การอินทิเกรตตามวิถีของฟายน์แมนสำหรับการขนส่งแบบอิเล็กตรอนที่เคลื่อนที่ผ่านดีเอ็นเอ

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FEYNMAN PATH INTEGRAL APPROACH TO ELECTRON TRANSPORT THROUGH DNA

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การเคลื่อนที่ของอิเล็กตรอนตามดีเอ็นเอถูกจำลองให้เป็นอิเล็กตรอนที่เคลื่อนที่และเกิดอันตรกิริยากับตัวสั่นแบบฮาร์โมนิกจำนวนมาก เราได้ประยุกต์ใช้การอินทิเกรตตามวิถีของฟายน์แมนแบบวิธีการแปรผัน เพื่อหาพลังงานสถานะพื้นจากส่วนเมทริกซ์ทแยงมุม และคำนวณหามวลยังผลแบบฟายน์แมนจากส่วนเมทริกซ์ไม่ทแยงมุม เราสามารถคำนวณผลเชิงตัวเลขสำหรับสองปริมาณนี้ และได้นำเสนอไว้ในที่นี้ด้วย นอกจากนี้ยังพบการเปลี่ยนเฟสของอิเล็กตรอนเมื่อค่ามวลยังผลมีค่าน้อย ๆ เปลี่ยนเป็นอนุภาคที่หนักขึ้นเมื่อขนาดของความแรงของการควบเพิ่มขึ้น

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An electron moving along DNA is modelled as an electron moving and interacting with a large number of harmonic oscillators. Feynman's path integral with a variational method is used to derive the density matrix of the system. The ground state energy of the electron can be obtained from the diagonal part of the density matrix and the Feynman effective mass obtained from the off-diagonal part. These two quantities are calculated numerically and the results are presented. We found a phase transition when an electron with a light effective mass turns into a very heavy particle as the coupling strength increases.

Department	Physics	Student's signature..
Field of study	Physics	Advisor's signature..
Academic year	2002	Co-advisor's signature.......................................

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Chapter 1
Introduction

DNA, or deoxyribonucleic acid, is known as one of the most interesting and mysterious biological molecules. It belongs to a class of biopolymer and has a very important biological function especially its ability to conserve and transfer genetic information. In 1953, Watson and Crick [1] discovered the double helix structure of DNA. It is composed of two linear polymers. Each polymer consists of monomeric units called nucleotide. Each nucleotide is made up of three components: sugar (furanose-derivative deoxyribose), phosphate (PO_4^-) and one of the four bases, adenine (A), guanine (G), thymine (T) and cytosine (C). Two linear polymers are held together between some combinations of these bases by hydrogen bonds which is called the Watson-Crick base pairing. They are wound around a common axis to form a double helix (Fig.1.1). The A base only pairs with T, and the G base only pairs with C. These pairs are the formation of double helix. The diameter of the helix is 20 $\mathring{A}$ and the adjacent bases are 3.4 $\mathring{A}$ apart along the axis with 36° angle respect to one another.

In 1962, Eley and Spivey [2] were the first to suggest that DNA could
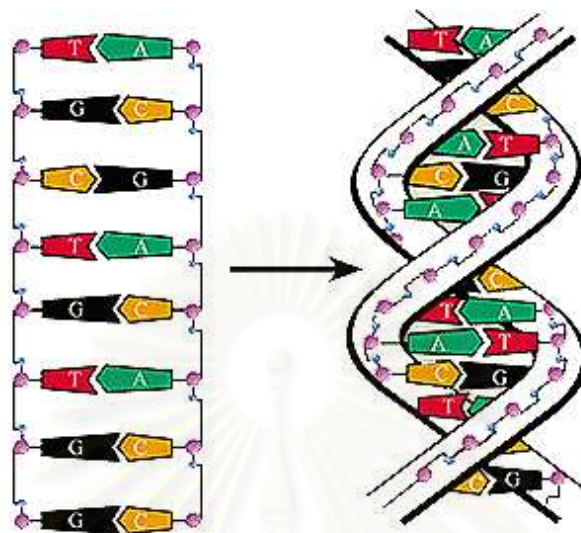
Figure 1.1: Diagram showing the double helix structure of DNA [3].

be a conductor because of the formation of a π- band across the different bases.
Recently, physicists and chemists have become increasingly interested in the electronic properties of the DNA. The process of a charge transfer, the movement of a charge from one molecule to another molecule or one end of the molecule to the other is one of the most fundamental concept in chemistry and material science. They are widely used in studying corrosion and photosynthesis.

Many experiments are conducted in order to find the first clue about the charge transfer mechanisms in DNA. Indirect measurements of the charge transfer in DNA and direct measurements of Current–Voltage or I-V characteristics are the two major experiments being investigated.

Fink *et al.* [4] performed the first direct measurement of the conducting properties of DNA. The resulting I-V characteristics are shown in Fig.(1.2). It was found that λ-DNA (a DNA of virus named lamda) is a good conductor, with a resistance comparable to that of conducting polymers. The experiment was done in vacuum, where a drop of solution containing DNA was placed onto a gold-covered carbon foil with 2 μm holes. The holes were imaged with a low-energy electron point source (LEEPS) microscope, which is claimed that it does not radioactively damage DNA [4, 5].
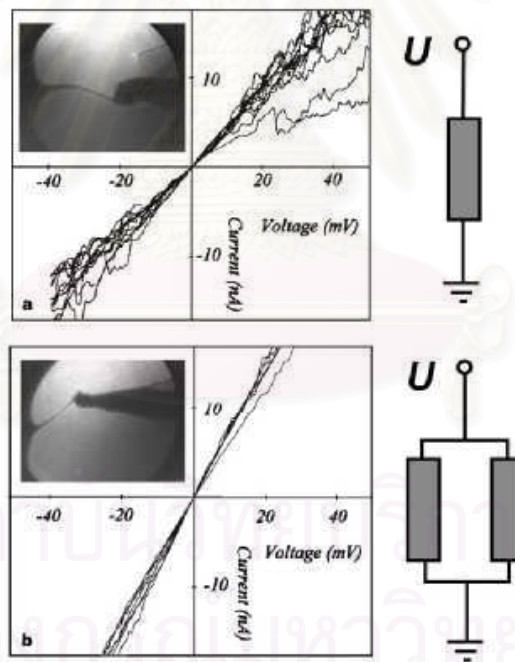
Figure 1.2: Diagram showing I-V characteristics of DNA ropes. (a) I-V curve for a single rope 600 nm long. (b) I-V curve for two ropes in parallel [5].

In other direct measurements, researchers have found that DNA acts as a large band gap semiconductor. For instance, Porath *et al.*[6] measured the conductivity in poly(dG)-poly(dC) DNA. The homogenous sequence of DNA is ideal for overlap of π-orbital in adjacent base pairs. These experiments were done using a 10.4-nm-long DNA and electrostatically trapping technique to position single DNA molecules between two electrodes. The I-V characteristics of these experiments are shown in Fig.(1.3). It can be seen that poly(dG)-poly(dC) DNA behaved like a semiconductor with a large band gap.
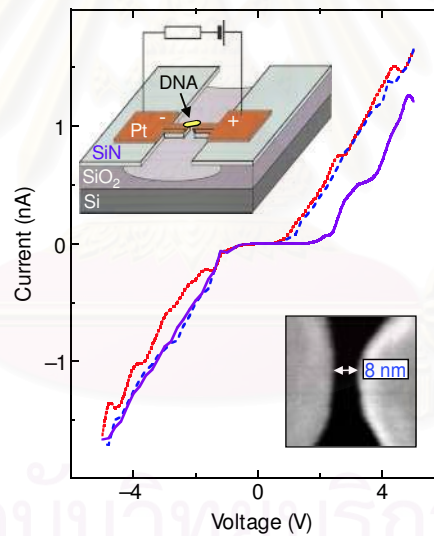
Figure 1.3: Diagram showing I-V characteristics for poly(dG)-poly(dC) DNA molecule. The difference curves show repeated measurements. The upper inset shows the experimental set up and the lower inset shows the electrodes separated by a 8 nm gap [6].

Recently, Pablo *et al.*[7] have performed measurements on the resistance

of λ-DNA and their results suggested that λ-DNA is an insulator. The contradictory results arise from many experimental conditions i.e, base sequences, lengths, temperatures, experimental techniques and so on.

Over the past several years, many theoretical models for the charge transfer have been proposed to account for differing experimental results. For instance, the coherent tunnelling have been proposed by Eley and Spivey in 1962, the incoherent phonon-assisted hopping have been proposed by Ly *et al.*[8] in 1996 and Jortner [9] in 1998, the classical diffusion under thermal fluctuations have been proposed by Bruinsma *et al.* in 2000 [10], the variable range hopping between localized state have been proposed by Yu and Song [11] in 2001 and the charge carriers assisted by polarons have been proposed by Conwell *et al.*[12] in 2000 and Rakhmanova *et al.* [13] in 2001.

In this work, we are interested in an electron moving in DNA. The DNA molecule is usually immersed in some thermal bath. The base pairs which are held together with a weak hydrogen are vibrated by thermal bath. We propose a model Hamiltonian for an electron moving in DNA, consisting of three parts: the kinetic energy of the electron, the energy of the base pair vibrations which are modelled simply as the harmonic oscillators, and the interaction between the electron and the base pair vibrations. In this model, it is easy to evaluate the

ground state energy and the effective mass of the electron by using Feynman's path integral which has been applied widely to other problems and various fields of theoretical physics, such as the polaron problem [14] of which the ground state energy and the effective mass can be evaluated successfully .

In this thesis, Feynman's path integral method with an example is presented in Chapter 2. In Chapter 3, our model Hamiltonian for an electron moving in DNA is presented. The approximate propagator and the density matrix including the off-diagonal part will also be calculated by using a variational method with the two-particle model trial action introduced by Samathiyakanit [15] . In Chapter 4, the ground state energy and the effective mass of the electron are obtained from the density matrix from Chapter 3 as well as numerical results and discussions. Conclusion for our model Hamiltonian and the results are given in the last chapter.

Chapter 2

Feynman's Path Integral Theory

To solve the problem of electron moving in DNA the powerful technique of Feynman's path integral is chosen. Using this method, the problem can be simplified from many body problem into one body problem by exact integrating over harmonic oscillator coordinates. The ground state energy and the effective mass can be evaluated analytically. Before we present our calculation in the next chapter, we would like to review the Feynman's path integral and some applications which can be applied to our work.

2.1 The classical action

In classical mechanics, the principle of least action expresses the condition that determines the particular path $\mathbf{x}_{cl}(t)$ out of all the possible paths for a particle, from an initial point $\mathbf{x}_a$ at time t_a to a final point $\mathbf{x}_b$ at time t_b. Therefore, a certain quantity S for each path can be computed. Moreover, the classical path $\mathbf{x}_{cl}(t)$ is the path that S is extremum. Then the value of S is unchanged in the

first order if the path $\mathbf{x}_{cl}(t)$ is modified slightly. The action S is expressed as

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

where L is the Lagrangian of the system. For a particle of mass m moving in a potential $V\left(\mathbf{x}, t\right)$, the Lagrangian is a function of position and time:

$$L = \frac{m}{2}\dot{\mathbf{x}}^2 - V\left(\mathbf{x}, t\right). \tag{2.2}$$

2.2 The quantum-mechanical amplitude

In quantum mechanics, the total amplitude to go from a point a to another point b is contributed by every paths, including the classical path, $\mathbf{x}_{cl}(t)$, and every paths gets the same weight, nevertheless, contributes at different phase. The phase of contribution from each path is $S/\hbar$. The probability $P\left(b, a\right)$ to go from a point $\mathbf{x}_a$ at the time t_a to a point $\mathbf{x}_b$ at time t_b is

$$P\left(b, a\right) = \left|K\left(b, a\right)\right|^2. \tag{2.3}$$

The $K\left(b, a\right)$, which is called the propagator, is an amplitude to go from a to b, is the sum of contribution $\phi\left[\mathbf{x}\left(t\right)\right]$ from each path, thus the propagator is

$$K\left(b, a\right) = \sum_{\substack{\text{over all paths} \\ \text{from a to b}}} \phi\left[\mathbf{x}\left(t\right)\right], \tag{2.4}$$

where the phase is proportional to the action S as

$$\phi\left[\mathbf{x}\left(t\right)\right] = const.\exp\left\{\frac{i}{\hbar}S\left[\mathbf{x}\left(t\right)\right]\right\}. \tag{2.5}$$

The constant term is a normalizing factor. Fig.(2.1) shows the continuum of paths linking the end points. In classical approximation, each path has a different action and contributes with a different phase. The contributions of the paths essentially cancel each other, so that no net contribution arises. On the other hand for the special path $\mathbf{x}_{cl}(t)$, which S is an extremum, a small change in path produces, in first order at least, no change in S. In this region, all the contributions from the paths are closely in phase (S_{cl}). For this reason, only for paths in the vicinity of $\mathbf{x}_{cl}(t)$ is important. In this way the classical laws of motion originate from the quantum laws

2.3   The sum over paths

Actually, the way to evaluate the propagator in Eq.(2.4), which is called path integration, is very complicated. In 1948 Feynman [16] proposed another way to perform a new formalism of propagator $[K\left(b,a\right)]$, by dividing the time intervals into small interval, i.e. $\varepsilon \to 0$. This provides, a set of times $t_1, t_2, t_3...$ between the values t_a and t_b, where $t_{i+1} = t_{i+\varepsilon}$. At each time , t_i, one selects some special point $\mathbf{x}_i$ and constructs a path by a straight line. This is shown in Fig.(2.2). It
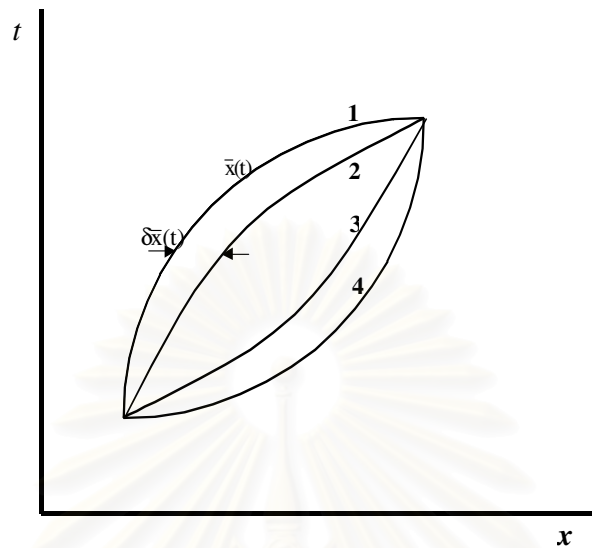
Figure 2.1: Diagram showing the classical path 1, $\bar{x}(t)$, which has the action S minimum. If the path is varied by $\delta x(t)$, to path 2, the integral suffers no first-order change.

is possible to define a sum over all paths constructed in this manner by taking a

multiple integral over all values of $\mathbf{x}_i$ for i from 1 to $N-1$, where

$$
\begin{aligned}
N\varepsilon &= t_b - t_a, \varepsilon = t_{i+1} - t_i, \\
t_0 &= t_a, t_N = t_b, \\
\mathbf{x}_0 &= \mathbf{x}_a, \mathbf{x}_N = \mathbf{x}_b.
\end{aligned}
\tag{2.6}
$$

The resulting equation is

$$
K(b,a) = \lim_{\varepsilon \to 0} \frac{1}{A} \int \int \cdots \int \exp\left\{ \frac{i}{\hbar} S[b,a] \right\} \frac{d\mathbf{x}_1}{A} \frac{d\mathbf{x}_2}{A} \ldots \frac{d\mathbf{x}_{N-1}}{A}, \tag{2.7}
$$
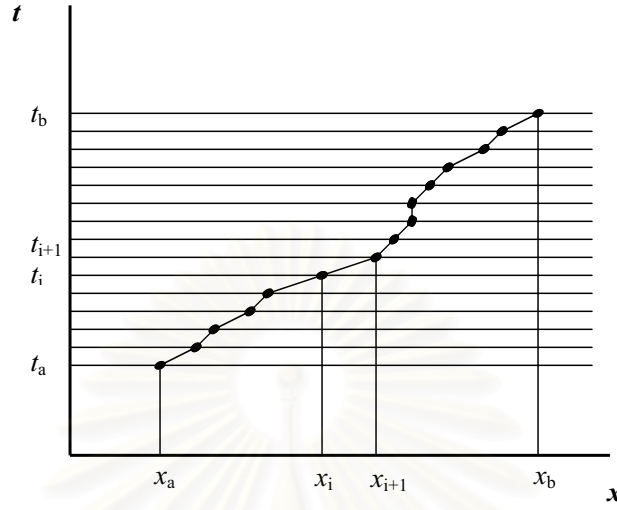
Figure 2.2: A diagram showing the sum over all paths.

where

$$S\left[b,a\right] = \int_{t_a}^{t_b} L\left(\dot{\mathbf{x}}, \mathbf{x}, t\right) dt, \tag{2.8}$$

and the normalizing factor is

$$A = \left(\frac{2\pi i \hbar \varepsilon}{m}\right)^{1/2} \tag{2.9}$$

Eq.(2.7) is suggested by Feynman in a less restrictive notation as

$$K\left(b,a\right) = \int \mathcal{D}\mathbf{x}\left(t\right) \exp\left\{\frac{i}{\hbar} S\left[b,a\right]\right\}. \tag{2.10}$$

It is called the Feynman's path integral. The symbol $\int \mathcal{D}\mathbf{x}\left(t\right)$ refers to an integration over all possible paths connecting the point $\left(\mathbf{x}_b, t_b\right)$ to point $\left(\mathbf{x}_a, t_a\right)$.

2.3.1   Path integral of a free particle

The first example is a free particle with the Lagrangian

$$L = \frac{m}{2}\dot{\mathbf{x}}^2\left(t\right).$$

(2.11)

From previous section, the one dimensional propagator is presented as

$$K\left(\mathbf{x}_b, t_b; \mathbf{x}_a, t_a\right) = \lim_{\varepsilon \to 0} \int \exp\left[\frac{im}{2\hbar\varepsilon}\sum_{i=1}^{N}\left(\mathbf{x}_i - \mathbf{x}_{i-1}\right)^2\right] d\mathbf{x}_1...d\mathbf{x}_{N-1}\left(\frac{2\pi i\hbar\varepsilon}{m}\right)^{-N/2}.$$

(2.12)

This is an integral of the form $\int_{-\infty}^{\infty} dx \exp\left[-ax^2 + bx\right]$, which is called a gaussian integral. Since the integral of gaussian is again gaussian, we may carry out the integrations on one variable after the other with the help of the formula

$$\int_{-\infty}^{\infty} d\mathbf{x}_1 \left[\frac{m}{2\pi i\hbar\left(\varepsilon\right)}\right]^{-2/2} \exp\left\{\left[\frac{m}{2\pi i\hbar\left(\varepsilon\right)}\right]\left[\left(\mathbf{x}_2 - \mathbf{x}_1\right)^2 - \left(\mathbf{x}_1 - \mathbf{x}_0\right)^2\right]\right\}$$

$$= \left[\frac{m}{2\pi i\hbar\left(2\varepsilon\right)}\right]^{1/2} \exp\left\{\left[\frac{m}{2\pi i\hbar\left(2\varepsilon\right)}\right]\left[\left(\mathbf{x}_2 - \mathbf{x}_0\right)^2\right]\right\}.$$

(2.13)

When the integration is finished, and the limit is taken, the result is.

$$K\left(\mathbf{x}_b, t_b; \mathbf{x}_a, t_a\right) = \left[\frac{m}{2\pi i\hbar\left(t_b - t_a\right)}\right]^{1/2} \exp\left\{\left[\frac{im}{2\hbar\left(t_b - t_a\right)}\right]\left(\mathbf{x}_b - \mathbf{x}_a\right)^2\right\}.$$

(2.14)

2.4   The quadratic Lagrangian

In general, since the path integral is still in gaussian form, it is possible to carry out the integral over all paths by the method that described in the previous

section. Nevertheless, in general problem which it is complicated to perform, for example, the forced harmonic oscillator problem. Consequently, some additional mathematical techniques will be introduced, which help us to sum over paths in some certain situations. Generally, the Lagrangian will be in the quadratic form which the corresponding action S contains the path $\mathbf{x}(t)$ up to the second power. Accordingly, to explain how the method work in such cases so we starting with the Lagrangian in the form,

$$L(\mathbf{x}, \dot{\mathbf{x}}, t) = a(t)\dot{\mathbf{x}}^2 + b(t)\mathbf{x}\dot{\mathbf{x}} + c(t)\mathbf{x}^2 + d(t)\dot{\mathbf{x}} + e(t)\mathbf{x} + f(t),\qquad(2.15)$$

where the action is the integral of this Lagrangian with respect to time between two fixed end points. Certainly the propagator that we wish to determine is

$$K(\mathbf{x}_b, t_b; \mathbf{x}_a, t_a) = \int \mathcal{D}\mathbf{x}(t)\exp\left\{\frac{i}{\hbar}\int_{t_a}^{t_b} L(\dot{\mathbf{x}}, \mathbf{x}, t)\,dt\right\},\qquad(2.16)$$

This is the integral over all paths which go from position $\mathbf{x}_a$ at time t_a to position $\mathbf{x}_b$ at time t_b. Therefore, a different way to solve this difficult problem is required. Now let us start with the classical path between the specified end points, $\mathbf{x}_{cl}(t)$, which the corresponding action S is extremum. Moreover, any path $\mathbf{x}(t)$ can be expressed as the sum of the classical path, $\mathbf{x}_{cl}(t)$, and a new variable $\mathbf{y}(t)$. That is

$$\mathbf{x}(t) = \mathbf{x}_{cl}(t) + \mathbf{y}(t).\qquad(2.17)$$

Because the classical path is completely fixed, $d\mathbf{x}_i = d\mathbf{y}_i$ and the path differential

$\mathcal{D}\mathbf{x}\left(t\right)$ can be replaced by $\mathcal{D}\mathbf{y}\left(t\right)$. That is to say, instead of defining a point on the

path by its distance $\mathbf{x}(t)$ from an arbitrary coordinate axis, we measure instead

the deviation $\mathbf{y}\left(t\right)$ from the classical path shown in Fig.(2.3) The function $\mathbf{y}\left(t\right)$

satisfies under the condition

$$\mathbf{y}\left(t_a\right) = \mathbf{y}\left(t_b\right) = 0. \tag{2.18}$$
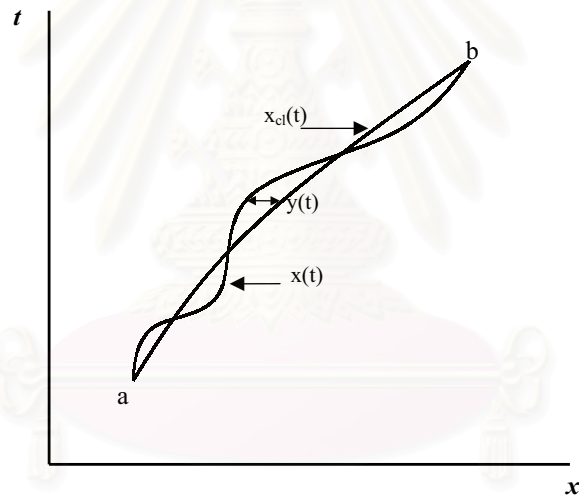
Figure 2.3: Difference between the classical path $\mathbf{x}_{cl}(t)$ and the some possible alternative paths $\mathbf{x}(t)$ is a function of $\mathbf{y}\left(t\right)$ with fixed end points .

Here, we start with the time $t = t_a$ and end at time $t = t_b$. So that the

the action S can be written as,

$$
\begin{aligned}
S\left[\mathbf{x}\left(t\right)\right] &= S\left[\mathbf{x}_{cl}(t)+\mathbf{y}\left(t\right)\right] \\
&= \int_{t_a}^{t_b}\left\{a\left(t\right)\left[\dot{\mathbf{x}}_{cl}^2(t)+2\dot{\mathbf{x}}_{cl}(t)\dot{\mathbf{y}}\left(t\right)+\dot{\mathbf{y}}^2\left(t\right)\right]+...f\left(t\right)\right\}dt. \quad (2.19)
\end{aligned}
$$

It is obvious that the integral of all terms involving exclusively $\mathbf{x}_{cl}(t)$ is exactly

the classical action and the integral of all terms that are linear in $\mathbf{y}\left(t\right)$ precisely

vanishes. So, all the remaining terms in the integral are second-order terms in

$\mathbf{y}\left(t\right)$ only. That is

$$
S\left[\mathbf{x}\left(t\right)\right] = S\left[\mathbf{x}_{cl}(t)\right] + \int_{t_a}^{t_b} dt\left[a\left(t\right)\dot{\mathbf{y}}^2\left(t\right)+b\left(t\right)\dot{\mathbf{y}}\left(t\right)\mathbf{y}\left(t\right)+c\left(t\right)\mathbf{y}^2\left(t\right)\right]. \quad (2.20)
$$

The integral over paths does not depend upon the classical path, so that the

propagator becomes

$$
\begin{aligned}
K\left(\mathbf{x}_b, t_b; \mathbf{x}_a, t_a\right) &= \exp\left\{\frac{i}{\hbar}S\left[\mathbf{x}_{cl}(t)\right]\right\} \\
&\quad \times \int \mathcal{D}\mathbf{y}\left(t\right)\exp\left\{\frac{i}{\hbar}\int_{t_a}^{t_b}dt\left[\begin{array}{c}a\left(t\right)\dot{\mathbf{y}}^2\left(t\right)\\+b\left(t\right)\dot{\mathbf{y}}\left(t\right)\mathbf{y}\left(t\right)+c\left(t\right)\mathbf{y}^2\left(t\right)\end{array}\right]\right\}.
\end{aligned}
$$

$$
(2.21)
$$

Since all paths $\mathbf{y}\left(t\right)$ start from and return to the point $\mathbf{y}=0$, the integral over

paths can be an only function of time, at the end points. This means that the

propagator can be expressed as,

$$
K\left(\mathbf{x}_b, t_b; \mathbf{x}_a, t_a\right) = F\left(t_b, t_a\right)\exp\left\{\frac{i}{\hbar}S_{cl}(\mathbf{x}_b, \mathbf{x}_a)\right\}. \quad (2.22)
$$

Accordingly, the propagator is determined except for multiplying factor $F(t_b, t_a)$, which may be determined by some other known properties of the solution. However, for a quadratic Lagrangian, Van-Vleck and Pauli had verified that the pre-factor $F(t_b, t_a)$ can be evaluated exactly by using the formula

$$F(t_b, t_a) = \sqrt{\det\left[\frac{i}{2\pi\hbar}\frac{\partial^2}{\partial x_b \partial x_a}S_{cl}(\mathbf{x}_b, \mathbf{x}_a)\right]}. \tag{2.23}$$

So that Eq.(2.22) becomes

$$K(\mathbf{x}_b, t_b; \mathbf{x}_a, t_a) = \sqrt{\det\left[\frac{i}{2\pi\hbar}\frac{\partial^2}{\partial \mathbf{x}_b \partial \mathbf{x}_a}S_{cl}(\mathbf{x}_b, \mathbf{x}_a)\right]} \times \exp\left\{\frac{i}{\hbar}S_{cl}(\mathbf{x}_b, \mathbf{x}_a)\right\}. \tag{2.24}$$

It is interesting to note that the expression $K \sim \exp\left\{\frac{i}{\hbar}S_{cl}\right\}$ is exact for the case that S is in quadratic form.

2.5   The path integral formulation of density matrices

The density matrix can be written in the form

$$\rho(\mathbf{x}', \mathbf{x}) = \sum_i \phi_i(\mathbf{x}')\phi_i^*(\mathbf{x})e^{-\beta E_i}, \tag{2.25}$$

where $\beta = \frac{1}{kT}, T$ is the absolute temperature. It is remarkable that the above expression bears a close resemblance to the general expression for the propagator which is written as

$$K(\mathbf{x}_b, t_b; \mathbf{x}_a, t_a) = \sum_j \phi_j(\mathbf{x}_b)\phi_j^*(\mathbf{x}_a)e^{-(i/\hbar)E_j(t_b-t_a)}. \tag{2.26}$$

The validity of this expression is restricted to situations in which the Hamiltonian is constant in time and $t_b > t_a$. However, this situation is implied in statistical mechanics; for only if the Hamiltonian is constant in time can equilibrium be achieved. The difference between the form of Eq.(2.25) and that of Eq.(2.26) is in the argument of the exponential. If the time difference $t_b - t_a$ of Eq.(2.26) is replaced by $-i\beta\hbar$, we see that expression for the density matrix is formally identical to the expression for the propagator corresponding to an imaginary negative time interval.

We can develop the similarity between these two expression from another point of view. Suppose we write the density matrix in a way which makes it look a little bit more like a propagator, thus, $k\left(\mathbf{x}_b, t_b; \mathbf{x}_a, t_a\right)$ for $\rho\left(\mathbf{x}_b, \mathbf{x}_a\right)$, where

$$k\left(\mathbf{x}_b, t_b; \mathbf{x}_a, t_a\right) = \sum_i \phi_i\left(\mathbf{x}_b\right) \phi_i^*\left(\mathbf{x}_a\right) e^{-[(u_b - u_a)/\hbar]E_i}. \qquad (2.27)$$

Then the Eq.(2.27) becomes identical with Eq.(2.25) if $\mathbf{x}_b = \mathbf{x}'$, $\mathbf{x}_a = \mathbf{x}$, $u_b = \beta\hbar$ and $u_a = 0$. If we differentiate k partially with respect to u_b, we get

$$-\hbar\frac{\partial k}{\partial u_b} = \sum_i \phi_i\left(\mathbf{x}_b\right) \phi_i^*\left(\mathbf{x}_a\right) e^{-[(u_b - u_a)/\hbar]E_i}. \qquad (2.28)$$

Now we recall that $E_i\phi_i\left(\mathbf{x}'\right) = H\phi_i\left(\mathbf{x}'\right)$ and let H_b imply operations only upon the variables $\mathbf{x}_b$, we can write

$$-\hbar\frac{\partial k\left(b, a\right)}{\partial u_b} = H_b k\left(b, a\right), \qquad (2.29)$$

or, to put the same thing another way

$$-\frac{\partial \rho\left(b, a\right)}{\partial \beta} = H_b \rho\left(b, a\right), \tag{2.30}$$

with simple Hamiltonian involving only momenta and coordinates, we have been able to write the propagator as a path integral. For example, if the Hamiltonian is given by

$$H = \frac{\hbar^2}{2m} \frac{d^2}{d\mathbf{x}^2} + V\left(\mathbf{x}\right), \tag{2.31}$$

then the solution for then propagator over a very short time interval $t_2 - t_1 = \varepsilon$ is

$$G\left(b, a\right) = \left(\frac{m}{2\pi i \hbar \varepsilon}\right)^{1/2} \exp\left[\frac{im}{2\hbar} \frac{\left(\mathbf{x}_b - \mathbf{x}_a\right)^2}{\varepsilon} - \frac{i}{\hbar} \varepsilon V\left(\frac{\mathbf{x}_b + \mathbf{x}_a}{2}\right)\right], \tag{2.32}$$

which can be directly verified by substitution Eq.(2.32) into Eq.(2.31). By building up a product of many propagators of Eq.(2.32) and taking the limit as the time interval ε goes to 0 and the number of terms in the product becomes infinite, we have produced a path integral describing the propagator over a finite period of time. We can produce a solution to Eq.(2.29) in the same manner. The solution for an infinitesimal interval of $u_b - u_a = \eta$ is given by substituting $\varepsilon = i\eta$ into Eq.(2.32). Thus

$$k\left(\mathbf{x}_b, \eta; \mathbf{x}_a, 0\right) = \left(\frac{m}{2\pi \hbar \eta}\right)^{1/2} \exp\left[-\frac{\left(m/2\eta\right)\left(\mathbf{x}_b - \mathbf{x}_a\right)^2 + \eta V\left[\left(\mathbf{x}_b + \mathbf{x}_a\right)/2\right]}{\hbar}\right].$$

$$\tag{2.33}$$

Where this is a valid solution of Eq.(2.29) and can be demonstrated by direct substitution of Eq.(2.33) into Eq.(2.29). The rule for the combination of functions defined for successive values of u is the same as the rule for the combination of propagators for successive intervals of time. That is,

$$k(b, a) = \int k(b, c) \, k(c, a) \, d\mathbf{x}_c. \tag{2.34}$$

That this result still holds follows from the fact that Eq.(2.28) is a first-order derivative in u. This rule can be used to obtain the path integral to define $k(b, a)$ as

$$k(\mathbf{x}_b, u_b; \mathbf{x}_a, u_a) = \int \left[\exp \left\{ -\sum_{i=0}^{N-1} \left[\frac{m}{2\hbar\eta} (\mathbf{x}_{i+1} - \mathbf{x}_i)^2 + \frac{\eta}{\hbar} V(\mathbf{x}_i) \right] \right\} \right]_{i=1}^{N-1} \frac{d\mathbf{x}_i}{a}. \tag{2.35}$$

The normalizing constant a now becomes

$$a = \left(\frac{2\pi\hbar\eta}{m} \right)^{1/2}, \tag{2.36}$$

and the integral is carried out over all paths going from $\mathbf{x}_a$ to $\mathbf{x}_b$ (that is, $\mathbf{x}_i$ is $\mathbf{x}_a$ for $i = 0$ and $\mathbf{x}_b$ for $i = N$) in the interval $u_b - u_a = N\eta$. The result of this derivation is that if we consider a path $\mathbf{x}(u)$ as a function which gives a coordinate in terms of the parameter u, and if we call $\dot{x}$ the derivative $d\mathbf{x}/du$, then

$$\rho(\mathbf{x}_b, \mathbf{x}_a) = \int \left[\exp \left\{ -\frac{1}{\hbar} \int_0^{\beta\hbar} \left[\frac{m}{2} \dot{\mathbf{x}}^2(u) + V(\mathbf{x}) \right] du \right\} \right] \mathcal{D}\mathbf{x}(u). \tag{2.37}$$

It is noticed that Eq.(2.37) can be obtained by just substituting $-iu$ and $-i\beta\hbar$ into τ and t_b respectively of the propagator $G\left(\mathbf{x}_b, t_b; \mathbf{x}_a, t_a\right)$ as follows

$$\rho\left(\mathbf{x}_b, \mathbf{x}_a\right) = G\left(\mathbf{x}_b, t_b = -i\beta\hbar; \mathbf{x}_a, t_a = 0\right). \qquad (2.38)$$

In Feynman's path integral, the very important quantity is the propagator which contains all informations of the system such as wave function, ground state energy, effective mass and so on. To evaluate the propagator the Largargian is modelled and the action is obtained. For quadratic Lagrangian the propagator can be evaluated exactly by integrating over all paths and the density matrix can be obtained from the propagator directly.

Chapter 3

The model Hamiltonian for an electron moving along DNA

In this chapter, the one dimensional model Hamiltonian for an electron moving in DNA is presented. In order to approximate our model propagator the Feynman's path integral and a variational method are applied. In the last section the density matrix corresponding to our model is evaluated.

3.1   An electron moving along DNA model

In our simplified model, the helicoidal structure of DNA is modelled as a long cylinder where each base pair vibrates classically and harmonically. In this model we consider an electron moving in the axial direction along DNA in one dimension and interacting with the base pair vibrations while localizing on them. The Hamiltonian model for an electron moving along DNA consists of three parts,

$$H = H_{el} + H_{har} + H_{int}. \qquad (3.1)$$
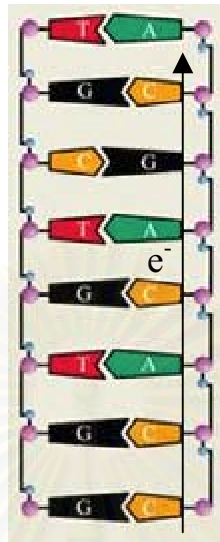
Figure 3.1: A model of an electron moving and interacting with the base pair vibrations $(A - T, G - C)$.

The first part H_{el} represents the kinetic energy of an electron moving over the base pairs,

$$H_{el} = \frac{1}{2}m\dot{x}^2(t),$$

(3.2)

where m is the mass of an electron in DNA and $x(t)$ presents the coordinate of an electron with respect to the origin. $\dot{x}(t)$ is the velocity of an electron. The second part H_{har} describes the dynamics of the base pair vibrations as the harmonic oscillators,

$$H_{har} = \frac{1}{2}M' \sum_k \left[\dot{y}_k^2(t) + \Omega^2 y_k^2(t) \right],$$

(3.3)

where index k denotes the kth base pair or an oscillator. The reduced mass and the vibration frequency of each base pair are M' and Ω, respectively. Also, $y_{o,k}(t)$ is the displacement of a kth oscillator from its equilibrium. The last term H_{int} represents the interaction between an electron and the oscillators which modelled as a Dirac delta function,

$$H_{int} = M'\Omega^2 \alpha \sum_k y_k(t) \, \delta \left[x(t) - y_{0,k} \right].$$ (3.4)

The coefficient α is a coupling constant and $y_{0,k}$ represents the position of the kth oscillator from the origin.
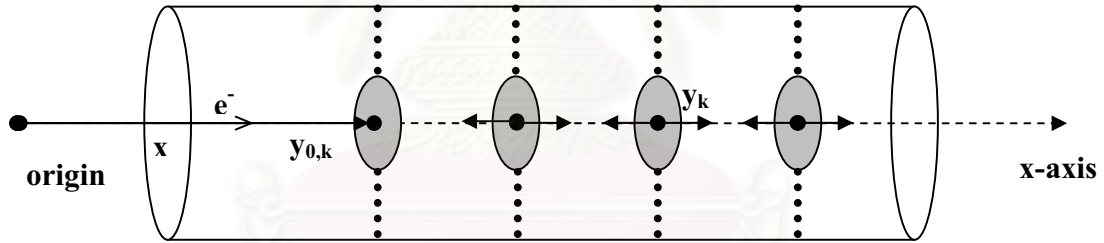
Figure 3.2: Sketch of the helicoidal structure of DNA model, the base pairs being presented by the ellipses. The parameters $x, y_{0,k}$ and y_k are as indicated.

Then the Lagrangian corresponding to the Hamiltonian in Eq.(3.1) can be easily evaluated using Legendre transform, as followed

$$L = \sum_i p_i \dot{q}_i - H.$$ (3.5)

Therefore,

$$L = \frac{1}{2}m\dot{x}^2(t) + \frac{1}{2}M'\sum_k \left[\dot{y}_k^2(t) - \Omega^2 y_k^2(t)\right] - M'\Omega^2\alpha\sum_k y_k(t)\,\delta\left[x(t) - y_{0,k}\right].$$

(3.6)

Next, the oscillator coordinates y_k can be eliminated by defining the transformation function for the electron and the oscillators, from an initial point at time $t = 0$ to a final point at time $t = T$ and with the boundary conditions $x(0) = x_a$, $x(T) = x_b$ and $y_k(0) = y_k(T) = y_k$. Thus, we have

$$\langle x_b, y_1, ... y_N, T; x_a, y_1, ... y_N, 0; \rangle$$

$$= \int_{x_a}^{x_b} \mathcal{D}x(t) \int_{y_1}^{y_1} \mathcal{D}y_1(t) ... \int_{y_N}^{y_N} \mathcal{D}y_N(t)\exp[\frac{i}{\hbar}S],$$

$$= \int_{x_a}^{x_b} \mathcal{D}x(t)\exp\left[\frac{i}{\hbar}\int_0^T dt\frac{1}{2}m\dot{x}^2(t)\right]\prod_k \int_{y_k}^{y_k} \mathcal{D}y_k(t)\exp\left[\frac{i}{\hbar}\int_0^T dt\,S(y_k)\right],$$

(3.7)

where

$$S = \int_0^T dt \left\{\frac{1}{2}m\dot{x}^2(t) + \frac{1}{2}M'\sum_k \left[\dot{y}_k^2(t) - \Omega^2 y_k^2(t)\right] - M'\Omega^2\alpha\sum_k y_k(t)\,\delta\left[x(t) - y_{0,k}\right]\right\},$$

(3.8)

and

$$S(y_k) = \int_0^T dt \left\{\frac{1}{2}M'\left[\dot{y}_k^2(t) - \Omega^2 y_k^2(t)\right] - M'\Omega^2\alpha y_k(t)\,\delta\left[x(t) - y_{0,k}\right]\right\}.$$

(3.9)

The path integrals over the oscillator coordinates y_k can be performed using the result [1] for the forced harmonic oscillator of which the Lagrangian is equal to

$\frac{1}{2}M'\left[\dot{y}_k^2\left(t\right)-\Omega^2 y_k^2\left(t\right)\right]-f\left(t\right)y_k\left(t\right)$. The time dependent force, in this case, is

$f\left(t\right)=M'\Omega^2\alpha\delta\left[x\left(t\right)-y_{0,k}\right]$. After integrating over the oscillator coordinates the

transformation function can be written as

$$\langle x_b,T;x_a,0;\rangle = \int_{-\infty}^{\infty}\langle x_b,y_1,...y_N,T;x_a,y_1,...y_N,0;\rangle\,dy_1 dy_2...dy_N,$$

$$= \left[2i\sin\left(\frac{\Omega T}{2}\right)\right]^{-N}\int\mathcal{D}x\left(t\right)\exp\left\{\frac{i}{\hbar}\int_0^T dt\frac{1}{2}m'\dot{x}^2\left(t\right)\right.$$

$$+\frac{i}{\hbar}\frac{M'\Omega^3\alpha^2}{4}\sum_k\int_0^T\int_0^T dtds\delta\left[x\left(t\right)-y_{0,k}\right]\delta\left[x\left(s\right)-y_{0,k}\right]$$

$$\left.\times\frac{\cos\left[\Omega\left(\frac{T}{2}-|t-s|\right)\right]}{\sin\left(\Omega\frac{T}{2}\right)}\right\}.\tag{3.10}$$

Because the interested quality is the effect of the coupling between an

electron and the oscillators, the prefactor in Eq.(3.10) can be ignored. Therefore

the transformation function without the prefactor is now called "our model's

propagator $K\left(x_b,x_a;T\right)$". From the relation $\sum_k\delta\left[x\left(t\right)-y_{0,k}\right]\delta\left[x\left(s\right)-y_{0,k}\right]=$

$\rho\delta\left[x\left(t\right)-x\left(s\right)\right]$ where ρ is a number of the oscillators per length, the propagator

$K\left(x_b,x_a;T\right)$ can be written as

$$K\left(x_b,x_a;T\right)=\int\mathcal{D}x\left(t\right)\exp\left(\frac{i}{\hbar}S_D\right),\tag{3.11}$$

where S_D is the action of our model

$$S_D=\int_0^T dt\frac{1}{2}m\dot{x}^2\left(t\right)+\frac{1}{4}M'\Omega^3\alpha^2\rho\int_0^T\int_0^T dtds\delta\left[x\left(t\right)-x\left(s\right)\right]\frac{\cos\left[\Omega\left(\frac{T}{2}-|t-s|\right)\right]}{\sin\left(\Omega\frac{T}{2}\right)}.$$

$$\tag{3.12}$$

Since an integral representation of the δ function is [17]

$$\delta\left[x\left(t\right) - x\left(s\right)\right] = \frac{1}{2\pi} \int_{-\infty}^{\infty} dq \exp\left\{iq\left[x\left(t\right) - x\left(s\right)\right]\right\},\qquad(3.13)$$

an action of our model S_D can be written in a new form,

$$S_D = \int_0^T dt \frac{1}{2}m\dot{x}^2\left(t\right) + C\int_0^T\int_0^T dtds \int_{-\infty}^{\infty} dq \exp\left\{iq\left[x\left(t\right) - x\left(s\right)\right]\right\} \frac{\cos\left[\Omega\left(\frac{T}{2} - |t - s|\right)\right]}{\sin\left(\Omega\frac{T}{2}\right)},$$
$$(3.14)$$

where $C = \frac{1}{8\pi}M'\Omega^3\alpha^2\rho$.

3.2 Variational method

Since our model's action S_D in Eq.(3.14) is not in a quadratic form, our model's propagator $K\left(x_b, x_a; T\right)$ cannot be evaluated exactly. To perform further calculations, a variational method is applied to carry out the path integral for the propagator $K\left(x_b, x_a; T\right)$. A trial action S_0 is chosen so that the propagator in Eq.(3.11) can be approximated [18] as

$$K\left(x_b, x_a; T\right) = K_0\left(x_b, x_a; T\right) \left\langle \exp\left\{\frac{i}{\hbar}\left(S_D - S_0\right)\right\}\right\rangle_{S_0},\qquad(3.15)$$

where the propagator $K_0\left(x_b, x_a; T\right)$ is defined as

$$K_0\left(x_b, x_a; T\right) = \int \mathcal{D}x\left(t\right)\exp\left(\frac{i}{\hbar}S_0\right),\qquad(3.16)$$

and the average over S_0, $\langle O\rangle_{S_0}$ is defined as

$$\langle O\rangle_{S_0} = \frac{\int \mathcal{D}x\left(t\right)\exp\left(\frac{i}{\hbar}S_0\right)O}{\int \mathcal{D}x\left(t\right)\exp\left(\frac{i}{\hbar}S_0\right)},\qquad(3.17)$$

where O is the quantity to be averaged.

The averaged quantity in Eq.(3.15) is expanded using the cumulant expansion. To approximate the propagator, the first-order cumulant approximation is chosen, because the first-order term is the averaged but the next terms are the fluctuation. That is

$$\left\langle \exp\left\{ \frac{i}{\hbar} (S_D - S_0) \right\} \right\rangle_{S_0} \sim \exp\left\{ \frac{i}{\hbar} \langle S_D - S_0 \rangle_{S_0} \right\}, \qquad (3.18)$$

therefore, the approximate propagator $K_1 (x_b, x_a; T)$ can be obtained as

$$K (x_b, x_a; T) \approx K_1 (x_b, x_a; T),$$

$$K_1 (x_b, x_a; T) = K_0 (x_b, x_a; T) \exp\left\langle \frac{i}{\hbar} (S_D - S_0) \right\rangle_{S_0}. \qquad (3.19)$$

3.3 The trial action

In this problem we choose a trial action with two variation parameters $S_0 (\kappa, \omega)$ following Samathiyakanit [7]. This trial action is modelled from a free electron interacting harmonically with a fictitious particle of mass M with κ is a spring constant and the harmonic frequency is $\omega = \sqrt{\kappa/M}$. The Lagrangian corresponding to this model is

$$L_0 (\kappa, M) = \frac{m}{2} \dot{x}^2 (t) + \frac{M}{2} \dot{y}^2 (t) - \frac{\kappa}{2} |x (t) - y (t)|^2, \qquad (3.20)$$

where $y(t)$ is a coordinate of fictitious particle. The coordinate $y(t)$ can be eliminated by using the path integral for a forced harmonic oscillator and setting $y_a(t) = y_b(t)$, where $y_a(t)$ and $y_b(t)$ are the starting point and the ending point respectively . After integrating over $y(t)$ by using the Gaussian formula

$$\int_{-\infty}^{\infty} dp e^{-ap^2 + bp} = \sqrt{\frac{\pi}{a}} e^{\frac{b^2}{4a}}, \tag{3.21}$$

the trial action of this model is

$$S_0(\kappa, \omega) = \int_0^T dt \frac{1}{2} m \dot{x}^2(t) - \frac{\kappa \omega}{8} \int_0^T \int_0^T dt ds \, |x(t) - x(s)|^2 \frac{\cos\left[\omega\left(\frac{T}{2} - |t - s|\right)\right]}{\sin\left(\omega \frac{T}{2}\right)}, \tag{3.22}$$

where κ and ω are two variational parameters. The propagator $K_0(x_b, x_a; T)$ associating to the trial action in Eq.(3.22) has already been evaluated exactly by Samathiyakanit [7]. That is

$$K_0(x_b, x_a; T) = \left(\frac{m}{2\pi i \hbar T}\right)^{1/2} \left[\frac{\upsilon \sin\left(\frac{\omega T}{2}\right)}{\omega \sin\left(\frac{\upsilon T}{2}\right)}\right] \exp\left\{\frac{i}{\hbar}\left[\frac{\mu \upsilon}{4} \cot\left(\frac{\upsilon T}{2}\right) + \left(\frac{m \mu}{2MT}\right)\right]|x_b - x_a|^2\right\}, \tag{3.23}$$

where a reduced mass $\mu = \dfrac{mM}{m + M}$ and a frequency $\upsilon = \sqrt{\kappa/\mu}$ and $\upsilon^2 = \omega^2 + \kappa/m$.

3.4   The approximate propagator

The approximate propagator $K_1(x_b, x_a; T)$ can be evaluated by first evaluating this quantity $\langle S_D - S_0 \rangle_{S_0}$, where

$$\langle S_D - S_0 \rangle_{S_0} = \langle S_D \rangle_{S_0} - \langle S_0 \rangle_{S_0}. \tag{3.24}$$

Noting that the kinetic energy term $\frac{1}{2}m\dot{x}^2(t)$ is canceled out. From Eq.(3.22) the first term of the right hand side in Eq.(3.24) is

$$\langle S_D \rangle_{S_0} = C \int_0^T \int_0^T dt ds \int_{-\infty}^{\infty} dq \frac{\cos\left[\Omega\left(\frac{T}{2} - |t - s|\right)\right]}{\sin\left(\Omega\frac{T}{2}\right)} \langle \exp\{iq[x(t) - x(s)]\}\rangle_{S_0},$$
(3.25)

and from Eq.(3.14) the second term of the right hand side in Eq.(3.24) is

$$\langle S_0 \rangle_{S_0} = -\frac{\kappa\omega}{8} \int_0^T \int_0^T dt ds \frac{\cos\left[\omega\left(\frac{T}{2} - |t - s|\right)\right]}{\sin\left(\omega\frac{T}{2}\right)} \langle |x(t) - x(s)|^2 \rangle_{S_0}. \quad (3.26)$$

The quantity $\langle \exp\{iq[x(t) - x(s)]\}\rangle_{S_0}$ in Eq.(3.25) is expanded using the cumulant expansion. Because the trial action S_0 is a quadratic action, the valid terms are the first and the second order terms and the next terms vanish. Thus the quantity $\langle \exp\{iq[x(t) - x(s)]\}\rangle_{S_0}$ can be approximated as

$$\langle \exp\{iq[x(t) - x(s)]\}\rangle_{S_0} \approx \exp\left\{iq\langle x(t) - x(s)\rangle_{S_0} \right.$$
$$\left. -\frac{q^2}{2}\left(\langle [x(t) - x(s)]^2\rangle_{S_0} - \langle x(t) - x(s)\rangle_{S_0}^2\right)\right\}.$$
(3.27)

Next, for evaluating the two quantities $\langle x(t) - x(s)\rangle_{S_0}$ and $\langle [x(t) - x(s)]^2\rangle_{S_0}$ the generating functional must be taken into account (see Appendix A). From this technique we obtain

$$\langle x(t) - x(s)\rangle_{S_0} = A(x_b - x_a), \quad (3.28)$$

and

$$\left\langle [x(t) - x(s)]^2 \right\rangle_{S_0} = B + A^2 (x_b - x_a)^2 \tag{3.29}$$

where

$$A = \mu \left\{ \frac{\sin\left[\frac{\nu}{2}(t-s)\right] \cos\left[\frac{\nu}{2}(T-(t+s))\right]}{m \sin\left(\frac{\nu}{2}T\right)} + \frac{(t-s)}{MT} \right\}, \tag{3.30}$$

and

$$B = \frac{i\hbar\mu}{m\nu^2} \left\{ \frac{2\nu \sin\left[\frac{\nu}{2}(t-s)\right] \sin\left[\frac{\nu}{2}(T-|t-s|)\right]}{m \sin\left(\frac{\nu}{2}T\right)} + \frac{\nu^2}{MT} |t-s| (T-|t-s|) \right\}. \tag{3.31}$$

From Eq.(3.27), Eq.(3.28), Eq.(3.29), Eq.(3.30) and Eq.(3.31), the averaged quantities $\langle S_0 \rangle_{S_0}$ and $\langle S_D \rangle_{S_0}$ in Eqs.(3.25) and (3.26) can be evaluated. Therefore, we obtained

$$\begin{aligned}
\langle S_D \rangle_{S_0} - \langle S_0 \rangle_{S_0} \cdot &= C \int_0^T \int_0^T dt ds \int_{-\infty}^{\infty} dq \frac{\cos\left[\Omega\left(\frac{T}{2} - |t-s|\right)\right]}{\sin\left(\Omega\frac{T}{2}\right)} \\
&\quad \times \exp\left[iqA(x_b - x_a) - \frac{q^2}{2}B\right] \\
&\quad + \frac{\kappa\omega}{8} \int_0^T \int_0^T dt ds \frac{\cos\left[\omega\left(\frac{T}{2} - |t-s|\right)\right]}{\sin\left(\omega\frac{T}{2}\right)} \left[B + A^2(x_b - x_a)^2\right].
\end{aligned} \tag{3.32}$$

Substituting the averaged quantity in Eq.(3.32) into Eq.(3.19) the approximate

propagator of our model $K_1(x_b, x_a; T)$ can be written as

$$
\begin{aligned}
K_1(x_b, x_a; T) = \; & K_0(x_b, x_a; T) \times \exp\left\{ \frac{i}{\hbar} C \int_0^T \int_0^T dtds \int_{-\infty}^{\infty} dq \frac{\cos\left[\Omega\left(\frac{T}{2} - |t - s|\right)\right]}{\sin\left(\Omega\frac{T}{2}\right)} \right. \\
& \times \exp\left[iqA(x_b - x_a) - \frac{q^2}{2} B \right] \\
& \left. + \frac{i}{\hbar} \frac{\kappa\omega}{8} \int_0^T \int_0^T dtds \frac{\cos\left[\omega\left(\frac{T}{2} - |t - s|\right)\right]}{\sin\left(\omega\frac{T}{2}\right)} \left[B + A^2(x_b - x_a)^2\right] \right\}.
\end{aligned}
$$

$$(3.33)$$

3.5 The density matrix

For convenience in taking a limit for finding the interested quantity such as the ground state energy and the effective mass, the approximate propagator has to be transformed into the density matrix by just replacing T, t, s as $T \to -i\beta\hbar$, $t \to -it$ and $s \to -is$. After performing this process the density matrix $\rho_1(x_b, x_a; \beta)$ which corresponds to the approximate propagator $K_1(x_b, x_a; T)$ will be obtained.

$$
\begin{aligned}
\rho_1(x_b, x_a; \beta) = \; & \rho_0(x_b, x_a; \beta) \times \exp\left\{ \frac{C}{\hbar} \int_0^{\beta\hbar} \int_0^{\beta\hbar} dtds \int_{-\infty}^{\infty} dq \frac{\cosh\left[\Omega\left(\frac{\beta\hbar}{2} - |t - s|\right)\right]}{\sinh\left(\Omega\frac{\beta\hbar}{2}\right)} \right. \\
& \times \exp\left[iq(x_b - x_a) A_1 - \frac{q^2\hbar}{2m\nu^2} f(|t - s|, \beta) \right] \\
& + \frac{1}{2}\left(1 - \frac{\omega^2}{\nu^2}\right)\left[\frac{\nu}{2}\beta\hbar \coth\left(\frac{\nu}{2}\beta\hbar\right) - 1\right] \\
& \left. + \frac{\kappa\omega}{8\hbar} \int_0^{\beta\hbar} \int_0^{\beta\hbar} \frac{\cosh\left[\omega\left(\frac{\beta\hbar}{2} - |t - s|\right)\right]}{\sinh\left(\omega\frac{\beta\hbar}{2}\right)} A_1^2(x_b - x_a)^2 \right\},
\end{aligned}
$$

$$(3.34)$$

where $\rho_0\left(x_b, x_a; \beta\right)$ is the density matrix which corresponds to the propagator $K_0\left(x_b, x_a; T\right)$,

$$
\begin{aligned}
\rho_0\left(x_b, x_a; \beta\right) &= \left(\frac{m}{2\pi\beta\hbar^2}\right)^{1/2}\left[\frac{\upsilon \sinh\left(\frac{\omega}{2}\beta\hbar\right)}{\omega \sinh\left(\frac{\upsilon}{2}\beta\hbar\right)}\right] \\
&\times \exp\left\{-\frac{1}{\hbar}\left[\frac{\mu\upsilon}{4}\coth\left(\frac{\upsilon}{2}\beta\hbar\right) + \left(\frac{m\mu}{2M\beta\hbar}\right)\right]|x_b - x_a|^2\right\},
\end{aligned}
$$

$$(3.35)$$

$$
A_1 = \mu\left\{\frac{\sinh\left[\frac{\nu}{2}(t-s)\right]\cosh\left[\frac{\nu}{2}(\beta\hbar - (t+s))\right]}{m \sinh\left(\frac{\nu}{2}\beta\hbar\right)} + \frac{(t-s)}{M\beta\hbar}\right\}, \qquad (3.36)
$$

and

$$
\begin{aligned}
f\left(|t-s|, \beta\right) &= \mu\left\{\frac{2\nu \sinh\left[\frac{\nu}{2}(t-s)\right]\sinh\left[\frac{\nu}{2}(\beta\hbar - |t-s|)\right]}{m \sinh\left(\frac{\nu}{2}\beta\hbar\right)}\right. \\
&\left. + \frac{\nu^2}{M\beta\hbar}|t-s|\beta\hbar - |t-s|\right\}.
\end{aligned}
$$

$$(3.37)$$

Noting that the term $\frac{1}{2}\left(1-\frac{\omega^2}{\nu^2}\right)\left[\frac{\nu}{2}\beta\hbar\coth\left(\frac{\nu}{2}\beta\hbar\right) - 1\right]$ in Eq.(3.35) has been derived using the expansion

$$
\begin{aligned}
\frac{\kappa\omega}{8}\frac{\mu}{m\nu^2}\int_0^{\beta\hbar}\int_0^{\beta\hbar}dtds&\frac{\cosh\left[\omega\left(\frac{\beta\hbar}{2} - |t-s|\right)\right]}{\sinh\left(\omega\frac{\beta\hbar}{2}\right)} \\
&\times\left\{\frac{2\nu \sinh\left[\frac{\nu}{2}(t-s)\right]\sinh\left[\frac{\nu}{2}(\beta\hbar - |t-s|)\right]}{m \sinh\left(\frac{\nu}{2}\beta\hbar\right)} + \frac{\nu^2}{M\beta\hbar}|t-s|(\beta\hbar - |t-s|)\right\},
\end{aligned}
$$

by setting $|t-s| = u$ and using the relation

$$
\int_0^\beta\int_0^\beta dtds g\left(|t-s|\right) = 2\int_0^\beta du\left(\beta - u\right)g\left(u\right). \qquad (3.38)
$$

In this chapter, the model Hamiltonian for an electron moving along DNA is proposed and the Lagrangian is obtained using Legendre transform. The oscillator coordinates are eliminated using the path integrals over the oscillator coordinates. To evaluate the propagator, a variational method is applied by choosing a trial action S_0. The first cumulant approximation is chosen to approximate the propagator. Lastly, the density matrix is obtained from the propagator by replacing T by $-i\beta\hbar$.

Chapter 4

The ground state energy and the effective mass

In this chapter, the ground state energy and the effective mass are computed. According to the density matrix obtained in Chapter 3, the off-diagonal part provides the formula for the effective mass called "Feynman mass". In the last section, a numerical method is applied to calculate the ground state energy and the effective mass.

4.1 The definition of the effective mass

In this thesis, an electron moving along DNA and interacting with the oscillators (the base pair vibrations) is considered by neglecting oscillator-oscillator interactions. By considering an electron in this way, it will have an effective mass higher than that of an isolated electron mass. The effective mass is denoted by m^*.

The definition of the effective mass can be determined in several ways. The most common way is to extract it from the coefficient of the momentum in

the following equation,

$$E = E_0 + \frac{p^2}{2m^*}, \tag{4.1}$$

where E_0 is the ground state energy or self-energy and m^* is the effective mass.

The effective mass can be determined by another way, suggested by Feynman [14]. We assume that the particle moves between the initial point R_1 and final point R_2 with a time interval T. Its mean group velocity U is then

$$U = \frac{R_2 - R_1}{T}. \tag{4.2}$$

By considering an electron at low velocities, the density matrix can be expressed in an approximate form of a free particle as

$$\rho \overset{\beta \to \infty}{\sim} \exp\left[-E_0\beta - \frac{m_F |R_2 - R_1|^2}{2\beta\hbar^2} \right], \tag{4.3}$$

where m_F is the effective mass called Feynman mass. It can be derived from the $|R_2 - R_1|^2$ dependent term, called the off-diagonal part. The ground state energy E_0 can be derived from the diagonal part.

4.2 Evaluation of the effective mass

In order to evaluate the effective mass, the off-diagonal part of the density matrix obtained in Chapter 3 is exploited. The limiting condition $(x_b - x_a) \to 0$ is taken

into account. The exponential term $\exp\left[iq\left(x_b - x_a\right) A_1\right]$ can then be expanded in a power series of $\left(x_b - x_a\right)$. By keeping these expansion terms up to the second order, we obtain

$$
\begin{aligned}
\rho_1\left(x_b, x_a; \beta\right) = {} & \rho_0\left(x_b, x_a; \beta\right) \times \exp\left\{\frac{C}{\hbar}\int_0^{\beta\hbar}\int_0^{\beta\hbar} dt\,ds \int_{-\infty}^{\infty} dq \frac{\cosh\left[\Omega\left(\frac{\beta\hbar}{2} - |t - s|\right)\right]}{\sinh\left(\Omega\frac{\beta\hbar}{2}\right)}\right. \\
& \times \exp\left[-\frac{q^2\hbar}{2m\nu^2}f\left(|t - s|, \beta\right)\right]\left[1 - \frac{q^2}{2}\left(x_b - x_a\right)^2 A_1^2\right] \\
& + \frac{1}{2}\left(1 - \frac{\omega^2}{\nu^2}\right)\left[\frac{\nu}{2}\beta\hbar\coth\left(\frac{\nu}{2}\beta\hbar\right) - 1\right] \\
& \left. + \frac{\kappa\omega}{8\hbar}\int_0^{\beta\hbar}\int_0^{\beta\hbar} dt\,ds \frac{\cosh\left[\omega\left(\frac{\beta\hbar}{2} - |t - s|\right)\right]}{\sinh\left(\omega\frac{\beta\hbar}{2}\right)}A_1^2\left(x_b - x_a\right)^2\right\}, \quad (4.4)
\end{aligned}
$$

where the function $\rho_0\left(x_b, x_a; \beta\right)$, A_1 and $f\left(|t - s|, \beta\right)$ are shown in Eq.(3.33), Eq.(3.34) and Eq.(3.35), respectively. Next, the system is considered at very low temperatures and a very low velocity, so the limiting conditions become $\beta \to \infty$, and $\left(x_b - x_a\right) \to 0$. Accordingly the hyperbolic function in volving $(t + s)$ is damped out and hyperbolic function in volving $(t - s)$ in the density matrix Eq.(4.4) can be approximated as,

$$
\begin{aligned}
& \frac{\cosh\left[\Omega\left(\frac{\beta\hbar}{2} - |t - s|\right)\right]}{\sinh\left(\Omega\frac{\beta\hbar}{2}\right)} \\
= {} & \frac{\exp\left[\Omega\left(\frac{\beta\hbar}{2} - |t - s|\right)\right] + \exp\left[-\Omega\left(\frac{\beta\hbar}{2} - |t - s|\right)\right]}{\exp\left(\Omega\frac{\beta\hbar}{2}\right) - \exp\left(-\Omega\frac{\beta\hbar}{2}\right)} \xrightarrow{\beta\to\infty} \exp\left(-\Omega\left|t - s\right|\right),
\end{aligned}
$$

$$
\frac{\cosh\left[\omega\left(\frac{\beta\hbar}{2} - |t - s|\right)\right]}{\sinh\left(\omega\frac{\beta\hbar}{2}\right)} \xrightarrow{\beta\to\infty} \exp\left(-\omega\left|t - s\right|\right).
$$

By using the relation

$$\int_0^\beta \int_0^\beta dtds\, g\left(|t-s|\right) = 2\int_0^\beta du\,(\beta-u)\,g\left(u\right),$$
$$\xrightarrow{\beta\to\infty} 2\beta \int_0^\infty du\, g\left(u\right), \qquad (4.5)$$

the expression

$$-\frac{C}{\hbar} \int_0^{\beta\hbar} \int_0^{\beta\hbar} dtds \int_{-\infty}^\infty dq \frac{\cosh\left[\Omega\left(\frac{\beta\hbar}{2}-|t-s|\right)\right]}{\sinh\left(\Omega\frac{\beta\hbar}{2}\right)} \frac{q^2}{2} A_1^2 \exp\left[-\frac{q^2\hbar}{2m\nu^2} f\left(|t-s|,\beta\right)\right] (x_b-x_a)^2,$$

in the density matrix Eq.(4.4) becomes

$$-C\beta \int_{-\infty}^\infty dq\, q^2 \int_0^\infty du\, \mu^2 \left[\frac{u}{M\beta\hbar}\right]^2 \times \exp\left[-\frac{q^2\hbar}{2m\nu^2} f\left(u,\beta\to\infty\right) - \Omega u\right] (x_b-x_a)^2, \qquad (4.6)$$

where $f\left(u,\beta\to\infty\right)$ can be written in terms of parameters ω and ν only as

$$f\left(u,\beta\to\infty\right) = \nu\left(1-\frac{\omega^2}{\nu^2}\right)\left(1-e^{-\nu u}\right) + \omega^2 u.$$

Also, the last term of the density matrix becomes

$$\frac{\kappa\omega}{2} \int_0^\infty du\, u^2 \frac{\mu^2}{M^2} \exp\left(-\omega u\right)] \frac{(x_b-x_a)^2}{2\beta\hbar^2}. \qquad (4.7)$$

Finally, the electron coordinates $(x_b - x_a)$ are transformed into the center of mass coordinates of the two particle model system, as

$$R_2 - R_1 = \frac{m}{m_0}\left(x_b - x_a\right), \qquad (4.8)$$

where $m_0 = m + M$ is the total mass.

According to Eq.(4.8), Eq.(4.6), Eq.(4.7) and Eq.(4.8), the off-diagonal part of the density matrix can be approximately written as

$$\rho_1\left(x_b, x_a; \beta \to \infty\right) \ \sim \ \exp\left\{-\left[m_o + 2C\int_{-\infty}^{\infty} dq q^2 \int_0^{\infty} du u^2 \right.\right.$$

$$\times \exp\left(-\frac{q^2\hbar}{2m\nu^2}f\left(|t-s|, \beta \to \infty\right) - \Omega u\right)$$

$$\left.\left. -\frac{\kappa\omega}{2}\int_0^{\infty} du u^2 \exp\left(-\omega u\right)\right]\frac{|R_2 - R_1|^2}{2\beta\hbar^2}\right\}. \qquad (4.9)$$

The last term of Eq.(4.9) can be integrated to give $-M$. This M together with m_o will give m, the bare mass of the electron in DNA.

Noting that the hyperbolic term $\frac{\nu\mu}{4\hbar}\coth\left(\frac{\nu}{2}\beta\hbar\right)$ in $\rho_0\left(x_b, x_a; \beta\right)$ does not enter into the calculation, because it is damped out as $\beta \to \infty$ [19].

Then by comparing Eq.(4.9) with Eq.(4.3) and integrating over q variable, the effective mass m^* can be expressed as

$$m^*\left(\nu, \omega\right) = m + C\sqrt{\pi}\nu^3\left(\frac{2m}{\hbar}\right)^{3/2}\int_0^{\infty} du u^2 \exp\left(-\Omega u\right)\left[f\left(|t-s|, \beta \to \infty\right)\right]^{-3/2},$$

$$(4.10)$$

or

$$\frac{m^*\left(\nu, \omega\right)}{m} = 1 + \frac{C\sqrt{\pi}\nu^3}{m}\left(\frac{2m}{\hbar}\right)^{3/2}\int_0^{\infty} du u^2 \exp\left(-\Omega u\right)\left[f\left(|t-s|, \beta \to \infty\right)\right]^{-3/2}.$$

$$(4.11)$$

The integral in Eq.(4.11) cannot be performed in a closed form, so the numerical integration is required for complete determination.

4.3 Evaluation the ground state energy

To evaluate the ground state energy the diagonal part of the density matrix is considered. So we have

$$
\begin{aligned}
\rho_1\left(0,0;\beta\right) \;=\; & \left(\frac{m}{2\pi\beta\hbar^2}\right)^{1/2}\left[\frac{\upsilon\sinh\left(\frac{\omega}{2}\beta\hbar\right)}{\omega\sinh\left(\frac{\upsilon}{2}\beta\hbar\right)}\right] \\
& \times\exp\left\{\frac{1}{2}\left(1-\frac{\omega^2}{\nu^2}\right)\left[\frac{\nu}{2}\beta\hbar\coth\left(\frac{\nu}{2}\beta\hbar\right)-1\right]\right. \\
& +\frac{2C}{\hbar}\int_0^{\beta\hbar}du\left(\beta\hbar-u\right)\int_{-\infty}^{\infty}dq\frac{\cosh\left[\Omega\left(\frac{\beta\hbar}{2}-u\right)\right]}{\sinh\left(\Omega\frac{\beta\hbar}{2}\right)} \\
& \left.\times\exp\left[-\frac{q^2\hbar}{2m'\nu^2}f\left(u,\beta\right)\right]\right\}.
\end{aligned}
\tag{4.12}
$$

Next, the limiting condition is taken as $\beta\rightarrow\infty$. So the density matrix Eq.(4.12) can be written approximately as

$$
\begin{aligned}
\rho_1\left(0,0;\beta\rightarrow\infty\right) \;\sim\; & \left(\frac{m}{2\pi\beta\hbar^2}\right)^{1/2}\left(\frac{\upsilon}{\omega}\right) \\
& \left\{\exp\left(\frac{\beta\hbar}{2}\left(\omega-\nu\right)\right)\times\exp\left[\frac{\nu}{4}\beta\hbar\left(1-\frac{\omega^2}{\nu^2}\right)\right]\right. \\
& \left.\times\exp\left(2C\beta\int_0^{\infty}du\int_{-\infty}^{\infty}dq\exp\left[-\frac{q^2\hbar}{2m\nu^2}f\left(u,\beta\rightarrow\infty\right)-\Omega u\right]\right)\right\}.
\end{aligned}
\tag{4.13}
$$

The ground state energy of our system can be evaluated by comparing Eq.(4.13) with Eq.(4.3)and integrating over q variable. Thus we get

$$
E_0\left(\nu,\omega\right)=\frac{\hbar\nu}{4}\left(1-\frac{\omega}{\nu}\right)^2-2C\sqrt{\pi}\left[\frac{\hbar}{2m\nu^2}\right]^{-1/2}\int_0^{\infty}duf\left(u,\beta\rightarrow\infty\right)^{-1/2}\exp\left(-\Omega u\right),
\tag{4.14}
$$

where the quantities ν, ω are considered as two variational parameters which may be varied separately to obtain a minimum value of E_0. Similar to the $\frac{m^*(\nu,\omega)}{m}$, the integral in $E_0(\nu,\omega)$ requires the numerical integration for complete calculation.

4.4   Numerical method

In sections 4.2 and 4.3 the formulas of the effective mass and the ground state energy of our system are evaluated. In this section, the ground state energy which is dependent on the two variable parameters is minimized. After that the best value of the two parameters are kept to calculate the effective mass.

4.4.1   The minimization process

For convenience in the minimization process the variational parameters are changed so that $E_0(\nu,\omega) \rightarrow E_0(\nu,r)$ and $\frac{m^*(\nu,\omega)}{m} \rightarrow \frac{m^*(\nu,r)}{m}$, where $r = \frac{\omega}{\nu}$. So the new expressions of the ground state energy $E_0(\nu,r)$ and the effective mass per mass $\frac{m^*(\nu,r)}{m}$ in Eq.(4.14) and Eq.(4.11) respectively, become

$$E_0(\nu,r) = \frac{\hbar\nu}{4}(1-r)^2 - 2C\sqrt{\pi}\left[\frac{\hbar}{2m\nu^2}\right]^{-1/2}\int_0^\infty duf(u,\beta\rightarrow\infty)^{-1/2}\exp(-\Omega u),$$
$$(4.15)$$

$$\frac{m^*(\nu,r)}{m} = 1 + \frac{C\sqrt{\pi}\nu^3}{m}\left(\frac{2m}{\hbar}\right)^{3/2}\int_0^\infty duu^2\exp(-\Omega u)\left[f(|t-s|,\beta\rightarrow\infty)\right]^{-3/2},$$
$$(4.16)$$

where $C = \frac{1}{8\pi}M'\Omega^3\alpha^2\rho$. Similarly $f(u, \beta \rightarrow \infty)$ can be rewritten in terms of parameters r and ν as

$$f(u, \beta \rightarrow \infty) = \nu\left(1 - r^2\right)\left(1 - e^{-\nu u}\right) + \nu^2 r^2 u. \qquad (4.17)$$

The realistic input parameters for DNA molecules are given as follows [23]: $\Omega = 6.252 \times 10^{12}\ s^{-1}$, $M' = 4.982 \times 10^{-25}\ kg$, $\rho = 0.294118\ \mathring{A}^{-1}$.

In order to minimize the ground state energy, the curve surface of E_0 is plotted versus two parameters ν, r and the minimum area of the E_0 is searched by eyes (see Appendix B). After that the MATHEMATICA program with Find-Minimum function is applied (see Appendix B) to choose the best values of the two parameters ν, r which minimize E_0.

4.4.2 Results and discussions

After applying the MATHEMATICA program to the formula of the ground state energy in Eq.(4.15), the ground state energy versus the coupling constant α is plotted in Fig.(4.1). It is shown that the ground state energy E_0 decreases slowly in the first region of small α (the weak coupling region). After that it decreases rapidly as α increases in the large α region (the strong coupling region). By substituting the values of the two parameters ν and r which minimize E_0 into Eq.(4.16) the results of $\dfrac{m^*}{m}$ are shown in Fig.(4.2) and Table (4.1). The results

of $\dfrac{m^*}{m}$ start from 1 and increase slowly in the weak coupling region and more rapidly in the strong coupling region.
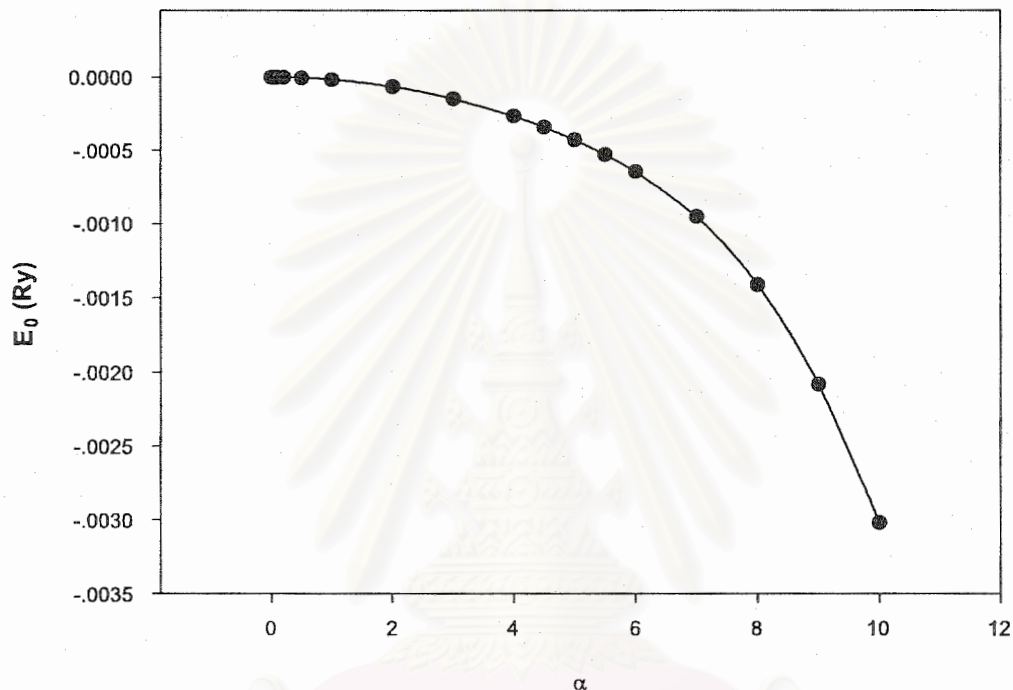

Figure 4.1: The relation between the ground state energy E_0 and the coupling constant α.

The characteristic of the parameter ν plotted versus α is shown in Fig.(4.3). It can be seen that ν varies from 0 and increases slowly in the weak coupling region but it increases rapidly in the strong coupling region. The curve of r versus α is shown in Fig.(4.4). It shows that r $(r = \dfrac{\omega}{\nu})$ varies from 1 to 0 as α increases
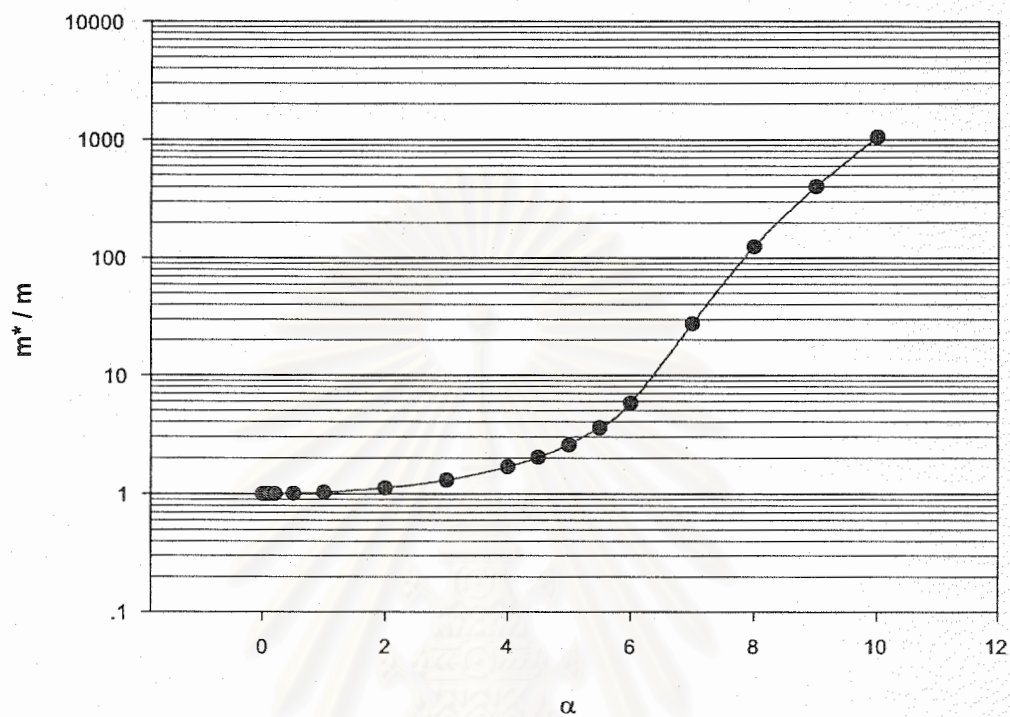
Figure 4.2: The relation between $\frac{m^*}{m}$ and the coupling constant α.

and it has an interesting characteristic that its slope decreases rapidly around α

between 4 and 7. The value of $\dfrac{dr}{d\alpha}$ is plotted versus α in Fig.(4.5). The lowest

point of the curve in Fig.(4.5) indicates the phase transition occurs at $\alpha = 5.76$.

When we look closely at the $\dfrac{m^*}{m}$ curve in Fig.(4.2), we see that $\dfrac{m^*}{m}$ is close to 1

in the weak coupling region and turns smoothly into large values in the strong

coupling region. The physical interpretation is that an electron behaves as a free

electron in the week coupling region and becomes a massive particle in the strong

α	m^*/m	α	m^*/m
0.001	1.00	3	1.30
0.002	1.00	4	1.68
0.005	1.00	4.5	2.02
0.01	1.00	5	2.57
0.02	1.00	5.5	3.58
0.05	1.00	6	5.78
0.1	1.00	7	27.42
0.2	1.00	8	124.481
0.5	1.01	9	400.38
1	1.03	10	1048.52
2	1.12		

Table 4.1: The relation between m^*/m and the coupling constant α.

coupling region.

An analytical form of the ground state energy in the weak coupling region can be derived. Following the curves in Fig.(4.3) and Fig.(4.4), some limiting conditions can be taken in this region. This is of interest because it leads to an analytic expression. Since $r \to 1$ and $\nu \ll 1$, the ground state energy in Eq.(4.15) can be approximated analytically. By considering the function $f(u, \beta \to \infty)$ first, the exponential term in Eq.(4.17) can be expanded in a power series and by keeping only the second order term, we get

$$f(u, \beta \to \infty) \approx \nu \left(1 - r^2\right) \left[1 - (1 - \nu u)\right] + \nu^2 r^2 u, \qquad (4.18)$$

$$\approx \nu^2 u.$$

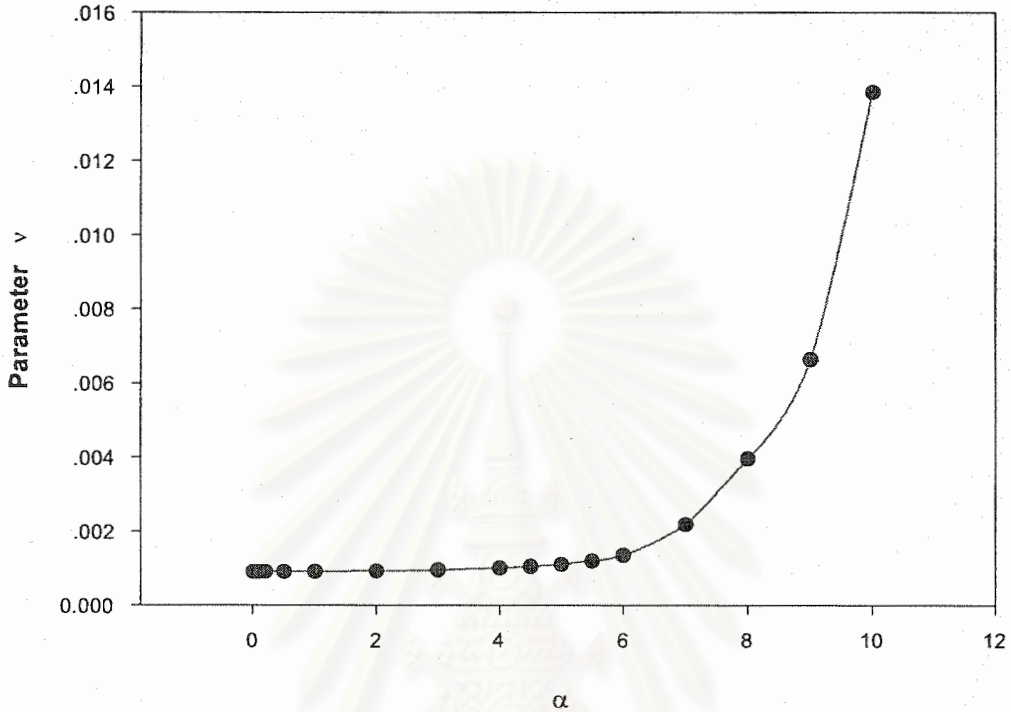Therefore, the ground state energy in the weak coupling limit $E_0(weak)$ in

Figure 4.3: The relation between the parameter ν and the coupling constant α.

Eq.(4.15) can be approximated as

$$E_0\left(weak\right) \approx \frac{\hbar\nu}{4}\left(1-r\right)^2 - 2C\sqrt{\pi}\left[\frac{\hbar}{2m\nu^2}\right]^{-1/2}\int_0^\infty du\nu^2 u\exp\left(-\Omega u\right). \quad (4.19)$$

Because $r \to 1$, the term $\frac{\hbar\nu}{4}\left(1-r\right)^2$ in Eq.(4.19) is negligible. After integrating over u, the analytical formula of the ground state energy in the weak coupling limit is

$$E_0\left(weak\right) \approx 2C\pi\sqrt{\frac{2m}{\hbar\Omega}}, \quad (4.20)$$
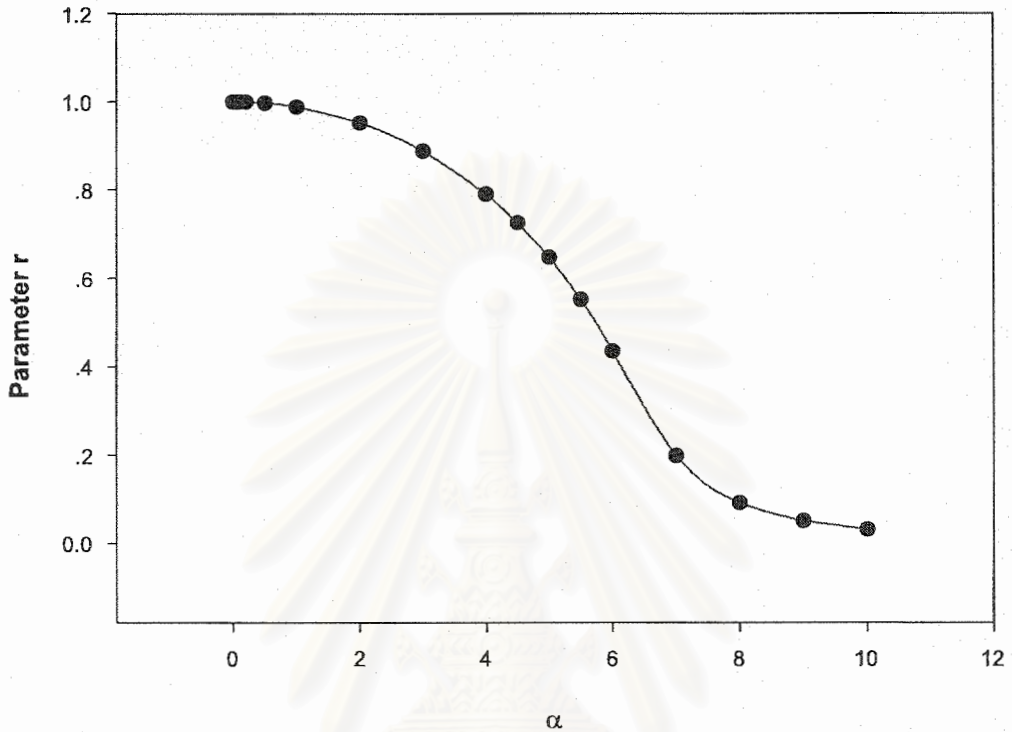
Figure 4.4: The relation between the parameter r and the coupling constant α.

where $C = \frac{1}{8\pi} M'\Omega^3 \alpha^2 \rho$. By substituting the realistic values of M', Ω and ρ into Eq.(4.20), we obtain

$$E_0\,(weak) \approx -1.61 \times 10^{-5} \alpha^2 Ry. \tag{4.21}$$

The analytical approximation of the ground state energy in the strong coupling region is too complicated to perform. The fitted curve using the least-squares
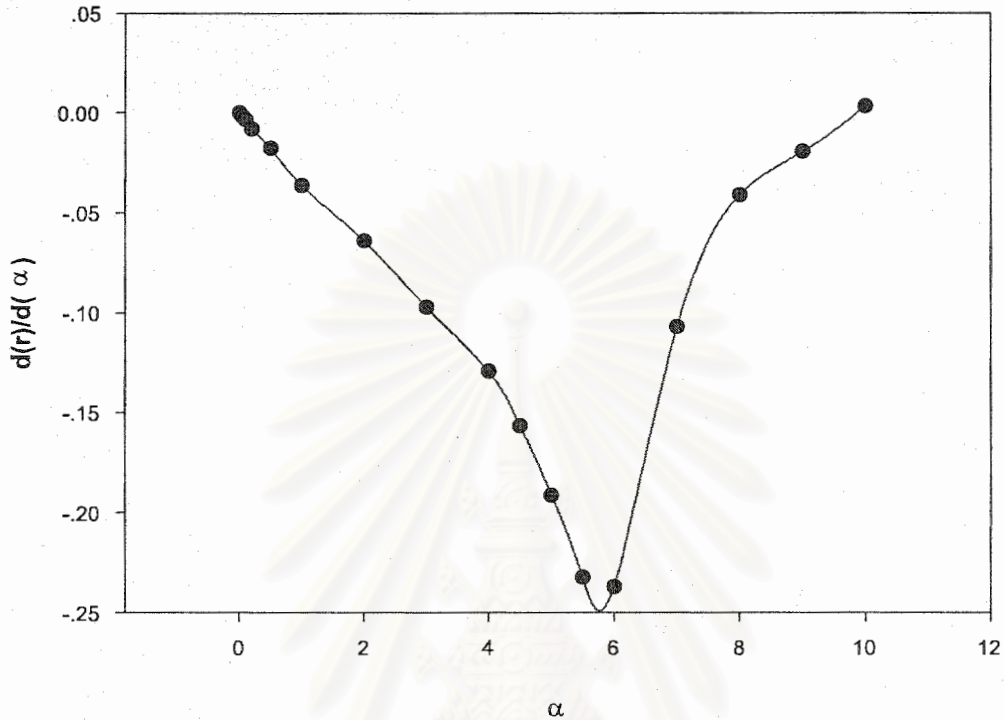
Figure 4.5: The relation between the $\frac{dr}{d\alpha}$ and the coupling constant α.

method of the ground state energy E_0 is

$$E_0 = 1.23 \times 10^{-5} - 9.29 \times 10^{-5}\alpha + 2.51 \times 10^{-5}\alpha^2 - 4.57 \times 10^{-6}\alpha^3 Ry. \quad (4.22)$$

The numerical results of E_0 are compared to the analytical formula of E_0 (*weak*)

and the fit curve of the ground state energy E_0 in Fig.(4.6). We find that in the

weak coupling region the approximate E_0 (*weak*) and the fit curve of the ground

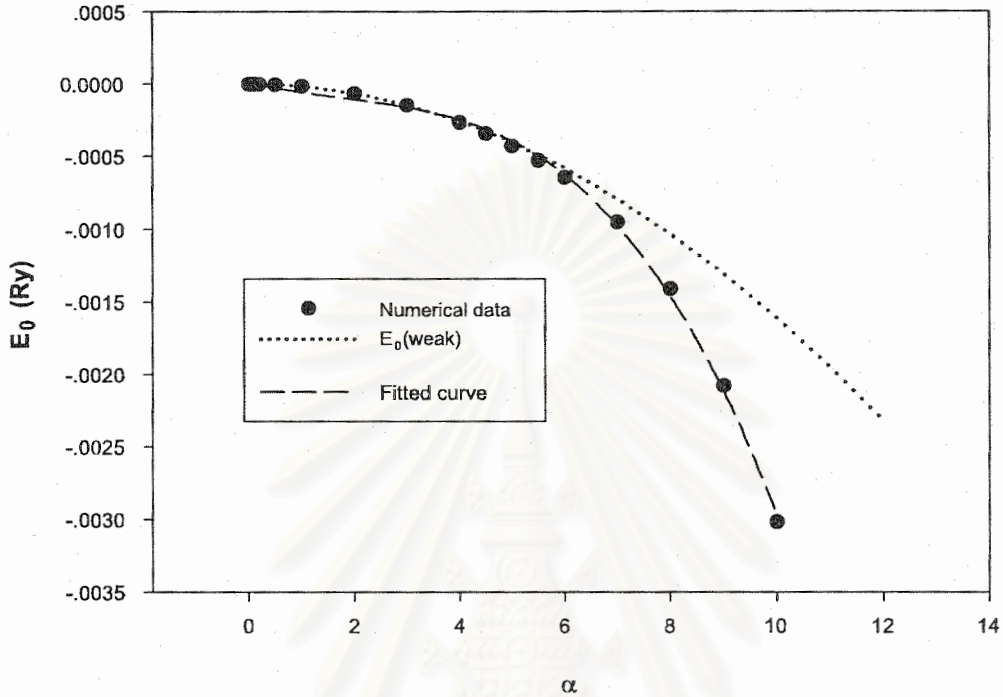state energy E_0 are close to the numerical results. But in strong coupling region,

Figure 4.6: Comparison of the numerical ground state energy E_0 with the approximate E_0 (*weak*) and the fitted curve of E_0.

only the fitted curve of the ground state energy E_0 is close to the numerical results.

It is also shown that the physical behavior in the two regions are different.

Our model can be used to explain other systems which compose of a moving electron interacting with harmonic oscillators. The formulas of the ground state energy and the effective mass per bare mass $\frac{m^*}{m}$ can be used by inserting the value of the oscillator mass M', the vibration frequency Ω, and the number

of the oscillator per length ρ which correspond to the true system into Eq.(4.14) and Eq.(4.11) respectively. In this model we consider an electron moving in one dimension but in the real DNA this is not a true one dimensional system. It is thus considered as a quasi one dimensional system. More realistic calculations should include an angular part of electron wave functions but it is too difficult to be performed by using Feynman's path integration.
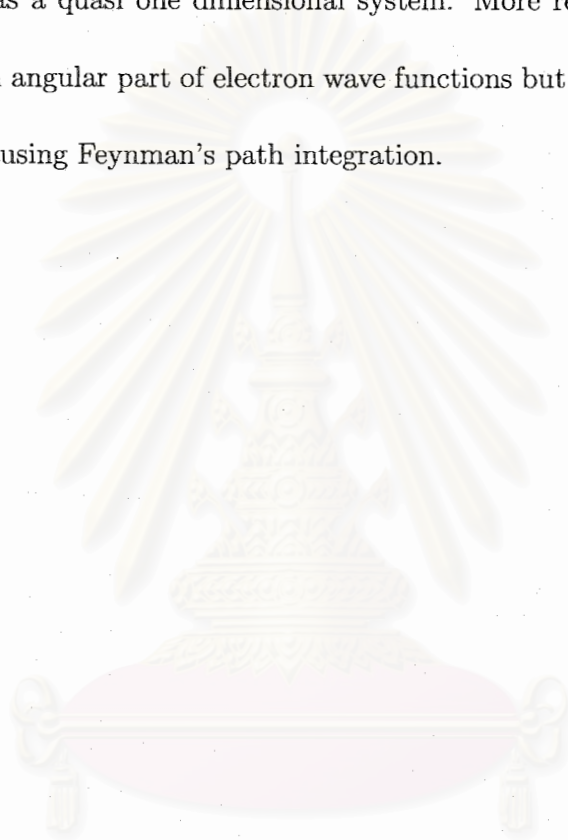
Chapter 5

Conclusion

In this work, the model for an electron moving along DNA is presented. It is modelled as an electron moving and interacting with harmonic oscillators while the interaction term is modelled as a Dirac delta function. The oscillator-oscillator interaction term is neglected. The ground state energy and the effective mass of the electron are evaluated by using Feynman's path integral method.

First of all, the oscillators' coordinates can be eliminated by setting up a transformation function which connects the initial and the final states of the electron and the oscillators. After eliminating the oscillators' coordinates, the transformation function without the prefactor is called the propagator. This propagator cannot be evaluated exactly. The approximate propagator can be evaluated by using the variational method with a trial action proposed by Sayakanit [15]. The approximate propagator is transformed into the density matrix.

The formulas of the ground state energy and the effective mass are derived from the diagonal part and the off-diagonal part respectively. The MATHEMAT-

ICA program is chosen to calculate the ground state energy and the Feynman effective mass numerically.

In the weak coupling region, the ground state energy E_0 decreases slowly as the coupling constant α increases. While it increases rapidly in the strong coupling region, the analytical formula of the ground state energy in the weak coupling region is $E_0\,(weak) \approx -1.61 \times 10^{-5}\alpha^2\ Ry$ and the fitted curve of the ground state energy is $E_0 = 1.23 \times 10^{-5} - 9.29 \times 10^{-5}\alpha + 2.51 \times 10^{-5}\alpha^2 - 4.57 \times 10^{-6}\alpha^3 Ry$. The effective mass per mass $\dfrac{m^*}{m}$ starts from 1 and increases slowly in the weak coupling region then it increases rapidly when the phase transition occurs at the coupling constant which is approximately equal to 5.76. It shows that, in the weak coupling region the behavior of the electron is like a free electron while it behaves like a heavy particle in the strong coupling region. This means that if we apply an external force such as an electric field to this system, an electron in the weak coupling will move easily than that in the strong coupling region. The conductivity of DNA molecules is measured experimentally and found that it behaves like either a conductor or an insulator as shown in Fig.(1.2) and Fig.(1.3) in Chapter 1. This conflict of the results may come from the difference of the coupling constant range operated in those experiments.

To improve our model, the interaction term should be modified by using

more realistic interactions such as a Coulomb interaction. Furthermore, if the oscillator vibrations are very strong, these must be modelled as the anharmonic oscillators also the distribution of the frequency Ω can be included that is the vibration frequency of each base pair is different. If the dynamics in the angular part is included into the model Hamiltonian, the degree of freedom of our system will be more realistic. Our model can be used to explaining other systems (such as an electron moving in polymer chain problem) which have a moving electron interacting with the harmonic oscillators.

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Appendices

Appendix A:
The generating function

The average over quantities like $\langle x(t) \rangle$ or $\langle x(t) x(s) \rangle$ can be evaluated from the generating functional

$$\left\langle \exp[\frac{i}{\hbar} \int f(t) x(t) \, dt] \right\rangle_{S_0} = \frac{\int \mathcal{D}x(t) \exp[\frac{i}{\hbar} \left(S + \int_0^T dt f(t) x(t) \right)]}{\int \mathcal{D}x(t) \exp(\frac{i}{\hbar} S)}, \qquad (A.1)$$

with end point condition $x(T) = x_b$, $x(0) = x_a$ and $f(t)$ is a time- dependent arbitrary function. By following the standard way of evaluation of the path integration from Feynman and Hibbs [1] the path integral on the right-hand side of above equation can be reduced to an exponential of a two classical function, that is

$$\left\langle \exp[\frac{i}{\hbar} \int f(t) x(t) \, dt] \right\rangle_{S_0} = \int \mathcal{D}x(t) \exp[\frac{i}{\hbar} \left(S_{cl}^f - S_{cl} \right)], \qquad (A.2)$$

where S_{cl}^f is the classical action which corresponds to the action S^f,

$$S^f = S + \int_0^T dt f(t) x(t)$$

and S_{cl} is the classical action which corresponds to the action S.

The interesting quantities $\langle x(t) \rangle$ and $\langle x(t) x(s) \rangle$ can be obtained by differentiating Eq.(A.2) with respect to the function $f(t)$ and setting it to zero.

That is

$$\left\langle x\left(t\right)\exp[\frac{i}{\hbar}\int f\left(t\right)x\left(t\right)dt]\right\rangle_{S_0} = \frac{\hbar}{i}\frac{\partial}{\partial f\left(t\right)}\left\{\exp[\frac{i}{\hbar}\left(S_{cl}^f - S_{cl}\right)]\right\},$$

$$= \frac{\partial S_{cl}^f}{\partial f\left(t\right)}\left\{\exp[\frac{i}{\hbar}\left(S_{cl}^f - S_{cl}\right)]\right\}.$$

Therefore, by evaluating both sides when $f\left(t\right) = 0$, we obtain

$$\langle x\left(t\right)\rangle_{S_0} = \left.\frac{\partial S_{cl}^f}{\partial f\left(t\right)}\right|_{f=0}. \tag{A.3}$$

We can continue this process to get the second derivative as

$$\langle x\left(t\right)x\left(s\right)\rangle = \left(\frac{\hbar}{i}\right)^2\frac{\partial^2}{\partial f\left(t\right)\partial f\left(s\right)}\exp[\frac{i}{\hbar}\left(S_{cl}^f - S_{cl}\right)]\Bigg|_{f=0}. \tag{A.4}$$
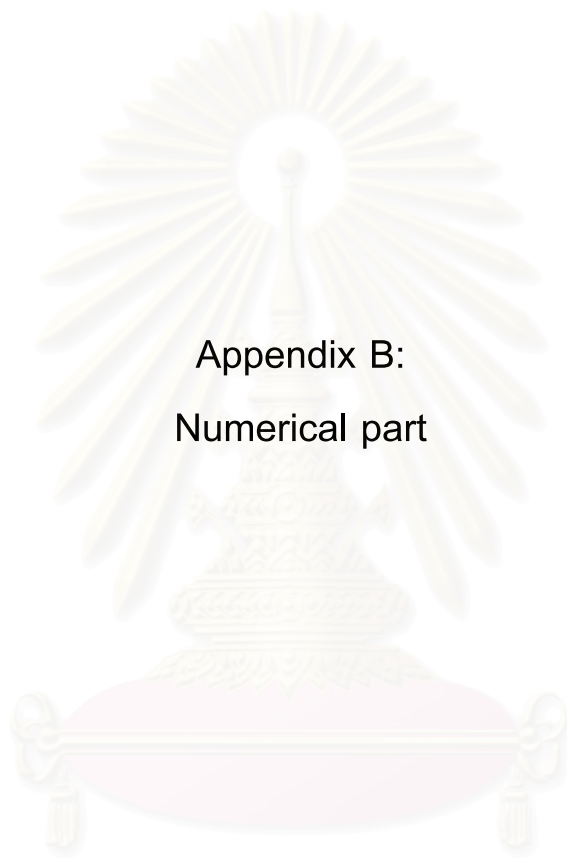
Appendix B:

Numerical part
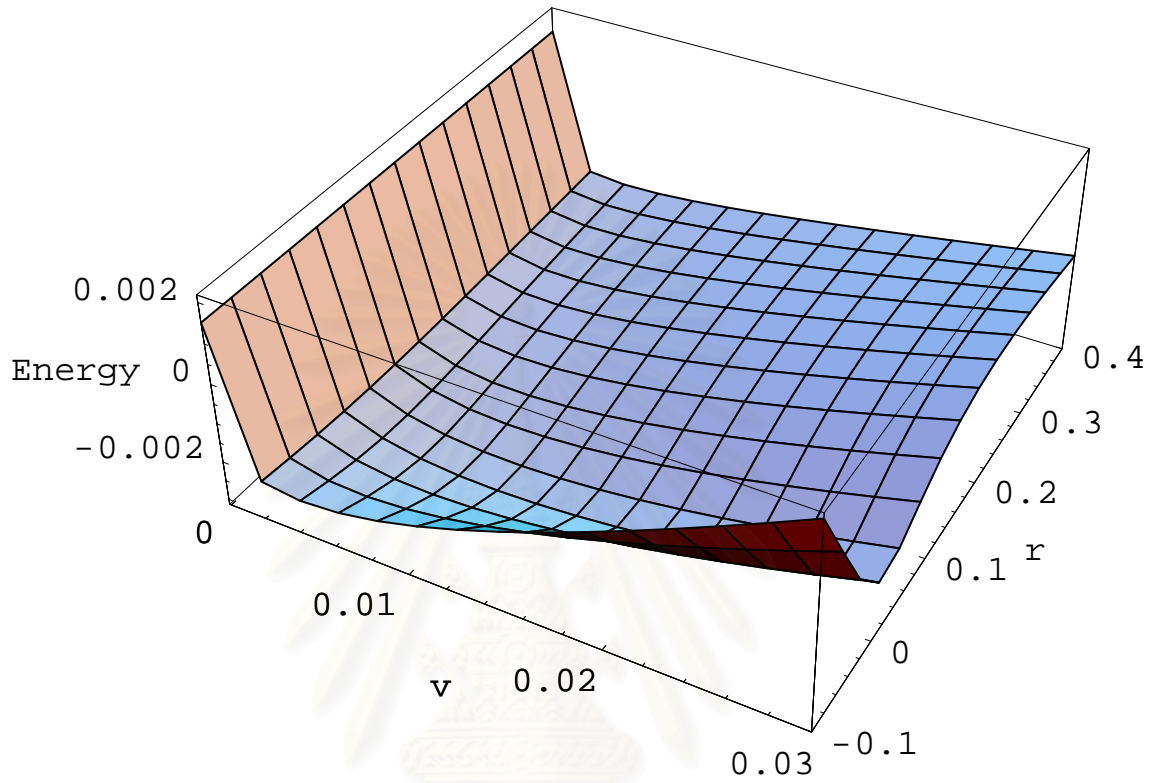
Figure B.1: The curve surface of the ground state energy E_0 and the two variational parameters ν and r where α equal to 10.

```
(* This program minimizes the ground state energy
   E0 where the coupling constant α equal to 1*)

Clear[h, m, Ω, α, M, c, ρ, r, ν, u]
h = 1;
m = 0.5;
Ω = 6.252 * 10^12 * (2.0600687 * 10^16)^-1;
α = 1;
M = 4.982 * 10^-25 (1.8218779 * 10^-30)^-1;
ρ = 0.5 (3.4)^-1;
c = ρ * M * Ω^3 * α^2 (8 * π)^-1;
```

$$\text{FindMinimum}\Big[\frac{h*\nu}{4} * (1-r)^2 - \Big(2*c*\nu \sqrt{\frac{2*\pi*m}{h}} \Big)$$

$$\text{NIntegrate}\Big[\text{Exp}[-\Omega*u]$$

$$* \Big(\sqrt{\frac{1}{(\nu * (1-r^2) * (1-\text{Exp}[-\nu*u]) + \nu^2 * r^2 * u)}} \Big),$$

$$\{u, 0, \text{Infinity}\}\Big], \{r, 1\}, \{\nu, 0.000915\}\Big]$$

(* The effective mass/mass can be calculated by
   substituting the values of r and v from the
   minimization program into the following program*)

```
Clear[h, m, Ω, α, M, c, ρ, r, v, u]
h = 1;
m = 0.5;
Ω = 6.252 * 10^12 * (2.0600687 * 10^16)^-1;
α = 1;
M = 4.982 * 10^-25 (1.8218779 * 10^-30)^-1;
ρ = 0.5 (3.4)^-1;
c = ρ * M * Ω^3 * α^2 (8 * π)^-1;
r = 0.9881222210114119;
v = 0.0009152083072018303;
```

$$1 + \frac{c}{m} * \sqrt{\pi} * v^3 \left(\frac{2*m}{h}\right)^{\frac{3}{2}} *$$

```
NIntegrate[Exp[-Ω*u] *u^2 *
```

$$\left(\frac{1}{(v*(1-r^2)*(1-Exp[-v*u]) + v^2*r^2*u)}\right)^{\frac{3}{2}}$$

```
, (u, 0, Infinity)]
```

Vitae

Miss Natda Nusso was born on March 4, 1977 in Bangkok. She received her B.Sc. degree in physics from King Mongkut's University of Technology Thonburi in 1999. During her graduate study she received a teaching assistantship from Chulalongkorn University in 2001.

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