m} 2\vec{\zeta}_m \cdot \left(\vec{\nabla}_{R_m} V_{mn}\right)_{\substack{\vec{R}_m=\vec{R}_m^0 \\ \vec{R}_n=\vec{R}_n^0}} a_n \ . \end{aligned} \qquad (4.11)$$

4.1.3 The Nearest-Neighbor Approximation

In most other works, polymers are assumed to be a one dimensional linear chain with nearest neighbor interaction (excluding volume effects). So we can approximate the interaction of the system to have nearest neighbor interaction only, $n = m \pm 1$, then the off-diagonal terms of Eq. (4.11) become

$$\begin{aligned} &V_{m,m-1}^0 a_{m-1} + 2\vec{\zeta}_m \cdot \left(\vec{\nabla}_{R_m} V_{m,m-1}\right)_{\substack{\vec{R}_m=\vec{R}_m^0 \\ \vec{R}_n=\vec{R}_n^0}} a_{m-1} \\ &+ V_{m,m+1}^0 a_{m+1} + 2\vec{\zeta}_m \cdot \left(\vec{\nabla}_{R_m} V_{m,m+1}\right)_{\substack{\vec{R}_m=\vec{R}_m^0 \\ \vec{R}_n=\vec{R}_n^0}} a_{m+1} \quad . \end{aligned} \qquad (4.12)$$

For a linear chain, we approximate both sums in Eq. (4.12) to have the same value $\left(\vec{\nabla}_{R_m} V\right)_{\substack{\vec{R}_m=\vec{R}_m^0 \\ \vec{R}_n=\vec{R}_n^0}}$ and we shall write $\vec{\zeta}_m = \vec{\zeta}$. Thus Eq. (4.11) becomes

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}a_m &= \varepsilon_m^0 a_m + V^0\left(a_{m+1} + a_{m-1}\right) + \hat{H}^N a_m + \vec{\zeta} \cdot \left(\vec{\nabla}_{R_m}\varepsilon_m\right)_{\substack{\vec{R}_m=\vec{R}_m^0 \\ \vec{R}_n=\vec{R}_n^0}} a_m \\ &+ 2\vec{\zeta} \cdot \left(\vec{\nabla}_{R_m} V\right)_{\substack{\vec{R}_m=\vec{R}_m^0 \\ \vec{R}_n=\vec{R}_n^0}} \left(a_{m+1} + a_{m-1}\right) \ , \end{aligned} \qquad (4.13)$$

where $V^0 = V^0_{m,m\pm1}$. Assuming that the functions a_{m+1} and a_{m-1} can be expanded about the function a_m at site m, we then have

$$\begin{aligned} a_{m+1}\left(\vec{R},t\right) &\equiv a\left((m+1)\vec{b},\vec{R},t\right) = a\left(m\vec{b}+\vec{b},\vec{R},t\right) = a\left(m\vec{b},\vec{R},t\right) \\ &\quad +\vec{b}\cdot\vec{\nabla}_{mb}a\left(m\vec{b},\vec{R},t\right) + \frac{b^2}{2}\nabla^2_{mb}a\left(m\vec{b},\vec{R},t\right) + \ \ldots\ , \end{aligned} \tag{4.14}$$

and

$$\begin{aligned} a_{m-1}\left(\vec{R},t\right) &\equiv a\left((m-1)\vec{b},\vec{R},t\right) = a\left(m\vec{b}-\vec{b},\vec{R},t\right) = a\left(m\vec{b},\vec{R},t\right) \\ &\quad -\vec{b}\cdot\vec{\nabla}_{mb}a\left(m\vec{b},\vec{R},t\right) + \frac{b^2}{2}\nabla^2_{mb}a\left(m\vec{b},\vec{R},t\right) + \ \ldots\ , \end{aligned} \tag{4.15}$$

where $\vec{\nabla}_{mb}$ is the gradient at site m and $\left|\vec{b}\right|$ is the lattice constant of the system and we assume that $b^2 \ll 1$; then b^2V^0 becomes constant. Thus we have

$$\begin{aligned} V^0\left(a_{m+1}+a_{m-1}\right) &= 2V^0a\left(m\vec{b},\vec{R},t\right) + b^2V^0\nabla^2_{mb}a\left(m\vec{b},\vec{R},t\right) \\ &= 2V^0a\left(m\vec{b},\vec{R},t\right) - \frac{\hbar^2}{2m}\nabla^2_{mb}a\left(m\vec{b},\vec{R},t\right)\ , \end{aligned} \tag{4.16}$$

where $b^2V^0 = -\frac{\hbar^2}{2m}$ [13]. Expanding

$$2\vec{\zeta}\cdot\left(\vec{\nabla}_{R_m}V\right)_{\substack{\vec{R}_m=\vec{R}^0_m \\ \vec{R}_n=\vec{R}^0_n}}\left(a_{m+1}+a_{m-1}\right)\ , \tag{4.17}$$

we have

$$2\vec{\zeta}\cdot\left(\vec{\nabla}_{R_m}V\right)_{\substack{\vec{R}_m=\vec{R}^0_m \\ \vec{R}_n=\vec{R}^0_n}}\left[2a\left(m\vec{b},\vec{R},t\right) - \frac{\hbar^2}{2mV^0}\nabla^2_{mb}a\left(m\vec{b},\vec{R},t\right)\right]\ . \tag{4.18}$$

Thus the time-dependent Schrödinger equation can be rewriten as

$$
\begin{aligned}
i\hbar\frac{\partial}{\partial t}a\left(m\vec{b},\vec{R},t\right) \;=\; & \Big[\varepsilon^0(m\vec{b}) - \vec{\zeta}\cdot\vec{g}\left(m\vec{b}\right) + 2V^0 \\
& -\frac{\hbar^2}{2m}\left(1+\frac{2}{V^0}\left(\vec{\nabla}_{R_m}V_{mn}\right)_{\substack{\vec{R}_m=\vec{R}_m^0\\ \vec{R}_n=\vec{R}_n^0}}\cdot\vec{\zeta}\right)\nabla^2_{mb}+\hat{H}^N\Big]a\left(m\vec{b},\vec{R},t\right) .
\end{aligned}
\tag{4.19}
$$

where $\vec{g}\left(m\vec{b}\right) = -\left[\vec{\nabla}_{R_m}\varepsilon_m + 4\left(\vec{\nabla}_{R_m}V\right)_{\vec{R}_n=\vec{R}_n^0}\right]_{\vec{R}_m=\vec{R}_m^0}$ as the electronic excitation-lattice vibration coupling.

4.1.4 The Continuous Limit

From now on, we will neglect the term $\frac{2}{V^0}\left(\vec{\nabla}_{R_m}V_{mn}\right)_{\substack{\vec{R}_m=\vec{R}_m^0\\ \vec{R}_n=\vec{R}_n^0}}$ in Eq. (4.19) (assume $\left|\frac{2}{V^0}\left(\vec{\nabla}_{R_m}V_{mn}\right)_{\substack{\vec{R}_m=\vec{R}_m^0\\ \vec{R}_n=\vec{R}_n^0}}\right| \ll 1$). In the continuum limit, we can write Eq. (4.19) as

$$
i\hbar\frac{\partial}{\partial t}a\left(\vec{r},\vec{\zeta},t\right) = [\varepsilon^0\left(\vec{r}\right) + 2V^0 - \frac{\hbar^2}{2m}\nabla_r^2 + \hat{H}^N - \vec{g}\left(\vec{r}\right)\cdot\vec{\zeta}]a\left(\vec{r},\vec{\zeta},t\right) \quad , \tag{4.20}
$$

where $\vec{r}$ is the electronic excitation coordinates and $\hat{H}^N$ is the vibrational monomer Hamiltonian which is assumed as the harmonic oscillator Hamiltonian:

$$
\hat{H}^N = \frac{\hat{P}^2}{2M} + \frac{M}{2}\Omega^2\vec{\zeta}^2 \ , \tag{4.21}
$$

where $\hat{P}$ is the monomer momentum operator, Ω is monomer-vibration frequency and M is the mass of each monomer. Thus we can write Hamiltonian as

$$
\hat{H} = \frac{\hat{p}^2}{2m} + \varepsilon^0\left(\vec{r}\right) + 2V^0 + \frac{\hat{P}^2}{2M} + \frac{M}{2}\Omega^2\vec{\zeta}^2 - \vec{g}\left(\vec{r}\right)\cdot\vec{\zeta} \ , \tag{4.22}
$$

where $\hat{p}$ is the momentum operator of the electronic excitation.

4.2 Path Integral Representation

4.2.1 The Feynman Propagator

We now consider the probability amplitude for a quantum process starting from the initial position $\vec{r}\,'$, $\vec{\zeta}\,'$ at t' and by returning to the final position $\vec{r}$, $\vec{\zeta}$ at t. The propagator can be written as coordinate space matrix element of the time development operator $\hat{U}\left(t,t'\right)$:

$$K\left(\vec{r},\vec{\zeta},t;\vec{r}\,',\vec{\zeta}\,',t'\right)=\left\langle \vec{r},\vec{\zeta},t\,\middle|\,\vec{r}\,',\vec{\zeta}\,',t'\right\rangle =\left\langle \vec{r},\vec{\zeta}\middle|\hat{U}\left(t,t'\right)\middle|\vec{r}\,',\vec{\zeta}\,'\right\rangle , \qquad (4.23)$$

where the time development operator $\hat{U}\left(t,t'\right)$ is defined by

$$\hat{U}\left(t,t'\right)=\exp\left[-\frac{i}{\hbar}\hat{H}\left(t-t'\right)\right]\theta\left(t-t'\right), \qquad (4.24)$$

with $\hat{H}$ is the time-independent Hamiltonian operator and $\theta\left(t-t'\right)$ is the step function defined by

$$\theta\left(t-t'\right)=\left\{\begin{array}{cc} 1 & t>t' \\ 0 & t<t' \end{array}\right. . \qquad (4.25)$$

Substituting Eq. (4.24) into Eq. (4.23), thus we can rewrite the propagator as

$$K\left(\vec{r},\vec{\zeta},t;\vec{r}\,',\vec{\zeta}\,',t'\right)=\left\langle \vec{r},\vec{\zeta}\middle|\exp\left[-\frac{i}{\hbar}\hat{H}\left(t-t'\right)\right]\middle|\vec{r}\,',\vec{\zeta}\,'\right\rangle . \qquad (4.26)$$

From the above equation we will divide the time interval $t - t'$ into n discrete steps of size $\epsilon = \frac{t-t'}{n}$

$$
\begin{aligned}
K\left(\vec{r}, \vec{\zeta}, t; \vec{r}\,', \vec{\zeta}\,', t'\right) \;=\; & \int_{-\infty}^{+\infty} d^3r_1 ... d^3r_{n-1} \int_{-\infty}^{+\infty} d^3\zeta_1 ... d^3\zeta_{n-1} \times \\
& \left\langle \vec{r}_n, \vec{\zeta}_n \left| \exp\left[-\frac{i}{\hbar}\epsilon \hat{H}\right] \right| \vec{r}_{n-1}, \vec{\zeta}_{n-1} \right\rangle \times \\
& \left\langle \vec{r}_{n-1}, \vec{\zeta}_{n-1} \left| \exp\left[-\frac{i}{\hbar}\epsilon \hat{H}\right] \right| \vec{r}_{n-2}, \vec{\zeta}_{n-2} \right\rangle \times \\
& ... \left\langle \vec{r}_1, \vec{\zeta}_1 \left| \exp\left[-\frac{i}{\hbar}\epsilon \hat{H}\right] \right| \vec{r}_0, \vec{\zeta}_0 \right\rangle . \qquad (4.27)
\end{aligned}
$$

In the limit of large n the time slices become infinitesimal

$$
\begin{aligned}
& \left\langle \vec{r}_l, \vec{\zeta}_l \left| \exp\left[-\frac{i}{\hbar}\epsilon \hat{H}\right] \right| \vec{r}_{l-1}, \vec{\zeta}_{1-1} \right\rangle \\
= & \left\langle \vec{r}_l, \vec{\zeta}_l \left| \exp\left[-\frac{i}{\hbar}\epsilon \left(\frac{\hat{p}^2}{2m} + \varepsilon^0\left(\vec{r}\right) + 2V^0 + \frac{\hat{P}^2}{2M} + \frac{M}{2}\Omega^2 \vec{\zeta}^2 - \overrightarrow{g}\left(\vec{r}\right) \cdot \vec{\zeta} \right)\right] \right| \vec{r}_{l-1}, \vec{\zeta}_{1-1} \right\rangle \\
\cong & \left\langle \vec{r}_l, \vec{\zeta}_l \left| 1 - \frac{i}{\hbar}\epsilon \left(\frac{\hat{p}^2}{2m} + \varepsilon^0\left(\vec{r}\right) + 2V^0 + \frac{\hat{P}^2}{2M} + \frac{M}{2}\Omega^2 \vec{\zeta}^2 - \overrightarrow{g}\left(\vec{r}\right) \cdot \vec{\zeta} \right) \right| \vec{r}_{l-1}, \vec{\zeta}_{1-1} \right\rangle \\
\cong & \left\langle \vec{r}_l, \vec{\zeta}_l \left| \exp\left[-\frac{i}{\hbar}\epsilon \left(\frac{\hat{p}^2}{2m} + \frac{\hat{P}^2}{2M} \right)\right] \right| \vec{r}_{l-1}, \vec{\zeta}_{1-1} \right\rangle \exp\left[-\frac{i}{\hbar}\epsilon \left(\varepsilon^0\left(\vec{r}_l\right) + 2V^0 \right.\right. \\
& \left.\left. + \frac{M}{2}\Omega^2 \vec{\zeta}^2 - \overrightarrow{g}\left(\vec{r}\right) \cdot \vec{\zeta} \right)\right] + \mathcal{O}\left(\epsilon^2\right), \qquad (4.28)
\end{aligned}
$$

and we can evaluate the coordinate space matrix element of the momentum $\hat{p}$ operator

$$
\left\langle \vec{r}_l, \vec{\zeta}_l \left| \exp\left[-\frac{i}{\hbar}\epsilon \frac{\hat{p}^2}{2m}\right] \right| \vec{r}_{l-1}, \vec{\zeta}_{1-1} \right\rangle . \qquad (4.29)
$$

By introducing a complete set of momentum states for electronic excitation, we have $\int \frac{d^3p}{(2\pi\hbar)^3} \left|\vec{p}\right\rangle \left\langle\vec{p}\right| = 1$ and inserting into Eq. (4.29), we get

$$\begin{aligned} & \int \frac{d^3p}{(2\pi\hbar)^3} \left\langle \vec{r}_l, \vec{\zeta}_l \mid \vec{p} \right\rangle \exp\left[-\frac{i}{\hbar}\epsilon\frac{\hat{p}^2}{2m}\right] \left\langle \vec{p} \mid \vec{r}_{l-1}, \vec{\zeta}_{1-1} \right\rangle \\ = & \int \frac{d^3p}{(2\pi\hbar)^3} \left\langle \vec{r}_l, \vec{\zeta}_l \mid \vec{p} \right\rangle \left\langle \vec{p} \mid \vec{r}_{l-1}, \vec{\zeta}_{1-1} \right\rangle \exp\left[-\frac{i}{\hbar}\epsilon\frac{\vec{p}^2}{2m}\right]. \end{aligned} \tag{4.30}$$

Since the plane wave is define as

$$\left\langle \vec{r}_l, \vec{\zeta}_l \mid \vec{p} \right\rangle = \exp\left[\frac{i}{\hbar}\vec{p}\cdot\vec{r}_l\right] \text{ and } \left\langle \vec{p} \mid \vec{r}_{l-1}, \vec{\zeta}_{1-1} \right\rangle = \exp\left[-\frac{i}{\hbar}\vec{p}\cdot\vec{r}_{l-1}\right]. \tag{4.31}$$

Inserting the plane wave into Eq. (4.30), we obtain

$$\left\langle \vec{r}_l, \vec{\zeta}_l \left| \exp\left(-\frac{i}{\hbar}\epsilon\frac{\vec{p}^2}{2m}\right) \right| \vec{r}_{l-1}, \vec{\zeta}_{1-1} \right\rangle = \int \frac{d^3p}{(2\pi\hbar)^3} \exp\left(-\frac{i}{\hbar}\epsilon\frac{\vec{p}^2}{2m} + \frac{i}{\hbar}\vec{p}\cdot(\vec{r}_l - \vec{r}_{l-1})\right). \tag{4.32}$$

Performing the $\vec{p}$-integration by using the Gaussian integral

$$\int_{-\infty}^{+\infty} dx \exp\left[ax^2 + bx\right] = \left(\frac{\pi}{-a}\right)^{\frac{1}{2}} \exp\left[-\frac{b^2}{4a}\right] , \tag{4.33}$$

thus we can write the kinetic energy of electronic excitation as

$$\left\langle \vec{r}_l, \vec{\zeta}_l \left| \exp\left[-\frac{i}{\hbar}\epsilon\frac{\vec{p}^2}{2m}\right] \right| \vec{r}_{l-1}, \vec{\zeta}_{1-1} \right\rangle = \left(\frac{m}{2\pi i\hbar\epsilon}\right)^{\frac{3}{2}} \exp\left[\frac{i}{\hbar}\frac{m}{2}\epsilon\left(\frac{\vec{r}_l - \vec{r}_{l-1}}{\epsilon}\right)^2\right]. \tag{4.34}$$

Similarly we can write the kinetic energy of polymers as

$$\left\langle \vec{r}_l, \vec{\zeta}_l \left| \exp\left[-\frac{i}{\hbar}\epsilon\frac{\vec{P}^2}{2M}\right] \right| \vec{r}_{l-1}, \vec{\zeta}_{1-1} \right\rangle = \left(\frac{M}{2\pi i\hbar\epsilon}\right)^{\frac{3}{2}} \exp\left[\frac{i}{\hbar}\frac{M}{2}\epsilon\left(\frac{\vec{\zeta}_l - \vec{\zeta}_{1-1}}{\epsilon}\right)^2\right]. \tag{4.35}$$

Substituting Eqs. (4.28), (4.34) and (4.35) into (4.27) and taking the continuum limit, we find the path integral prescription

$$\begin{aligned} K\left(\vec{r},\vec{\zeta},t;\vec{r}\,',\vec{\zeta}\,',t'\right) &= \lim_{n\to\infty}\left(\frac{m}{2\pi i\hbar\epsilon}\right)^{\frac{3n}{2}}\left(\frac{M}{2\pi i\hbar\epsilon}\right)^{\frac{3n}{2}}\int_{-\infty}^{+\infty}d^3r_1...d^3r_{n-1}\int_{-\infty}^{+\infty}d^3\zeta_1...d^3\zeta_{n-1} \\ &\quad \exp\frac{i}{\hbar}\sum_{\ell=1}^{n}\left(m\frac{\left(\vec{r}_l-\vec{r}_{l-1}\right)^2}{2\epsilon}-\epsilon\varepsilon^0\left(\vec{r}_l\right)-\epsilon 2V^0+\right. \\ &\quad \left. M\frac{\left(\vec{\zeta}_l-\vec{\zeta}_{l-1}\right)^2}{2\epsilon}-\epsilon\frac{M}{2}\Omega^2\vec{\zeta}_l^2+\epsilon\vec{g}\left(\vec{r}_l\right)\cdot\vec{\zeta}_l\right), \end{aligned} \tag{4.36}$$

where the quantities $\left(\frac{m}{2\pi i\hbar\epsilon}\right)^{\frac{3}{2}}and\left(\frac{M}{2\pi i\hbar\epsilon}\right)^{\frac{3}{2}}$are normalization factor of particles of mass m and mass M, respectively. So the time-dependent Schrödinger equation can be rewriten in the path integral representation as

$$\begin{aligned} K\left(\vec{r}_2,\vec{\zeta}_2,t_2;\vec{r}_1,\vec{\zeta}_1,t_1\right) &= \int D\left[\vec{r}\left(\tau\right)\right]\int D\left[\vec{\zeta}\left(\tau\right)\right]\exp[\frac{i}{\hbar}\int_{t_1}^{t_2}d\tau(\frac{m}{2}\dot{\vec{r}}^{\,2}\left(\tau\right)-\varepsilon^0\left(\vec{r}\left(\tau\right)\right) \\ &\quad -2V^0+\frac{M}{2}\dot{\vec{\zeta}}^{\,2}\left(\tau\right)-\frac{M}{2}\Omega^2\vec{\zeta}^2(\tau)+\vec{g}\left[\vec{r}\left(\tau\right)\right]\cdot\vec{\zeta}\left(\tau\right))], \end{aligned} \tag{4.37}$$

where the symbol $\int D\left[\vec{r}\left(\tau\right)\right]$ and $\int D\left[\vec{\zeta}\left(\tau\right)\right]$ are defined by Eq. (4.36) and represent the integration over all possible path connecting the points $\left(\vec{r}_1,t_1\right)$ and $\left(\vec{r}_2,t_2\right)$,$\left(\vec{\zeta}_1,t_1\right)$ and $\left(\vec{\zeta}_2,t_2\right)$ respectively.

4.2.2 The Path Integral as a Functional

When a Kernel contains more than one variable and can not be separated, the analysis therefore is very difficult. However because of the quadratic action in the coordinate $\vec{\zeta}$, we can simply write the Kernel by eliminating $\vec{\zeta}(\tau)$ coordinates. The resulting propagator can be written in “functional form” as

$$\begin{aligned} K\left(\vec{r}_2, \vec{\zeta}_2, t_2; \vec{r}_1, \vec{\zeta}_1, t_1\right) &= \int D\left[\vec{r}\left(\tau\right)\right]\Big[\exp[\frac{i}{\hbar}\int_{t_1}^{t_2} d\tau(\frac{m}{2}\dot{\vec{r}}^{\,2}\left(\tau\right) - \varepsilon^0\left(\vec{r}\left(\tau\right)\right) \\ &\qquad -2V^0\Big] \times T\left[\vec{r}\left(\tau\right)\right], \end{aligned} \tag{4.38}$$

where

$$T\left[\vec{r}\left(\tau\right)\right] = \int D\left[\vec{\zeta}\left(\tau\right)\right]\exp[\frac{i}{\hbar}\int_{t_1}^{t_2} d\tau\left(\frac{M}{2}\dot{\vec{\zeta}}^{\,2}\left(\tau\right) - \frac{M}{2}\Omega^2\vec{\zeta}^2(\tau) + \vec{g}\left[\vec{r}\left(\tau\right)\right]\cdot\vec{\zeta}\left(\tau\right)\right)]. \tag{4.39}$$

Integrating over all paths available to the $\vec{\zeta}$ coordinates produces a functional T. From Eq. (4.39) it is just the path integrals of a forced harmonic oscillator. We shall assume the electronic excitation-lattice vibration coupling $\vec{g}\left[\vec{r}\left(\tau\right)\right]$ (forcing function) as an external force. Then Eq. (4.39) can be determined exactly [21].

$$\begin{aligned} T\left[\vec{r}\left(\tau\right)\right] &= \int D\left[\vec{\zeta}\left(\tau\right)\right]\exp[\frac{i}{\hbar}\int_{t_1}^{t_2} d\tau\left(\frac{M}{2}\dot{\vec{\zeta}}^{\,2}\left(\tau\right) - \frac{M}{2}\Omega^2\vec{\zeta}^2(\tau) + \vec{g}\left[\vec{r}\left(\tau\right)\right]\cdot\vec{\zeta}\left(\tau\right)\right) \\ &= \left(\frac{M\Omega}{2\pi i\hbar\sin\Omega\left(t_2-t_1\right)}\right)^{\frac{1}{2}}\exp\left\{\frac{iM\Omega}{2\hbar\sin\Omega\left(t_2-t_1\right)}[\left(\vec{\zeta}_1^2 + \vec{\zeta}_2^2\right)\cos\Omega\left(t_2-t_1\right)\right. \\ &\quad -2\vec{\zeta}_1\cdot\vec{\zeta}_2 + \frac{2\vec{\zeta}_2}{M\Omega}\cdot\int_{t_1}^{t_2} d\tau\vec{g}\left[\vec{r}\left(\tau\right)\right]\sin\Omega\left(\tau-t_1\right) \\ &\quad +\frac{2\vec{\zeta}_1}{M\Omega}\cdot\int_{t_1}^{t_2} d\tau\vec{g}\left[\vec{r}\left(\tau\right)\right]\sin\Omega\left(t_2-\tau\right) \\ &\quad \left. -\frac{2}{M^2\Omega^2}\int_{t_1}^{t_2} d\tau\int_{t_1}^{\tau} d\sigma\vec{g}\left[\vec{r}\left(\tau\right)\right]\cdot\vec{g}\left[\vec{r}\left(\sigma\right)\right]\sin\Omega\left(t_2-\tau\right)\sin\Omega\left(\sigma-t_1\right)]\right\}. \end{aligned} \tag{4.40}$$

Thus we can rewrite the propagator as

$$\begin{aligned} K\left(\vec{r}_2, \vec{\zeta}_2, t_2; \vec{r}_1, \vec{\zeta}_1, t_1\right) \; = \; & \left(\frac{M\Omega}{2\pi i\hbar \sin\Omega\left(t_2 - t_1\right)}\right)^{\frac{3}{2}} \int D\left[\vec{r}\left(\tau\right)\right] \exp\bigg\{\frac{i}{\hbar}\int_{t_1}^{t_2} d\tau\big(\frac{m}{2}\dot{\vec{r}}^{\,2}\left(\tau\right) \\ & -\varepsilon^0\left(\vec{r}\left(\tau\right)\right) - 2V^0 \\ & +\frac{iM\Omega}{2\hbar\sin\Omega\left(t_2 - t_1\right)}\big[\left(\vec{\zeta}_1^{\,2} + \vec{\zeta}_2^{\,2}\right)\cos\Omega\left(t_2 - t_1\right) \\ & -2\vec{\zeta}_1 \cdot \vec{\zeta}_2 + \frac{2\vec{\zeta}_2}{M\Omega} \cdot \int_{t_1}^{t_2} d\tau \vec{g}\left[\vec{r}\left(\tau\right)\right] \sin\Omega\left(\tau - t_1\right) \\ & +\frac{2\vec{\zeta}_1}{M\Omega} \cdot \int_{t_1}^{t_2} d\tau \vec{g}\left[\vec{r}\left(\tau\right)\right] \sin\Omega\left(t_2 - \tau\right)\big] \\ & -\bigg(\frac{2}{M^2\Omega^2}\int_{t_1}^{t_2} d\tau \vec{g}\left[\vec{r}\left(\tau\right)\right] \\ & \quad \cdot \int_{t_1}^{\tau} d\sigma \vec{g}\left[\vec{r}\left(\sigma\right)\right] \sin\Omega\left(t_2 - \tau\right) \sin\Omega\left(\sigma - t_1\right)\bigg)\bigg\}. \end{aligned} \tag{4.41}$$

The coordinate $\vec{\zeta}$ can be eliminated by first setting $\vec{\zeta}_1 = \vec{\zeta}_2$ and integrating Eq. (4.41) with respect to the variable $\vec{\zeta}_2$. As a result, we obtain

$$\begin{aligned}
K\left(\vec{r}_2, t_2; \vec{r}_1, t_1\right) &= \int d\vec{\zeta}_2 d\vec{\zeta}_1 \delta\left(\vec{\zeta}_2 - \vec{\zeta}_1\right) K\left(\vec{r}_2, \vec{\zeta}_2, t_2; \vec{r}_1, \vec{\zeta}_1, t_1\right) \\
&= \left(\frac{M\Omega}{2\pi i\hbar \sin\Omega\left(t_2 - t_1\right)}\right)^{\frac{3}{2}} \int D\left[\vec{r}\left(\tau\right)\right] \Bigg\{ \exp[\frac{i}{\hbar}\int_{t_1}^{t_2} d\tau(\frac{m}{2}\dot{\vec{r}}^{2}\left(\tau\right) \\
&\quad -\varepsilon^0\left(\vec{r}\left(\tau\right)\right) - 2V^0 \\
&\quad -\frac{i}{\hbar M\Omega\sin\Omega\left(t_2 - t_1\right)} \int_{t_1}^{t_2} d\tau \vec{g}\left[\vec{r}\left(\tau\right)\right] \\
&\quad \cdot \int_{t_1}^{\tau} d\sigma \vec{g}\left[\vec{r}\left(\sigma\right)\right] \sin\Omega\left(t_2 - \tau\right) \sin\Omega\left(\sigma - t_1\right)] \Bigg\} \\
&\quad \times \int d\vec{\zeta} \Bigg(\exp\frac{iM\Omega}{2\hbar\sin\Omega\left(t_2 - t_1\right)} [2\vec{\zeta}^2 \cos\Omega\left(t_2 - t_1\right) - 2\vec{\zeta}^2 \\
&\quad +\frac{2\vec{\zeta}}{M\Omega} \cdot \int_{t_1}^{t_2} d\tau \vec{g}\left[\vec{r}\left(\tau\right)\right] \sin\Omega\left(\tau - t_1\right) \\
&\quad\quad +\frac{2\vec{\zeta}}{M\Omega} \cdot \int_{t_1}^{t_2} d\tau \vec{g}\left[\vec{r}\left(\tau\right)\right] \sin\Omega\left(t_2 - \tau\right)] \Bigg)
\end{aligned} \tag{4.42}$$

For simplicity, let us consider the case when the nearest neighbor interaction V^0 and exciton-lattice vibration coupling $\vec{g}\left[\vec{r}\left(\tau\right)\right]$ are constant. Performing the $\vec{\zeta}$ integration by using Eq. (4.33), we obtain

$$\begin{aligned}
K\left(\vec{r}_2, t_2; \vec{r}_1, t_1\right) &= \left(\frac{1}{2\left(\cos\Omega\left(t_2 - t_1\right)\right)}\right)^{\frac{3}{2}} \int D\left[\vec{r}\left(\tau\right)\right] \exp[\frac{i}{\hbar}\int_{t_1}^{t_2} d\tau(\frac{m}{2}\dot{\vec{r}}^{2}\left(\tau\right) \\
&\quad -\varepsilon^0\left(\vec{r}\left(\tau\right)\right) - 2V^0 + \frac{g^2}{2M\Omega^2})].
\end{aligned} \tag{4.43}$$

4.2.3 Inclusion of Randomness

We now introduce randomness into the system and study the case when $\varepsilon^0(\vec{r})$ is distributed in a Gaussian random fashions with zero mean $\langle \varepsilon^0 \rangle = 0$ and finite correlation length L. Therefore, the correlation function of the second moments is defined by

$$\left\langle \varepsilon^0(\vec{r})\,\varepsilon^0(\vec{r}\,')\right\rangle = W(\vec{r}-\vec{r}\,'). \tag{4.44}$$

We can write the correlation function as

$$W\left(\vec{r}(\tau)-\vec{r}(\sigma)\right) = \xi_L \exp\left(-\frac{\left|\vec{r}(\tau)-\vec{r}(\sigma)\right|^2}{L^2}\right), \tag{4.45}$$

where ξ_L is the variance of the random Gaussian potential. The quantity ξ_L, having the dimension of energy squared, was first introduced by Halperin and Lax [35]. In order to calculate the average propagator with respect to probabillity distribution of $\varepsilon^0(\vec{r})$ ($P[\varepsilon^0(\vec{r})]$), we write the average propagator in the form

$$G\left(\vec{r}_2,t_2;\vec{r}_1,t_1\right) = \left\langle K\left(\vec{r}_2,t_2;\vec{r}_1,t_1\right)\right\rangle_{P[\varepsilon^{\circ}(\vec{r})]}. \tag{4.46}$$

By using cumulant expansion (exact semi-invariant expansion)[25] defined by

$$\langle \exp[A]\rangle = \exp\left[\langle A\rangle + \frac{1}{2!}\left(\left\langle A^2\right\rangle - \langle A\rangle^2\right) + \frac{1}{3!}\left(\left\langle A^3\right\rangle - 3\langle A\rangle\left(\left\langle A^2\right\rangle - \langle A\rangle^2\right) - \langle A\rangle^3\right) + ...\right], \tag{4.47}$$

up to the second order, we obtain the propagator with randomness as

$$\begin{aligned} G\left(\vec{r}_2, t_2; \vec{r}_1, t_1\right) &= \left(\frac{1}{2\left(\cos\Omega\left(t_2-t_1\right)\right)}\right)^{\frac{3}{2}} \int D\left[\vec{r}\left(\tau\right)\right] \exp[\frac{i}{\hbar}\left\{\left(\left(\int_{t_1}^{t_2} d\tau(\frac{m}{2}\dot{\vec{r}}^{2}\left(\tau\right)\right.\right.\right. \\ &\left.\left. -2V^0+\frac{g^2}{2M\Omega^2}\right)+\frac{i}{2\hbar}\int\int W\left(\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right)d\tau d\sigma\right\}] \\ &= \left(\frac{1}{2\left(\cos\Omega\left(t_2-t_1\right)\right)}\right)^{\frac{3}{2}} \int D\left[\vec{r}\left(\tau\right)\right] \exp\left(\frac{i}{\hbar}S\right), \end{aligned} \tag{4.48}$$

where S is the action of the system and we have set the propagator starting from $\vec{r}_1$ at $t_1 = 0$ to $\vec{r}_2$ at $t_2 = t$.

4.2.4 The Approximated Propagator

In many path integral problems one cannot carry out the path integral easily. Thus we need an approximation method to handle this problem. In this research we apply the method given by Sa-yakanit [13, 24] and introduce the nonlocal harmonic trial action :

$$S_0\left(\omega\right) = \int_0^t d\tau\left(\frac{m}{2}\dot{\vec{r}}^{2}\left(\tau\right)-\frac{m}{2}\frac{\omega^2}{2t}\int_0^t d\sigma\left|\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right|^2\right), \tag{4.49}$$

where ω is a parameter to be determined. $S_0\left(\omega\right)$ is chosen to be translation invariant since we are not considering the localized states. The average propagator may be written in terms of the trial action as

$$G\left(\vec{r}_2, \vec{r}_1; t, \omega\right) = G_0\left(\vec{r}_2, \vec{r}_1; t, \omega\right)\left\langle \exp\frac{i}{\hbar}\left(S-S_0\right)\right\rangle_{S_0(\omega)}, \tag{4.50}$$

where the non-local harmonic oscillator propagator is defined by

$$G_0\left(\vec{r}_2, \vec{r}_1; t, \omega\right) = \left(\frac{1}{2\left(\cos \Omega t\right)}\right)^{\frac{3}{2}} \int D[\vec{r}\left(\tau\right)] \exp \frac{i}{\hbar} S_0\left(\omega\right), \tag{4.51}$$

and the average $\langle ... \rangle_{S_0(\omega)}$ is defined by

$$\langle O \rangle_{S_0(\omega)} = \frac{\int D[\vec{r}\left(\tau\right)] \exp\left(\frac{i}{\hbar} S_0\left(\omega\right)\right) O}{\int D[\vec{r}\left(\tau\right)] \exp\left(\frac{i}{\hbar} S_0\left(\omega\right)\right)}, \tag{4.52}$$

where O denotes a physical quantity to be averaged. Consequently, it is convenient to use the cumulant expansion and keep only the first order cumulant, Eq. (4.50) becomes

$$G_1\left(\vec{r}_2, \vec{r}_1; t, \omega\right) = G_0\left(\vec{r}_2, \vec{r}_1; t, \omega\right) \exp[\frac{i}{\hbar} \langle S - S_0 \rangle_{S_0(\omega)}]. \tag{4.53}$$

To obtain $G_1\left(\vec{r}_2, \vec{r}_1; t, \omega\right)$ we have to find $G_0\left(\vec{r}_2, \vec{r}_1; t, \omega\right)$ and the average $\langle S - S_0 \rangle_{S_0(\omega)}$. Since their kinetic energy terms are identical and always cancelled each other, the exponent $\langle S - S_0 \rangle_{S_0(\omega)}$ can be replaced by $\left\langle S^{'} - S_0^{'} \right\rangle_{S_0(\omega)}$, where the prime symbol in both actions mean excluding out the kinetic energy terms. For convenient, we shall denote $\left\langle S^{'} \right\rangle_{S_0(\omega)}$ and $\left\langle S_0^{'}\left(\omega\right) \right\rangle_{S_0(\omega)}$ as the averages of the second term respectively. So we can write the average propagator to be

$$G_1\left(\vec{r}_2, \vec{r}_1; t, \omega\right) = G_0\left(\vec{r}_2, \vec{r}_1; t, \omega\right) \exp\left[\frac{i}{\hbar}\left(\langle S' \rangle_{S_0(\omega)} - \langle S_0'\left(\omega\right) \rangle_{S_0(\omega)}\right)\right]. \tag{4.54}$$

From Ref. (25) the propagator $G_0\left(\vec{r}_2, \vec{r}_1; t, \omega\right)$ can be calculated exactly to be

$$G_0\left(\vec{r}_2, \vec{r}_1; t, \omega\right) = \left(\frac{1}{2\left(\cos \Omega t\right)}\right)^{\frac{3}{2}} \left(\frac{m}{2\pi i \hbar t}\right)^{\frac{3}{2}} \left(\frac{\omega t}{2 \sin \frac{1}{2}\omega t}\right)^{3}. \tag{4.55}$$

We now consider average $\langle S' \rangle_{S_0(\omega)}$ from Eq. (4.54)

$$\langle S' \rangle_{S_0(\omega)} = -2V^0 t + \frac{g^2}{2M\Omega^2}t + \frac{i}{2\hbar}\int_0^t \int_0^t d\tau d\sigma \left\langle W\left(\vec{r}(\tau) - \vec{r}(\sigma)\right)\right\rangle_{S_0(\omega)}, \quad (4.56)$$

where $W\left(\vec{r}(\tau) - \vec{r}(\sigma)\right)$ is given by Eq. (4.45) for Gaussian potentials. To evaluate this average $\langle S' \rangle_{S_0(\omega)}$ we expand it in powers of Fourier transforms.

$$W\left(\vec{r}(\tau) - \vec{r}(\sigma)\right) = \int \frac{d^3k}{(2\pi)^3} W(\vec{k}) \exp\left[i\vec{k}\cdot\left(\vec{r}(\tau) - \vec{r}(\sigma)\right)\right], \quad (4.57)$$

where $W(\vec{k})$ denotes the Fourier transform of $W\left(\vec{r}(\tau) - \vec{r}(\sigma)\right)$ which appears to be

$$W(\vec{k}) = \xi_L \exp\left[-\frac{L^2}{4}\vec{k}^2\right]. \quad (4.58)$$

Thus we can rewrite $\left\langle S' \right\rangle_{S_0(\omega)}$ as

$$\begin{aligned} \left\langle S' \right\rangle_{S_0(\omega)} &= -2V^0 t + \frac{g^2}{2M\Omega^2}t + \frac{i}{2\hbar}\int_0^t d\tau \int_0^t d\sigma \int \frac{d^3k}{(2\pi)^3} W(\vec{k}) \times \\ &\quad \left\langle \exp\left[i\vec{k}\cdot\left(\vec{r}(\tau) - \vec{r}(\sigma)\right)\right]\right\rangle_{S_\text{o}(\omega)}. \end{aligned} \quad (4.59)$$

The average of the above equation can be expanded in cumulants. Because the average is quadratic, only the first two cumulants survive (see appendix A). Hence

$$\left\langle S' \right\rangle_{S_0(\omega)} = -2V^0 t + \frac{g^2}{2M\Omega^2}t + \frac{i}{2\hbar}\int_0^t d\tau \int_0^t d\sigma \int \frac{d^3k}{(2\pi)^3} W(\vec{k}) \exp\left(a_1 + a_2\right), \quad (4.60)$$

where

$$a_1 = i\vec{k}.\left\langle \vec{r}(\tau) - \vec{r}(\sigma)\right\rangle_{S_0(\omega)}, \quad (4.61)$$

$$a_2 = -\frac{\vec{k}^2}{2}\left[\frac{1}{3}\left\langle\left(\vec{r}(\tau) - \vec{r}(\sigma)\right)^2\right\rangle_{S_0(\omega)} - \left\langle r(\tau) - r(\sigma)\right\rangle^2_{S_0(\omega)}\right]. \quad (4.62)$$

Substituting $W(\vec{k})$ into Eq. (4.60) and performing the $\vec{k}$-integration, we obtain

$$\langle S' \rangle_{S_0(\omega)} = -2V^0 t \ + \frac{g^2}{2M\Omega^2}t + \frac{i}{2\hbar}\xi_L \int_0^t d\tau \int_0^t d\sigma \left(\frac{1}{4\pi}\right)^{\frac{3}{2}} A^{-\frac{3}{2}} \exp\left(-\frac{B^2}{4A}\right), \tag{4.63}$$

where

$$A = \frac{1}{4}L^2 + \frac{1}{2}\left[\frac{1}{3}\left\langle (\vec{r}(\tau) - \vec{r}(\sigma))^2 \right\rangle_{S_0(\omega)} - \langle r(\tau) - r(\sigma)\rangle^2_{S_0(\omega)}\right], \tag{4.64}$$

and

$$B = \langle \vec{r}(\tau) - \vec{r}(\sigma)\rangle_{S_0(\omega)}. \tag{4.65}$$

4.2.5 Calculations of A, B and $\left\langle (\vec{r}(\tau) - \vec{r}(\sigma))^2 \right\rangle_{S_0(\omega)}$

Next we consider the average of the trial action $\langle \ S_0'(\omega)\rangle_{\ S_0(\omega)}$ (from Eq. (4.49); excluding the kinetic energy terms) which is easily written as

$$\langle \ S_0'(\omega)\rangle_{\ S_0(\omega)} = -\frac{m}{2}\frac{\omega^2}{2t}\int_0^t d\tau \int_0^t d\sigma \left\langle (\vec{r}(\tau) - \vec{r}(\sigma))^2 \right\rangle_{S_0(\omega)}. \tag{4.66}$$

From Eq. (4.63) and Eq. (4.66) all averages can be expressed in terms of the averages $\langle \ \vec{r}(\tau)\rangle_{\ S_0(\omega)}$and $\langle \vec{r}(\tau) - \vec{r}(\sigma)\rangle_{S_0(\omega)}$. Such averages can be obtained from the characteristic functional $\left\langle \exp\left(\frac{i}{\hbar}\int_0^t d\tau \vec{f}(\tau) \cdot \ \vec{r}(\tau)\right) \ \right\rangle_{\ S_0(\omega)}$ where $\vec{f}(\tau)$ is any arbitrary function of time. To be explicit, we write the characteristic functional as

$$\left\langle \exp\left(\frac{i}{\hbar}\int_0^t d\tau \vec{f}(\tau) \cdot \ \vec{r}(\tau)\right) \ \right\rangle_{\ S_0(\omega)} = \frac{\int D[\vec{r}(\tau)] \exp\left(\frac{i}{\hbar}\left[S_0(\omega) + \int_0^t d\tau \vec{f}(\tau) \,.\, \vec{r}(\tau)\right]\right)}{\int D[\vec{r}(\tau)] \exp\left(\frac{i}{\hbar}S_0(\omega)\right)}. \tag{4.67}$$

From Eq. (4.67), if the trial action $S_0(\omega)$ is quadratic, then the forced action is defined by

$$S_0^f(\omega) = S_0(\omega) + \int_0^t d\tau \vec{f}(\tau) \cdot \vec{r}(\tau). \tag{4.68}$$

From Feynman and Hibbs (1965), the characteristic functional can be carried out exactly as

$$\left\langle \exp\left(\frac{i}{\hbar}\int_0^t d\tau \vec{f}(\tau) \cdot \vec{r}(\tau)\right) \right\rangle_{S_0(\omega)} = \left(\frac{i}{\hbar}\left[S_{0,cl}^f - S_{0,cl}\right]\right), \tag{4.69}$$

where $S_{0,cl}^f$, $S_{0,cl}$ are the forced classical trial action and classical trial action corresponding to classical actions of $S_0^f(\omega)$ and $S_0(\omega)$ respectively. We have derived these in Appendix B. From the transition element given by Eq. (4.69) we can obtain the transition element of $\vec{r}(\tau)$ by differentiating with respect to $\vec{f}(\tau)$. The result is

$$\left\langle \vec{r}(\tau) \exp\left(\frac{i}{\hbar}\int_0^t d\tau \vec{f}(\tau) \cdot \ \vec{r}(\tau)\right) \right\rangle_{S_0(\omega)} = \frac{\delta S_{0,cl}^f}{\delta \vec{f}(\tau)} \left(\exp\left[\frac{i}{\hbar} S_{0,cl}^f - S_{0,cl}\right]\right). \tag{4.70}$$

Therefore, by evaluating both sides when $\vec{f}(\tau) \equiv 0$, we obtain

$$\langle \vec{r}(\tau) \rangle_{S_0(\omega)} = \left.\frac{\delta S_{0,cl}^f}{\delta \vec{f}(\tau)}\right|_{\vec{f}(\tau)\equiv 0}, \tag{4.71}$$

and further differentiating Eq. (4.69), we get the second derivative as

$$\langle \vec{r}(\tau) \cdot \vec{r}(\sigma) \rangle_{S_0(\omega)} = \left.\left[\frac{\hbar}{i}\frac{\delta^2 S_{0,cl}^{f\prime}}{\delta \vec{f}(\tau) \cdot \delta \vec{f}(\sigma)} + \frac{\delta S_{0,cl}^f}{\delta \vec{f}(\tau)} \cdot \frac{\delta S_{0,cl}^f}{\delta \vec{f}(\sigma)}\right]\right|_{\vec{f}(\tau)\equiv 0}. \tag{4.72}$$

Using Eqs. (4.60), (4.71) and (4.72), the first and second functional derivatives can be evaluated, and we can get A and B for $\tau > \sigma$

$$\begin{aligned}
\langle \vec{r}\,(\tau)\ \rangle_{S_0(\omega)} &= \left.\frac{\delta S'_{0,cl}}{\delta \vec{f}\,(\tau)}\right|_{\vec{f}(\tau)\equiv 0} \\
&= \frac{m\omega}{2\sin\omega t}\left[\frac{2\vec{r}_2}{m\omega}\left(\sin\omega\tau - 2\sin\frac{\omega\tau}{2}\sin\frac{\omega}{2}\,(t-\tau)\sin\frac{\omega t}{2}\right)\right. \\
&\quad \left. +\frac{2\vec{r}_1}{m\omega}\left(\sin\omega\,(t-\tau) - 2\sin\frac{\omega\tau}{2}\sin\frac{\omega}{2}\,(t-\tau)\sin\frac{\omega t}{2}\right)\right],
\end{aligned} \tag{4.73}$$

and

$$\begin{aligned}
\langle \vec{r}\,(\tau)\cdot\vec{r}\,(\sigma)\ \rangle_{S_0(\omega)} &= \left.\frac{\delta^2 S'_{0,cl}}{\delta \vec{f}\,(\tau)\cdot\delta\vec{f}\,(\sigma)}\right|_{\vec{f}(\tau)\equiv 0} \\
&= \frac{3\hbar}{im\omega\sin\omega t}\left[\sin\omega\,(t-\tau)\sin\omega\sigma - 4\sin\frac{\omega\sigma}{2}\times\right. \\
&\quad \left.\sin\frac{\omega}{2}\,(t-\tau)\sin\frac{\omega\tau}{2}\sin\frac{\omega}{2}\,(t-\tau)\right].
\end{aligned} \tag{4.74}$$

Substituting Eqs. (4.73) and (4.74) into (4.64) and (4.65), we obtain

$$A \equiv A\,(t, \tau-\sigma; \omega) = \left(\frac{L^2}{4} + \frac{i\hbar}{m\omega}\frac{\sin\frac{1}{2}\omega\,(\tau-\sigma)\cos\frac{1}{2}\omega\,(t-(\tau-\sigma))}{\sin\frac{1}{2}\omega t}\right), \tag{4.75}$$

and

$$B \equiv B\,(\vec{r}_2-\vec{r}_1; t, \tau, \sigma; \omega) = \frac{\sin\frac{1}{2}\omega\,(\tau-\sigma)\cos\frac{1}{2}\omega\,(t-(\tau+\sigma))}{\sin\frac{1}{2}\omega t}\,(\vec{r}_2-\vec{r}_1)\,. \tag{4.76}$$

Using Eqs. (4.73) and (4.74) and performing the integration in Eq. (4.66), we obtain

$$\begin{aligned}\left\langle S_0^{'}(\omega)\right\rangle_{S_0(\omega)} &= \frac{3}{2}i\hbar\left(\frac{\omega t}{2}\cot\frac{\omega t}{2}-1\right)\\ &\quad+\frac{m}{2}\left[\frac{\omega t}{2}\cot\frac{\omega t}{2}-\left(\frac{\omega t}{2}\csc\frac{\omega t}{2}\right)^2\right]\frac{\left|\vec{r}_2-\vec{r}_1\right|^2}{2t},\end{aligned} \tag{4.77}$$

and substituting Eqs. (4.63) and (4.77) into (4.54), we obtain the propagator as

$$\begin{aligned}G_1\left(\vec{r}_2,t;\vec{r}_1,\omega\right) &= \left(\frac{1}{2\left(\cos\Omega t\right)}\right)^{\frac{3}{2}}\left(\frac{m}{2\pi i\hbar t}\right)^{\frac{3}{2}}\left(\frac{\omega t}{2\sin\frac{\omega t}{2}}\right)^3\exp[\frac{3}{2}\left(\frac{\omega t}{2}\cot\omega t-1\right)\\ &\quad-\frac{i}{\hbar}2V^0t+\frac{i}{\hbar}\frac{g^2}{2M\Omega^2}t-\frac{\xi_L}{2\hbar^2}\left(\frac{L}{4}\right)^{\frac{3}{2}}\int_0^t\int_0^\tau d\tau d\sigma A^{-\frac{3}{2}}\exp\left(\frac{B^2}{4A}\right)\\ &\quad+\frac{i}{2\hbar}\left[\frac{\omega t}{2}\cot\frac{\omega t}{2}-\left(\frac{\omega t}{2}\csc\frac{\omega t}{2}\right)^2\right]\frac{m}{2}\frac{\left|\vec{r}_2-\vec{r}_1\right|^2}{t}],\end{aligned} \tag{4.78}$$

where A and B are Eq. (4.75) and Eq. (4.76), respectively.

4.3 The Density of States

From the Kane theory , the density of states per unit volume Ω' at energy E is defined as

$$\rho\left(E\right)=\frac{1}{\Omega'}\sum_i\delta\left(E-E_i\right), \tag{4.79}$$

where the sum is over the energy E_i and δ is the Dirac delta function. The Dirac delta function can be represented in terms of a transformed propagator. With the energy expansion formula of the propagator [18,30]

$$G\left(\vec{r}_2, t; \vec{r}_1, 0\right) = \sum_i \phi_i\left(\vec{r}_2\right)\phi_i^*\left(\vec{r}_1\right)\exp\left[-\frac{i}{\hbar}E_i t\right], \tag{4.80}$$

we have the trace of the propagator of the form

$$TrG\left(\vec{r}_2, t; \vec{r}_1, 0\right) = \sum_i \exp\left[-\frac{i}{\hbar}E_i t\right]. \tag{4.81}$$

Taking Fourier transforms of both sides, the above equation leads to

$$\int_{-\infty}^{+\infty} dtTrG\left(\vec{r}_2, t; \vec{r}_1, 0\right)\exp\left[\frac{i}{\hbar}Et\right] = 2\pi\hbar\sum_i \delta\left(E - E_i\right). \tag{4.82}$$

Note that the following identities,

$$\delta\left(a\right) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} dx \exp[iax], \tag{4.83}$$

and

$$\delta\left(\frac{a}{b}\right) = b\delta\left(a\right), \tag{4.84}$$

are used in Eq. (4.82). Now the required relation between the density of states and the propagator can be obtained by comparing Eqs. (4.79) and (4.82), then we have

$$\rho\left(E\right) = \frac{1}{2\pi\hbar}\frac{1}{\Omega'}\int_{-\infty}^{+\infty} dtTrG\left(\vec{r}_2, \vec{r}_1, t, 0\right)\exp\left[\frac{i}{\hbar}Et\right]. \tag{4.85}$$

Because of translational invariant of the propagator, hence

$$TrG\left(\vec{r}_2, \vec{r}_1, t, 0\right) = \Omega' G\left(0, 0; t, 0\right). \tag{4.86}$$

From Eq. (4.86) the density of states can be writen to be

$$\rho\left(E\right)=\frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty}dtG\left(0,0;t,0\right)\exp\left[\frac{i}{\hbar}Et\right]. \tag{4.87}$$

.

4.3.1 Approximated Density of States

We obtained the DOS in first cumulant approximation by substituting Eq. (4.78) in Eq. (4.87)

$$\begin{aligned}\rho_1\left(E\right) \;=\; & \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty}dt\left(\frac{1}{2\left(\cos\Omega t\right)}\right)^{\frac{3}{2}}\left(\frac{m}{2\pi i\hbar t}\right)^{\frac{3}{2}}\left(\frac{\omega t}{2\sin\frac{\omega t}{2}}\right)^{3}\exp[\frac{3}{2}\left(\frac{\omega t}{2}\cot\omega t-1\right) \\ & -\frac{i}{\hbar}2V^0t+\frac{i}{\hbar}\frac{g^2}{2M\Omega^2}t+\frac{i}{\hbar}Et-\frac{\xi_L}{2\hbar^2}\left(\frac{L}{4}\right)^{\frac{3}{2}}\int_0^t\int_0^\tau d\tau d\sigma A\left(t,\tau-\sigma;\omega\right)^{-\frac{3}{2}}].\end{aligned} \tag{4.88}$$

Now using the property

$$A(t,\tau,\sigma;\omega)=A\left(t,t-\left(\tau-\sigma\right);\omega\right), \tag{4.89}$$

the double integral in Eq. (4.88) can be reduced to a single integral:

$$\int_0^t\int_0^t d\tau d\sigma A\left(t,\tau-\sigma;\omega\right)^{-\frac{3}{2}}=t\int_0^t dxA\left(t,x;\omega\right)^{-\frac{3}{2}}, \tag{4.90}$$

where

$$A\left(t,x;\omega\right)=\frac{L^2}{4}+\frac{i\hbar}{m\omega}\frac{\sin\frac{\omega}{2}x\sin\frac{\omega}{2}\left(t-x\right)}{\sin\frac{\omega t}{2}}. \tag{4.91}$$

Thus we can rewrite Eq. (4.88) to be

$$\begin{aligned}\rho_1\left(E\right) &= \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty}dt\left(\frac{1}{2\left(\cos\Omega t\right)}\right)^{\frac{3}{2}}\left(\frac{m}{2\pi i\hbar t}\right)^{\frac{3}{2}}\left(\frac{\omega t}{2\sin\frac{\omega t}{2}}\right)^{3}\exp[\frac{3}{2}\left(\frac{\omega t}{2}\cot\omega t-1\right) \\ &\quad -\frac{i}{\hbar}2V^0 t+\frac{i}{\hbar}\frac{g^2}{2M\Omega^2}t+\frac{i}{\hbar}Et-\frac{\xi_L}{2\hbar^2}\left(\frac{L}{4}\right)^{\frac{3}{2}}t\int_0^t dxA\left(t,x;\omega\right)^{-\frac{3}{2}}].\end{aligned} \tag{4.92}$$

Since the density of states are complicated to calculate, we shall consider the density of states in another energy limit which is easy to solve. In this thesis we are interested in the low-energy limit.

4.3.2 Low-Energy Limit

In the low-energy limit, we consider the system at large imaginary time ($it \rightarrow \infty$). This is called the "ground state " approximation. Hence, we are able to approximate

$$\cos\Omega t \cong \frac{1}{2}\exp\left[i\Omega t\right], \tag{4.93}$$

$$\sin\frac{\omega t}{2} \cong \frac{1}{2i}\exp\left[\frac{i\omega t}{2}\right], \tag{4.94}$$

$$\frac{\omega t}{2}\cot\omega t-1 \cong \frac{i\omega t}{2}, \tag{4.95}$$

$$\frac{\sin\frac{\omega}{2}x\sin\frac{\omega}{2}\left(t-x\right)}{\sin\frac{\omega t}{2}} \cong \frac{1}{2i}. \tag{4.96}$$

Thus Eq. (4.92) becomes

$$\begin{aligned}\rho_1\left(E\right) &= \frac{1}{2\pi\hbar}\int_{-\infty}^{+\infty} dt\left(\frac{m}{2\pi\hbar}\right)^{\frac{3}{2}}\omega^3\left(it\right)^{\frac{3}{2}}\exp[-\frac{i}{\hbar}\left(-E+\frac{3}{4}\hbar\omega\right.\\ &\left.+\frac{1}{2}\hbar\Omega+2V^0-\frac{g^2}{2M\Omega^2}\right)t-\frac{\xi_L}{4\hbar^2}\frac{t^2}{\left(1+\frac{4E_L}{E_\omega}\right)^{\frac{3}{2}}}],\end{aligned}\tag{4.97}$$

where $E_\omega = \hbar\omega$ and $E_L = \frac{\hbar^2}{2mL^2}$ is the correlation energy (the kinetic energy of localization over a distance L, the correlation length of the random potential fluctuations). By using the tabulated formula (Gradshteyn and Ryzhik)[31]

$$\int_{-\infty}^{+\infty} dt\left(it\right)^p\exp\left(-\beta^2t^2-iqt\right) = 2^{-\frac{p}{2}}\sqrt{\pi}\beta^{-p-1}\exp\left(-q^2/8\beta^2\right)D_p\left(q/\beta\sqrt{2}\right)\ ,\tag{4.98}$$

where $D_p\left(z\right)$ is the parabolic cylinder function, Eq. (4.97) can be rewritten as

$$\rho_1\left(E\right) = \frac{1}{2\pi\hbar}\left(\frac{m}{2\pi\hbar}\right)^{\frac{3}{2}}\omega^3 2^{-\frac{3}{4}}\sqrt{\pi}\beta^{-\frac{5}{2}}\exp\left(-q^2/8\beta^2\right)D_{\frac{3}{2}}\left(q/\beta\sqrt{2}\right)\ ,\tag{4.99}$$

where

$$\left.\begin{array}{c} p=\frac{3}{2} \\ q=\frac{1}{\hbar}\left(\frac{3}{4}\hbar\omega+E_0-E\right) \\ E_0=\frac{1}{2}\hbar\Omega+2V^0-\frac{g^2}{2M\Omega^2} \\ \beta^2=\frac{\xi_L}{4\hbar^2}\left(1+\frac{4E_L}{E_\omega}\right)^{-\frac{3}{2}} \end{array}\right\}\ .\tag{4.100}$$

We are now interested in the case of the low-energy limit of the density of states. There are two equivalent ways, following Halperin and Lax (1974), [24], by letting $E \to -\infty$ ($q \to +\infty$) or keeping E constant and reducing the magnitude of fluctuation by letting $\xi \to 0$. The asymptotic properties of the parabolic-cylinder function is

$$D_p\left(z\right) = \exp\left(-\frac{1}{4}z^2\right) z^p \left(1 - \frac{p\left(p-1\right)}{2}\frac{1}{z^2} + \ ...\right). \qquad (4.101)$$

For $z \rightarrow \infty$, keeping only the first order, Eq. (4.99) becomes

$$\begin{aligned} \rho_1\left(E\right) &= \frac{1}{2\pi\hbar}\left(\frac{m}{2\pi\hbar}\right)^{\frac{3}{2}} \omega^3 2^{-\frac{3}{4}}\sqrt{\pi}\beta^{-4}q^{\frac{3}{2}}\exp\left(-q^2/4\beta^2\right) \\ &= \left[\left(E_L/L\right)^3/\xi_L^2\right] a\left(\nu, x\right)\exp\left[-E_L^2 b\left(\nu, x\right)/2\xi_L\right]. \qquad (4.102) \end{aligned}$$

where the dimensionless variational parameter, $x = E_\omega/E_L$, energy normalization with respect to the correlation energy $\nu = \left(E_0 - E\right)/E_L$

$$a\left(\nu, x\right) = \left(\frac{3}{4}x + \nu\right)^{\frac{3}{2}} \left(4 + x\right)^3/8\sqrt{2}\ , \qquad (4.103)$$

and

$$b\left(\nu, x\right) = \left(\frac{3}{4}x + \nu\right)^2 \left(1 + 4/x\right)^{\frac{3}{2}}. \qquad (4.104)$$

At the moment the parameter ω introduced in the trial action S_0 has not yet been determined.

4.3.3 The Variational Equation

In order to adjust the variational parameter x, it is introduced in the trial action. We know that the justification of this procedure was given by Lloyd and Best (1975) [28]. Lloyd and Best have shown that, the exact density of states is the function which maximizes the pressure $P(E)$ of the system

$$P(E) \equiv \int\limits_{-\infty}^{E} dE^{'} \int\limits_{-\infty}^{E^{'}} dE^{''} \rho\left(E\right) = \int\limits_{-\infty}^{E} dE^{'} \left(E - E^{'}\right) \rho\left(E^{'}\right). \tag{4.105}$$

This means that, for calculating the approximated density of states, the variational parameter should be that the pressure function reaches its maximum value. Therefore, the variational equation is obtained in the form

$$\frac{\partial}{\partial x} P(E.x) = 0 \ , \tag{4.106}$$

or

$$\int\limits_{-\infty}^{E} dE^{'} \left(E - E^{'}\right) \frac{\partial}{\partial x} \rho\left(E^{'}; x\right) = 0. \tag{4.107}$$

The asymptotic behavior of this variational principle is to maximize the density of states, which is so-called the Halerin and Lax's variational principle (1966,1967). That is

$$\frac{\partial}{\partial x} \rho\left(E^{'}; x\right) = 0. \tag{4.108}$$

In Halperin and Lax's work, this equation has been reduced to a more simple one by assuming that the prefactor of the exponential varies slowly with respect to the exponential term. The left-hand side of Eq. (4.108) then becomes a partial derivative of the exponent of the density of states. In symbol

$$\frac{\partial}{\partial x} b\left(\nu, x\right) = 0. \tag{4.109}$$

From Eq. (4.102), it is clear that when $\xi_L \to 0$, the exponential factor becomes very sensitive to the choice of x while the prefactor is not. Thus the best choices of x with using Eq. (4.109) found to satisfy the equation

$$x^2 + x - 4\nu = 0, \tag{4.110}$$

by keeping only the positive root

$$x = \frac{1}{2}\left[(1 + 16\nu)^{1/2} - 1\right], \tag{4.111}$$

and then substituting Eq. (4.111) into both $a(\nu, x)$ and $b(\nu, x)$, we obtain

$$a(\nu) = \left[(1 + 16\nu)^{1/2} - 1\right]^{3/2}\left[(1 + 16\nu)^{1/2} + 7\right]^{9/2} / 2^{12} 2^{1/2} \pi^2, \tag{4.112}$$

and

$$b(\nu) = \left[(1 + 16\nu)^{1/2} - 1\right]^{1/2}\left[(1 + 16\nu)^{1/2} + 7\right]^{7/2} / 2^8, \tag{4.113}$$

respectively. By introducing the dimensionless quantity

$$\xi' = \frac{\xi_L}{E_L^2}, \tag{4.114}$$

we can rewrite the density of states in the final form

$$\rho_1(\nu) = \left[1/E_L L^3 \xi'^2\right] a(\nu) \exp\left[-b(\nu)/2\xi'\right]. \tag{4.115}$$

4.4 The Spectral Density Function

The spectral density function for the electronic excitation in a random potential from Ref. (34) can be adoped to

$$A\left(\vec{K},E\right)=\frac{1}{\Omega'}\left\langle\sum_i\left|\int d\vec{r}e^{i\vec{K}\cdot\vec{r}}\phi_i\left(\vec{r}\right)\right|^2\delta\left(E-E_i\right)\right\rangle\ , \tag{4.116}$$

where $\phi_i\left(\vec{r}\right)$ is the wave function of the i^{th} electronic excitation state with a corresponding energy E_i, $\vec{K}$ is the excitation wave vector and Ω' is the normalization volume. Eq. (4.116) is averaged over all possible configurations of the random potential fluctuations ($\langle\ldots\rangle$ indicating an average over the statistical ensemble). We are now interested in calculating the optical density function of which the wave function for electronic transition is in the eV range while molecular size is of order the Angstrom unit. Then we have

$$\vec{K}\cdot\vec{r}\sim 1eV\times 1A^{\circ}\frac{1}{\hbar c}\sim\frac{1}{2000}\ll 1, \tag{4.117}$$

so that it is reasonable to replace

$$e^{\vec{K}\cdot\vec{r}}\approx 1. \tag{4.118}$$

This is called the electric dipole approximation. Thus Eq. (4.116) becomes

$$A\left(E\right)=\frac{1}{\Omega'}\left\langle\sum_i\left|\int d\vec{r}\phi_i\left(\vec{r}\right)\right|^2\delta\left(E-E_i\right)\right\rangle. \tag{4.119}$$

In the low-energy range we shall be interested only in the ground state contribution to the density of states (since we have taken the limit of large imaginary time in obtaining it), and we can consider that the main contribution to the above equation comes from the ground state wave function in a harmonic potential well, i.e.,

$$\phi_0\left(\vec{r}\right) = \left(\frac{m\omega}{\pi\hbar}\right)^{\frac{3}{4}} \exp\left[-\left(\frac{m\omega}{2\hbar}\right)\vec{r}^{\ 2}\right]. \tag{4.120}$$

This is a Gaussian envelope function. We now introduce γ which is the Gaussian parameter:

$$\gamma = \frac{m\omega}{2\hbar} = \frac{x}{4L^2}\ , \tag{4.121}$$

where x is a variational parameter. Substituting Eq. (4.121) into Eq. (4.120), we get

$$\phi_0\left(\vec{r}\right) = \left(\frac{2\gamma}{\pi}\right)^{\frac{3}{4}} \exp\left[-\gamma\vec{r}^{\ 2}\right]. \tag{4.122}$$

By taking the factor $\left|\int d\vec{r}\phi_i\left(\vec{r}\right)\right|^2$out of the functional integral in Eq. (4.119) and performing the integral over $d\vec{r}$, the remaining functional integral is, by definition, the density of states. We obtain

$$A\left(\nu\right) = \left|\int d\vec{r}\phi_0\left(\vec{r}\right)\right|^2 \rho_1\left(\nu\right) = \left(\frac{2\pi}{\gamma}\right)^{\frac{3}{2}} \rho_1\left(\nu\right). \tag{4.123}$$

Substituting Eq. (4.121) and Eq. (4.111) into the above equation, we obtain the final result of our spectral density function

$$A\left(\nu\right) = \left(\frac{16\pi L^2}{\left(1+16\nu\right)^{1/2}-1}\right)^{\frac{3}{2}} \rho_1\left(\nu\right)\ , \tag{4.124}$$

where $\rho_1\left(\nu\right)$ is given in Eq. (4.115).

Chapter 5

Discussions and Conclusions

In this thesis we have developed a quantum mechanical description of the spectral density function of a single electronic excitation in randomly distributed identical polymer chains. The proposed method is based on the path integral technique for the calculation of the density of states of disordered systems. In this model we consider a long linear polymer chain under the influence of lattice vibration, nearest neighbor intermolecular coupling and assume that each monomer has only a single excited electronic state.

The model system is described by the polymer Hamiltonian in tight binding approximation which consists of a sum over electronic and vibrational lattices where we assume absence of internal vibration. The starting point of our calculation is the time-dependent Schrödinger equation using delocalization of the excitation state vector (Eq. (4.2)).

In the absence of internal vibrations, we assume the quantities ε_m and V_{mn} to be a function only of the lattice coordinates. In the adiabatic limit the lattice coordinates move slower than the electronic coordinates. Thus the quantity ε_m and V_{mn} can be expanded about the equilibrium position.

For a one-dimensional linear chain, the interaction of the system are assumed to have only nearest neighbor interactions (excluded volume effect) only, i.e. $n = m \pm 1$.

Upon introducing of the electronic excitation-lattice vibration coupling , $\overrightarrow{g}$, and approximating the vibrational lattice Hamiltonian to be harmonic (Eq. (4.21)) we show that in the continuous limit the discrete model can be formulated in terms of the Feynman path integrals by using coordinate space matrix elements of the time development operator (Hamiltonian path integral). Thus the "propagator" (or kernel) represents the probability amplitude that a single particle (electronic excitation) produced at a position $\vec{r}_1$, $\vec{\zeta}_1$ at time t_1 "propagates" to another position $\vec{r}_2$, $\vec{\zeta}_2$ at time t_2.

In this system, the path integral is a "functional form" containing more than one variable, which cannot be separated because it contains a coupling term between coordinates $\vec{r}$ and $\vec{\zeta}$. For convenience, the coordinates $\vec{\zeta}$ can be eliminated by integration over the variable $\vec{\zeta}$ giving the functional $T[\vec{r}(\tau)]$. From Eq. (4.39) one can see that the functional $T[\vec{r}(\tau)]$ is a path integral of the forced harmonic oscillator. For the external oscillator (this is a force function) the electronic excitation-monomer vibration coupling $\vec{g}[\vec{r}(\tau)]$ is assumed and we can calculate exactly [21] .

In the path integral method, it is easy to include randomness in the system. We study the case of nearest neighbor interaction V^0, consider the electronic excitation-monomers vibration coupling $\vec{g}[\vec{r}(\tau)]$ as a constant and introduce randomness into the system. Specifically we study the case where the electronic exciton energy $\varepsilon^0(\vec{r})$ is distributed in a Gaussian random fashion with finite correlation length L, in order to calculate the average propagator with respect to probability of $\varepsilon^0(\vec{r})$ $(P[\varepsilon^0(\vec{r})])$. Then we obtain the propagator which includes randomness (Eq. (4.48)).

We approximate the propagator by introducing a trial action S_0 based on the harmonic oscillator potential. This is equivalent to assuming that all the fluctuating potentials have the same quadratic shape. Thus, we need to approximate the full action by a nonlocal harmonic oscillator (Eq. (4.49)). The average propagator can be rewritten in terms of the trial action, using the path integral normalization, corresponding to a zero-order approximation G_0 and keeping only the first-order term in the cumulant expansion, the propagator in the first cumulant approximation G_1 is obtained.

The DOS is given by the Fourier transform of the diagonal path of the configuration averaged one-particle propagator. The DOS in the first-cumulant approximation was derived by Sa-yakanit [22] and generalized for the case of d-dimensions in Ref. (30), which led to the optical density function.

Considering the ground state contribution to the DOS in the limit of large imaginary time (Eq. (4.97)) and performing the t-integration using Gradshteyn and Ryzhik [31], we can rewrite the DOS in its asymptotic form which results in the pre-exponential factor $a\left(\nu, x\right)$ and the factor in the exponent $b\left(\nu, x\right)$ being obtained. We introduce the dimensionless variational parameter $x = \frac{E_\omega}{E_L}$ and energy normalizing with respect to the correlation energy $\nu = \frac{E_0 - E}{E_L}$. We have minimized the DOS exponent and obtained the variational parameter x. Keeping only the positive root and introducing the dimensionless disorder parameter, $\xi' = \frac{\xi_L}{E_L^2}$, we obtain the final DOS in the form of $a\left(\nu\right)$ and $b\left(\nu\right)$ defined in (Eq. (4.115)).

Since we are interested in the spectral density function, we wish to calculate the spectral density function that represents the case $\vec{K} \cdot \vec{r} << 1$ ($e^{\vec{K} \cdot \vec{r}} \approx 1$; dipole approximation) in the low-energy (Eq. (4.119)). Introducing the ground-state electronic excitation wave function in a harmonic potential well as the Gaussian envelope function and using the Gaussian parameter γ, we can take the factor $\left| \int d\vec{r} \phi_0 \left(\vec{r}\right) \right|^2$out of the functional integral. The remaining integral is, by definition, the density of states $\rho(\nu)$. So we have Eq. (4.124) as the final result for the spectral density.

From Eq. (4.124), we are interested in the spectral density function in the low-energy range ($\frac{E-E_0}{E_L} \to -\infty$, or, equivalently, $\nu \gg 1$). For the limiting case, $\nu \gg 1$, we have the spectral density function

$$A(\nu) = \frac{2^{\frac{5}{2}}\nu^{\frac{9}{4}}}{E_L \xi'^2 \sqrt{\pi}} \exp\left[-\frac{\nu^2}{2\xi'}\right]$$

which is dependent on the dimensionless energy ν and dimensionless disorder parameter ξ'. In order to plot the spectral density function $A(\nu)$ which is a function of the dimensionless energy ν, we have fixed the correlation energy E_L and varied the dimensionless energy ν for any values of dimensionless disorder parameter ξ'. We obtain the asymmetric line shape shown in Fig. (5.1)

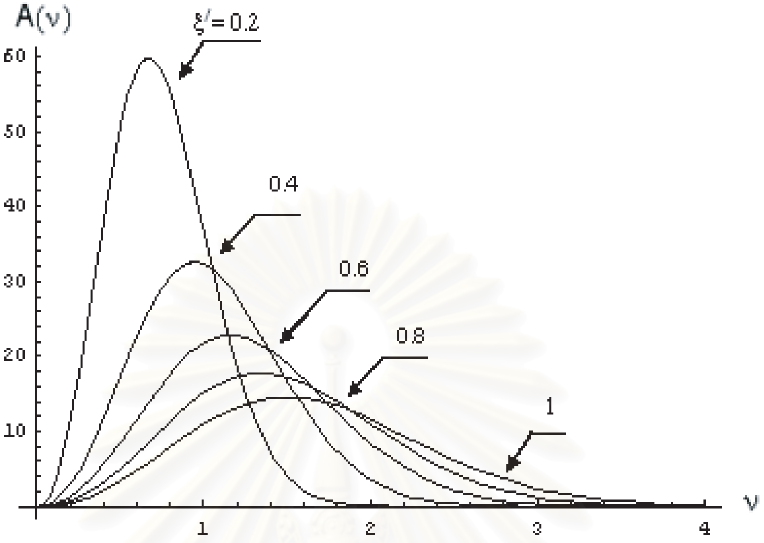

Fig. (5.1) Plot of the spectral density functional $A(\nu)$ v.s. dimensionless energy $\nu = \frac{E_0 - E}{E_L}$ and dimensionless disorder parameters $\xi' = 0.2$, 0.4, 0.6, 0.8 and 1. The plot are calculated using the path-integral method for the low energy limit of the spectrum and assuming a constant correlation energy $E_L = 1\ meV$.

In Fig. (5.1) the plot of the spectral density functional of the dimensionless energy with varying disorder parameters are shown for the low-energy limit. The electronic excitation absorption line shape influenced by the random potential are broad and decreased in magnitude of the peak with increasing disorder. Thus, the width of the electronic excitation line shape is directly proportional to the fluctuations (ξ': disorder parameter) of the system. If the width is wide (narrow) then there is high (low) fluctuation.

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Appendices

Appendix A:
Approximated cumulant

We approximate $\left\langle \exp\left[i\vec{k}\cdot\left(\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right)\right]\right\rangle_{S_0(\omega)}$ by using cumulant expansion,

$$\left\langle \exp\left[a\right]\right\rangle = \exp\left[\left\langle a\right\rangle + \frac{1}{2!}\left(\left\langle a^2\right\rangle - \left\langle a\right\rangle^2\right) + \frac{1}{3!}\left[...\right] + ...\right]. \tag{A.1}$$

Considering only up to the second order, we therefore have

$$\begin{aligned}\left\langle \exp\left[i\vec{k}\cdot\left(\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right)\right]\right\rangle &= \exp\left[\left\langle i\vec{k}\cdot\left(\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right)\right\rangle\right. \\ &\quad + \frac{1}{2!}\left\{\left\langle\left(i\vec{k}\cdot\left(\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right)\right)^2\right\rangle\right. \\ &\quad \left.\left. - \left\langle\left(i\vec{k}\cdot\left(\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right)\right)\right\rangle^2\right\}\right]. \end{aligned} \tag{A.2}$$

We are seperating (A.2) into 3 terms and manipulating these terms as follows

$$a_1 = \left\langle i\vec{k}\cdot\left(\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right)\right\rangle = i\vec{k}\cdot\left\langle\left(\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right)\right\rangle \tag{A.3}$$

and

$$\begin{aligned}\left\langle\left(i\vec{k}\cdot\left(\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right)\right)^2\right\rangle &= -\frac{\vec{k}^2}{3}\left\langle\left(\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right)^2\right\rangle \\ &\quad -2k_xk_y\left\langle\left(r_x\left(\tau\right)-r_x\left(\sigma\right)\right)\left(r_y\left(\tau\right)-r_y\left(\sigma\right)\right)\right\rangle \\ &\quad -2k_xk_z\left\langle\left(r_x\left(\tau\right)-r_x\left(\sigma\right)\right)\left(r_z\left(\tau\right)-r_z\left(\sigma\right)\right)\right\rangle \\ &\quad -2k_yk_z\left\langle\left(r_y\left(\tau\right)-r_y\left(\sigma\right)\right)\left(r_z\left(\tau\right)-r_z\left(\sigma\right)\right)\right\rangle \end{aligned} \tag{A.4}$$

and the last term is

$$\begin{aligned}\left\langle\left(i\vec{k}\cdot\left(\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right)\right)\right\rangle^{2} &= -\vec{k}^{2}\left\langle\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right\rangle^{2}\\ &\quad+2k_{x}k_{y}\left\langle r_{x}\left(\tau\right)-r_{x}\left(\sigma\right)\right\rangle\left\langle r_{y}\left(\tau\right)-r_{y}\left(\sigma\right)\right\rangle\\ &\quad+2k_{x}k_{z}\left\langle r_{x}\left(\tau\right)-r_{x}\left(\sigma\right)\right\rangle\left\langle r_{z}\left(\tau\right)-r_{z}\left(\sigma\right)\right\rangle\\ &\quad+2k_{y}k_{z}\left\langle r_{y}\left(\tau\right)-r_{y}\left(\sigma\right)\right\rangle\left\langle r_{z}\left(\tau\right)-r_{z}\left(\sigma\right)\right\rangle.\end{aligned} \tag{A.5}$$

From (A.3) and (A.4), we give

$$C_{x}=r_{x}\left(\tau\right)-r_{x}\left(\sigma\right), \tag{A.6}$$

$$C_{y}=r_{y}\left(\tau\right)-r_{y}\left(\sigma\right), \tag{A.7}$$

$$C_{z}=r_{z}\left(\tau\right)-r_{z}\left(\sigma\right). \tag{A.8}$$

Therefore, we have

$$\begin{aligned}&\left\langle\left(i\vec{k}\cdot\left(\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right)\right)^{2}\right\rangle-\left\langle\left(i\vec{k}\cdot\left(\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right)\right)\right\rangle^{2}\\ =\;&-\frac{\vec{k}^{2}}{3}\left\langle\left(\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right)^{2}\right\rangle+\vec{k}^{2}\left\langle\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right\rangle^{2}-2k_{x}k_{y}\left[\left\langle C_{x}C_{y}\right\rangle-\left\langle C_{x}\right\rangle\left\langle C_{y}\right\rangle\right]\\ &-2k_{x}k_{z}\left[\left\langle C_{x}C_{z}\right\rangle-\left\langle C_{x}\right\rangle\left\langle C_{z}\right\rangle\right]-2k_{y}k_{z}\left[\left\langle C_{y}C_{z}\right\rangle-\left\langle C_{y}\right\rangle\left\langle C_{z}\right\rangle\right]\\ =\;&-\frac{\vec{k}^{2}}{3}\left\langle\left(\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right)^{2}\right\rangle+\vec{k}^{2}\left\langle\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right\rangle^{2}\end{aligned} \tag{A.9}$$

where

$$\left\langle C_{x}C_{y}\right\rangle=\left\langle C_{x}C_{y}\right\rangle=\left\langle C_{x}C_{y}\right\rangle=0. \tag{A.10}$$

See Feynman and Hibbs [21]. Hence, we have

$$a_{2}=-\frac{1}{2}\vec{k}^{2}\left[\frac{1}{3}\left\langle\left(\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right)^{2}\right\rangle-\left\langle\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right\rangle^{2}\right]. \tag{A.11}$$

Appendix B:
Find trial action

In this appendix, we find $S_{0,cl}^{f}$ and $S_{0,cl}$ which are used to evaluate $\langle \vec{r}(\tau) \rangle_{S(0)}$ and $\langle \vec{r}(\tau) \cdot \vec{r}(\sigma) \rangle_{S_0(\omega)}$. In order to obtain $S_{0,cl}^{f}$ and $S_{0,cl}$, we have to find the classical path by considering a variation on $S_0^f(\omega)$

$$\begin{aligned} S_0^f(\omega) &= \int_0^t d\tau \; L\left(\dot{\vec{r}}(\tau), \vec{r}(\tau), t\right) \\ &= \int_0^t d\tau \left[\frac{m}{2} \dot{\vec{r}}^{\,2}(\tau) - \frac{m}{2}\left(\frac{\omega^2}{2t}\right) \int_0^t d\sigma \left| \vec{r}(\tau) - \vec{r}(\sigma) \right|^2 + \vec{f}(\tau) . \vec{r}(\tau) \right]. \end{aligned} \tag{B.1}$$

At the extremum point,

$$\begin{aligned} \delta S_0^f(\omega) = \int_0^t d\tau \Big[& m\dot{\vec{r}}(\tau)\,\delta\dot{\vec{r}}(\tau) + \vec{f}(\tau) . \delta\vec{r}(\tau) \\ & - \frac{m\omega^2}{2t} \int_0^t d\sigma \left(\vec{r}(\tau) - \vec{r}(\sigma)\right) \cdot \delta\left(\vec{r}(\tau) - \vec{r}(\sigma)\right) \Big] \end{aligned} \tag{B.2}$$

where $\delta\dot{\vec{r}}(\tau) = \delta\left[\frac{d\vec{r}(\tau)}{dt}\right] = \frac{d\delta\vec{r}(\tau)}{dt}$ and $\delta\vec{r}(t) = \delta\vec{r}(0) = 0$. Thus

$$\delta S_0^f(\omega) = -\int_0^t d\tau \left[m\ddot{\vec{r}}(\tau) + \frac{m\omega^2}{t} \int_0^t d\sigma \left(\vec{r}(\tau) - \vec{r}(\sigma)\right) - \vec{f}(\tau) \right] . \delta\vec{r}(\tau) = 0. \tag{B.3}$$

Therefore, we can obtain a classical equation

$$\ddot{\vec{r}}_c(\tau) + \omega^2 \vec{r}_c(\tau) = \frac{\omega^2}{t} \int_0^t d\sigma \vec{r}_c(\sigma) + \frac{\vec{f}(\tau)}{m} \tag{B.4}$$

and we can solve Eq. (B.4) by using the Green function method

$$g\left(\tau,\sigma\right)=-\frac{1}{\omega\sin\omega t}\left[\sin\omega\left(t-z\right)\sin\omega\sigma\ \Theta\left(\tau-\sigma\right)+\sin\omega\left(t-\sigma\right)\sin\omega\tau\ \Theta\left(\sigma-\tau\right)\right] \tag{B.5}$$

where Θ is the Heaviside step function and we use the boundary condition $\vec{r}\left(0\right)=\vec{r}_1$ and $\vec{r}\left(t\right)=\vec{r}_2$. From Eq. (B.4), we use Eq. (B.5) and get

$$\vec{r}_c\left(\tau\right)=\vec{r}_h\left(\tau\right)+\int_0^t\left[\frac{\omega^2}{t}\int_0^t d\sigma'\vec{r}_c\left(\sigma'\right)+\frac{\vec{f}\left(\sigma'\right)}{m}\right]g\left(\tau,\sigma\right)d\sigma \tag{B.6}$$

where $\vec{r}_h\left(\tau\right)$ is the homogeneous solution of Eq. (B.4). Integrating both sides of Eq. (B.6) and adding the same term together, we obtain

$$\begin{aligned}\int_0^t d\sigma\vec{r}_c\left(\tau\right) &= \frac{1}{1-\frac{\omega^2}{t}\int_0^t d\tau\int_0^t d\sigma g\left(\tau,\sigma\right)}\left[\int_0^t\vec{r}_h\left(\tau\right)d\tau+\int_0^t d\sigma\int_0^t d\tau\frac{\vec{f}\left(\sigma\right)}{m}g\left(\tau,\sigma\right)\right] \qquad \text{(B.7)}\\ &= \frac{t}{2\sin\omega t/2}\left[\left(\vec{r}_1+\vec{r}_2\right)\sin\frac{\omega t}{2}+\frac{2}{m\omega}\int_0^t\vec{f}\left(\sigma\right)\left(\sin\frac{\omega\sigma}{2}\sin\frac{\omega\left(\sigma-\tau\right)}{2}\right)d\sigma\right] \qquad \text{(B.8)}\end{aligned}$$

and

$$\int_0^t d\sigma\int_0^t d\tau\frac{\vec{f}\left(\sigma\right)}{m}g\left(\tau,\sigma\right)=\frac{2}{m\omega^2\cos\omega t/2}\int_0^t d\sigma\vec{f}\left(\sigma\right)\left(\sin\frac{\omega\sigma}{2}\sin\frac{\omega\left(\sigma-\tau\right)}{2}\right). \tag{B.9}$$

Substituting Eq. (B.8) and Eq. (B.9) into Eq. (B.6), we have

$$\begin{aligned}\vec{r}_c\left(\tau\right) &= \frac{1}{\sin\omega t}\left(\vec{r}_2\sin\omega\tau+\vec{r}_1\sin\omega\left(t-\tau\right)\right)-\frac{2}{\sin\omega t}\left(\sin\frac{\omega\tau}{2}\sin\frac{\omega\left(t-\tau\right)}{2}\right)\\ &\quad\times\left[\left(\vec{r}_2+\vec{r}_1\right)\sin\frac{\omega t}{2}-\frac{2}{m\omega}\int_0^t d\sigma\vec{f}\left(\sigma\right)\left(\sin\frac{\omega\sigma}{2}\sin\frac{\omega\left(\tau-\sigma\right)}{2}\right)\right]\\ &\quad+\int_0^t\frac{\vec{f}\left(\sigma\right)}{m}g\left(\sigma,\tau\right)d\sigma.\end{aligned} \tag{B.10}$$

The forced classical trial action $S^{f}_{s,cl}\left(\vec{r}_2,\vec{r}_1;t,\omega\right)$ is obtained by substituting Eq. (B.10) into the expression

$$S^{f}_{0,cl}\left(\vec{r}_2,\vec{r}_1;t,\omega\right)=S_{0,cl}\left(\vec{r}_2,\vec{r}_1;t,\omega\right)+\int\limits_0^t d\tau\;\vec{f}\left(\tau\right).\vec{r}_c\left(\tau\right) \tag{B.11}$$

which we have

$$\begin{aligned} S^{f}_{0,cl}\left(\vec{r}_2,\vec{r}_1;t,\omega\right) &= \frac{m}{2}\left[\int\limits_0^t d\tau\;\dot{\vec{r}}_c^{\,2}\left(\tau\right)-\frac{\omega^2}{2t}\int\limits_0^t d\tau\int\limits_0^t d\sigma\left|\vec{r}\left(\tau\right)-\vec{r}\left(\sigma\right)\right|^2\right.\\ &\quad\left.+\int\limits_0^t d\tau\;\vec{f}\left(\tau\right)\vec{r}_c\left(\tau\right)\right]\\ &= \frac{m}{2}\left[\dot{\vec{r}}_c\left(\tau\right)\vec{r}_c\left(\tau\right)-\dot{\vec{r}}_c\left(0\right)\vec{r}_c\left(0\right)\right]+\frac{1}{2}\int\limits_0^t d\tau\;\vec{f}\left(\tau\right)\vec{r}_c\left(\tau\right). \end{aligned} \tag{B.12}$$

Thus, we get

$$\begin{aligned} S^{f}_{0,cl}\left(\vec{r}_2,\vec{r}_1;t,\omega\right) &= \frac{m\omega}{4}\cot\frac{\omega t}{2}\left|\vec{r}_2-\vec{r}_1\right|^2\\ &\quad+\frac{m\omega}{2\sin\omega t}\left[\frac{2\vec{r}_2}{m\omega}\int\limits_0^t d\tau\;\vec{f}\left(\tau\right)\left(\sin\omega\tau-2\sin\frac{\omega t}{2}\sin\frac{\omega}{2}\left(t-\tau\right)\sin\frac{\omega\tau}{2}\right)\right.\\ &\quad+\frac{2\vec{r}_1}{m\omega}\int\limits_0^t d\tau\;\vec{f}\left(\tau\right)\left(\sin\omega\left(t-\tau\right)-2\sin\frac{\omega t}{2}\sin\frac{\omega}{2}\left(t-\tau\right)\sin\frac{\omega\tau}{2}\right)\\ &\quad-\frac{2}{m^2\omega^2}\int\limits_0^t d\tau\int\limits_0^t d\sigma\vec{f}\left(\tau\right)\vec{f}\left(\sigma\right)\left\{\sin\omega\left(t-\tau\right)\sin\omega\sigma\right.\\ &\quad\left.\left.-4\sin\frac{\omega}{2}\left(t-\tau\right)\sin\frac{\omega\tau}{2}\sin\frac{\omega}{2}\left(t-\sigma\right)\sin\frac{\omega\sigma}{2}\right\}\right]. \end{aligned} \tag{B.13}$$

By means of Eq. (B.11), the classical trial action $S_{0,cl}$ can be obtained if we set $\vec{f}\left(\tau\right)$ equal zero. Hence, we find

$$S_{0,cl}\left(\vec{r}_2,\vec{r}_1;t,\omega\right)=\frac{1}{2}m\omega\cot\frac{\omega t}{2}\left|\vec{r}_2-\vec{r}_1\right|^2. \tag{B.14}$$

Vitae

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