Efficient Modeling Techniques for Time-Dependent Quantum System with Applications to Carbon Nanotubes

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EFFICIENT MODELING TECHNIQUES FOR
TIME-DEPENDENT QUANTUM SYSTEM WITH
APPLICATIONS TO CARBON NANOTUBES

A Thesis Presented
by
ZUOJING CHEN

Submitted to the Graduate School of the
University of Massachusetts Amherst in partial fulfillment
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Electrical and Computer Engineering
EFFICIENT MODELING TECHNIQUES FOR TIME-DEPENDENT QUANTUM SYSTEM WITH APPLICATIONS TO CARBON NANOTUBES

A Thesis Presented

by

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ABSTRACT

EFFICIENT MODELING TECHNIQUES FOR TIME-DEPENDENT QUANTUM SYSTEM WITH APPLICATIONS TO CARBON NANOTUBES

MAY 2010

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Nowadays, for nano-electronic devices, inter-atomic interactions and quantum effects are becoming increasingly important. For time dependent problem, such as high frequency electronics responses, the description of the system behavior necessitate insights on the time dependent electron dynamics. In this thesis, we will be identifying all the numerical difficulties and propose new effective modeling and numerical schemes to address the current limitations in time-dependent quantum simulations. A real-space mesh techniques framework and TDDFT type calculations are used for obtaining time dependent properties for nanowire type device(such as CNT). Direct Hamiltonian diagonalizations are performed by using the innovative linear scaling eigenvalue solver FEAST, and a Gauss Quadrature scheme is proposed to enhance the speed and accuracy of the time evolution calculation.
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INTRODUCTION

The famous Moore’s law states: Since the invention of the integrated circuit, the number of transistors that can be placed on an integrated circuit has increased exponentially, doubling approximately every two years. As a result of the downscaling of the size of the transistor, quantum effects have become increasingly important while affecting significantly the device performances. Nowadays, at the nanometer scale, inter-atomic interactions and quantum mechanical properties need to be studied extensively. Device and material simulations are important to achieve these goals because they are flexible and less expensive than experiments. They are also important for designing and characterizing new generation of electronic device such as silicon nanowire or carbon nanotube (CNT) transistors.

Several modeling methods have been developed and applied to electronic structure calculations, such as: Hartree-Fock, density functional theory (DFT), empirical tight-binding, etc. For transport simulations, most of the device community focuses on studying the stationary problem for obtaining characteristics such as I-V curves. The non-equilibrium transport problem is then often addressed by solving a multitude of time-independent Schrödinger-type equation for all possible energies. On the other hand, for many other electronic applications including high-frequency electronics response (e.g. when a time-dependent potential is applied to the system), the description of the system behavior necessitate insights on the time dependent electron dynamics. To address this problem, it is then necessary to solve a time-dependent Schrödinger-type equation. In this thesis, we will focus on solving time-dependent problems with application to CNTs. We will be identifying all the numerical difficul-
ties and propose new effective modeling and numerical schemes to address the current limitations in time-dependent quantum simulations.

One approach for solving the time-dependent Schrödinger equation consists of using a partial differential equation (PDE) representation; generally we can discretize the time domain using finite difference method (FDM) while discretizing the space domain using FDM or finite element method (FEM). The specific techniques include both explicit and implicit schemes, with the commonly used Crank-Nicolson scheme [3]. These numerical techniques can be cast as direct approaches, however, they do not always guarantee numerical accuracy and robustness for large simulation times.

Another approach consists of performing the integration of the time evolution operator. Two cases can then be generally considered: (i) The Hamiltonian is time-independent; (ii) The Hamiltonian is time-dependent. The first case (i) is relatively straightforward, since the Hamiltonian is independent of time, the problem is then equivalent to solving the exponential of the Hamiltonian. The most obvious way to address this numerical problem would be to directly diagonalize the Hamiltonian while selecting the relevant number of modes needed to accurately expand the solutions. Direct diagonalization techniques, however, are known to be very computationally demanding especially for large systems. The mainstream in time dependent simulations is then to use approximations based on expansions such as split operator techniques, etc. In this thesis, however, we do propose to perform exact diagonalizations rather than approximations by taking advantage of a new linear scaling eigenvalue solver FEAST (solver recently developed by E. Polizzi [10]).

The second case (ii), when the Hamiltonian is time-dependent, increases significantly the modeling complexity since the Hamiltonian operators do not commute with each other at different times (i.e. \( \exp(A + B) \neq \exp(A) \ast \exp(B) \)) – A and B here are the Hamiltonian at different times). One solution strategy consists of dividing the simulation time into small time steps \( dt \) so that the anti-commutation error can be
ignored. At each individual time step, the Hamiltonian can then be viewed as time
independent and the system can be solved with techniques similar to case (i). Again,
the FEAST solver can be used to speed up the process, which is more efficient than
using any other conventional eigenvalue solvers. However, this direct approach is still
a very computational challenging approach since now, not one but many eigenvalue
problems need to be solved at each time step, which are chosen very small in order
to preserve the numerical accuracy. It should be noted that, as compared to the
traditional PDE approach which is recursive in time, a parallelizing procedure could
potentially be proposed here.

In this thesis, we will point out that two numerical errors may occur in the case
(ii): an integration error and the anti-commutation issue error; the direct computa-
tion above being mathematically equivalent to performing the integration of the
time dependent Hamiltonian using a rectangle numerical quadrature formula along
the total simulation times. After careful study and many numerical experiments, we
found that the Gaussian quadrature scheme provides a good trade off between com-
putational consumption and numerically accuracy, meanwhile unitary, stability and
time reversal properties are well preserved. The new Gaussian quadrature integration
scheme uses (i) much fewer points in time to approximate the integral of the Hamil-
tonian, (ii) ordered exponential to factorize the time evolution operator, (iii) FEM
discretize techniques (iv) and at last, the FEAST eigenvalue solver to diagonalize and
solve each exponential.

The time dependent modeling strategies that will be investigated in this thesis
are summarized in the flow chart given in Fig. 1. Especially, the red circles indicate
the main schemes we will propose and discuss in this thesis.

The outline of this thesis is as follows.

In Chapter 1, we briefly review the basics of time independent Schrödinger equa-
tion and time dependent Schrödinger equation.
Figure 1: Flow-chart summary of our time-dependent simulation framework.

In Chapter 2, we discuss in detail the numerical modeling methods for TDSE. First we use PDE approach for both time-independent and time-dependent problems: including Explicit, Implicit, and Crank Nicolson scheme respectively. A few examples are provided, such as: stationary states evolves in triangular potential, Gaussian wave packet in infinite well, and Gaussian wave packet tunneling through a potential barrier. After that, we solve the time dependent 1D problem by integrating time evolution propagators within the framework of real-space TDDFT (Time Dependent Density Functional Theory). First, we introduce a direct approach, which means diagonalizing Hamiltonian within very small dt. The finite element method is used for the space discretization, then problem is transformed into a generalized eigenvalue problem. Unitary, stability and time reversal properties are analyzed and examined. Then we use direct approach result as a reference, relative errors for Gaussian Quadrature scheme are investigated. Ordered exponential, FEAST, and banded matrix format are applied to the calculation.
In Chapter 3 and 4, we apply the time dependent analysis to single wall carbon nanotube under time dependent external field. First we deal with a 1D system with empirical atomic potential, and then full 3D modeling and simulation of carbon nanotube is performed. Real-space mesh techniques framework and DFT type calculations are used, mode approach is also implemented. Electron energy, current density, electron density and kinetic inductance of the SWCNT are investigated using our simulation and are compared to measured results.
Quantum mechanics is a set of principles describing the behavior of systems at the atomic scale level or smaller. These descriptions include the simultaneous wave-like and particle-like behavior of both matter and radiation. The behavior of quantum processes can be described by the Schrödinger equation, which indicates how the quantum state of a physical system changes in time. It is as central to quantum mechanics as Newton’s laws are to classical mechanics.

1.1 Time-Independent Schrödinger Equation (TISE)

One of the fundamental concepts of quantum physics is that of wave-particle duality. For example, Einstein showed that a photon, which is considered to be a wave packet, has momentum just like a particle moving with the same energy. The one-dimensional time-dependent Schrödinger Equation for a single particle is given by Equation (1.1)

\[
\frac{i\hbar}{\partial t} \psi(x, t) = -\frac{\hbar^2}{2m} \nabla^2 \psi(x, t) + V(x)\psi(x, t),
\]

where \( m \) is the mass of the particle, \( \hbar = \frac{h}{2\pi} \) is the reduced Plank constant and \( V(x) \) is a real function representing the potential energy of the system, which is considered here independent of time. Before considering the full time-dependent equation, we propose to give a brief derivation of the time-independent version.

Starting with the one dimensional classical wave equation,
\[
\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u}{\partial t^2},
\]  
(1.2)

and using separation of variables,

\[
u(x, t) = \psi(x)f(t),
\]  
(1.3)

we obtain

\[
f(t) \frac{d^2}{dx^2} \psi(x) = \frac{1}{v^2} \psi(x) \frac{d^2}{dt^2} f(t).
\]  
(1.4)

Then, using a standard solution of the wave equation, \( f(t) = e^{i\omega t} \), we obtain

\[
\frac{d^2}{dx^2} \psi(x) = -\frac{\omega^2}{v^2} \psi(x).
\]  
(1.5)

This gives an ordinary differential equation describing the spatial amplitude of the matter wave as a function of position. This can be put in the standard form for the Schrödinger Equation by using the fact that the energy of a particle is the sum of kinetic and potential parts,

\[
E = \frac{p^2}{2m} + V(x).
\]  
(1.6)

Finally, using duality wave-particle relationship \( \omega = 2\pi \nu, v = \nu \lambda, \) and \( h = p\lambda, \) we have

\[
\frac{\omega^2}{v^2} = \frac{4\pi^2 \nu^2}{v^2} = \frac{4\pi^2}{\lambda^2} = \frac{2m(E - V(x))}{\hbar^2},
\]  
(1.7)

which when combined with Equation (1.5) gives

\[
\frac{d^2}{dx^2} \psi(x) + \frac{2m}{\hbar^2} [E - V(x)] \psi(x) = 0.
\]  
(1.8)

This one dimensional equation can be extended to the case of three dimensions, after rearranging it becomes
the solutions to this equation then represent the state function of a particle of mass $m$ in a potential $V(x)$.

### 1.2 Time-Dependent Schrödinger Equation (TDSE)

Time-dependent Schrödinger equation cannot be derived so is generally considered as a postulate of quantum mechanics. However, we are able to show that the time-dependent equation is a reasonable model of the dynamic evolution of a particle’s states function even though it is not derivable. As before, using separation of variables,

$$\psi(x, t) = \psi(x)f(t), \quad (1.10)$$

and substituting this into Equation (1.1) we have

$$\frac{i\hbar}{f(t)} \frac{df}{dt} = \frac{1}{\psi(x)} \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(x) \right] \psi(x). \quad (1.11)$$

Now, as the left hand side is a function of $t$ only and the right hand side is a function of $x$ only, the two sides must be equal to a constant. Assigning this constant as $E$, as the right hand side clearly has dimensions of energy, we can then extract two ordinary differential equations:

$$\frac{1}{f(t)} \frac{df(t)}{dt} = -\frac{iE}{\hbar}, \quad (1.12)$$

and where the other is the time independent Schrödinger equation, Equation (1.9). Simply solving Equation (1.12) we have
\[ f(t) = e^{-iEt/\hbar}. \]  

(1.13)

The energy operator, given by Equation (1.9), known as the Hamiltonian is a Hermitian operator, therefore its eigenvalues are real, so \( E \) is real. This means that the solutions of Equation (1.12) are purely oscillatory. Therefore, if

\[ \psi(x, t) = \psi(x)e^{-iEt/\hbar}, \]  

(1.14)

then the total wave function \( \psi(x, t) \) differs from \( \psi(x) \) only by a phase factor of constant magnitude. This then implies that the probability, of the particle state is time independent,

\[ |\psi(x, t)|^2 = \psi^*(x, t)\psi(x, t) = e^{iEt/\hbar}\psi^*(x)e^{-iEt/\hbar}\psi(x) = \psi^*(x)\psi(x) = |\psi(x)|^2, \]  

(1.15)

it also implies that the expectation value for any time-independent operator is also time independent.

\[ < A > = \int_{-\infty}^{\infty} \psi^*(x, t)\hat{A}\psi(x, t)dv = \int_{-\infty}^{\infty} \psi^*(x)\hat{A}\psi(x)dv, \]  

(1.16)

for this reason the states described by the wavefunction in Equation (1.14) are called stationary states.

When \( V(x, t) \) is time dependent, however, the separation of variables is not applicable and the equation (1.14) is not valid anymore. Therefore, the general time dependent problems usually require a numerical treatment. In the following chapters, we propose and describe two numerical methods for solving the TDSE: using a PDE approach and using a Integral approach of the evolution operator.
CHAPTER 2
NUMERICAL MODELING OF TDSE

2.1 PDE Approach and Direct Space/Time Discretization

The Time-dependent Schrödinger equation is a Partial Differential Equation (PDE) which is second-order in space and first-order in time, so one direct way to solve the equation consists in discretizing the differential operator in time using finite difference method (FDM) and in space using the finite element method (FEM).

2.1.1 Finite Difference Discretization

2.1.1.1 Time Independent Problems

In the case of complicated potential fields \( V(x) \), the numerical finite difference method has been used for many years to solve the Schrödinger equation [3]. For the time independent case we can simply discretize the Schrödinger equation and put it into matrix form, which can then be numerically solved. For the one dimensional case, the Schrödinger equation at each point along \( x \) can be written as:

\[
E\psi_{x_n} = -\frac{\hbar^2}{2m}\left(\frac{d^2\psi}{dx^2}\right)_{x_n} + V_n(x)\psi_{x_n},
\]

(now using the basic finite difference approximation,

\[
\left(\frac{d^2\psi}{dx^2}\right)_{x_n} = \frac{\psi_{x_{n+1}} - 2\psi_{x_n} + \psi_{x_{n-1}}}{a^2},
\]

where \( a \) is an uniform interval spacing, we can write Equation (2.1) as
\[ E\psi_n = k(2\psi_n - \psi_{n+1} - \psi_{n-1}) + v_n(x)\psi_n, \quad (2.3) \]

where \( k = \frac{\hbar^2}{2ma^2} \). This can also be written in matrix form as

\[
E\begin{pmatrix}
\psi_1 \\
\psi_2 \\
\psi_3 \\
\vdots \\
\psi_{N-1} \\
\psi_N
\end{pmatrix} = \begin{pmatrix}
2k + V_1 & -k & 0 & 0 & 0 & \cdots \\
-k & 2k + V_2 & -k & 0 & 0 & \cdots \\
0 & -k & 2k + V_3 & -k & 0 & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\cdots & 0 & 0 & -k & 2k + V_{N-1} & -k \\
\cdots & 0 & 0 & 0 & -k & 2k + V_N
\end{pmatrix}\begin{pmatrix}
\psi_1 \\
\psi_2 \\
\psi_3 \\
\vdots \\
\psi_{N-1} \\
\psi_N
\end{pmatrix}.
\quad (2.4)
\]

This can also be written in operator form as

\[ EI\vec{\psi} = H\vec{\psi}, \quad (2.5) \]

where \( I \) is the identity matrix. This eigenvalue problem can be solved numerically, and the corresponding eigenvectors, which represent the eigenstate of the particle, can be found.

### 2.1.1.2 Time Dependent Problems

For time domain FDM discretization, there are mainly three different schemes: Explicit scheme, Implicit scheme and Crank-Nicolson scheme. Explicit methods calculate the state of a system at a later time from the state of the system at the current time, while an Implicit method finds it by solving an equation involving both the current state of the system and the later one. The Crank-Nicolson scheme is a special case of Implicit scheme.

**Explicit Scheme**
Mathematically, if \( Y(t) \) is the state of the current system and \( Y(t + \Delta t) \) is the state at the later time (\( \Delta t \) is a small time step), then for an explicit method:

\[
Y(t + \Delta t) = F(Y(t)) .
\] (2.6)

As before we can discretize the spatial part of Equation (1.1) using the approximation in Equation (2.2). Then applying the explicit time-difference approximation,

\[
\left[ \frac{d\psi(x, t)}{dt} \right]_{t=t_j, x=x_n} = \frac{\psi_{x_n}^{t+1} - \psi_{x_n}^{t}}{b} ,
\] (2.7)

where \( b \) is the uniform temporal interval spacing, we are able to construct the explicit finite difference approximation to the Schrödinger equation:

\[
\psi_{x_n}^{t+1} = \psi_{x_n}^{t} - \frac{ib}{\hbar} \left[ \frac{\hbar}{ma^2} (\psi_{x_n+1}^{t} - 2\psi_{x_n}^{t} + \psi_{x_n-1}^{t}) + V_{x_n} \psi_{x_n}^{t} \right] .
\] (2.8)

In operator form this can be written:

\[
\bar{\psi}_{t+1}^{t} = \left( I - \frac{i}{\hbar} bH \right) \bar{\psi}_{t}^{t} ,
\] (2.9)

where as before \( H \) is the discretized Hamiltonian (with the potential matrix \( V \)) and \( I \) is the unit matrix. The explicit scheme is not always numerically stable, actually the condition under which explicit scheme is stable is:

\[
0 < | \frac{kh}{2ma^2} | < \frac{1}{2} .
\] (2.10)

Because \( (I - \frac{i}{\hbar} bH)^\times (I - \frac{i}{\hbar} bH) = I + \frac{\psi^2}{\hbar^2} H^2 \), the operator \( I - \frac{i}{\hbar} bH \) is not unitary, which is a required property in order to conserve probability.

**Implicit Scheme**

In Implicit Scheme, the state of a system at later time is calculated by solving a equation involving states both at current time and later time. That is we solve:
\[ G(Y(t), Y(t + \Delta t)) = 0 , \quad (2.11) \]

to find \( Y(t + \Delta t) \).

Now performing an implicit discretization we have:

\[ \psi_{x_n}^{t_j} = \psi_{x_n}^{t_{j+1}} + \frac{ib}{\hbar} \left[ -\frac{\hbar^2}{2ma^2}(\psi_{x_{n+1}}^{t_{j+1}} - 2\psi_{x_n}^{t_{j+1}} + \psi_{x_{n-1}}^{t_{j+1}}) + V_{x_n} \psi_{x_n}^{t_{j+1}} \right] , \quad (2.12) \]

which can also be put into operator form as:

\[ \tilde{\psi}_{j+1} = \left( I + \frac{i}{\hbar} bH \right)^{-1} \tilde{\psi}_j . \quad (2.13) \]

The fully implicit scheme is unconditionally stable. Similarly we can show this scheme do not correspond to a unitary transformation.

**Crank Nicolson Scheme**

The Crank Nicolson scheme is based on central difference in space, and the trapezoidal rule in time, giving second order convergence in time. Equivalently, it is the average of the Euler forward method and the Euler backward method in time. For example, in one dimension, if the partial differential equation is

\[ \frac{\partial u}{\partial t} = F \left( u, x, t, \frac{\partial u}{\partial x}, \frac{\partial^2 u}{\partial x^2} \right) , \quad (2.14) \]

then, letting

\[ u(n \Delta x, j \Delta t) = u_n^j . \quad (2.15) \]

Crank Nicolson method is the average of the forward Euler method at \( j \) and the backward Euler method at \( j + 1 \):
\[
\frac{u_j^{n+1} - u_j^n}{\Delta t} = F^j_n \left( u, x, t, \frac{\partial u}{\partial x}, \frac{\partial^2 u}{\partial x^2} \right) \quad \text{(forward Euler), } (2.16)
\]

\[
\frac{u_j^{n+1} - u_j^n}{\Delta t} = F^{j+1}_n \left( u, x, t, \frac{\partial u}{\partial x}, \frac{\partial^2 u}{\partial x^2} \right) \quad \text{(backward Euler), } (2.17)
\]

\[
\frac{u_j^{n+1} - u_j^n}{\Delta t} = \frac{1}{2} \left[ F^j_n \left( u, x, t, \frac{\partial u}{\partial x}, \frac{\partial^2 u}{\partial x^2} \right) + F^{j+1}_n \left( u, x, t, \frac{\partial u}{\partial x}, \frac{\partial^2 u}{\partial x^2} \right) \right] \quad \text{(Crank Nicolson). } (2.18)
\]

The function \( F \) must be discretized spatially with a central difference. Note that this is an implicit method: to get the next value of \( u \) in time, a system of algebraic equations must be solved. If the partial differential equation is nonlinear, the discretization will also be nonlinear so that advancing in time will involve the solution of a system of nonlinear algebraic equations, though linearizations are possible. In many problems, especially linear diffusion, the algebraic problem is tridiagonal and may be efficiently solved with the tridiagonal matrix algorithm, avoiding a costly full matrix inversion.

First, using Crank Nicolson Scheme to construct the temporal discretization:

\[
i h \psi_{j+1}^n - \psi_j^n \frac{b}{b} = \frac{1}{2} \left[ \frac{-h^2}{2m} \frac{d^2 \psi(x, t)}{dx^2} + V(x) \psi(x, t) \right]_{n}^{j+1} + \frac{1}{2} \left[ \frac{-h^2}{2m} \frac{d^2 \psi(x, t)}{dx^2} + V(x) \psi(x, t) \right]_{n}^{j}, \quad (2.19)
\]

after spatial discretization we have:

\[
i h \psi_{j+1}^n - \psi_j^n \frac{b}{b} = \frac{1}{2} \left[ \frac{-h^2}{2ma^2} (\psi_{x_{n+1}}^{tj+1} - 2\psi_{x_n}^{tj+1} + \psi_{x_{n-1}}^{tj+1}) + V_{x_n} \psi_{x_n}^{tj+1} \right] + \frac{1}{2} \left[ \frac{-h^2}{2ma^2} (\psi_{x_{n+1}}^{tj} - 2\psi_{x_n}^{tj} + \psi_{x_{n-1}}^{tj}) + V_{x_n} \psi_{x_n}^{tj} \right]. \quad (2.20)
\]
After rearranging we obtain:

\[
\psi_{x_n}^{t+1} + if_{x_n} \psi_{x_n}^{t+1} + 2ig \psi_{x_n}^{t+1} - ig \psi_{x_{n+1}}^{t+1} - ig \psi_{x_{n-1}}^{t+1} = \psi_{x_n}^t - if_{x_n} \psi_{x_n}^t - 2ig \psi_{x_n}^t + ig \psi_{x_{n+1}}^t + ig \psi_{x_{n-1}}^t ,
\]  

(2.21)

where \( f_{x_n} = \frac{b}{2\pi} V_{x_n} \), and \( g = \frac{bh}{4ma\tau} \). Simplifying further we have:

\[
(1 + if_{x_n} + 2g) \psi_{x_n}^{t+1} - ig \psi_{x_{n+1}}^{t+1} - ig \psi_{x_{n-1}}^{t+1} = (1 - if_{x_n} - 2g) \psi_{x_n}^t + ig \psi_{x_{n+1}}^t + ig \psi_{x_{n-1}}^t ,
\]  

(2.22)

this can then be put in matrix form as:

\[
\begin{pmatrix}
\psi_1 \\
\psi_2 \\
\psi_3 \\
\vdots \\
\psi_{N-1} \\
\psi_N
\end{pmatrix}_{t+1} = (I + iH) \begin{pmatrix}
\psi_1 \\
\psi_2 \\
\psi_3 \\
\vdots \\
\psi_{N-1} \\
\psi_N
\end{pmatrix}_t
= (I - iH) \begin{pmatrix}
\psi_1 \\
\psi_2 \\
\psi_3 \\
\vdots \\
\psi_{N-1} \\
\psi_N
\end{pmatrix}_t
\]  

(2.23)

As before \( I \) is the unit matrix, but now \( H \) is given by

\[
H = \begin{pmatrix}
f_1 + 2g & -g & 0 & 0 & 0 & \cdots \\
-g & f_2 + 2g & -g & 0 & 0 & \cdots \\
0 & -g & f_3 + 2g & -g & 0 & \cdots \\
\vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\
\cdots & 0 & 0 & -g & f_{N-1} + 2g & -g \\
\cdots & 0 & 0 & 0 & -g & f_N + 2g
\end{pmatrix}.
\]  

(2.24)
So we have the numerical difference equation in the Crank Nicolson form, assuming \( \frac{1}{1 + iH} \) stands for \( (I + iH)^{-1} \):

\[
\bar{\psi}_{t+1}^j = \frac{I - iH}{I + iH} \bar{\psi}_t^j .
\] (2.25)

The temporal operator that relate \( \psi^j \) to \( \psi^{j+1} \) is now not only numerically stable but also unitary; this can be shown as:

\[
\left( \frac{I - iH}{I + iH} \right)^* \left( \frac{I - iH}{I + iH} \right) = \left( \frac{I + iH}{I - iH} \right) \left( \frac{I - iH}{I + iH} \right) = I .
\] (2.26)

Through this unitary property, Equation (2.26) then satisfies conservation of probability as required.

### 2.1.2 Finite Element Method in Space

#### 2.1.2.1 Introduction

One of the biggest advantages of FEM over FDM is its ability to handle complicated geometries and boundaries. Even though handling complex geometries in FEM is theoretically straightforward, the computation time is strongly influenced by the choice of the most appropriate element type for the problem.

We are using a variational approach (which will be described below) to apply FEM to the problem, so it requires a discretization of the functional associated with the problem. Then, by minimizing the discretized functional and assembling the system for all the individual elements we can obtain the FEM equation of the system.

In quantum mechanics, we could use FEM method to solve the one-dimensional stationary Schrödinger equation:

\[
-\frac{\hbar^2}{2m} \nabla^2 \psi(x) + V(x)\psi(x) = E\psi(x) .
\] (2.27)
We can find out energy level configurations for particles in various potentials and space. First we consider the case of a closed system, where Dirichlet boundary condition is applied.

Multiplying Equation (2.27) by a test function $\psi(x)$ and integrating over $\Omega$

$$
-\frac{\hbar^2}{2m} \int_\Omega \triangle \psi(x)\psi(x)d\Omega + \int_\Omega V(x)\psi(x)\psi(x)d\Omega = E \int_\Omega \psi(x)\psi(x)d\Omega, \quad (2.28)
$$

the FEM method is based on an approximation of the solution of the Schrödinger equation while the original operator remains unchanged.

The solution which is expanded in a local basis set $\{\omega_i(x)\}$ [see Fig. 2.1], satisfies the Schrödinger equation only in an approximate way.

![Figure 2.1: Discretization of a 1D wave function using FEM with local shape functions in uniform mesh](image)

The meshes can be both uniform or nonuniform here.

The first term of the variational form can be decomposed using Green’s identity:

$$
-\frac{\hbar^2}{2m} \int_\Omega \triangle \psi(x)d\Omega = \frac{\hbar^2}{2m} \int_\Omega \nabla \psi(x)\nabla \psi(x)d\Omega + B.C., \quad (2.29)
$$

with
\begin{equation}
  B.C. = -\frac{\hbar^2}{2m} \int_{\gamma} (\nabla \psi(x) \cdot \vec{\eta}) \psi(x) d\gamma ,
\end{equation}

where $\gamma(\equiv \partial \Omega)$ denotes the boundary of the domain $\Omega$ and $\vec{\eta}$ is the normal vector exterior along $\gamma$. The integral term $B.C.$ over the boundary $\gamma$ specifies the boundary conditions.

In a closed system, the system is an isolated one, and the problem becomes a generalized eigenvalue problem which in the matrix notation takes the following form:

\begin{equation}
  [H_0] \Psi = E[S] \Psi ,
\end{equation}

with

\begin{equation}
  [H_0]_{ii'} = \frac{\hbar^2}{2m} \int_{\Omega} \nabla \omega_i(x) \nabla \omega_{i'}(x) d\Omega + \int_{\Omega} V(x) \omega_i(x) \omega_{i'}(x) d\Omega ,
\end{equation}

\begin{equation}
  [S]_{ii'} = \int_{\Omega} \omega_i(x) \omega_{i'}(x) d\Omega ,
\end{equation}

where $[H_0]$ is the discretized version of the variational form of the Hamiltonian where the boundary term B.C. is equal to zero, and $[S]$ is the mass matrix which represents the overlap between the basis function $\{\omega_i\}$ see Fig. 2.1. These matrices are real and symmetric. $[H_0]$ is Hermitian in most cases for multi-band models, and sparse. Because $\omega_i$ has only a finite overlap with its nearest functions neighbors $\omega_{i-1}$ and $\omega_{i+1}$, $[H_0]_{ii'}$ and $[S]_{ii'}$ are equal to zero if $|i - i'| > 1$.

Using FEM method described above, we could solve the one dimensional time independent Schrödinger equation. Fig. 2.2 and 2.3 are simple examples, Fig. 2.2 shows the first 3 stationary states under parabolic potential, and Fig. 2.3 is the same result with triangular potential.
Figure 2.2: First three stationary states under parabolic potential

Figure 2.3: First three stationary states under triangular potential
2.1.2.2 FDM/FEM Time-Space Discretization

For Time Dependent Problems, we could solve the spatial part of the problem using the previous FEM approach, then the temporal part will use FDM approach.

Multiplying Equation 1.1 with a test function and integrating by parts, we have

\[
\int_0^L V(x)\psi(x)\phi(x)dx + \frac{\hbar^2}{2m} \int_0^L \frac{\partial \phi}{\partial x} \frac{\partial \psi}{\partial x}dx = i\hbar \int_0^L \phi \frac{\partial \psi}{\partial t}dx .
\]
(2.34)

If we discretize the temporal part with explicit time integration, the matrix form will be:

\[
[H_0]\tilde{\psi}^t_j = \frac{i\hbar}{b} [S] (\tilde{\psi}^{t+1} - \tilde{\psi}^t) .
\]
(2.35)

So:

\[
\tilde{\psi}^{t+1} = \left\{ 1 + \frac{b[H_0]}{i\hbar[S]} \right\} \tilde{\psi}^t_j ,
\]
(2.36)

where \([H_0]\) and \([S]\) are defined the same as Equation (2.32) and Equation (2.33)

We can also use Implicit Crank Nicolson time integration

\[
i\hbar[S]\dot{\psi} = \frac{1}{2} [[H_0]\tilde{\psi}^{t+1} + [H_0]\tilde{\psi}^t] ,
\]
(2.37)

which consists of solving the equation:

\[
i\hbar[S] \frac{\tilde{\psi}^{t+1} - \tilde{\psi}^t}{b} = \frac{1}{2} [[H_0]\tilde{\psi}^{t+1} + [H_0]\tilde{\psi}^t] .
\]
(2.38)

2.2 Numerical Integration of Propagators for TDSE

The Crank Nicolson scheme can solve the time dependent Schrödinger equation, it is stable and unitary, but it needs very small time steps to be numerically accurate, and this renders it inapplicable to realistic problem simulations. Also even when \(V(x)\) is time-independent, we must perform many iterations to evolve the system from \(t_0\) to the final time.
In this chapter, we will address the problem of integrating of the evolution operator for the time dependent Schrödinger equation, which is another alternative approach to the FDM/FEM method. In particular, we are concerned with the important case where $\hat{H}$ is the self-consistent Kohn-Sham Hamiltonian that stems from time-dependent density functional theory. As the Kohn-Sham potential depends parametrically on the time dependent density, $\hat{H}$ is in general time dependent, even in the absence of an external time dependent field. This analysis also holds for the description of the excited state dynamics of a many-electron system under the influence of arbitrary external time-dependent electromagnetic fields.

2.2.1 Approximations to the Evolution Operator

We want to solve the problem of approximating the evolution operator $\hat{U}(t+\Delta t, t)$, i.e., finding an approximation for $\psi(t + \Delta t, t)$ from the knowledge of $\psi(t)$ and $\hat{H}(\tau)$ for $0 \leq \tau \leq t$. Most methods also require the knowledge of the Hamiltonian at some points in time between $t \leq \tau \leq t + \Delta t$. To obtain this quantity, one can extrapolate the Hamiltonian using a polynomial fit to $n$ previous steps. However, this can reduce the accuracy of the propagator. To be fully consistent the following method can be employed: (i) Obtain $\hat{H}(\tau)$ through extrapolation; (ii) Propagate $\psi$ to get $\psi(t + \Delta t)$; (iii) From $\psi(t + \Delta t)$ calculate $\hat{H}(t + \Delta t)$; (iv) Obtain $\hat{H}(\tau)$ by interpolating between $\hat{H}(t)$ and $\hat{H}(t + \Delta t)$; (v) Repeat steps (i)-(iv) until self consistency is reached. For small time steps, the step (i) may be sufficient.

We will briefly describe several propagators that we have been investigating within the framework of real space TDDFT calculations. For the theoretical description of the properties of the propagators (unitary, time reversibility), we assume that $\hat{H}(\tau)$ is properly obtained using the above mentioned self consistent procedure, and that all numerical operations (calculation of the exponential of an operator, solution of a linear system, etc.) are performed exactly.
2.2.1.1 Implicit Midpoint Rule

The implicit midpoint rule is defined by:

\[
\hat{U}(t + \Delta t, t) = \frac{1 - \frac{i}{2} \Delta t \hat{H}(t + \Delta t/2)}{1 + \frac{i}{2} \Delta t \hat{H}(t + \Delta t/2)} .
\] (2.39)

The problem of propagating an orbital with this scheme is usually cast in the solution of the linear system:

\[
\hat{L}\psi(t + \Delta t) = b, \tag{2.40}
\]

where \(\hat{L} = \hat{I} + i(\Delta t/2)\hat{H}(t + \Delta t/2)\) and \(b = [\hat{I} - i(\Delta t/2)\hat{H}(t + \Delta t/2)]\psi(t)\). This scheme is unitary and preserves time reversal symmetry.

2.2.1.2 Exponential Midpoint Rule

The exponential midpoint rule consists in approximating the propagator by the exponential calculated at time \(t + \Delta t/2\),

\[
\hat{U}(t + \Delta t, t) = \exp\{-i\Delta t \hat{H}(t + \Delta t/2)\} .
\] (2.41)

If we assume that the exponential is calculated exactly and that \(\hat{H}(t + \Delta t/2)\) is obtained self consistently, then this method is also unitary and time reversible. In practice this method requires small time steps to be stable.

2.2.1.3 Time-reversal Symmetry based Propagator

In a time reversible method, propagating backwards \(\Delta t/2\) starting from \(\psi(t + \Delta t)\) or propagating forwards \(\Delta t/2\) starting from \(\psi(t)\) should lead to the same result. By using the simplest approximation to the propagator, this statement leads to the condition
\[
\exp\{i \frac{\Delta t}{2} \hat{H}(t + \Delta t)\} \psi(t + \Delta t) = \exp\{-i \frac{\Delta t}{2} \hat{H}(t)\} \psi(t),
\]

(2.42)

rearranging the terms, we arrive at an approximation to the propagator

\[
\hat{U}(t + \Delta t) = \exp\{-i \frac{\Delta t}{2} \hat{H}(t + \Delta t)\} \times \exp\{-i \frac{\Delta t}{2} \hat{H}(t)\}.
\]

(2.43)

2.2.1.4 Splitting Techniques

The split Operator technique takes advantage of the fact that the Hamiltonian is composed of two terms, one diagonal in Fourier space (the kinetic operator \(\hat{T}\)) and the other diagonal in real space (the potential operator \(\hat{V}\)). The idea is to approximate the propagator by the following product of exponentials:

\[
\text{split}\{-i \Delta t \hat{H}, v\} = S_2(-i \Delta t \hat{H})v = \exp\{-i \frac{\Delta t}{2} \hat{T}\} \times \exp\{-i \Delta t \hat{V}\} \exp\{-i \frac{\Delta t}{2} \hat{T}\}v.
\]

(2.44)

This decomposition neglects terms involving the anti-commutation \([\hat{T}, \hat{V}]\) and higher order commutators, and is of \(O(\Delta t^2)\). Equation (2.44) is sometimes called ”potential referenced split operator”, since the potential term appears sandwiched between the two kinetic terms. A ”kinetic referenced” scheme is equally legitimate. Since the three exponentials may be computed exactly, it is always unitary and unconditionally stable, providing a very reliable second order method. The split operator was first introduced in physics or chemistry by Feit and co workers. [4]

Besides the simplest SO method, a wide variety of other splitting schemes have been proposed and studied. [1,9] One of these, the fourth order symmetric decomposition, was studied and applied to TDDFT by Sugino and Miyamoto [13],
\[ suzuki\{−iΔt\hat{H}, v\} = \prod_{j=1}^{5} S_2(−ip_jΔt\hat{H})v, \quad (2.45) \]

where the \( p_j \) are a properly chosen set of real numbers.

We can combine the exponential midpoint with the split operator method. In practice, this consists in setting \( \hat{V} = t + \hat{\Delta}t/2 \) in Equation (2.45). If this potential is obtained accurately we end up with a second-order method, otherwise the method is of first order. There is, however, a simpler alternative:

\[
\hat{U}(t+\Delta t, t) = S_2[−i\Delta t(\hat{T}+\hat{V}′)] = \exp\{−\frac{1}{2}i\Delta t\hat{T}\} \exp\{−i\Delta t\hat{V}'\} \exp\{\frac{1}{2}i\Delta t\hat{T}\}, \quad (2.46)
\]

where the potential operator \( \hat{V}' \) is defined by

\[
\hat{V}' = v_{ext}(\mathbf{r}, t + \Delta t/2) + \int d^3r' \frac{n'(\mathbf{r}'\}}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n'](\mathbf{r}, t). \quad (2.47)
\]

In this expression \( n' \) is the density built after applying the first kinetic exponential in Equation (2.46). In other words, the modified method is the following: (i) apply the first kinetic term; (ii) recalculate the density and obtain the Kohn Sham potential, and (iii) apply the potential term and the second kinetic term. In this simple way we recover an order 2 method.

2.2.1.5 Magnus Expansions

As noted previously, \( \hat{U}(t + \Delta t, t) \) does not reduce to a simple exponential of the form \( \exp(−i\Delta t\hat{H}(t)) \) unless the Hamiltonian is time independent. One may ask if there exists an operator \( \hat{\Omega}(t + \Delta t, t) \) such that \( \hat{U}(t + \Delta t, t) = \exp\{\hat{\Omega}(t + \Delta t, t)\} \).

Magnus [8] answered this question positively in 1954: There exists an infinite series, convergent at least for some local environment of \( t \), such that
\[ \hat{\Omega}(t + \Delta t, t) = \sum_{k=1}^{\infty} \hat{\Omega}_k(t + \Delta t, t). \]  

(2.48)

There also exists a procedure to generate the exact \( \hat{\Omega}_k \) operators:

\[ \hat{\Omega}_k(t + \Delta t, t) = \sum_{j=0}^{k-1} B_j \frac{1}{j!} \int_t^{t+\Delta t} \hat{S}_j^k(\tau) d\tau, \]  

(2.49)

where \( B_j \) are Bernoulli numbers and the operator \( S \) are recursively generated

\[ \hat{S}_0^0(\tau) = -i\hat{H}; \quad \hat{S}_0^k(\tau) = 0 \quad (k > 1), \]  

(2.50)

\[ \hat{S}_j^k(\tau) = \sum_{m=1}^{k-j} [\hat{\Omega}_m(t + \Delta t, t), \hat{S}_{k-m}^{j-1}(\tau)] \quad (1 \leq j \leq k - 1). \]  

(2.51)

### 2.2.2 Direct Approach: Fast Eigenvalue Problem Solver

In practice, it is normally not feasible to obtain \( \psi(t) \) directly from \( \psi_0 \) for a long time interval \([0, t] \). Instead, one can break \([0, t] \) into smaller time intervals, and by using the property \( \hat{U}(t_1, t_2) = \hat{U}(t_1, t_3)\hat{U}(t_3, t_2) \), the full unitary time propagator is written as:

\[ \hat{U}(t, 0) = \prod_{i=0}^{N-1} \hat{U}(t_i + \Delta t_i, t_i), \]  

(2.52)

where \( t_0 = 0, t_{i+1} = t_i + \Delta t_i \), and \( t_N = t \). Usually we use a constant time step, \( i.e. \), \( \Delta t_i = \Delta t \). However, it is possible to use variable time step methods, especially if the algorithm implemented is able to choose optimally the time step to enhance the efficiency without compromising the accuracy. In any case, we deal with the problem of performing the short time propagation,
\[ \psi(t + \Delta t) = \hat{U}(t + \Delta t, t)\psi(t) = T \exp \left\{ -i \int_{t}^{t+\Delta t} d\tau \hat{H}(\tau) \right\} \psi(t), \quad (2.53) \]

where \( T \exp \) is an operator called 'Time Ordered Exponential', it is a mathematical object defined in non-commutative algebras, which is equivalent to exponential function of the integral in the commutative algebras. Therefore it is a function defined by means of a function from real numbers to a real or complex associative algebra. In practice the values lie in matrix and operator algebras.

When \( \Delta t \) is very small, it is reasonable to consider \( \hat{H}(\tau) \) constant during time interval \([t, t + \Delta t]\), so the problem becomes:

\[ \hat{U}(t + \Delta t, t) = \exp \left\{ -i \Delta t \hat{H}(t) \right\} \cdot \quad (2.54) \]

Then it is possible diagonalize \( H(t) \) by solving the time independent Schrödinger equation:

\[ \left[ -\frac{\hbar^2}{2m} \Delta + V(x) \right] \psi(x) = E\psi(x). \quad (2.55) \]

This equation can be reformulated as the eigenvalue problem \( HX = \lambda X \) by using FDM.

After solving the eigenvalue problem, the Hamiltonian \( H \) then is diagonalized as \( \hat{H} = \hat{P}\hat{D}\hat{P}^{-1} \). The columns of the matrix \( \hat{P} \) are the eigenvectors, the matrix \( \hat{D} \) is a diagonal matrix and the diagonal entries are the eigenvalues \( \lambda \).

Then Equation (2.54) can be written as:
\[
\hat{U}(t + \Delta t, t) = \exp\left\{-i\Delta t \hat{P} \hat{D} \hat{P}^{-1}\right\}
= \sum_{k=0}^{\infty} \frac{1}{k!} \left[-i\Delta t \hat{P} \hat{D} \hat{P}^{-1}\right]^k
= \hat{P} \sum_{k=0}^{\infty} \left[\frac{1}{k!}(-i\Delta t \hat{D})^k\right] \hat{P}^{-1}
= \hat{P} \exp\{-i\Delta t \hat{D}\} \hat{P}^{-1}
\]

\[
= \hat{P} \exp\{-i\Delta t \lambda_1\} \hat{P}^{-1}
\quad \begin{pmatrix}
    e^{-i\Delta t \lambda_1} & 0 & 0 & 0 & \cdots \\
    0 & e^{-i\Delta t \lambda_2} & 0 & 0 & \cdots \\
    \vdots & \vdots & \ddots & \vdots & \\
    \cdots & 0 & 0 & e^{-i\Delta t \lambda_{N-1}} & 0 \\
    \cdots & 0 & 0 & 0 & e^{-i\Delta t \lambda_N}
\end{pmatrix} \hat{P}^{-1}. \quad (2.56)
\]

We can also use Finite Element Method for space discretization, as mentioned before, FEM method is more capable of handling complicated geometries and boundaries. In this case, the problem is rearranged to a generalized eigenvalue problem:

\[
[H_0] \Psi = E[S] \Psi . \quad (2.57)
\]

Noting that \([S] \) is symmetric positive-definite and can be decomposed as \([S] = LL^T\), multiplying Equation (2.57) by \(L^{-1}\) at both sides, we have:

\[
L^{-1}[H_0](L^T)^{-1} L^T \Psi = E L^T \Psi . \quad (2.58)
\]

The time evolution operator is:

\[
\hat{U}(t + \Delta t, t) = \exp\left\{-i\Delta t \hat{H}\right\} = L^T \hat{P} \exp(-i\Delta t \hat{D}) \hat{P}^T L , \quad (2.59)
\]
then, the final wave function can be represented by:
\[ \psi(t + \Delta t) = \hat{U}(t + \Delta t, t)\psi(t) = L^T \hat{P} \exp(-i\Delta t \hat{D}) \hat{P}^T L\psi(t). \] (2.60)

In order to keep the final state orthogonalized, set \( \psi = L^T \Psi(t + \Delta t) \) as the new final wave function, So we have

\[ \psi^T \psi = \Psi^T LL^T \Psi = \Psi^T S \Psi = I , \] (2.61)

according to the S-normalization of generalized eigenvalue problem solver (e.g., LA-PACK or FEAST)

Now the matrix form of time evolution operator using FEM is:

\[ \Psi(t + \Delta t) = \hat{P} \exp(-i\Delta t \hat{D}) \hat{P}^T S \Psi(t) . \] (2.62)

Usually the direct approach, which requires the solution of many time-independent problems, is not considered applicable, because the numerical complexity of eigenvalue solvers varies as the cube of the number of degrees of freedom \( N \). For large systems where hundreds of atoms are taken into consideration, the solution of the Schrödinger equation is the limiting step. Unlike linear equations that are easier to solve, accurate eigensolutions for thousands of eigenpairs are computationally demanding and algorithmically challenging, since the eigenfunctions also have to meet the orthogonality constraint.

In this thesis, we will apply the Density matrix based algorithm (FEAST) by E. Polizzi [10] to the direct approach. This algorithm addresses all the problems above and it is fast and robust for solving the generalized eigenvalue problem.
2.2.3 Gaussian Quadrature Integration and Time Ordered Exponential

In the solution form of integration of propagators

$$
\psi(t) = \hat{U}(t,0)\psi_0 = T \exp \left\{ -i \int_0^t d\tau \hat{H}(\tau) \right\} \psi_0 , \tag{2.63}
$$

in order to get the final state, first we need to deal with the integration of $\hat{H}$. The direct approach in the previous section approximates the integration by the rectangle rule, (see Fig. 2.4$^1$), based on the fact that Hamiltonian $H$ varies very little in the small time interval $\Delta t$. Second, because Hamiltonians $H$ do not commute with each other at different times, time ordered exponential $T \exp$ is needed.

The direct approach is still too computationally demanding to be applicable to a realistic system, considering that we have to make each time step small enough to keep the numerical accuracy and for each time step we must solve a eigenvalue problem.

In this work, we apply Gaussian Quadrature to interpolate the integration of Hamiltonian. A quadrature rule is an approximation of the definite integral of a function, usually stated as a weighted sum of function values at specified points within the domain of integration. An $n$ point Gaussian quadrature rule is a quadrature rule constructed to yield an exact result for polynomials of degree $2n-1$ by a suitable

$^1$From http://en.wikipedia.org/wiki/Numerical_integration
choice of the points \( x_i \) and weights \( w_i \). Gaussian Quadrature can use relatively fewer points to yield a high order approximation of the integral of a function.

An integral over \([a, b]\) must be changed into an integral over \([-1, 1]\) before applying the Gaussian quadrature rule. This change of interval can be done in the following way:

\[
\int_{a}^{b} f(x) \, dx = \frac{b-a}{2} \int_{-1}^{1} f \left( \frac{b-a}{2} x + \frac{a+b}{2} \right) \, dx,
\]

(2.64)

after applying the Gaussian quadrature rule, the following approximation is obtained:

\[
\frac{b-a}{2} \sum_{i=1}^{n} w_i f \left( \frac{b-a}{2} x_i + \frac{a+b}{2} \right).
\]

(2.65)

In our case, the equation becomes:

\[
\psi(t) = \mathcal{T} \exp \left\{ -i \int_{t_0}^{t} \hat{H}(\tau) \, d\tau \right\} \psi(t_0)
\]

\[
= \mathcal{T} \exp \left\{ -\xi \sum_{i=1}^{n} \omega_i H(t_i) \right\} \psi(t_0)
\]

\[
= \mathcal{T} \left\{ \exp \left[ -\xi \omega_1 H(t_1) \right] \exp \left[ -\xi \omega_2 H(t_2) \right] \cdots \exp \left[ -\xi \omega_N H(t_N) \right] \right\} \psi(t_0),
\]

(2.66)

where \( \mathcal{T} \) is time ordering operator, it means that operators at later time are placed further left in the expression, and each exponential can be calculated in the same way we did in direct approach (by diagonalizing \( H \)). And \( \xi = i \left( \frac{t-t_0}{2} \right) \).

Using FEM, we obtained:

\[
\psi(t) = \mathcal{T} \left\{ \prod_{i} \left[ \hat{P}(t_i) \exp \left( -\xi \omega_i \Delta(t_i) \right) \hat{P}^T(t_i) \right] \right\} S\psi(t_0),
\]

(2.67)

where \( \hat{P}_i \Delta(t_i) \hat{P}_i^T = H(t_i) \) and \( t_i = \frac{t-t_0}{2} x_i + \frac{t+t_0}{2} \).
Fig. 2.5 give us a comparison of different time discretization schemes. The direct approach needs more time steps which means longer computation time, but it can give detailed results between $t_i$ and $t_f$. Gauss approach needs fewer points, but the points in the middle do not have any physical meanings.

A comparison between these two approaches is shown in Table 2.1,

<table>
<thead>
<tr>
<th></th>
<th>Direct approach</th>
<th>Gauss approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very fine mesh</td>
<td>Very computationally demanding</td>
<td>Significant computational saving</td>
</tr>
<tr>
<td>Detailed results at intermediate time</td>
<td>No physical meaning at intermediate time</td>
<td></td>
</tr>
</tbody>
</table>
2.3 Numerical Results and Benchmark

Using FEM and FDM methods, we have obtained numerical results by solving
time dependent Schrödinger equation in many cases, some of which can be solved
analytically, so that our numerical results can be compared to the analytical results.
The Direct approach and Gaussian quadrature are also implemented to small systems
in order to compare these two techniques.

2.3.1 Nonstationary Initial State in Static Potential

Although stationary states are solutions and very important solutions of the time-
dependent Schrödinger equation, they are by no means the only solutions. To see this,
suppose that we have two stationary states,

\[ \psi_1(x,t) = \psi_1(x)e^{-i\omega_1 t} \quad \text{and} \quad \psi_2(x,t) = \psi_2(x)e^{-i\omega_2 t}, \]

where \( \hbar \omega_1 = E_1 \) and \( \hbar \omega_2 = E_2 \) are the corresponding energies. To be definite, we could
consider \( \psi_1 \) and \( \psi_2 \) to be the lowest two wave functions of the infinite potential well.
Because each of these functions satisfies the time dependent Schrödinger equation, it
is easy to see that the same is true of any linear combination of the form

\[ \psi(x,t) = \alpha \psi_1(x,t) + \beta \psi_2(x,t), \]

for any two fixed number \( \alpha \) and \( \beta \).

\[
i\hbar \frac{\partial}{\partial t} \psi(x,t) = \alpha i\hbar \frac{\partial}{\partial t} \psi_1(x,t) + \beta i\hbar \frac{\partial}{\partial t} \psi_2(x,t) \\
= \alpha \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi_1(x,t) + \beta \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi_2(x,t) \\
= \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi(x,t). \quad (2.70)
\]
However, when we form a linear combination of two stationary state wave functions, the resulting state is not a stationary state.

\[ \psi(x, t) = \frac{1}{\sqrt{2}} \left[ \psi_1(x) e^{-i\omega_1 t} + \psi_2(x) e^{-i\omega_2 t} \right] , \quad (2.71) \]

and

\[ |\psi(x, t)|^2 = \frac{1}{2} |\psi_1(x) + \psi_2(x) e^{-i\omega_{21} t}|^2 . \quad (2.72) \]

Therefore:

\[ |\psi(x, t)|^2 = \frac{1}{2} [\psi_1(x)^2 + \psi_2(x)^2 + 2\psi_1(x)\psi_2(x)\cos(\omega_{21} t)] . \quad (2.73) \]

The most obvious thing about this result is that, because of the factor \( \cos(\omega_{21} t) \) the probability density does vary with time. Notice that in this case the time dependence is actually periodic, with period \( T = \frac{2\pi}{\omega_{21}} \).

Fig. 2.6 shows the initial state of our experiment, which is the combination of the lowest two stationary states. Fig. 2.7 shows the evolution obtained using the Crank-Nicolson scheme. Thw green curve shows the final states of \( T/8, T/4, 3T/8 \) and \( T/2 \) respectively, we can see the numerical results fit analytical results very well for this simple example.

### 2.3.2 Stationary States in Time Dependent External Potential

Another experiment consists in solving the 1D time dependent Schrödinger equation within the infinite potential well, we choose the lowest stationary state as initial state, meanwhile a time-independent triangular potential is applied. Because the initial state is not the eigenstate of the triangular potential, it will evolve with time according to time dependent Schrödinger equation.

Fig. 2.8 is a illustration of the problem we are solving:
The parameters we used in the the simulation are: Well Length $L=1.42$ nm Space Discretization $n=100$ Time step $k = 3.2 \times 10^{-18}$ s, number of time steps=1000.

When we apply the triangular potential instantaneously to the system at beginning, Fig. 2.9 shows the final wave function after time evolution under this potential using Direct Approach. And Fig. 2.10 is the 3D plot of how wave function evolves with time.

After we obtained the final state, then we decompose it with respect to the eigenstates of the triangular potential:

$$
\psi_f = \sum_m C_m \times \psi_m .
$$

The spectrum ($C_m$ versus m) is plotted in Fig. 2.11, $C_m$ is all the eigenstates of triangular potential:

We can see that because we used the first stationary state as initial state, the first eigenstate of the triangular potential dominates the spectrum. From the decomposition above, we could see that $\sum C_m = 1$. 

Figure 2.6: Evolution of combination of two lowest stationary states at tim $t = 0$
Figure 2.7: Time evolution of combination of lowest two stationary states

Figure 2.8: Problem Description
Figure 2.9: Initial and Final states of the lowest stationary state under triangular potential

Figure 2.10: 3D plot of Initial and final states of the lowest stationary state
When using second stationary state as initial state, the result is shown in Fig. 2.12. As we speculate, this time the second eigenstate is the dominate state in the spectrum.

The calculations above are for the case of a potential which is time-independent. However in real cases potentials are usually time dependent, e.g., applying external electrical field to carbon nanotube.

With the Crank Nicolson Scheme we can calculate how wave function evolves when triangular potential is increasing with time. So the potential is different for each time step, now stop the iteration when triangular potential reaches 1ev.

The time dependent potential can be written as below:

\[ V(x,t) = \frac{t}{t_f} \times \frac{x}{L}, \]  

where \( x \in [0, L] \), \( t \in [0, t_f] \)
Figure 2.12: Use 2nd lowest state as the initial guess

We choose to run 1000 time steps, and the corresponding frequency is about 10THz.

The results for sudden potential move ($V(x,t)$ is time-independent) and slow potential move ($V(x,t)$ is time-dependent) are put up for comparison in Fig. 2.13.

Also the spectrum plot for time dependent triangular potential is shown in Fig. 2.14 with comparison to time independent case.

In slow potential moving case, system needs more time to response or evolve compared to the case of a sudden change of potential.

2.3.3 Wave Packet in Infinite Well

In this simulation, we put a wave packet initially centered in the infinite well, using direct approach to see how the wave packet evolves with time in the infinite well.

The wave packet we use is a Gaussian Wave packet.

$$
\psi(x) = \left( \frac{1}{2\pi \sigma^2} \right)^{1/4} e^{ik_0 x} e^{-\frac{(x-x_0)^2}{4\sigma^2}},
$$

(2.76)
Figure 2.13: Initial and Final states of the lowest stationary state under triangular potential

Figure 2.14: Spectrum of final state comparison
where $x_0$ denotes the center of the wave packet, $\hbar k_0$ is the mean momentum of the packet, and $\sigma$ is the uncertainty in the position of the particle ($\Delta x$). This wave function satisfies the lower bound of uncertainty relation:

$$\Delta x \Delta P_x = \frac{\hbar}{2}. \quad (2.77)$$

In Fig. 2.15 it can be seen that the wave packet moves to the right until it collides with the infinite potential barrier on the right. It is reflected, and then it continues to the left side of the well. Upon colliding with the infinite walls the Gaussian envelope undergoes a distortion. This is due to the fact that the real and imaginary parts of the wave packet, even though they are not physically observable, undergo phase changes on reflection. If this simulation runs long enough, the Gaussian envelope will spread out until it covers the entire well.

Here we have used $L=1.42\text{nm}$, $n=200$, $T=8 \times 10^{-19}\text{s}$, results are obtained with Gauss 40 points scheme.

### 2.3.4 Wave Packet in Infinite Well with Potential Barrier

When there is a potential barrier in the center of the well and the wave packet is initially placed to the left part of the well, we could see the procedure of wave packet interacting with the potential barrier, and also the tunneling process.

In Fig. 2.16, we can see that the wave packet moves towards right until it hit the barrier. A small part of it is transmitted through the barrier and the rest is reflected, and transmitted parts continue moving until they collide with the walls of the well.

### 2.4 Comparison between Direct approach and Gauss approach

In this section, we want to compare the the direct approach and Gaussian Quadrature approach.
Figure 2.15: Results of Gaussian wave packet propagating in infinite potential well
Figure 2.16: Results of Gaussian wave packet interacting with potential barrier
Here we propose in a 1D closed system, potential is shown as the red curve in Fig. 3.2. We use direct approach 2000 step during one period \( T = 0.5 \times 10^{-14} \) as a reference because we believe this is close enough to the actual solution. We also use direct approach 200 points, 500 points and Gauss 10 points, Gauss 16 and 40 points respectively to calculate the relative errors.

In Appendix A, we can see that for a few periods, Gaussian Quadrature is very effective: 40 points is equivalent to 500 points in direct approach. But as the simulation goes on (for more periods), the error for Gaussian Quadrature started to accumulate. In our assumptions, there are mainly two errors in integration of the propagators method to solve the time-dependent Schrödinger equation: (i) Numerical Integral error. (ii) anti-commutation error. The anti-commutation error is less when more time points are selected, but of course more computation resources are required. There is always a trade-off between these two errors. For Gaussian Quadrature Scheme, the integral error can be very well controlled, but as the simulation time grows, the anti-commutation error becomes more important. However, we could always divide the period in order to get better accuracy.

In next chapter, we will discuss the possibility of applying both direct approach and Gaussian Quadrature Scheme to Carbon nanotube simulations.
CHAPTER 3
APPLICATION TO CARBON NANOTUBE IN 1D

3.1 TDDFT and Kohn-Sham Equations

The Time Dependent Schrödinger equation:

\[ i\hbar \frac{\partial}{\partial t} \psi(t) = \hat{H} \psi(t) \]  \hspace{1cm} (3.1)

describes the evolution of a wave function \( \psi \) in a system defined by the Hamiltonian operator \( \hat{H} \). In the simple case, the Hamiltonian is composed of two terms, one of kinetic origin and another describing the interaction of the particle with local potential:

\[ \hat{H} = \hat{T} + \hat{V}(t) = -\frac{\hbar^2}{2m} \nabla^2 + v(r, t), \]  \hspace{1cm} (3.2)

in some cases, the external potential may contain nonlocal contributions, \textit{e.g.}, nonlocal pseudopotentials.

This Hamiltonian is nonbounded and, in most cases, Hermitian. Besides appropriate boundary conditions, without which the kinetic term is not properly defined, the time dependent Schrödinger equation requires an initial value condition \( \psi(t = 0) = \psi_0 \) that completely determines the dynamics of the system.

In this thesis, we are especially concerned with a special form of \( v(r, t) \) that stems from time dependent density functional theory (TDDFT). TDDFT can be viewed as a reformulation of time dependent quantum mechanics where the basic variable is no longer the many body wave function, but the time dependent electron density \( n(r, t) \).
The density can be obtained from the solution of a set of one body equations, the so called Kohn Sham equations, that have the same form as Equation (3.1). The potential that enters the Kohn Sham equations is normally written as a sum of three terms.

\[ v_{KS}(\mathbf{r}, t) = v_{ext}(\mathbf{r}, t) + \int d^3\mathbf{r}^\prime \frac{n(\mathbf{r}^\prime, t)}{|\mathbf{r} - \mathbf{r}^\prime|} + v_{xc}[n](\mathbf{r}, t). \] (3.3)

The first term is the external potential felt by the electrons, usually generated by some set of nuclei, and possibly by an external electromagnetic field. This term may also include an imaginary part describing absorbing boundary conditions, the Hamiltonian in this case becomes non Hermitian. The next term, the Hartree potential, describes the classical part of the interaction between the electrons, while the exchange correlation potential \( v_{xc} \) accounts for all other nontrivial many body contributions. Note that both the Hartree and exchange correlation potentials are functionals of the density and are therefore intrinsically time dependent.

Formally, the solution of Equation (3.1) can be written as

\[ \psi(t) = \hat{U}(t, 0)\psi_0 = T \exp \left\{ -i \int_0^t d\tau \hat{H}(\tau) \right\} \psi_0, \] (3.4)

where \( T \exp \), the time ordered exponential, is a shorthand notation for

\[ \hat{U}(t, 0) = \sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_0^t d\tau_1 \int_0^t d\tau_2 \ldots \int_0^t d\tau_n \times T\{ \hat{H}(\tau_1)\hat{H}(\tau_2)\ldots\hat{H}(\tau_n) \}. \] (3.5)

Equation (3.5) is an exact reformulation of the Schrödinger equation, here we give a short derivation of it.

In the interaction picture, we have the following equations:
\[ i \hbar \frac{\partial}{\partial t} \Psi_I(t) = \hat{H}_I(t) \Psi_I(t) \]  
\[ \Psi_I(t) = \hat{U}(t, t_0) \Psi_I(t_0), \]  
(3.6)

subscript \( I \) means in the interaction picture, \( \hat{U}(t, t_0) \) is a unitary operator that determines the state vector at time \( t \) in terms of the state vector at time \( t_0 \).

It is clear that \( \hat{U} \) satisfies the differential equation:

\[ i \hbar \frac{\partial}{\partial t} \hat{U}(t, t_0) = \hat{H}_I(t) \hat{U}(t, t_0), \]  
(3.8)

Integrating this equation from \( t_0 \) to \( t \), yields an integral equation

\[ \hat{U}(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^{t} dt' \hat{H}(t') \hat{U}(t', t_0), \]  
(3.9)

The solution takes the form:

\[ \hat{U}(t, t_0) = 1 + \left( -\frac{i}{\hbar} \right) \int_{t_0}^{t} dt' \hat{H}(t') + \left( -\frac{i}{\hbar} \right)^2 \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' \hat{H}(t') \hat{H}(t'') + \cdots \]  
(3.10)

Consider the third term in this expansion, it may be rewritten as:

\[ \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' \hat{H}(t') \hat{H}(t'') = \frac{1}{2} \int_{t_0}^{t} dt' \int_{t_0}^{t} dt'' \hat{H}(t') \hat{H}(t'') + \frac{1}{2} \int_{t_0}^{t} dt'' \int_{t''}^{t} dt' \hat{H}(t') \hat{H}(t'') , \]  
(3.11)

since the last term on the right is just obtained by reversing the order of the integrations, we now changed dummy variables in the second term, interchanging the label \( t' \) and \( t'' \):
\[
\frac{1}{2} \int_{t_0}^{t} dt'' \int_{t''}^{t} dt' \hat{H}(t') \hat{H}(t'') = \frac{1}{2} \int_{t_0}^{t} dt' \int_{t'}^{t} dt'' \hat{H}(t'') \hat{H}(t').
\] (3.12)

These two terms may now be recombined to give

\[
\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \hat{H}(t') \hat{H}(t'') = \frac{1}{2} \int_{t_0}^{t} dt' \int_{t'}^{t} dt'' \times \left[ \hat{H}(t') \hat{H}(t'') \theta(t' - t'') + \hat{H}(t'') \hat{H}(t') \theta(t'' - t') \right],
\] (3.13)

where \(\theta(x)\) denotes the step function

\[
\theta(x) = \begin{cases} 
1 & \text{if } x \geq 0 \\
0 & \text{if } x < 0
\end{cases}
\]

the step function is essential here because the operators \(\hat{H}\) do not necessarily commute at different times. Equation (3.13) has the characteristic feature that the operator containing the latest time stands farthest to the left. We call this a \textit{time-ordered product of operators}, denoted by the symbol \(\mathcal{T}\). Thus Equation (3.13) can be rewritten as

\[
\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \hat{H}(t') \hat{H}(t'') = \frac{1}{2} \int_{t_0}^{t} dt' \int_{t'}^{t} dt'' \mathcal{T}[\hat{H}(t') \hat{H}(t'')].
\] (3.14)

This result is readily generalized and the resulting expansion for \(\hat{U}\) becomes

\[
\hat{U}(t, t_0) = \sum_{n=0}^{\infty} \left( \frac{-i}{\hbar} \right)^n \frac{1}{n!} \int_{t_0}^{t} dt_1 \cdots \int_{t_0}^{t} dt_n \mathcal{T}[\hat{H}(t_1) \cdots \hat{H}(t_n)],
\] (3.15)

where the \(n = 0\) term is just the unit operator. The proof of Equation (3.15) is as follows. Consider the \(n\)th term in this series. There are \(n!\) possible time orderings of label \(t_1 \cdots t_n\). Pick a particular one, say \(t_1 > t_2 > t_3 \cdots > t_n\). Any other time ordering gives the same contribution to \(\hat{U}\). This results is easily seen by relabeling the
dummy integration variables $t_i$ to agree with the previous ordering, and then using the symmetry of the $T$ product under interchange of its arguments:

$$T[\cdots \hat{H}(t_i) \cdots \hat{H}(t_j) \cdots] = T[\cdots \hat{H}(t_j) \cdots \hat{H}(t_i) \cdots]. \quad (3.16)$$

Equation (3.16) follows from the definition of the $T$ product, which puts the operator at the latest time farthest to the left, the operator at the next latest time next, and so on, since the prescription holds equally well for both sides of Equation (3.16). In this way, Equation (3.15) reproduces the iterated series of Equation (3.10).

If the Hamiltonian commutes with itself at different times, we can drop the time ordering product; Moreover, if the Hamiltonian is time independent, the solution is simply

$$\psi(t) = \exp\{-it\hat{H}\}\psi_0, \quad (3.17)$$

unfortunately, this is not the case relevant for TDDFT, and in particular when applied to the description of the electronic dynamics under time dependent external perturbations (as electric and magnetic fields, pulsed lasers, currents, particle scattering, etc.) That is why we need the numerical techniques described in Chapter 2.

### 3.2 Wave Functions in 1D Empirical Atomic Potential

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanosstructure. Nanotubes have been constructed with length-to-diameter ratio of up to 28,000,000:1, which is significantly larger than any other material. These cylindrical carbon molecules have novel properties that make them potentially useful in many applications in nanotechnology, electronics, optics and other fields of materials science, as well as potential uses in architectural fields. They exhibit extraordinary strength and unique electrical properties, and are efficient thermal conductors. Some experiment results on Terahertz in single wall carbon nanotubes has been published [5], we
are trying to do time dependent simulations of carbon nanotube properties in order to understand it better theoretically.

First, we view the single wall carbon nanotube in Fig. 3.1 as a 1D system, under an empirical 1D atomic potential which comes from the results of mode approach. Then a time dependent triangular potential (represented by Equation (3.18)) is applied to the system. This potential stays zero in the middle, and moves up and down at both ends periodically like a seesaw.

\[
V(x,t) = U_0(x) + V(x) \times \sin(\omega t),
\]

(3.18)

where \( V(x) \) is the triangular potential whose zero point is in the middle of the 1D system.

Then, we apply the above time dependent triangular potential to the atomic potential, see Fig. 3.2. Then time dependent properties such as electron density, energy and current are calculated using Gauss approach.

First, we solve the stationary problems with potential configuration at \( t = 0 \) and \( t = T/4 \) (\( T = 2\pi/\omega = 0.5 \times 10^{-14}s \) is the period of the external triangular
Figure 3.2: Potential at $t = 0$, $t = T/4$ and $t = 3T/4$

Figure 3.3: Eigenvectors under Potential at $t = 0$
potential) respectively, each wavefunction is re-scaled in order to be placed on the same figure with the potential, and the origins of wavefunctions are proportional to their eigenenergies.

We can see from Fig. 3.3 and Fig. 3.4 that each eigenstate is confined in the wave bottoms. In Fig. 3.4, low states are very localized and higher states start to appear delocalized.

Now we use Gauss Approach 40 points to calculate wavefunction at $t = T/4$ from the knowledge of initial state at $t = 0$ and $H(t)$.(Fig. 3.5) We can see that wavefunctions are more delocalized compared to Fig. 3.4.

We can also see the evolution of energies of each mode with time (Fig. 3.6). The calculation is within one period using equation (3.19). One thing to note is that the sum of the energies of the lowest six states stays unchanged, which make sense to us because electrons in the valence band are confined.
Figure 3.5: Time Evolution of wave function under Potential at $t = T/4$

\[ E(t) = \langle \psi(t) | \hat{H}(t) | \psi(t) \rangle. \]  \hspace{1cm} (3.19)

Current is another important property, in this case, we use the probability current density which has the form below:

\[ \vec{j} = \frac{\hbar}{2mi} \left( \Psi^* \vec{\nabla} \Psi - \Psi \vec{\nabla} \Psi^* \right). \]  \hspace{1cm} (3.20)

Current is calculated in the middle of 1D system, Fig. 3.7 shows the results of evolution of current during 8 periods using both Direct and Gauss approach. We can see from the figure that the Direct approach always give us more detail but if we are not interested in what happen in between, Gauss approach is more efficient to give us a overview and long range curve values. Another thing to notice is that the sum of current density for valence band stays zero, this is consistent with the energy results shown in Fig. 3.6.
Figure 3.6: Evolution of Eigenenergies, mode 1-6 constitute the valence band and higher modes constitute conduction band

Figure 3.7: Evolution of current during 8 periods using Direct and Gauss approach
At last, we calculate the electron density from the wave functions and obtain:

\[ n(x) = \sum_i |\psi_i(x)|^2 f_{FD}(E_i - E_F), \]

where \(|\psi_i(x)|^2\) is the density of probability to find an electron in a given subband i.

The electron density at \(t = 0\) and \(t = T/4\) is shown respectively in Fig. 3.8 and Fig. 3.9.

![Figure 3.8: Electron density at \(t = 0\)](image-url)
In Fig. 3.8 and Fig. 3.9, the red curve represents the lowest six states which are the valence band, and the green curve represents mode 7 and 8 which are in the conduction band. We can see that the density including the lowest six states (the valence band) does not change with the potential, because the eigenenergies are too low to overcome the potential barriers. However, if the higher energy states are included, the electron density is moving according to the time dependent potential.

The following Fig. 3.10 shows how the potential movement (see Fig. 3.2) affects the density; here we include the first 8 states, which include both valence and conduction bands. From these figures we can see clearly how electron density is affected according to the external potential.
Figure 3.10: Electron Density (first 8 modes) under moving potential
CHAPTER 4
APPLICATION TO CARBON NANOTUBE IN 3D

In this chapter we perform full 3D modeling and simulation of carbon nanotube using real-space mesh technique and coupled mode approach. The (5, 5) carbon nanotube is studied in this chapter, the unit cell is composed of 2 rings [AB], each ring contains 10 atoms. Electron density, current density, and kinetic inductance will be investigated.

First of all, let us review the TDDFT/Time-Dependent Kohn-Sham Equations in 3D. Runge-Gross theorem asserts that all observables can be calculated with the knowledge of the one-body density. In order to avoid solving the interacting Schrödinger equation, Kohn and Sham had the idea of utilizing an auxiliary system of non-interacting electrons, subject to an external local potential, $v_{KS}$. This potential is unique, by virtue of the Runge-Gross theorem applied to the non-interacting system, and is chosen such that the density of the Kohn-Sham electrons is the same as the density of the orginal interacting system. In the time-dependent case, these Kohn-Sham electrons obey the time-dependent Schrödinger equation.

Consider an N-electron system, starting from a stationary state, solve a set of static Kohn-Sham equations to get a set of N ground state orbitals:

$$\left[ -\frac{\hbar^2}{2m} + v_{ext}(r, t_0) + v_{Hartree}(r) + v_{xc}(r) \right] \Psi_j^{(0)}(r) = E_j \Psi_j^{(0)}(r), \quad (4.1)$$

The N static Kohn-Sham orbitals are taken as initial orbitals and will be propagated in time:
\[ \Psi_j^{(0)}(\mathbf{r}) = \Psi_j(\mathbf{r}, t_0) \quad j = 1, \ldots, N \] (4.2)

\[ \imath \hbar \frac{\partial}{\partial t} \Psi_j(\mathbf{r}, t) = \left[ -\frac{\hbar^2}{2m} \nabla^2 + v_{KS}(\mathbf{r}, t) \right] \Psi_j(\mathbf{r}, t). \] (4.3)

The density of the interacting system can be obtained from the time-dependent Kohn-Sham orbitals

\[ n(\mathbf{r}, t) = \sum_j |\Psi_j(\mathbf{r}, t)|^2, \] (4.4)

The Kohn-Sham potential is conventionally separated in the following way:

\[ v_{KS}(\mathbf{r}, t) = v_{ext}(\mathbf{r}, t) + v_{Hartree}(\mathbf{r}, t) + v_{xc}(\mathbf{r}, t), \] (4.5)

The first term is again the external potential, the Hartree potential accounts for the classical electrostatic interaction between the electrons:

\[ v_{Hartree}(\mathbf{r}, t) = \int d^3\mathbf{r}' n(\mathbf{r}, t) \frac{n(\mathbf{r}, t)}{|\mathbf{r} - \mathbf{r}'|}, \] (4.6)

The last term, the xc potential, comprises all the non-trivial many-body effects.

In our case, we combine the Hartree term and xc term into a given empirical potential, so the only time dependent term is external potential and self consistent procedure is not needed.

### 4.1 Mode Approach for Time Dependent Systems

The size of system matrix is very large in 3D case if we make full 3D discretization, however, if we solve the 3D Schrödinger equation by a coupled mode approach, we can obtain both computational efficiency and high accuracy. Since the mode approach treats quantum confinement and transport separately, the general procedure of the calculation takes two steps [14]: (i) Solving a two-dimensional Schrödinger equation
with a closed boundary condition to obtain the electron subbands and eigenfunctions. In order to solve it, we use potential $U_1(y, z)$ which captures the atomistic potential variation in transport direction (Fig 4.1). (ii) Solving a coupled one-dimensional Schrödinger equations to obtain the electron density.

For 3D case and one Kohn-Sham eigenvector ($\Psi \equiv \Psi_j$), the time dependent Schrödinger equation is given by:

$$i\hbar \frac{\partial}{\partial t} \Psi(x, y, z, t) = \hat{H}_{3D}(x, y, z, t)\Psi(x, y, z, t) , \quad (4.7)$$

and $\hat{H}_{3D}$ is defined as:

$$\hat{H}_{3D} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + U(x, y, z, t) , \quad (4.8)$$

$U(x, y, z, t)$ can be decomposed as:

Figure 4.1: Slices are uniformly discretized on longitudinal direction of nanotube and 2D non-uniformly meshes are created on the cross section.
\[ U(x, y, z, t) = U_1(y, z, t_0) + u(x, y, z, t) , \quad (4.9) \]

\( u(x, y, z, t) \) is a correction potential, where \( U_1(y, z, t_0) \) is an average potential (weighted with lineic density) obtained by:

\[ U_1(y, z, t_0) = \frac{\int_x U(x, y, z, t)n(x, y, z)}{\int_x n(x, y, z)} , \quad (4.10) \]

\( n(x, y, z) \) is the electron density. \( U_1(y, z, t_0) \) is expected to capture the atomistic variation in \( x \) direction (\( x \) is longitudinal direction), and it is time independent.

Then the 3D wave function in the subband eigenfunction space can be expanded as:

\[ \Psi_{3D}(x, y, z, t) = \sum_{n=1}^{\infty} \psi_n(x, t)\chi_n(y, z) , \quad (4.11) \]

where \( \chi_n(y, z) \) is the nth eigenfunction of the following 2D Schrödinger equation (Fig. 4.2 illustrate several 2D wave functions):

\[ -\left[ \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + \frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} \right] \chi_n(y, z) + U_1(y, z, t_0)\chi_n(y, z) = E_n\chi_n(y, z) , \quad (4.12) \]

Here \( E_n \) is the nth subband energy level. \( \chi_n(y, z) \) satisfy orthonormalization condition:

\[ \int \int \chi_m(y, z)\chi_n(y, z)dydz = \delta_{m,n} , \quad (4.13) \]

Eqn. 4.11 can be rewritten into a matrix format as below:

\[ \Psi_{3D}(x, y, z, t) = [Q] \cdot \vec{\psi}(x, t) , \quad (4.14) \]

where the dimensions of matrixes \([Q]\) and \(\vec{\psi}\) are \(N3 \times NM\) and \(NM \times 1\) respectively. \((N3 = N1 \cdot N2, NM = N1 \cdot M)\), \(N1\) is the number of nodes in 1d direction, \(N2\) is the number of nodes on cross section, \(M\) is the number of modes when solving the 2D
Schrödinger equation). Let us denote $\hat{M}$ as $N2 \times M$ block, each column is one mode of the 2D Schrödinger equation 4.12. it comes:

$$[Q] = 
\begin{bmatrix}
\hat{M} & 0 & \cdots & 0 \\
0 & \hat{M} & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & \hat{M}
\end{bmatrix}
\quad \hat{M} = 
\begin{bmatrix}
\cdots & \cdots & \cdots \\
\chi_1(y, z) & \chi_2(y, z) & \cdots & \chi_M(y, z) \\
\vdots & \vdots & \ddots & \vdots
\end{bmatrix}
$$

and $\bar{\psi}$ is a vector of $N1 \times M$ entries, in format below:

$$\bar{\psi}(x, t) = 
\begin{pmatrix}
\psi_1(x_1, t) \\
\psi_2(x_1, t) \\
\vdots \\
\psi_M(x_1, t) \\
\psi_1(x_2, t) \\
\psi_2(x_2, t) \\
\vdots \\
\psi_M(x_2, t) \\
\vdots \\
\psi_1(x_N, t) \\
\psi_2(x_N, t) \\
\vdots \\
\psi_M(x_N, t)
\end{pmatrix}
$$

Insert matrix format Eqn. 4.14 into the 3D time dependent Schrödinger equation, we have:
(a) The 1st mode  
(b) The 2nd mode

(c) The 3rd mode  
(d) The 5th mode

(e) The 20th mode  
(f) The 50th mode

Figure 4.2: Representation of 2D wave-function
\[ i\hbar \frac{\partial}{\partial t} [Q] \bar{\psi} = [H][Q] \bar{\psi} , \]  
(4.15)

Since \([Q]\) only consists of 2d basic functions which are time-independent, the equation can be further written as:

\[ i\hbar \frac{\partial}{\partial t} \bar{\psi} = [H_Q] \bar{\psi} , \]  
(4.16)

Because \([Q^T][Q] = \mathbf{I}\), \([H_Q]\) can be expressed as \([H_Q] = [Q^T][H][Q]\).

This time dependent formula looks like the 1d time dependent Schrödinger equation we discussed in the previous chapters, and of course we can use all the time evolution schemes we have developed. Once \(\psi\) is obtained at any time, we can also get the 3D wave function at any time by Eqn. 4.14.

As discussed in Chapter 2, in order to solve time-dependent Schrödinger equation (Eqn. 4.16), we need to solve a set of eigenvalue problems (diagonalizing Hamiltonian \(H_Q\) at different time \(t\)):

\[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi_m(x) + \sum_n^{\infty} \left( \int_{y,z} (U(t) - U_1) \chi_m \chi_n dydz \right) \psi_n(x) = (E - E_m) \psi_m(x) , \]  
(4.17)

Let

\[ \hat{U}_{mn}(t) = \int_{y,z} (U(t) - U_1) \chi_m \chi_n dydz , \]  
(4.18)

thus, 1D Schrödinger equation becomes:

\[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi_m(x) + \sum_n \hat{U}_{mn}(t) \psi(x) + E_m \psi_m(x) = E \psi_m(x) , \]  
(4.19)

If \(M\) modes are taken into consideration, there will be an equation group that contains \(M\) coupled equations, each representing a selected mode. The \(M\) equations can be written in a matrix format, which is given by:
In order to obtain matrix form of the group equations, multiply both sides of Eqn. 4.19 by a test function and integrated on x direction. The obtained variational form is given by:

\[
\begin{pmatrix}
-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + E_1 + \hat{U}_{11} & \hat{U}_{12} & \hat{U}_{13} & \cdots & \hat{U}_{1M} \\
\hat{U}_{21} & -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + E_2 + \hat{U}_{22} & \hat{U}_{23} & \cdots & \hat{U}_{2M} \\
\vdots & \cdots & \ddots & \cdots & \vdots \\
\hat{U}_{M1} & \hat{U}_{M2} & \hat{U}_{M3} & \cdots & -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + E_M + \hat{U}_{MM}
\end{pmatrix}
\begin{pmatrix}
\psi_1(x) \\
\psi_1(x) \\
\vdots \\
\psi_M(x)
\end{pmatrix}
= E
\begin{pmatrix}
\psi_1(x) \\
\psi_1(x) \\
\vdots \\
\psi_M(x)
\end{pmatrix}
\]

Using FEM, the system matrix becomes a tridiagonal block matrix and each one is \(M \times M\) dense block.

\[
\begin{align*}
-\frac{\hbar^2}{2m} \int_x \frac{\partial^2}{\partial x^2} \psi_m(x) \phi(x) dx &+ \sum_{n}^{\infty} \int_x \hat{U}_{mn} \psi_n(x) dx \\
+ E_m \int_x \psi_m(x) \phi(x) dx & = E \int_x \psi(x) \phi(x) dx,
\end{align*}
\]
$$[H_Q] = \begin{bmatrix}
H_{11} & H_{12} & 0 & 0 & \cdots & 0 \\
H_{21} & H_{22} & H_{23} & 0 & \cdots & 0 \\
0 & H_{32} & H_{33} & H_{34} & \cdots & 0 \\
0 & 0 & H_{43} & H_{44} & \cdots & 0 \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
0 & 0 & 0 & \cdots & H_{N,N-1} & H_{NN}
\end{bmatrix}$$

with

$$[H_{ij}]_{mn} = \frac{\hbar^2}{2m} \int_x \nabla \omega_i \nabla \omega_j dx + \int_x (\hat{U}_{mn}(t) + E_m) \omega_i \omega_j dx , \quad (4.22)$$

The generalized eigenvalue matrix equation we want to solve is:

$$[H_Q] \tilde{\psi} = E[S] \tilde{\psi} , \quad (4.23)$$

Matrixes $\hat{P}$ and $\Delta$ are constructed from the obtained eigenvalue $E$ and eigenvector $\bar{\psi}$.

$$\Delta(t_i) = \begin{bmatrix}
E_1(t_i) & 0 & \cdots & 0 \\
0 & E_2(t_i) & \cdots & 0 \\
\vdots & \vdots & \ddots & \vdots \\
0 & 0 & \cdots & E_n(t_i)
\end{bmatrix} \quad \hat{P}(t_i) = \begin{bmatrix}
\tilde{\psi}_1(t_i) & \tilde{\psi}_2(t_i) & \cdots & \tilde{\psi}_n(t_i)
\end{bmatrix}$$

Finally, the time dependent wavefunction is:

$$\Psi_{3D}(x, y, z, t) = [Q] \cdot \tilde{\psi}(x, t) , \quad (4.24)$$

where
\[
\tilde{\psi}(x, t) = T \exp \left\{ -i \int_{t_0}^{t} H_Q(\tau) d\tau \right\} \tilde{\psi}(x, t_0)
\]
\[
= T \exp \left\{ -\xi \sum_{i=1}^{n} \omega_i H_Q(t_i) \right\} \tilde{\psi}(x, t_0)
\]
\[
= T \left\{ \exp \left[ -\xi \omega_1 H_Q(t_1) \right] \cdot \exp \left[ -\xi \omega_2 H_Q(t_2) \right] \cdots \exp \left[ -\xi \omega_N H_Q(t_N) \right] \right\} \tilde{\psi}(x, t_0)
\]
\[
= T \left\{ \prod_{i} \left[ \hat{P}(t_i) \exp \left( -\xi \omega_i \Delta(t_i) \right) \hat{P}^T(t_i) \right] \right\} [S] \cdot \tilde{\psi}(x, t_0).
\] (4.25)

\[\xi = i \left( \frac{t-t_0}{2} \right), \quad \hat{P}(t_i) \Delta(t_i) \hat{P}^T(t_i) = H_Q(t_i) \quad \text{and} \quad t_i = \frac{t-t_0}{2} x_i + \frac{t+t_0}{2}, \quad x_i \quad \text{and} \quad \omega_i \quad \text{are the selected points of Quadrature.}\]

4.2 Simulation Results

The carbon nanotub studied here is an isolated (5,5) single wall carbon nanotube, the unit cell is composed of 2 rings [AB]. A and B are two different rings, each ring has 10 atoms. The total number of atoms is 120 and the length of CNT is 1.983 nm.

As mentioned before, we combine the Hartree term and xc term into a given empirical potential, the only time-dependent term is external potential. So the potential can be represented as the formula below:

\[
U(x, y, z, t) = U_0(x, y, z) + V_{ext}(x) \times \sin(\omega t) \quad V_{ext}(x) = \frac{2x - L}{L} \times 5eV, \quad (4.26)
\]

where \(x \in [0, L], t \in [0, t_f], t_f = 2\pi/\omega.\)

Because the potential is 3D, a good way to visualize is to plot the potential along longitude direction at given atom positions (transparent plot). The 1D transparent plot of empirical potential is given in Fig. 4.3, the green curve is for atoms in ring type A, the red curve is for atoms in ring type B:
When the time-dependent external potential is applied to the CNT, it maintains zero in the middle of CNT, but oscillates at both ends with the phase of alternating current. The 1D transparent plots of potential at different time steps are Fig. 4.4:
4.2.1 Electron Density

First, we perform eigenvalue calculation and use the eigenfunctions as the initial states, initial electron density is calculated by the formula:

\[
n(x, y, z) = \sum_{i} |\psi_{i}(x, y, z)|^{2} f_{FD}(E_{i} - E_{F}) ,
\]

(4.27)

Similarly, we can plot 1D transparent electron density at atom positions (Fig. 4.5a). More importantly, we can integrate the electron density over cross section (\(\int_{y,z} n(x, y, z, t)\)) to get a 1D electron density (Fig. 4.5b).

Since we can obtain the wave function at any time using the Eqn. 4.25, which has been developed in the last section, now we can investigate many properties of the CNT. One important thing is to see how the electron density evolves over time.
\[ n_{1D}(x,t) = \int_{y,z} n(x,y,z,t) dydz = \int_{y,z} \sum_m |\psi_m(x,t)\chi_m(y,z)|^2 dydz \]

\[ = \int_{y,z} \left[ \sum_{m,n} \psi_m(x,t)\psi_n(x,t)\chi_m(y,z)\chi_n(y,z) \right] dydz \]

\[ = \sum_m |\bar{\psi}_m(x,t)|^2 , \]

Fig. 4.6 shows how the 1D integrated electron density evolves over time at \( t = 0, T/4, T/2, 3T/4, T \) \( (T = 2\pi/\omega = 0.5 \times 10^{-14} s) \). The amplitude for external potential is 5ev, and the scheme used is direct approach 120 points.

Fig. 4.7 shows how does 1D electron density at given position evolves over time. The two particular points are chosen as the middle point of x=0 and the first ring, and the middle point of the last ring and x=L.

Fig. 4.8 shows the "continues" evolvement of the 1D electron potential over time, and a contour plot is also provided. From these figures, we can see that the evolvement of 1D electron density corresponds with the variation of the external potential.

### 4.2.2 Kinetic Inductance

The carbon nanotube (CNT) bundles have been proposed as a promising candidate for next-generation interconnect applications because of their superior electronic and thermal properties. Using theoretical models, the bundles of single wall carbon nanotubes (SWCNTs) have resistance, inductance, and capacitance values at high frequencies that are consistent with predictions for ballistic conductors with quantized energy states [12] [11]. In this section, we will carry out a quantum simulation to the kinetic inductance of SWCNTs.

The CNT has two kinds of inductance: kinetic inductance and magnetic inductance. The kinetic inductance is the manifestation of the inertial mass of mobile charge carriers in alternating electric fields as an equivalent series inductance. The magnetic inductance depends on the magnetic fields inside and between the tubes.
Figure 4.6: Time evolvement of 1D integrated electron density
Figure 4.7: 1D electron density at given position over time

Figure 4.8: 1D electron density over time
For small tubes (width: 10-100 nm), the kinetic inductance is of several orders higher than the magnetic inductance, so we will only deal with kinetic inductance.

Kinetic inductance arises naturally in the Drude model of electrical conduction when the relaxation time (collision time) \( \tau \) is taken to be non-zero. This model defines a complex number—complex conductivity in a time-varying electric field of frequency \( \omega \) given by \( \sigma(\omega) = \sigma_1 - i\sigma_2 \), the imaginary part arising due to kinetic inductance. This complex conductivity can be expanded into its real and imaginary components:

\[
\sigma = \frac{ne^2\tau}{m(1 + i\omega\tau)} = \frac{ne^2\tau}{m(1 + \omega^2\tau^2)} - i\frac{ne^2\omega\tau^2}{m(1 + \omega^2\tau^2)}.
\] (4.29)

where \( m \) is the mass of the charge carrier (i.e.; effective electron mass in metallic electrical conductor—conductors) and \( n \) is the carrier number density. In normal metals the collision time is normally \( \approx 10^{-14} \) s, so for frequencies < 100 GHz the term \( \omega^2\tau^2 \) is very small and can be ignored. Kinetic inductance is therefore only really noticeable at optical frequencies and in superconductors when \( \tau \to \infty \). Since the SWCNT can hold current density up to \( 10^{10} A/cm^2 \), which exceed copper by a factor of 1000, and we apply very high frequencies in our simulation, kinetic inductance becomes very important in our case.

To derive the kinetic inductance for a conducting material is straightforward, the average excess kinetic energy of the charge carriers energy is given by:

\[
E_k = \frac{1}{2}nmv^2.
\] (4.30)

where \( m \) is the electron mass and \( v \) the drift velocity and \( n \) is the number of electrons per unit volume. The current can be described in terms of cross sectional area of conductor (A), the drift velocity and the charge \( q \):

\[
I = nAvq.
\] (4.31)
The total kinetic energy can be expressed in terms of the current $I$ and equivalence to inductance used:

$$E_k = \frac{mI^2}{2nA^2q^2} = \frac{1}{2}L_kI^2. \quad (4.32)$$

So in order to get the kinetic inductance, we need kinetic energy and current. From the wavefunction we got, we can calculate the probability current density in the middle of the CNT. In non-relativistic quantum mechanics, the probability current $\vec{j}$ of the wave function $\Psi$ is defined as

$$\vec{j} = \frac{\hbar}{2mi} \left( \psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^* \right) = \frac{\hbar}{m} \text{Im}(\psi^* \vec{\nabla} \psi). \quad (4.33)$$

Integrating over the cross section ($I = \int_{y,z} \vec{j}dydz$), we have probability current in the middle of the CNT. Fig. 4.9 shows the result of probability current over 10 periods using 120 points direct approach. Kinetic energy can also be calculated from...
malfunction using the formula:

\[ E_k = -\frac{\hbar^2}{2m} (\psi^* \nabla^2 \psi). \]  (4.34)

Because \( L_k = \frac{2E_k}{I^2} \), current \( I \) could be zero at some time, so we take an average of \( E_k \) and \( I \) over each period, and then calculate the average kinetic inductances in each period. Fig. 4.10a shows the average kinetic inductance for 10 periods, with fitting lines in Fig. 4.10b we can see the average kinetic inductance converges over time. The value for kinetic inductance is 2.5 pH, as the actual length of CNT is around 1.4 nm, so we have unit kinetic inductance of 3.57 pH/nm (considering spin). One theoretical estimate for unit kinetic inductance of SWCNT is 6.7 pH/nm [6], which is consistent with Léonard’s book [7]. P.J.Burke has unit kinetic inductance of 4 pH/nm by using a nano-transmission line model [2]. And a measured kinetic inductance result is 7.8 pH/nm (15 parallel tubes) [15]. We can see our result is consistent with other theoretical estimates and measured results. However, because the kinetic inductance has only been applied to much longer device than what we have, we should optimize our numerical techniques and simulate longer CNT, then compare these results.

If we increase the amplitude of external potential to 10ev and calculate the kinetic inductance again, we have the result in Fig. 4.11a. Moreover, if we reduce the size of CNT to 1/2 of its original size, keep 5ev potential variation, the kinetic inductance is shown in Fig. 4.11b. From these simulation result, we find the kinetic inductance is a property that does not depend on the external potential, it is only proportional to the size of the SWCNT.

\subsection*{4.2.3 Energy Evolution of Modes}

Since we have the wavefunction of time for every modes, we can obtain energy variation for each mode. And it would be a good way to examine the accuracy and
(a) Kinetic inductance of SWCNT
(b) Fitting result

Figure 4.10: Kinetic inductance of SWCNT of 6 unit cells when potential variation is 5ev

(a) Kinetic inductance of SWCNT when amplitude of external potential is 10ev
(b) Kinetic inductance of SWCNT with 3 unit cells

Figure 4.11: Kinetic inductance of SWCNT of 6 unit cells and 3 unit cells
Figure 4.12: Energy for mode 1 to 5 calculated using direct approach 120 points and gauss 16 points

efficiency of Gaussian quadrature approach compared to direct approach. The energy for each mode can be represented as Eqn. 4.35

\[ E(t) = \langle \Psi(t) | \hat{H}(t) | \Psi(t) \rangle = \bar{\psi}^* [H_Q] \bar{\psi}. \] (4.35)

Fig. 4.12 shows the energy for mode 1 to 5 calculated using direct approach 120 points and gauss 16 points. We can find that gauss approach can capture the energy variation pretty well (relative error 5%), with only 1/7 computation compared to direct approach.

Fig. 4.17 shows the energy for mode 1 to 5 calculated using direct approach 120 points and gauss 40 points. Gauss 40 points approach is even more accurate than gauss 16 points approach.
Figure 4.13: Energy for mode 1 to 5 calculated using direct approach 120 points and gauss 40 points

And Fig. 4.14 shows the energy for mode 56 to 60 calculated using direct approach 120 points and gauss 16 points. We can see that Gauss 16 no longer capture the variation of energy well.

At last, Fig. 4.15 shows the energy for mode 56 to 60 calculated using direct approach 120 points and gauss 40 points. Again, Gauss 40 approach is very good approximation of the full direct approach.

In order to compare direct approach and gauss approach more clearly, we take the first mode and the last mode up to the fermi energy as examples, and calculate energies using both direct and gauss approach. Results are shown in Fig. 4.12 and Fig. 4.17, which contains different simulation results using direct approach 40, 120 points, gauss 16 points, 40 points and 64 points for mode 1 and mode 60.

Our conclusion is: For lower states the electrons are very confined, and the anti-commutation error is then expected to be small, so gauss 16 approach can be efficient and accurate enough to do the calculations. However, for higher modes where states
Figure 4.14: Energy for mode 56 to 60 calculated using direct approach 120 points and gauss 16 points

Figure 4.15: Energy for mode 56 to 60 calculated using direct approach 120 points and gauss 40 points
are more coupled (i.e. electrons are highly delocalized), the anti-commutation error would then increase, and more points are needed in order to keep the same accuracy such as Gauss 40. It should be noted that using a direct approach 40, the result diverges from direct approach 120 from the beginning of the simulation. Indeed, the main error here is then the integration error which is minimize using Gauss quadrature.

Here we also propose a combination of direct and gauss approach, which means using gauss approach first to save computation, and then apply direct approach to get the detailed information in interested time range. This could be a balance between computational effort and simulation accuracy.

![Figure 4.16: Energy for mode 1 calculated using direct approach 40, 120 points, gauss 16 points, 40 points and 64 points](image)

Figure 4.16: Energy for mode 1 calculated using direct approach 40, 120 points, gauss 16 points, 40 points and 64 points
Table 4.1: Integration error and anti-commutation error

<table>
<thead>
<tr>
<th>Method</th>
<th>Integration error</th>
<th>Anti-commutation error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct approach 40 points</td>
<td>Not acceptable</td>
<td>✓</td>
</tr>
<tr>
<td>Direct approach 120 points</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Gauss approach 16 points</td>
<td>✓</td>
<td>Not acceptable</td>
</tr>
<tr>
<td>Gauss approach 64 points</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

Figure 4.17: Energy for mode 60 calculated using direct approach 40, 120 points, gauss 16 points, 40 points and 64 points

Table 4.1 below summarize the integration error and anti-commutation error when using direct approach and gauss approach respectively.
CONCLUSION

In this thesis, we investigate different modeling techniques for time dependent quantum system. Two main categories are discussed, (i) Solving the time-dependent Schrödinger Equation using a partial differential equation (PDE) representation, FDM/FEM schemes will be used in both space and time discretization. (ii) Performing integration of the time evolution operator, in this approach solving many eigenvalue problems will be involved. The PDE approach can solve some time dependent problems, but it do not always guarantee numerical accuracy and robustness for long simulation time, so we mainly focus on (ii) in this thesis. Instead of using approximations based on expansions such as split operator techniques, we propose to perform exact diagonalizations taking advantage of FEAST. We also propose direct approach and revised gauss quadrature approach when integrating the time evolution operator, efficiency and accuracy for both of them are investigated. After developing the numerical schemes, we apply them to an isolated single wall carbon nanotube, using real-space mesh techniques framework and Density Functional Theory (Kohn-Sham equation) type calculations. During the calculation, a empirical potential is used and a time dependent external potential is applied to the system, self-consistent procedure is not taken into the simulation. Mode approach is another techniques we use to simply the 3D calculation. For the CNT application, we obtained time dependent properties such as electron density, current density, energy for each mode (electron). Unique property of the CNT like kinetic inductance is also examined and compared to other theoretical estimation and measured results.
APPENDIX

APPENDIX A

In this section, we still solve the 1D system with external potential in Fig. 3.2 like in Chapter 3. Direct approach 2000 steps is considered as a reference because we believe this is close enough to the actual solution. Then we use direct approach 200 points, 500 points and Gaussian 10 points, Gaussian 16 and 40 points respectively to calculate the relative errors. The results are shown in the Table below:
### Figure A.1: Relative error comparison between direct approach and Gaussian Quadrature Scheme 1

<table>
<thead>
<tr>
<th>Mode</th>
<th>1/2 period</th>
<th>1/2 * 2 periods</th>
<th>1 period</th>
<th>2 periods</th>
<th>1/2 * 4 periods</th>
<th>5 periods</th>
<th>1/2 * 10 periods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gauss 10</td>
<td>2.80%</td>
<td>4.09%</td>
<td>12.50%</td>
<td>18.30%</td>
<td>40.80%</td>
<td>19.60%</td>
<td>4.80%</td>
</tr>
<tr>
<td>Gauss 16</td>
<td>1.00%</td>
<td>1.72%</td>
<td>8.50%</td>
<td>13.30%</td>
<td>2.90%</td>
<td>4.72%</td>
<td>1.48%</td>
</tr>
<tr>
<td>Gauss 40</td>
<td>0.55%</td>
<td>0.62%</td>
<td>1.90%</td>
<td>2.30%</td>
<td>0.71%</td>
<td>4.72%</td>
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