A THEORETICAL STUDIES QUANTUM PROSPECT FOR SILICON METALORGANIC ATOMIC LAYER DEPOSITION

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ABSTRACT

We are studied theoretical prospect of adsorption process in molecular dynamics via quantum dynamical principle.The quantum propagator or transition amplitude use to explain the probability of dynamic between the initial to another state. In this work we interested in the system of surface science, that is the clean silicon sheet in process of atomic layer deposition. During the adsorbed atom that occupies in the excited state then transfer to the molecule of substrate. The work reviews the phenomena of atom the atom with the substrate surface.

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CHAPTER I

INTRODUCTION

1.1 Background and Motivation

In the recent century, the quantum theory was developed by several scientists for example, Erwin Schrödinger, Paul M. A. Dirac, Richard P. Feynman, and Julian Schwinger. We are the new physicist in current century that just study the enormous prospect of the giant of this major. We have been studied a lot of quantum theory until impress and appreciate for valuable of knowledge in quantum theory. The joint of any knowledge is the joint between the theoretical study and the experimental result. Therefore in this work we try to walk together between theoretical analysis and experimental complexity. The motivation of this work is the fulfillment of our knowledge and we attempt to apply this prospect with the low energy physics.

Modern microelectronic devices, solar cells, ultra thin invisible corrosion resistant coating are prepared by using an exciting technique that is called Atomic Layer Deposition, ALD.

In the recent century Julian Schwinger introduced and developed the Quantum Action(Dynamical) Principle[4] (we can called in short name "QDP") which is an important principle for quantum theory.

After Julian Schwinger the originality of quantum action principle published the context of quantum field theory which was seen by Professor Edward Berg Manoukian, he was totally appreciate that principle and renamed to the quantum dynamical principle in his text book.[5].

In the chapter 2, some of compositions in the literature review there are the explanation of the atomic layer deposition to create the thin film. In the present, ALD is one of almost the popular of creating thin film technology. The next one, in brief,we introduce quantum dynamical principle which is the powerful tool for the quantum theoretical physicists. This theory is useful to create the fundamental quantum quantity this is the transformation function which can be separated in two attribute $\langle \mathbf{x}t|\mathbf{x}'t'\rangle$ and $\langle \mathbf{x}t|\mathbf{p}'t'\rangle$. The first one is called the propagator and the second one is the transformation function. Both of type of transformation function are introduced by J. Schwinger, provide the viewpoint of quantum propagator. The last one of this chapter, is briefly of Green's function that is the important theorem in the quantum theory. Green's function is described how the system transfers from some state to the other state. In the chapter 3, significantly ,is described the cause of the project that why do we build the thesis. In the other chapter is accorded to the hypothesis, procedure and the expected result of the whole project.

1.2 Objctive

-To Study the quantum dynamical principle which is powerful method for quantum mechanics and quantum theory

-To apply this elegance method to other field by using the transformation function or propagator

-To obtain some mechanism or some parameter which could be explained the adsorption mechanism on the surface of metalorganic substrate work piece.

1.3 Framework

In this work study only the theoretical prospect of quantum theory and apply with the adsorption process on the metalorganic surface. Even though in the recent time there are a lot of programmings and tools to obtain an easy model of the system in quantum molecular dynamics such as Hatree-Fock approximation(HF), density functional theory(DFT) but in this work we just present a small piece of theoretical idea by quantum propagator which is an important behind the scene of their theory.

CHAPTER II

REVIEW GREEN'S FUNCTION

In this chapter, we shall introduce important principle, namely, the Green's function which sometimes is called the transfer function in the linear time invariance (LTI) for the engineers.

2.1 Introduction to Green's Function

Mainly idea of this theorem come from British mathematician Gorge Green in recent century[6]. This useful theorem is explain the relation between the source commonly we introduce the Dirac-delta function $\delta(x-x')$ for the general influence that be able to change the equilibrium state[7]. The structure of Green's function is the impulse response function from the differential equation of the influence source.[8, 9]

Green's function is the responded function of a linear differential equation require the both of boundary and initial conditions.

According to the superposition principle, we may write the arbitrary function $f(x)$ in form of linear combination $f(x) = c_0 f_0(x) + c_1 f_1(x) + c_2 f_2(x) + \cdots = \sum\limits_{n=0}^{\infty} c_n f_n(x)$, where $f_n(x)$ stand for the basis of linear combination. The convolution of Green's function with an arbitrary function $f(x)$ is the solution of linear differential equation for $f(x)$. By the way, if we given the linear operator $L\hat{(x)}$ acting on the transfer function in this case it is Green's function we must be got the source term. It implies that if there is a Green's function $G(x,x')$ of a linear differential operator $\hat{L}(x)$ acting on the distribution over some space, at a point x', is a solution of

$$\hat{L}G(x,x') = \delta(x,x') \tag{2.1}$$

where $\delta(x,x')$ is called Dirac-delta function. The property of Green's function is able be advantaged to solve the solution of differential equation of the form

$$Lu(x) = f(x). \tag{2.2}$$

However, in normally, the Green's function is imposed by the boundary and initial condition. If such a function G can be calculated by linear operator L, then, if we multiply Eq.(2.1) with the Green's function $f(x)$, and integrate over x', we get

$$\int \mathrm{d}x' LG(x-x')f(x') = \int \mathrm{d}x' \delta(x-x')f(x') = f(x) \tag{2.3}$$

the right hand side is referred to Eq.(2.2), hence $\int \mathrm{d}x\ LG(x-x')f(x')' = Lu(x) = f(x)$. Moreover, from the property of linear differential operator for arbitrary function $\psi(\xi)$ that is $\int \mathrm{d}\xi\ \hat{L}\psi(\xi) = \hat{L}\left(\int \mathrm{d}\xi\ \psi(\xi)\right)$, then we obtain

$$Lu(x) = \int \mathrm{d}x'\ LG(x-x')f(x') \tag{2.4}$$

$$Lu(x) = L\int \mathrm{d}x'\ G(x-x')f(x') \tag{2.5}$$

$$u(x) = \int \mathrm{d}x'\ G(x-x')f(x'). \tag{2.6}$$

Hence, one may obtain function of $u(x)$ through knowledge of Green's function and the source term, $\delta(x-x')$. The process relies upon the linearity of operator L.

The Green's function be able to split into a sum of two kind of function,namely, there are the retarded and advanced Green's function. Sometimes there are three kind of Green's function the another one is Feynman Green's function. The difference kind of Green's function is occurring because we need to avoid the singularities of poles in the complex plane, when we integrate the Fourier transform.

2.2 Green's function of Poisson Equation

Consider Poisson's equation for electrodynamics

$$\nabla\cdot\mathbf{E} = \frac{\rho}{\epsilon_0} \quad \text{where} \quad \mathbf{E} = -\nabla\phi - \frac{\partial}{\partial t}\mathbf{A}.$$

Then now we have the relation between electric potential $\phi(t,\mathbf{x})$ and Green's function $G(\mathbf{x}-\mathbf{x}')$

$$-\nabla^2\phi(t,\mathbf{x}) = -\int d^3\mathbf{x}\ \ \nabla^2 G(\mathbf{x}-\mathbf{x}')\frac{\rho(t,\mathbf{x}')}{\epsilon_0} \tag{2.7}$$

and from the representation of Green's function of scalar potential

$$-\nabla^2 G(\mathbf{x}-\mathbf{x}') = \delta^{(3)}(\mathbf{x}-\mathbf{x}'). \tag{2.8}$$

Substituting Eq.(2.8) into Eq.(2.7) to obtain

$$-\nabla^2 \phi(t,\mathbf{x}) = \int d^3\mathbf{x}\ \ \delta^{(3)}(\mathbf{x}-\mathbf{x}')\frac{\rho(t,\mathbf{x}')}{\epsilon_0} = \frac{\rho(t,\mathbf{x})}{\epsilon_0} \tag{2.9}$$

Consider above equation, it is amazed how the potential $\phi(t,\mathbf{x})$ can depend upon the charge density $\rho(t,\mathbf{x}')$: *at different points at the same time.* The scalar potential, $\phi(t,\mathbf{x})$, is immediate because of the Coulomb gauge condition $\nabla\cdot\mathbf{A}=0$, which is not Lorentz invariant. The gauge-invariant physical field **E** and **B** are not sudden and do describe Lorentz- invariant electrodynamics.

To evaluate the Fourier Transform of Green's function

$$G(\mathbf{x}) = \int \mathrm{d}^3\mathbf{k}\ e^{i\mathbf{k}\,\cdot\,\mathbf{x}} g(\mathbf{k}) \tag{2.10}$$

and the definition of Dirac-delta function in 3-dimensional reads

$$\delta^{(3)}(\mathbf{x}) = \int \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\,\cdot\,\mathbf{x}} \tag{2.11}$$

If we apply Fourier transform of Green's function in Poisson's equation, then

$$-\nabla^2 G(\mathbf{x}) = -(i\mathbf{k})^2 \int \mathrm{d}^3\mathbf{k}\ \ e^{i\mathbf{k}\cdot\mathbf{x}} g(\mathbf{k})$$

$$= |\mathbf{k}|^2 \int \mathrm{d}^3\mathbf{k}\ \ e^{i\mathbf{k}\cdot\mathbf{x}} g(\mathbf{k})$$

$$= \int \mathrm{d}^3\mathbf{k}\ \ e^{i\mathbf{k}\cdot\mathbf{x}} |\mathbf{k}|^2 g(\mathbf{k}).$$

Comparison the result of above equation with Eq.(2.8), hence

$$\int \mathrm{d}^3\mathbf{k}\ \ e^{i\mathbf{k}\cdot\mathbf{x}} |\mathbf{k}|^2 g(\mathbf{k}) = \int \frac{d^3\mathbf{k}}{(2\pi)^3}\ \ e^{i\mathbf{k}\cdot\mathbf{x}}$$

or

$$g(\mathbf{k}) = \frac{1}{|\mathbf{k}|^2}\frac{1}{(2\pi)^2} \tag{2.12}$$

The new version Fourier transform of Green's function by substitute Eq.(2.12) into Eq.(2.10), we obtain

$$G(\mathbf{x}) = \int \mathrm{d}^3\mathbf{k} \;\; e^{i\mathbf{k}\cdot\mathbf{x}} \frac{1}{|\mathbf{k}|^2} \frac{1}{(2\pi)^3} \tag{2.13}$$

To evaluate the Green's function by use the integration in spherical coordinate $\mathrm{d}^3\mathbf{k} = |\mathbf{k}|^2 \sin(\theta)\, \mathrm{d}|\mathbf{k}|\mathrm{d}\theta\mathrm{d}\phi$ and the dot product of $\mathbf{k}\cdot\mathbf{x} = |\mathbf{k}||\mathbf{x}|\cos(\theta)$

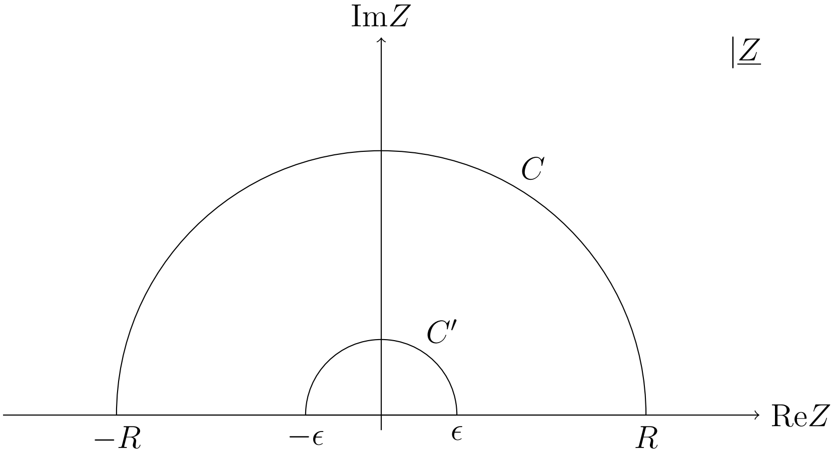
$$\begin{aligned}
G(\mathbf{x}) &= \int \mathrm{d}|\mathbf{k}| \; \mathrm{d}\theta \; \mathrm{d}\phi \; e^{i|\mathbf{k}||\mathbf{x}|\cos(\theta)} \frac{1}{\cancel{|\mathbf{k}|^2}} \frac{1}{(2\pi)^3} \cancel{|\mathbf{k}|^2} \sin(\theta) \\
&= \int \mathrm{d}|\mathbf{k}| \; \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi \; e^{i|\mathbf{k}||\mathbf{x}|\cos(\theta)} \frac{1}{(2\pi)^3} \; \sin(\theta) \\
&= \frac{2\pi}{(2\pi)^3} \int_0^\infty \mathrm{d}|\mathbf{k}| \; \int_{-1}^{1} \mathrm{d}\cos(\theta) \; e^{i|\mathbf{k}||\mathbf{x}|\cos(\theta)} \\
&= \frac{2\pi}{(2\pi)^3} \int_0^\infty \; \mathrm{d}|\mathbf{k}| \; \frac{e^{i|\mathbf{k}||\mathbf{x}|} - e^{-i|\mathbf{k}||\mathbf{x}|}}{i|\mathbf{k}||\mathbf{x}|} \\
&= \frac{2\pi}{(2\pi)^3} \frac{2}{|\mathbf{x}|} \int_0^\infty \; \mathrm{d}\left(|\mathbf{k}||\mathbf{x}|\right) \; \frac{e^{i|\mathbf{k}||\mathbf{x}|} - e^{-i|\mathbf{k}||\mathbf{x}|}}{2\cdot i} \frac{1}{|\mathbf{k}||\mathbf{x}|} \\
&= \frac{2\pi}{(2\pi)^3} \frac{2}{|\mathbf{x}|} \int_0^\infty \; \mathrm{d}\left(|\mathbf{k}||\mathbf{x}|\right) \; \frac{\sin|\mathbf{k}||\mathbf{x}|}{|\mathbf{k}||\mathbf{x}|}.
\end{aligned}$$

According to the calculus of residue we can compute $\int_0^\infty \frac{\sin(z)}{z}\,\mathrm{d}z = \frac{\pi}{2}$, then now we have

$$G(\mathbf{x}) = \frac{2\pi}{(2\pi)^3} \frac{2}{|\mathbf{x}|} \frac{\pi}{2} = \frac{1}{4\pi|\mathbf{x}|} \tag{2.14}$$

<u>Appendix:</u> Calculus of residue for evaluate $I = \int_0^\infty \frac{\sin(z)}{z}\,\mathrm{d}z = \frac{\pi}{2}$

There is a simple pole at $z = 0$ and we have to integrating upper half plane or semicircle and the limit integrate be $-\infty$ to ∞



$$
\begin{aligned}
I &= \int_{-\infty}^{\infty} \frac{\sin(x)}{x}\, dx = \int_{-\infty}^{\infty} \frac{e^{iz}}{z}\, dz \\
&= \text{Im}\left(2\pi i \text{ Residue of } \frac{e^{iz}}{z} \text{ at } z = 0\right) \cdot \left(\frac{1}{2} \text{ because integral semicircle}\right) \\
&= \text{Im}\left(2\pi i \lim_{z \to 0} (z - 0) \frac{e^{i}z}{(z - 0)} \cdot \frac{1}{2}\right) \\
&= \text{Im }(i\pi) \\
&= \pi
\end{aligned}
$$

Therefore $I = \displaystyle\int_{-\infty}^{\infty} \frac{\sin(x)}{x}\, dx = \pi$, then the half of integrating is half of total value or $\displaystyle\int_{0}^{\infty} \frac{\sin(z)}{z}\, dz = \frac{\pi}{2}$

2.3 Green's Function in Quantum Mechanics

In quantum mechanics the Green's function is one of important tools to solve the result of Schrödinger equation

2.3.1 1-Dimensional Free Particle

Let us see the free particle Hamiltonian is shown as the kinetic energy: $H = H_0 = \dfrac{p^2}{2m}$. Time - dependence Schrödinger's equaton as

$$i\hbar \frac{\partial}{\partial t} \psi = H\psi \tag{2.15}$$

or

$$\left(i\hbar \frac{\partial}{\partial t} - H\right) \psi = 0 \tag{2.16}$$

Take to Green's function formalism

$$\left(i\hbar\frac{\partial}{\partial t}-H\right)G\left(x_2t_2;x_1t_1\right)=\delta\left(x_2-x_1\right)\delta\left(t_2-t_1\right) \tag{2.17}$$

The Fourier transform of Green's function in $k-space$ is described by

$$G\left(x_2t_2;x_1t_1\right)=\int\frac{\mathrm{d}k\mathrm{d}\omega}{\left(2\pi\right)^2}e^{i[k(x_2-x_1)-\omega(t_2-t_1)]}G\left(\omega,k\right) \tag{2.18}$$

Substituting Eq.(2.18) in to Eq.(2.17), to obtain

$$\left(i\hbar\frac{\partial}{\partial t}-H\right)\int\frac{\mathrm{d}k\mathrm{d}\omega}{\left(2\pi\right)^2}\mathrm{e}^{i[k(x_2-x_1)-\omega(t_2-t_1)]}G\left(\omega,k\right)=\delta\left(x_2-x_1\right)\delta\left(t_2-t_1\right)$$

$$\begin{aligned}
\text{R.H.S.}&=\int\frac{\mathrm{d}k\mathrm{d}\omega}{\left(2\pi\right)^2}\left(i\hbar\frac{\partial}{\partial t}-H\right)\mathrm{e}^{i[k(x_2-x_1)-\omega(t_2-t_1)]}G\left(\omega,k\right)\\
&=\int\frac{\mathrm{d}k\mathrm{d}\omega}{\left(2\pi\right)^2}\left(i\hbar\frac{\partial}{\partial t}-\frac{p^2}{2\mathrm{m}}\right)\mathrm{e}^{i[k(x_2-x_1)-\omega(t_2-t_1)]}G\left(\omega,k\right)\\
&=\int\frac{\mathrm{d}k\mathrm{d}\omega}{\left(2\pi\right)^2}\left(i\hbar\frac{\partial}{\partial t}+\frac{\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial x^2}\right)\mathrm{e}^{i[k(x_2-x_1)-\omega(t_2-t_1)]}G\left(\omega,k\right)\\
&=\int\frac{\mathrm{d}k\mathrm{d}\omega}{\left(2\pi\right)^2}\left(i\hbar\left(-i\omega\right)+\frac{\hbar^2}{2\mathrm{m}}\left(ik\right)^2\right)\mathrm{e}^{i[k(x_2-x_1)-\omega(t_2-t_1)]}G\left(\omega,k\right)\\
&=\int\frac{\mathrm{d}k\mathrm{d}\omega}{\left(2\pi\right)^2}\left(\hbar\omega-\frac{\hbar^2k^2}{2\mathrm{m}}\right)\mathrm{e}^{i[k(x_2-x_1)-\omega(t_2-t_1)]}G\left(\omega,k\right)
\end{aligned}$$

Now we will have Green's function in $k-space$ as

$$\int\frac{\mathrm{d}k\mathrm{d}\omega}{\left(2\pi\right)^2}\left(\hbar\omega-\frac{\hbar^2k^2}{2\mathrm{m}}\right)\mathrm{e}^{i[k(x_2-x_1)-\omega(t_2-t_1)]}G\left(\omega,k\right)=\int\frac{\mathrm{d}k\mathrm{d}\omega}{\left(2\pi\right)^2}\mathrm{e}^{i[k(x_2-x_1)-\omega(t_2-t_1)]}G\left(\omega,k\right)$$

$$G(\omega,k)=\frac{1}{\left(\hbar\omega-\dfrac{\hbar^2k^2}{2\mathrm{m}}\right)} \tag{2.19}$$

Substituting Eq.(2.19) into Eq.(2.18) and then evaluating as a usual integration we should have

$$G\left(x_2t_2;x_1t_1\right) = \int \frac{\mathrm{d}k\mathrm{d}\omega}{\left(2\pi\right)^2}\frac{e^{i\left[k\left(x_2-x_1\right)-\omega\left(t_2-t_1\right)\right]}}{\left(\hbar\omega-\dfrac{\hbar^2k^2}{2\mathrm{m}}\right)}$$

$$= \frac{1}{\hbar}\int \frac{\mathrm{d}k\mathrm{d}\omega}{\left(2\pi\right)^2}\frac{e^{i\left[k\left(x_2-x_1\right)-\omega\left(t_2-t_1\right)\right]}}{\left(\omega-\dfrac{\hbar k^2}{2\mathrm{m}}\right)}.$$

We have the pole at $\omega = \dfrac{\hbar k^2}{2\mathrm{m}}$, let us transform $\omega \mapsto \omega - \dfrac{\hbar k^2}{2\mathrm{m}}$ and $\mathrm{d}\omega \mapsto \mathrm{d}\omega$, we have

$$G\left(x_2t_2;x_1t_1\right) = \frac{1}{\hbar}\int \frac{\mathrm{d}k\mathrm{d}\omega}{\left(2\pi\right)^2}\frac{\mathrm{e}^{i\left[k\left(x_2-x_1\right)-\left(\omega+\frac{\hbar k^2}{2\mathrm{m}}\right)\left(t_2-t_1\right)\right]}}{\omega}$$

$$= \frac{1}{\hbar}\int \frac{\mathrm{d}k}{\left(2\pi\right)}e^{i\left[k\left(x_2-x_1\right)-\left(\frac{\hbar k^2}{2\mathrm{m}}\right)\left(t_2-t_1\right)\right]}\int \frac{\mathrm{d}\omega}{\left(2\pi\right)}\frac{e^{-1\omega\left(t_2-t_1\right)}}{\omega}$$

<u>Remark</u> We have the special function is Heaviside-step function

$$\Theta(t_2-t_1) = \lim_{\epsilon\to 0^+}\int \frac{\mathrm{d}\omega}{2\pi i}\frac{e^{-i\omega(t_2-t_1)}}{\omega-i\epsilon}. \tag{2.20}$$

An above equation becomes

$$G\left(x_2t_2;x_1t_1\right) = \frac{1}{\hbar}\int \frac{\mathrm{d}k}{\left(2\pi\right)}e^{i\left[k\left(x_2-x_1\right)-\left(\frac{\hbar k^2}{2\mathrm{m}}\right)\left(t_2-t_1\right)\right]}\lim_{\epsilon\to 0^+} i\int \frac{\mathrm{d}\omega}{2\pi i}\frac{e^{-i\omega(t_2-t_1)}}{\omega-i\epsilon}$$

$$= \frac{i}{\hbar}\Theta(t_2-t_1)\int \frac{\mathrm{d}k}{\left(2\pi\right)}e^{i\left[k\left(x_2-x_1\right)-\left(\frac{\hbar k^2}{2\mathrm{m}}\right)\left(t_2-t_1\right)\right]} \tag{2.21}$$

This session we devote to integrate the last term by redefine the exponential integrand

$$i\left[k\left(x_2-x_1\right)-\left(\frac{\hbar k^2}{2\mathrm{m}}\right)\left(t_2-t_1\right)\right] = \frac{i\hbar\left(t_2-t_1\right)}{2\mathrm{m}}\left[\frac{2\mathrm{m}k\left(x_2-x_1\right)}{\hbar\left(t_2-t_1\right)}-k^2\right]$$

$$= -\frac{i\hbar\,(t_2 - t_1)}{2\mathrm{m}}\left[k^2 - \frac{2\mathrm{m}k\,(x_2 - x_1)}{\hbar\,(t_2 - t_1)} + \left(\frac{\mathrm{m}\,(x_2 - x_1)}{\hbar\,(t_2 - t_1)}\right)^2 - \left(\frac{\mathrm{m}\,(x_2 - x_1)}{\hbar\,(t_2 - t_1)}\right)^2\right]$$

$$= -\frac{i\hbar\,(t_2 - t_1)}{2\mathrm{m}}\left[\left(k - \frac{\mathrm{m}(x_2 - x_1)}{\hbar(t_2 - t_1)}\right)^2 - \frac{\mathrm{m}^2(x_2 - x_1)^2}{\hbar^2(t_2 - t_1)^2}\right] \tag{2.22}$$

Substituting Eq.(2.22) into Eq.(2.21), we have

$$G\,(x_2t_2; x_1t_1) = \frac{i}{\hbar}\Theta(t_2 - t_1)$$
$$\times \int \frac{\mathrm{d}k}{(2\pi)}\; e^{-\frac{i\hbar\,(t_2 - t_1)}{2\mathrm{m}}\left[\left(k - \frac{\mathrm{m}(x_2 - x_1)}{\hbar(t_2 - t_1)}\right)^2 - \frac{\mathrm{m}^2(x_2 - x_1)^2}{\hbar^2(t_2 - t_1)^2}\right]} \tag{2.23}$$

Let us transform $k \mapsto k - \dfrac{m(x_2 - x_1)}{\hbar(t_2 - t_1)}$ and $\mathrm{d}k \mapsto \mathrm{d}k$, to obtain

$$G\,(x_2t_2; x_1t_1) = \frac{i}{\hbar}\Theta(t_2 - t_1)e^{\frac{i\cancel{\hbar}\cancel{(t_2 - t_1)}}{2\,\cancel{\mathrm{m}}}\frac{\cancel{\mathrm{m}^2}(x_2 - x_1)^2}{\cancel{\hbar^2}\cancel{(t_2 - t_1)^2}}} \int \frac{\mathrm{d}k}{(2\pi)}\; e^{-\frac{i\hbar\,(t_2 - t_1)}{2\mathrm{m}}k} \tag{2.24}$$

We use the Gaussian integral

$$\int_{-\infty}^{\infty} \mathrm{d}u\; e^{-au^2} = \sqrt{\frac{\pi}{a}} \tag{2.25}$$

and setup

$$a = \frac{i(t_2 - t_1)}{2\mathrm{m}\hbar}$$

until now we obtain

$$G\,(x_2t_2; x_1t_1) = \frac{i}{\hbar}\Theta(t_2 - t_1)\frac{e^{\frac{i}{\hbar}\frac{\mathrm{m}(x_2 - x_1)^2}{2(t_2 - t_1)}}}{2\pi}\sqrt{\frac{2\mathrm{m}\pi}{i\hbar(t_2 - t_1)}}$$

$$= \frac{i}{\hbar}\Theta(t_2 - t_1)e^{\frac{i}{\hbar}\frac{\mathrm{m}(x_2 - x_1)^2}{2(t_2 - t_1)}}\sqrt{\frac{\cancel{2}\mathrm{m}\cancel{\pi}}{\underbrace{\cancel{4}\cancel{\pi^2}}_{2\pi}\, i\hbar(t_2 - t_1)}}$$

Eventually, we now obtain Green's function for 1-dimensional free particle

$$G\,(x_2t_2; x_1t_1) = \frac{i}{\hbar}\Theta(t_2 - t_1)\;\sqrt{\frac{\mathrm{m}}{2\pi i\hbar(t_2 - t_1)}}\;\; e^{\frac{i\mathrm{m}(x_2 - x_1)^2}{2\hbar(t_2 - t_1)}}\,. \tag{2.26}$$

2.3.2 3-Dimensional Free Particle

In this case we attempt to calculate Green's function of a 3-dimensional free particle. Define free Hamiltonian

$$H_0 = \frac{\mathbf{p}^2}{2\mathrm{m}} = \frac{p_x^2 + p_y^2 + p_z^2}{2\mathrm{m}} \tag{2.27}$$

Time-dependent Schrödinger's equation

$$\left(i\hbar\frac{\partial}{\partial t} - H_0\right)\psi(\mathbf{x}) = 0$$

Green's function for 3-dimensional is defined as

$$\left(i\hbar\frac{\partial}{\partial t} - H_0\right)G(\mathbf{x}_2 t_2; \mathbf{x}_1 t_1) = \delta^3(\mathbf{x}_2 - \mathbf{x}_1)\delta(t_2 - t_1) \tag{2.28}$$

Take to Green's function formalism

$$\left(i\hbar\frac{\partial}{\partial t} - H\right)G\left(\mathbf{x}_2 t_2; \mathbf{x}_1 t_1\right) = \delta\left(\mathbf{x}_2 - \mathbf{x}_1\right)\delta\left(t_2 - t_1\right) \tag{2.29}$$

The Fourier transform of Green's function in $k - space$ is described by

$$G\left(\mathbf{x}_2 t_2; \mathbf{x}_1 t_1\right) = \int \frac{\mathrm{d}^3\mathbf{k}\ \mathrm{d}\omega}{\left(2\pi\right)^4} e^{i\left[\mathbf{k}\cdot\left(\mathbf{x}_2 - \mathbf{x}_1\right) - \omega\left(t_2 - t_1\right)\right]} G\left(\omega, \mathbf{k}\right) \tag{2.30}$$

Substituting Eq.(2.30) in to Eq.(2.29), to obtain

$$\left(i\hbar\frac{\partial}{\partial t}-H\right)\int\frac{\mathrm{d}^3\mathbf{k}\,\mathrm{d}\omega}{(2\pi)^4}e^{i\left[\mathbf{k}\left(\mathbf{x}_2-\mathbf{x}_1\right)-\omega\left(t_2-t_1\right)\right]}G\left(\omega,\mathbf{k}\right)=\delta\left(\mathbf{x}_2-\mathbf{x}_1\right)\delta\left(t_2-t_1\right)$$

$$\int\frac{\mathrm{d}^3\mathbf{k}\,\mathrm{d}\omega}{(2\pi)^4}\left(i\hbar\frac{\partial}{\partial t}-H\right)e^{i\left[\mathbf{k}\left(\mathbf{x}_2-\mathbf{x}_1\right)-\omega\left(t_2-t_1\right)\right]}G\left(\omega,\mathbf{k}\right)=\text{R.H.S.}$$

$$\int\frac{\mathrm{d}^3\mathbf{k}\,\mathrm{d}\omega}{(2\pi)^4}\left(i\hbar\frac{\partial}{\partial t}-\frac{\mathbf{p}^2}{2\mathrm{m}}\right)e^{i\left[\mathbf{k}\cdot\left(\mathbf{x}_2-\mathbf{x}_1\right)-\omega\left(t_2-t_1\right)\right]}G\left(\omega,\mathbf{k}\right)=$$

$$\int\frac{\mathrm{d}^3\mathbf{k}\,\mathrm{d}\omega}{(2\pi)^4}\left(i\hbar\frac{\partial}{\partial t}+\frac{\hbar^2}{2\mathrm{m}}\frac{\partial^2}{\partial x^2}\right)e^{i\left[\mathbf{k}\left(\mathbf{x}_2-\mathbf{x}_1\right)-\omega\left(t_2-t_1\right)\right]}G\left(\omega,\mathbf{k}\right)=$$

$$\int\frac{\mathrm{d}^3\mathbf{k}\,\mathrm{d}\omega}{(2\pi)^4}\left[i\hbar\left(-i\omega\right)+\frac{\hbar^2}{2\mathrm{m}}\left(i\mathbf{k}\right)^2\right]e^{i\left[\mathbf{k}\cdot\left(\mathbf{x}_2-\mathbf{x}_1\right)-\omega\left(t_2-t_1\right)\right]}G\left(\omega,k\right)=$$

$$\int\frac{\mathrm{d}^3\mathbf{k}\,\mathrm{d}\omega}{(2\pi)^4}\left(\hbar\omega-\frac{\hbar^2\mathbf{k}^2}{2\mathrm{m}}\right)e^{i\left[\mathbf{k}\cdot\left(\mathbf{x}_2-\mathbf{x}_1\right)-\omega\left(t_2-t_1\right)\right]}G\left(\omega,\mathbf{k}\right)=\text{R.H.S.}$$

Now we will have Green's function in $\mathbf{k}-\textit{space}$ as

$$\int\frac{\mathrm{d}^3\mathbf{k}\,\mathrm{d}\omega}{(2\pi)^4}\left(\hbar\omega-\frac{\hbar^2\mathbf{k}^2}{2\mathrm{m}}\right)e^{i\left[\mathbf{k}\cdot\left(\mathbf{x}_2-\mathbf{x}_1\right)-\omega\left(t_2-t_1\right)\right]}G\left(\omega,\mathbf{k}\right)$$
$$=\int\frac{\mathrm{d}^3\mathbf{k}\,\mathrm{d}\omega}{(2\pi)^4}e^{i\left[\mathbf{k}\cdot\left(\mathbf{x}_2-\mathbf{x}_1\right)-\omega\left(t_2-t_1\right)\right]}G\left(\omega,\mathbf{k}\right)$$

Since we derive Green's function in *momentum* - *space* now we can express in Eq.(2.31)

$$G(\omega,\mathbf{k})=\frac{1}{\left(\hbar\omega-\dfrac{\hbar^2\mathbf{k}^2}{2\mathrm{m}}\right)}\tag{2.31}$$

Substituting Eq.(2.31) into Eq.(2.30) and then evaluating as a usual integration we should have

$$G\left(\mathbf{x}_2 t_2;\mathbf{x}_1 t_1\right)=\int\frac{\mathrm{d}^3\mathbf{k}\mathrm{d}\omega}{\left(2\pi\right)^4}\frac{e^{i\left[\mathbf{k}\cdot\left(\mathbf{x}_2-\mathbf{x}_1\right)-\omega\left(t_2-t_1\right)\right]}}{\left(\hbar\omega-\dfrac{\hbar^2\mathbf{k}^2}{2\mathrm{m}}\right)}$$

$$=\frac{1}{\hbar}\int\frac{\mathrm{d}^3\mathbf{k}\mathrm{d}\omega}{\left(2\pi\right)^4}\frac{e^{i\left[\mathbf{k}\cdot\left(\mathbf{x}_2-\mathbf{x}_1\right)-\omega\left(t_2-t_1\right)\right]}}{\left(\omega-\dfrac{\hbar\mathbf{k}^2}{2\mathrm{m}}\right)}.$$

We have the pole at $\omega=\dfrac{\hbar\mathbf{k}^2}{2\mathrm{m}}$, let us transform $\omega\mapsto\omega-\dfrac{\hbar\mathbf{k}^2}{2\mathrm{m}}$ and $\mathrm{d}\omega\mapsto\mathrm{d}\omega$, we have

$$G\left(\mathbf{x}_2 t_2;\mathbf{x}_1 t_1\right)=\frac{1}{\hbar}\int\frac{\mathrm{d}^3\mathbf{k}\mathrm{d}\omega}{\left(2\pi\right)^4}\frac{e^{i\left[\mathbf{k}\cdot\left(\mathbf{x}_2-\mathbf{x}_1\right)-\left(\omega+\dfrac{\hbar\mathbf{k}^2}{2\mathrm{m}}\right)\left(t_2-t_1\right)\right]}}{\omega}$$

$$=\frac{1}{\hbar}\int\frac{\mathrm{d}^3\mathbf{k}}{\left(2\pi\right)^3}e^{i\left[\mathbf{k}\cdot\left(\mathbf{x}_2-\mathbf{x}_1\right)-\left(\dfrac{\hbar\mathbf{k}^2}{2\mathrm{m}}\right)\left(t_2-t_1\right)\right]}\int\frac{\mathrm{d}\omega}{\left(2\pi\right)}\frac{e^{-i\omega\left(t_2-t_1\right)}}{\omega}\tag{2.32}$$

<u>Remark</u> We have the special function is Heaviside-step function

$$\Theta(t_2-t_1)=\lim_{\epsilon\to0^+}\int\frac{\mathrm{d}\omega}{2\pi i}\frac{e^{-i\omega(t_2-t_1)}}{\omega-i\epsilon}.$$

An above equation Eq.(2.32) becomes

$$G\left(\mathbf{x}_2 t_2;\mathbf{x}_1 t_1\right)=\frac{1}{\hbar}\int\frac{\mathrm{d}^3\mathbf{k}}{\left(2\pi\right)^3}e^{i\left[\mathbf{k}\cdot\left(\mathbf{x}_2-\mathbf{x}_1\right)-\left(\dfrac{\hbar\mathbf{k}^2}{2\mathrm{m}}\right)\left(t_2-t_1\right)\right]}\lim_{\epsilon\to0^+}i\int\frac{\mathrm{d}\omega}{2\pi i}\frac{e^{-i\omega(t_2-t_1)}}{\omega-i\epsilon}$$

$$=\frac{i}{\hbar}\Theta(t_2-t_1)\int\frac{\mathrm{d}^3\mathbf{k}}{\left(2\pi\right)^3}e^{i\left[\mathbf{k}\cdot\left(\mathbf{x}_2-\mathbf{x}_1\right)-\left(\dfrac{\hbar\mathbf{k}^2}{2\mathrm{m}}\right)\left(t_2-t_1\right)\right]}\tag{2.33}$$

This session we devote to integrate the last term by redefine the exponential integrand

$$i\left[\mathbf{k}\cdot\left(\mathbf{x}_2-\mathbf{x}_1\right)-\left(\frac{\hbar\mathbf{k}^2}{2\mathrm{m}}\right)\left(t_2-t_1\right)\right]=\frac{i\hbar\left(t_2-t_1\right)}{2\mathrm{m}}\left[\frac{2\mathrm{m}\mathbf{k}\cdot\left(\mathbf{x}_2-\mathbf{x}_1\right)}{\hbar\left(t_2-t_1\right)}-\mathbf{k}^2\right]$$

$$= -\frac{i\hbar\,(t_2 - t_1)}{2\mathrm{m}}\left[\mathbf{k}^2 - \frac{2\mathrm{m}\mathbf{k}\cdot(\mathbf{x}_2 - \mathbf{x}_1)}{\hbar\,(t_2 - t_1)} + \left(\frac{\mathrm{m}\,|\mathbf{x}_2 - \mathbf{x}_1|}{\hbar\,(t_2 - t_1)}\right)^2 - \left(\frac{\mathrm{m}\,|\mathbf{x}_2 - \mathbf{x}_1|}{\hbar\,(t_2 - t_1)}\right)^2\right]$$

$$= -\frac{i\hbar\,(t_2 - t_1)}{2\mathrm{m}}\left[\left(|\mathbf{k}| - \frac{\mathrm{m}|\mathbf{x}_2 - \mathbf{x}_1|}{\hbar(t_2 - t_1)}\right)^2 - \frac{\mathrm{m}^2(\mathbf{x}_2 - \mathbf{x}_1)^2}{\hbar^2(t_2 - t_1)^2}\right] \tag{2.34}$$

Substituting Eq.(2.34) into Eq.(2.33), we have

$$G\left(\mathbf{x}_2 t_2; \mathbf{x}_1 t_1\right) = \frac{i}{\hbar}\Theta(t_2 - t_1)$$

$$\times \int \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3}\, e^{-\frac{i\hbar\,(t_2 - t_1)}{2\mathrm{m}}\left[\left(|\mathbf{k}| - \frac{\mathrm{m}|\mathbf{x}_2 - \mathbf{x}_1|}{\hbar(t_2 - t_1)}\right)^2 - \frac{\mathrm{m}^2|\mathbf{x}_2 - \mathbf{x}_1|^2}{\hbar^2(t_2 - t_1)^2}\right]} \tag{2.35}$$

Let us transform $|\mathbf{k}| \mapsto |\mathbf{k}| - \dfrac{m|\mathbf{x}_2 - \mathbf{x}_1|}{\hbar(t_2 - t_1)}$ and $\mathrm{d}|\mathbf{k}| \mapsto \mathrm{d}|\mathbf{k}|$, to obtain

$$G\left(\mathbf{x}_2 t_2; \mathbf{x}_1 t_1\right) = \frac{i}{\hbar}\Theta(t_2 - t_1) e^{\frac{i\cancel{\hbar}\cancel{(t_2 - t_1)}}{2\,\cancel{\mathrm{m}}}\frac{\cancel{\mathrm{m}}^2(\mathbf{x}_2 - \mathbf{x}_1)^2}{\cancel{\hbar}^2\cancel{(t_2 - t_1)^2}}} \int \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3}\, e^{-\frac{i\hbar\,(t_2 - t_1)}{2\mathrm{m}}|\mathbf{k}|^2}$$

$$= \frac{i}{\hbar}\Theta(t_2 - t_1) e^{\frac{i}{\hbar}\frac{m|\mathbf{x}_2 - \mathbf{x}_1|^2}{2(t_2 - t_1)}} \frac{1}{(2\pi)^3} \int_0^\infty \mathrm{d}|\mathbf{k}| \int_0^\pi \mathrm{d}\theta\, \underbrace{\int_0^{2\pi} \mathrm{d}\phi}_{=2\pi}\; |\mathbf{k}|^2 \sin(\theta)\, e^{-\frac{i\hbar\,(t_2 - t_1)}{2\mathrm{m}}|\mathbf{k}|^2}$$

$$= \frac{i}{\hbar}\Theta(t_2 - t_1) e^{\frac{i}{\hbar}\frac{m|\mathbf{x}_2 - \mathbf{x}_1|^2}{2(t_2 - t_1)}} \frac{\cancel{2\pi}}{(2\pi)^{\cancel{3}=2}} \int_0^\infty \mathrm{d}|\mathbf{k}| \underbrace{\int_{-1}^{1} \mathrm{d}\cos(\theta)}_{=2}\, |\mathbf{k}|^2\, e^{-\frac{i\hbar\,(t_2 - t_1)}{2\mathrm{m}}|\mathbf{k}|^2} \tag{2.36}$$

We use the Gaussian integral

$$\int_0^\infty \mathrm{d}u\; u^{2n}\, e^{-au^2} = \frac{(2n-1)!!}{a^n\; 2^{n+1}}\sqrt{\frac{\pi}{a}} \tag{2.37}$$

and setup

$$a = \frac{i\hbar(t_2 - t_1)}{2\mathrm{m}}$$

until now we obtain

$$G\left(\mathbf{x}_2 t_2;\mathbf{x}_1 t_1\right) = \frac{i}{\hbar}\Theta(t_2-t_1)\frac{e^{\frac{i}{\hbar}\frac{\mathrm{m}(\mathbf{x}_2-\mathbf{x}_1)^2}{2(t_2-t_1)}}}{(2\pi)^2}\cancel{2}\,\frac{(2(1)-1)!!}{\left[\frac{i\hbar}{2\mathrm{m}}(t_2-t_1)\right]2^{\cancel{2}}}\sqrt{\frac{2\mathrm{m}\pi}{i\hbar(t_2-t_1)}}$$

$$= \frac{i}{\hbar}\Theta(t_2-t_1)e^{\frac{i}{\hbar}\frac{\mathrm{m}(\mathbf{x}_2-\mathbf{x}_1)^2}{2(t_2-t_1)}}\sqrt{\frac{\cancel{8}\mathrm{m}^3\cancel{\pi}}{\cancel{16}\pi^{\cancel{4}}\cancel{4}\left[i\hbar(t_2-t_1)\right]^3}}$$

$$= \frac{i}{\hbar}\Theta(t_2-t_1)e^{\frac{i}{\hbar}\frac{\mathrm{m}(\mathbf{x}_2-\mathbf{x}_1)^2}{2(t_2-t_1)}}\sqrt{\frac{\mathrm{m}^3}{8\pi^3\left[i\hbar(t_2-t_1)\right]^3}}$$

Eventually, we now obtain Green's function for 3-dimensional free particle

$$G\left(\mathbf{x}_2 t_2;\mathbf{x}_1 t_1\right) = \frac{i}{\hbar}\Theta(t_2-t_1)\,\left[\frac{\mathrm{m}}{2\pi i\hbar(t_2-t_1)}\right]^{\frac{3}{2}}\,e^{\frac{i\mathrm{m}|\mathbf{x}_2-\mathbf{x}_1|^2}{2\hbar(t_2-t_1)}}. \qquad (2.38)$$

2.3.3 Green's Function for Linear Schrödinger Equation

In mathematic, *non-linear differential equation* is in the form *degree* of the right hand side is greater than 1 as

$$Lf(x) = x^n.$$

An above equation will be non-linear differential equation where $n > 1$.

CHAPTER III

QUANTUM DYNAMICAL PRINCIPLE

This prospect has been demonstrated to useful tool about high energy physics and particle physics. Moreover the quantum dynamical principle is able to apply and study the low energy physics system i.e. atomic theory, scattering theory, the behavior of material science and etc. The theorical formalism is offered on the transition amplitude $\delta \langle \mathbf{b}, t | \mathbf{a}, t' \rangle$ is explained that the particle transfer from a position **a** and time t' to another position **b** with time t, as an occuring from any differing of some variables in Hamiltonian operator e.g. external source term, mass, charge, etc. The main idea for QDP is the functional derivative of Hamiltonian with respect to the external source term. The benefit of the QDP is used for functional treatment of the Hamiltonian in a formalism of Green's function of the propagator.

3.1 The Dynamical Principle

3.2 Summary of How to calculate Propagator via Dynamical Principle

Time dependence Schrödinger's equation

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \psi(t) = E\psi(t) \tag{3.1}$$

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \left[e^{-\frac{iHt}{\hbar}} \psi(t=0) \right] = H \left[e^{-\frac{iHt}{\hbar}} \psi(t=0) \right] \tag{3.2}$$

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \left[U(t) \psi(t=0) \right] = H \left[U(t) \psi(t=0) \right] \tag{3.3}$$

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \left[U(t) \cancel{\psi(t=0)} \right] = H \left[U(t) \cancel{\psi(t=0)} \right] \tag{3.4}$$

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} U(t) = H U(t) \tag{3.5}$$

Now we have the equation of motion for the time derivative of time-evolution operator

Summary

How to find the propagator by using the quantum dynamical principle

Definition

1) Notation of propagator

$$K(\mathbf{x}_2 t_2; \mathbf{x}_1 t_1) \tag{3.6}$$

2) Transition amplitude

$$\langle \mathbf{x}_2 t_2; \mathbf{x}_1 t_1 \rangle \tag{3.7}$$

3) Chronological Time-Ordering

$$(\dots)_+ \quad \text{or} \quad \hat{T}(\dots) \tag{3.8}$$

4) Green's function

$$G(\mathbf{x}_2 t_2; \mathbf{x}_1 t_1) \tag{3.9}$$

Procedure

1. Define the Hamiltonian operator in coordinate space $H = \dfrac{\mathbf{p}^2}{2\mathrm{m}} + V(\mathbf{x})$

Hamiltonian of source term

$$\hat{H}(\tau) = -\mathbf{x} \cdot \mathbf{F}(\tau) + \mathbf{p} \cdot \mathbf{S}(\tau) \tag{3.10}$$

The complete Hamiltonian

$$H'(\lambda, \tau) = \frac{p^2}{2\mathrm{m}} + \lambda V(\mathbf{x}) - \mathbf{x} \cdot \mathbf{F}(\tau) + \mathbf{p} \cdot \mathbf{S}(\tau) \tag{3.11}$$

Free particle Hamiltonian

$$H'(\lambda = 0, \tau) = \frac{\mathbf{p}^2}{2\mathrm{m}} - \mathbf{x} \cdot \mathbf{F}(\tau) + \mathbf{p} \cdot \mathbf{S}(\tau) \tag{3.12}$$

$$= H'(0, \tau)|_{\mathbf{F},\mathbf{S}=0} + \hat{H}(\tau) \tag{3.13}$$

$$= H_{\lambda=0} + \hat{H}(\tau) \tag{3.14}$$

2. Define the transition amplitude which satisfies above equation

$$\langle \mathbf{a}_2 t_2; \mathbf{b}_1 t_1 \rangle, \tag{3.15}$$

$$\langle \mathbf{a}_2 t_2; \mathbf{b}_1 t_1 \rangle^{(0)}, \tag{3.16}$$

$$\langle \mathbf{a}_2 t_2; \mathbf{b}_1 t_1 \rangle_0 \tag{3.17}$$

where the first symbol is for the propagator of bound system, the second one is the propagator of free particle with a difference time, and the last one is the transition of momentum to position state at the initial time.

We attempt to reduce the following step by step to obtain the transition amplitude $\langle \mathbf{a}_2 t_2; \mathbf{b}_1 t_1 \rangle$. This can be expressed as

$$\begin{aligned} \langle \mathbf{x} t_2; \mathbf{p} t_1 \rangle_0 = & \exp\left[\frac{i}{\hbar}\mathbf{x}\cdot\mathbf{p}\right] \exp\left[\frac{i}{\hbar}\left(\mathbf{x}\cdot\int \mathrm{d}\tau \mathbf{F}(\tau) - \mathbf{p}\cdot\int \mathrm{d}\tau \mathbf{S}(\tau)\right)\right] \\ & \times \exp\left[-\frac{i}{\hbar}\int \mathrm{d}\tau \int \mathrm{d}\tau' \mathbf{S}(\tau)\Theta(\tau-\tau')\mathbf{F}(\tau')\right] \end{aligned} \tag{3.18}$$

The first term in the right-hand side refers to the transition from **p** to **x** at the same time, namely,

$$\langle \mathbf{x} t | \mathbf{p} t \rangle = \langle \mathbf{x} | U(t-t) | \mathbf{p} \rangle \tag{3.19}$$

$$= \langle \mathbf{x} | \mathbf{p} \rangle \tag{3.20}$$

$$= \exp\left[\frac{i}{\hbar}\mathbf{x}\cdot\mathbf{p}\right] \tag{3.21}$$

$$\tag{3.22}$$

The expression of the transition amplitude at the difference time

$$\langle \mathbf{x}t|\mathbf{p}t\rangle^{(0)} = \exp\left[-\frac{i}{\hbar}\int \mathrm{d}\tau \frac{\mathbf{p}^2}{2\mathrm{m}}\right]\langle \mathbf{x}t_2;\mathbf{p}t_1\rangle_0 \tag{3.23}$$

$$= \exp\left[-\frac{i}{\hbar}\frac{1}{2\mathrm{m}}\int \mathrm{d}\tau \left(\frac{\delta}{\delta \mathbf{S}(\tau)}\right)^2\right]\langle \mathbf{x}t_2;\mathbf{p}t_1\rangle_0 \tag{3.24}$$

Substitute Eq.(3.18) into Eq.(3.24) and limit **S** approaches to zero,

$$\begin{aligned}\langle \mathbf{x}t|\mathbf{p}t\rangle^{(0)}\Big|_{\mathbf{S}=0} =& \exp\left[-\frac{i}{\hbar}\frac{1}{2\mathrm{m}}\int \mathrm{d}\tau \left(\frac{\delta}{\delta \mathbf{S}(\tau)}\right)^2\right] \\ & \times \exp\left[\frac{i}{\hbar}\mathbf{x}\cdot\mathbf{p}\right]\exp\left[\frac{i}{\hbar}\left(\mathbf{x}\cdot\int \mathrm{d}\tau \mathbf{F}(\tau) - \mathbf{p}\cdot\int \mathrm{d}\tau \mathbf{S}(\tau)\right)\right] \\ & \times \exp\left[-\frac{i}{\hbar}\int \mathrm{d}\tau \int \mathrm{d}\tau' \mathbf{S}(\tau)\Theta(\tau-\tau')\mathbf{F}(\tau')\right] \\ =& \exp\left[-\frac{i}{\hbar}\frac{\mathbf{p}^2}{2\mathrm{m}}(t-t')\right]\times\exp\left[\frac{i}{\hbar}\mathbf{x}\cdot\mathbf{p}\right] \\ & \exp\left[\frac{i}{\hbar}\left(\mathbf{x}\cdot\int \mathrm{d}\tau \mathbf{F}(\tau) - \frac{\mathbf{p}}{m}\cdot\int \mathrm{d}\tau \mathbf{F}(\tau)(t-\tau)\right)\right] \\ & \times \exp\left[-\frac{i}{\hbar}\frac{1}{2\mathrm{m}}\int \mathrm{d}\tau \int \mathrm{d}\tau' \mathbf{F}(\tau)(t-\tau_>)\mathbf{F}(\tau')\right]\end{aligned} \tag{3.25}$$

By using the fact that

$$\mathbf{S}(\tau) = \frac{\mathbf{F}(\tau)}{\mathrm{m}}(t-\tau) \tag{3.26}$$

and

$$\mathbf{S}(\tau)\Theta(\tau-\tau') = \frac{\mathbf{F}(\tau)}{\mathrm{m}}(t-\tau)\Theta(\tau-\tau') \tag{3.27}$$

$$= \frac{\mathbf{F}(\tau)}{\mathrm{m}}\left[\frac{t-\max(\tau,\tau')}{2}\right] \tag{3.28}$$

We define the new operation as $\tau_{>} = \max(\tau, \tau')$.

Now we come to the complete propagator with potential $V(\mathbf{x})$ which is the characteristic of these system,

$$\langle \mathbf{x}t|\mathbf{p}t\rangle = \exp\left[-\frac{i}{\hbar}\int \mathrm{d}\tau V\left(-i\hbar\frac{\delta}{\delta\mathbf{F}(\tau)}\right)\right]\langle \mathbf{x}t|\mathbf{p}t\rangle^{(0)}\Big|_{\mathbf{S}=0} \tag{3.29}$$

$$= \exp\left\{-\frac{i}{\hbar}\int \mathrm{d}\tau\left[\frac{\mathbf{p}^2}{2\mathrm{m}} + V\left(-i\hbar\frac{\delta}{\delta\mathbf{F}(\tau)}\right)\right]\right\}\langle \mathbf{x}t|\mathbf{p}t\rangle_0|_{\mathbf{S}=0} \tag{3.30}$$

Therefore, the transformation function can be expressed by the multiple of

$$\langle \mathbf{x}t|\mathbf{p}t\rangle = \exp\left[-\frac{i}{\hbar}\int \mathrm{d}\tau V\left(-i\hbar\frac{\delta}{\delta\mathbf{F}(\tau)}\right)\right]\langle \mathbf{x}t|\mathbf{p}t\rangle^{(0)}\Big|_{\mathbf{F},\mathbf{S}=0} \tag{3.31}$$

$$= \exp\left[-\frac{i}{\hbar}\int \mathrm{d}\tau V\left(-i\hbar\frac{\delta}{\delta\mathbf{F}(\tau)}\right)\right]\exp\left[-\frac{i}{\hbar}\frac{1}{2\mathrm{m}}\int \mathrm{d}\tau\left(\frac{\delta}{\delta\mathbf{S}(\tau)}\right)^2\right]$$

$$\times\ \langle \mathbf{x}t|\mathbf{p}t\rangle_0|_{\mathbf{F},\mathbf{S}=0} \tag{3.32}$$

These equation celebrate the quantum dynamical principle

$$\delta\langle at|bt'\rangle = -\frac{i}{\hbar}\int \mathrm{d}\tau\langle at|\delta H\left(q(\tau), p(\tau), \tau; \lambda\right)|bt'\rangle \tag{3.33}$$

$$\tag{3.34}$$

$$\int_{t=t'}^{t}\delta\langle at|bt'\rangle = \langle at|bt'\rangle - \langle at'|bt'\rangle \tag{3.35}$$

$$= \langle at|bt'\rangle - \langle a|b\rangle \tag{3.36}$$

$$= \text{R.H.S} \tag{3.37}$$

$$\text{L.H.S} = -\frac{i}{\hbar}\int \mathrm{d}\tau \langle at|\delta H\left(q(\tau), p(\tau), \tau; \lambda\right)|bt'\rangle \tag{3.38}$$

$$= -\frac{i}{\hbar}\int \mathrm{d}\tau \langle at|\delta H\left(-i\hbar\frac{\delta}{\delta \mathbf{F}(\tau)}, i\hbar\frac{\delta}{\delta \mathbf{S}(\tau)}, \tau; \lambda\right)|bt'\rangle \tag{3.39}$$

$$= -\frac{i}{\hbar}\int \mathrm{d}\tau H\left(-i\hbar\frac{\delta}{\delta \mathbf{F}(\tau)}, i\hbar\frac{\delta}{\delta \mathbf{S}(\tau)}, \tau; \lambda\right)\langle at|bt'\rangle \tag{3.40}$$

The final answer for dynamical principle is

$$\langle at|bt'\rangle = \exp\left[-\frac{i}{\hbar}\int \mathrm{d}\tau H\left(-i\hbar\frac{\delta}{\delta \mathbf{F}(\tau)}, i\hbar\frac{\delta}{\delta \mathbf{S}(\tau)}, \tau; \lambda\right)\right]\langle \mathbf{x}t|\mathbf{p}t\rangle_0\big|_{\mathbf{F},\mathbf{S}=0} \tag{3.41}$$

3.3 The Birth of Dynamical Principle

The general Hamiltonian operator

$$H(t,\lambda) = H_1(t) + H_2(t,\lambda) \tag{3.42}$$

where λ refers to any parameters such as mass, coupling constant, prescribed frequency, number of atomic, charge of particles, magnetic moment, external sources,etc.

Suppose, we have the adsorption coefficient to the parameter λ which is $0 < \lambda < 1$. This value of parameter λ or adsorption coefficient means that if the adsorption on the surface depends on this value.

Consider the time evolution operator, which is the exponential of Hamiltonian operator

$$U(t,\lambda) = \exp\left[-\frac{i}{\hbar}H(t,\lambda)t\right] \tag{3.43}$$

Prove with time-dependent Schrödinger's equation to show that the unitary operator is function of t and λ ,

$$U(t, \lambda) = \exp\left[-\frac{i}{\hbar} H(t, \lambda) t\right] \tag{3.44}$$

$$= \exp\left[-\frac{i}{\hbar}\Big(H_1(t) + H_2(t, \lambda)\Big) t\right] \tag{3.45}$$

$$= \exp\left[-\frac{i}{\hbar} H_1(t) t - \frac{i}{\hbar} H_2(t, \lambda) t\right] \tag{3.46}$$

$$= \exp\left[-\frac{i}{\hbar} H_1(t) t\right] \exp\left[-\frac{i}{\hbar} H_2(t, \lambda) t\right] \tag{3.47}$$

$$= U_1(t) \cdot U_2(t, \lambda) \tag{3.48}$$

apply with Eq.(3.5) to obtain

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \left[U_1(t) U_2(t, \lambda)\right] = i\hbar \left[\frac{\mathrm{d}}{\mathrm{d}t} U_1(t) U_2(t, \lambda) + U_1(t) \frac{\mathrm{d}}{\mathrm{d}t} U_2(t, \lambda)\right] \tag{3.49}$$

$$= i\hbar \left[\frac{H_1(t) U_1(t)}{i\hbar} U_2(t, \lambda) + U_1(t) \frac{H_2(t) U_2(t, \lambda)}{i\hbar}\right] \tag{3.50}$$

$$= \Big(H_1 + H_2\Big) U_1(t) U_2(t, \lambda) \tag{3.51}$$

$$= H(t, \lambda) U(t, \lambda) \tag{3.52}$$

Look at the bottom equation, forthe time-dependence Schrödinger's equation reads

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} \Psi(t) = H(t) \Psi(t) \tag{3.53}$$

or

$$i\hbar \frac{\mathrm{d}}{\mathrm{d}t} |\Psi(t)\rangle = H(t) |\Psi(t)\rangle \tag{3.54}$$

and we have the definition of state $\langle x' | \Psi(t)\rangle = \langle x', t | \Psi\rangle$, one has

$$\begin{aligned} i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\langle x',t|\Psi\rangle &= H(t)\langle x',t|\Psi\rangle = \langle x',t|H(t)|\Psi\rangle \\ i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\langle x',t| &= \langle x',t|H(t) \end{aligned} \tag{3.55}$$

and similarly to the adjoint conjugate

$$\left(i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\langle x',t|\right)^{\dagger} = \bigg(\langle x',t|H(t)\bigg)^{\dagger}$$

$$-i\hbar\frac{\mathrm{d}}{\mathrm{d}t}|x',t\rangle = H^{\dagger}(t)\langle x',t|^{\dagger} = H(t)\;|x',t\rangle \tag{3.56}$$

From $i\hbar\frac{\mathrm{d}}{\mathrm{d}t}U_1(t) = H_1(t)U_1(t)$ and $i\hbar\frac{\mathrm{d}}{\mathrm{d}t}\,{}_1\langle at| = {}_1\langle at|H_1(t)$ we can see that physical states $\langle at|$ are clearly related to the state ${}_1\langle at|$ or

$$\langle at| = {}_1\langle at|U_1^{\dagger}(t)U(t,\lambda) \tag{3.57}$$

Prove

$$U(t,\lambda) = U(t)U(t,\lambda) = U_1(t)U_2(t,\lambda)$$

$$U(t,\lambda)\Psi(x,t) = \langle x,t|U(t,\lambda)|\Psi\rangle = \langle x,t|U_1(t)U_2(t,\lambda)|\Psi\rangle$$

Therefore $\langle x,t|U(t) = \langle x,t|U_1(t)U_2(t,\lambda)$ or

$$\langle a,t|U(t) = \langle a,t|U_1(t)U_2(t,\lambda)$$

$$\langle a,t|U_1^{\dagger}(t)U(t) = \langle a,t|\underbrace{U_1^{\dagger}(t)U_1(t)}_{=1}U_2(t,\lambda)$$

$$\langle a,t|U_1^{\dagger}(t)U(t) = \langle a,t|U_2(t,\lambda)$$

3.4 Definition of Quantum Dynamical Principle

In this section, we devote to prove along mathematical structure of the quantum dynamical principle. By using the derivative of transformation function with respect to time. Define the transformation functions at a difference time t' and t by varying with $\tau = (t', t)$

$$\langle at|a'\tau\rangle \tag{3.58}$$

$$\langle b'\tau|bt'\rangle \tag{3.59}$$

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}\tau}\left[\langle at|a'\tau\rangle\,\langle b'\tau|b't'\rangle\right] = i\hbar\left[\langle at|\,\frac{\mathrm{d}}{\mathrm{d}\tau}\,|a'\tau\rangle\,\langle b'\tau|b't'\rangle + \langle at|a'\tau\rangle\,\langle b'\tau|\,\frac{\mathrm{d}}{\mathrm{d}\tau}\,|b't'\rangle\right] \tag{3.60}$$

$$= i\hbar\left[\langle at|\,\frac{\mathrm{d}}{\mathrm{d}\tau}e^{\frac{i}{\hbar}H_2(\tau,\lambda)\tau}\,|a'\rangle\,\langle b'\tau|b't'\rangle + \langle at|a'\tau\rangle\,\langle b'|\,\frac{\mathrm{d}}{\mathrm{d}\tau}e^{-\frac{i}{\hbar}H_2(\tau,\lambda')\tau}\,|b't'\rangle\right] \tag{3.61}$$

$$\begin{aligned} = i\hbar\Bigg[&\langle at|\left(\frac{i}{\hbar}H_2(\tau,\lambda)\right)e^{\frac{i}{\hbar}H_2(\tau,\lambda)\tau}\,|a'\rangle\,\langle b'\tau|b't'\rangle \\ &+ \langle at|a'\tau\rangle\,\langle b'|\left(-\frac{i}{\hbar}H_2(\tau,\lambda')\right)e^{-\frac{i}{\hbar}H_2(\tau,\lambda')\tau}\,|b't'\rangle\Bigg] \end{aligned} \tag{3.62}$$

$$= i\hbar\left[\langle at|\left(\frac{i}{\hbar}H_2(\tau,\lambda)\right)|a'\tau\rangle\,\langle b'\tau|b't'\rangle + \langle at|a'\tau\rangle\,\langle b'\tau|\left(-\frac{i}{\hbar}H_2(\tau,\lambda')\right)|b't'\rangle\right] \tag{3.63}$$

$$= i\cancel{\hbar}\,\langle at|\left(\frac{i}{\cancel{\hbar}}H_2(\tau,\lambda)\right)|a'\tau\rangle\,\langle b'\tau|b't'\rangle + i\cancel{\hbar}\,\langle at|a'\tau\rangle\,\langle b'\tau|\left(-\frac{i}{\cancel{\hbar}}H_2(\tau,\lambda')\right)|b't'\rangle \tag{3.64}$$

$$= \langle at| - H_2(\tau,\lambda)\, |a'\tau\rangle \langle b'\tau|bt'\rangle + \langle at|a'\tau\rangle \langle b'\tau|\, H_2(\tau,\lambda')\, |bt'\rangle \tag{3.65}$$

$$= \langle at|a'\tau\rangle \langle b'\tau|\, H_2(\tau,\lambda')\, |bt'\rangle + \langle at| - H_2(\tau,\lambda)\, |a'\tau\rangle \langle b'\tau|bt'\rangle \tag{3.66}$$

$$= \langle at|a'\tau\rangle\, H_2(\tau,\lambda') \langle b'\tau|bt'\rangle - \langle at|a'\tau\rangle\, H_2(\tau,\lambda) \langle b'\tau|bt'\rangle \tag{3.67}$$

$$= \langle at|a'\tau\rangle \left[H_2(\tau,\lambda') - H_2(\tau,\lambda)\right] \langle b'\tau|bt'\rangle \tag{3.68}$$

From $H(\tau,\lambda) = H_1(\tau) + H_2(\tau,\lambda)$, we substitute intoEq.(3.68), to obtain

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}\tau}\left[\langle at|a'\tau\rangle \langle b'\tau|b't'\rangle\right] = \langle at|a'\tau\rangle \left[H(\tau,\lambda') - \cancel{H_1(\tau)} - H(\tau,\lambda) + \cancel{H_1(\tau)}\right] \langle b'\tau|bt'\rangle \tag{3.69}$$

To determine λ' as $\lambda' = \lambda + \delta\lambda$ an

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}\tau}\left[\langle at|a'\tau\rangle \langle b'\tau|b't'\rangle\right] = \langle at|a'\tau\rangle \left[H(\tau,\lambda+\delta\lambda) - H(\tau,\lambda)\right] \langle b'\tau|bt'\rangle \tag{3.70}$$

$$= \langle at|a'\tau\rangle\, \delta H(\tau,\lambda) \langle b'\tau|bt'\rangle \tag{3.71}$$

Setup $a' = b'$ for arbitrary constant, we have

$$i\hbar\,\frac{\mathrm{d}}{\mathrm{d}\tau}\left[\langle at|a'\tau\rangle \langle b'\tau|b't'\rangle\right]\bigg|_{a'=b'} = i\hbar\frac{\mathrm{d}}{\mathrm{d}\tau}\left[\langle at|a'\tau\rangle \langle a'\tau|b't'\rangle\right] \tag{3.72}$$

$$= \langle at|\, \delta H(\tau,\lambda)\, |bt'\rangle \tag{3.73}$$

=>

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}\tau}\langle at|bt'\rangle = \langle at|\, \delta H(\tau,\lambda)\, |bt'\rangle \tag{3.74}$$

Integrate over τ from t' to t, to obtain

$$\int_{t'}^{t} \mathrm{d}\,\langle at|bt'\rangle = -\frac{i}{\hbar}\int_{t'}^{t} \mathrm{d}\tau\, \langle at|\, \delta H(\tau,\lambda)\, |bt'\rangle \tag{3.75}$$

$$\boxed{\delta\,\langle at|bt'\rangle = -\frac{i}{\hbar}\int_{t'}^{t} \mathrm{d}\tau\, \langle at|\, \delta H(\tau,\lambda)\, |bt'\rangle} \tag{3.76}$$

Hamiltonian correspondence as $H = H(q, p, \tau; \lambda)$ in Heisenberg picture

$$U \dagger (\tau, \lambda) H(q, p, \tau; \lambda)(\tau, \lambda) = H(q(\tau), p(\tau), \tau; \lambda) \tag{3.77}$$

It is allowed to the $\delta \langle at|bt'\rangle$

$$\boxed{\delta \langle at|bt'\rangle - \frac{i}{\hbar}\int_{t'}^{t} \mathrm{d}\tau \, \langle at|\, \delta H(q(\tau), p(\tau), \tau, \lambda) \,|bt'\rangle} \tag{3.78}$$

This equation is celebrated Schwinger's dynamical (action) principle or the quantum dynamical principle. It is expressed in terms of the physical states $|at\rangle$ and $|bt\rangle'$ which depend on λ. Needless to say, q and p in equation may carry indices corresponding to various degree of freedom.

3.5 Functional Treatment via Dynamical Principle

Given the Hamiltonian, in general, it is combined by two part of kinetic and potential energy

$$H = \frac{\mathbf{p}^2}{2\mathrm{m}} + V(\mathbf{x}) \tag{3.79}$$

Compact to the external source

$$H'(\tau, \lambda) = \frac{\mathbf{p}^2}{2\mathrm{m}} + \lambda V(\mathbf{x}) - \mathbf{x}\cdot\mathbf{F}(\tau) + \mathbf{p}\cdot\mathbf{S}(\tau) \tag{3.80}$$

If we setup $\lambda = 0$ this implies that we now consider the free particle, or

$$\begin{aligned} H'(\tau, \lambda)|_{\lambda=0} &= \frac{\mathbf{p}^2}{2\mathrm{m}} + \lambda V(\mathbf{x})|_{\lambda=0} - \mathbf{x}\cdot\mathbf{F}(\tau) + \mathbf{p}\cdot\mathbf{S}(\tau) \\ H'(\tau, 0) &= \frac{\mathbf{p}^2}{2\mathrm{m}} - \mathbf{x}\cdot\mathbf{F}(\tau) + \mathbf{p}\cdot\mathbf{S}(\tau) \end{aligned} \tag{3.81}$$

Consider Eq.(3.81) refers to the system which there is no potential, thus we can say this is to free particle system. Consequently, for show how QDP is an elegance and a powerful tool to find the transformation function

$$\langle \mathbf{x}t|\mathbf{p}t'\rangle \tag{3.82}$$

where $\mathbf{x}$ and $\mathbf{p}$ is position and coordinate by its imply that nonresponse at time t and t' or final and initial time respectively.

3.6 The dawn of quantum dynamical principle

We can prove from the variational of transformation function in Eq.(3.81), we obtain

$$\delta \langle \mathbf{x}t|\mathbf{p}t'\rangle = \left(-\frac{i}{\hbar}\right)\int_{t'}^{t} \mathrm{d}\tau\ \delta\left(\lambda V(\mathbf{x})\right)\langle \mathbf{x}t|\mathbf{p}t'\rangle \tag{3.83}$$

After we integrate along $\lambda = 0$ to 1 we can eliminate λ that appear in transformation function as

$$\int \delta \langle \mathbf{x}t|\mathbf{p}t'\rangle = \left(-\frac{i}{\hbar}\right)\int_{t'}^{t} \mathrm{d}\tau \int_{\lambda=0}^{1}\mathrm{d}\lambda\left(V(\mathbf{x})\right)\langle \mathbf{x}t|\mathbf{p}t'\rangle$$

$$\int \frac{\mathrm{d}\langle \mathbf{x}t|\mathbf{p}t'\rangle}{\langle \mathbf{x}t|\mathbf{p}t'\rangle} = \left(-\frac{i}{\hbar}\right)\int_{t'}^{t} \mathrm{d}\tau \int_{\lambda=0}^{1}\mathrm{d}\lambda\left(V(\mathbf{x})\right)$$

$$\langle \mathbf{x}t|\mathbf{p}t'\rangle^{(\lambda=1)} = \exp\left[\left(-\frac{i}{\hbar}\right)\int_{t'}^{t}\mathrm{d}\tau\ V(\mathbf{x})\right]\langle \mathbf{x}t|\mathbf{p}t'\rangle^{(\lambda=0)}$$

$$\langle \mathbf{x}t|\mathbf{p}t'\rangle = \exp\left[\left(-\frac{i}{\hbar}\right)\int_{t'}^{t}\mathrm{d}\tau\ V(\mathbf{x})\right]\langle \mathbf{x}t|\mathbf{p}t'\rangle^{(0)} \tag{3.84}$$

According to the Heisenberg equation we can replace $\mathbf{x}$ and $\mathbf{p}$ by $-i\hbar\dfrac{\delta}{\delta\mathbf{F}(\tau)}$ and $i\hbar\dfrac{\delta}{\delta\mathbf{S}(\tau)}$ respectively. To evaluate the vanishing of external source or $\mathbf{F} = \mathbf{S} = 0$, we can substitute $\mathbf{x} = -i\hbar\dfrac{\delta}{\delta\mathbf{F}(\tau)}$ into Eq.(3.84) we have

$$\langle \mathbf{x}t|\mathbf{p}t'\rangle = \exp\left[\left(-\frac{i}{\hbar}\right)\int_{t'}^{t}\mathrm{d}\tau\ V\left(-i\hbar\frac{\delta}{\delta\mathbf{F}(\tau)}\right)\right]\langle \mathbf{x}t|\mathbf{p}t'\rangle^{(0)}\Big|_{\mathbf{F},\mathbf{S}=0} \tag{3.85}$$

Look at Eq.(3.85), it may refer to the transformation function of the free particle system and is expressed as

$$\langle \mathbf{x}t|\mathbf{p}t'\rangle^{(0)} = \exp\left[-\frac{i}{\hbar}\int_{t'}^{t}\mathrm{d}\tau\left(\frac{\mathbf{p}^2}{2\mathrm{m}}\right)\right]\langle \mathbf{x}t|\mathbf{p}t'\rangle_{(0)} \tag{3.86}$$

or

$$\langle \mathbf{x}t|\mathbf{p}t'\rangle^{(0)}\Big|_{\mathbf{F},\mathbf{S}=0} = \exp\left[-\frac{i}{\hbar}\frac{1}{2\mathrm{m}}\int_{t'}^{t}\mathrm{d}\tau\left(i\hbar\frac{\delta}{\delta\mathbf{S}(\tau)}\right)\right]\Bigg|_{\mathbf{F},\mathbf{S}=0}\langle \mathbf{x}t|\mathbf{p}t'\rangle_{(0)} \tag{3.87}$$

We can see the last term, $\langle \mathbf{x}t|\mathbf{p}t'\rangle_{(0)}$, may refer to the transformation function of external sources which generate an equation of motion and satisfy

$$\hat{H}(\tau) = -\mathbf{x}\cdot\mathbf{F}(\tau) + \mathbf{p}\cdot\mathbf{S}(\tau). \tag{3.88}$$

This Hamiltonian has no both of kinetic and potential terms but there are the source term which satisfy that the external source $\mathbf{F}$ generates $\mathbf{x}$ or space translation and for source $\mathbf{S}$ generates $\mathbf{p}$ or momentum translation.

We arise to Hamilton equations which are

$$\frac{\mathrm{d}\mathbf{x}}{\mathrm{d}\tau} = \dot{\mathbf{x}} = \frac{\partial H}{\partial \mathbf{p}} = \mathbf{S}(\tau) \tag{3.89}$$

$$\frac{\mathrm{d}\mathbf{p}}{\mathrm{d}\tau} = \dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{x}} = \mathbf{F}(\tau) \tag{3.90}$$

and

$$\frac{\mathrm{d}H}{\mathrm{d}\tau} = \frac{\partial H}{\partial \tau} \tag{3.91}$$

From Heisenberg equation we can see that $\mathbf{x}$ operator at time τ in the interval $\tau = (t', t)$

$$\dot{\mathbf{x}} = \frac{\mathrm{d}}{\mathrm{d}\tau}\mathbf{x}(\tau) = \mathbf{S}(\tau) \tag{3.92}$$

$$\int_{\mathbf{x}(t')}^{\mathbf{x}(t)} \mathrm{d}\mathbf{x} = \int_{t'}^{t} \mathrm{d}\tau\ \mathbf{S}(\tau) \tag{3.93}$$

$$\mathbf{x}(t) - \mathbf{x}(t') = \int_{t'}^{t} \mathrm{d}\tau\ \mathbf{S}(\tau) \tag{3.94}$$

$$\mathbf{x}(t) - \mathbf{x}(\tau) = \underbrace{\int_{t'}^{t} \mathrm{d}\tau\ (0)\mathbf{S}(\tau)}_{\text{turn-off}} + \underbrace{\int_{t'}^{t} \mathrm{d}\tau\ (1)\mathbf{S}(\tau)}_{\text{turn-on}} \tag{3.95}$$

$$\mathbf{x}(t) - \mathbf{x}(\tau) = \int_{t'}^{t} \mathrm{d}\tau'\ \Theta(\tau - \tau')\mathbf{S}(\tau') \tag{3.96}$$

$$\mathbf{x}(\tau) = \mathbf{x}(t) - \int_{t'}^{t} \mathrm{d}\tau'\ \Theta(\tau - \tau')\mathbf{S}(\tau') \tag{3.97}$$

and similarly to $\mathbf{p}$ operator

$$\dot{\mathbf{p}} = \frac{\mathrm{d}}{\mathrm{d}\tau}\mathbf{p}(\tau) = \mathbf{F}(\tau) \tag{3.98}$$

$$\int_{\mathbf{p}(t')}^{\mathbf{p}(t)} \mathrm{d}\mathbf{p} = \int_{t'}^{t} \mathrm{d}\tau\ \mathbf{F}(\tau) \tag{3.99}$$

$$\mathbf{p}(t) - \mathbf{p}(t') = \int_{t'}^{t} \mathrm{d}\tau\ \mathbf{F}(\tau) \tag{3.100}$$

$$\mathbf{p}(\tau) - \mathbf{p}(t') = \underbrace{\int_{t'}^{t} \mathrm{d}\tau\ (0)\mathbf{F}(\tau)}_{\text{turn-off}} + \underbrace{\int_{t'}^{t} \mathrm{d}\tau\ (1)\mathbf{F}(\tau)}_{\text{turn-on}} \tag{3.101}$$

$$\mathbf{p}(\tau) - \mathbf{p}(t') = \int_{t'}^{t} \mathrm{d}\tau'\ \Theta(\tau - \tau')\mathbf{F}(\tau') \tag{3.102}$$

$$\mathbf{p}(\tau) = \mathbf{p}(t') + \int_{t'}^{t} \mathrm{d}\tau'\ \Theta(\tau' - \tau)\mathbf{F}(\tau') \tag{3.103}$$

Their implement on the source $\mathbf{p}$ turn-on at time $\tau = (t', \tau)$ and for $\mathbf{x}$ operator turn-on at time $\tau = (\tau, t)$ or after operator $\mathbf{p}$ turn-off.

where $\mathbf{x}$ and $\mathbf{p}$ in square bracket on the right-hand sides of the above two equations are Grasmann number and we have used the relation

$$ {}_0\langle \mathbf{x}t|\, \mathbf{x}(t) = \mathbf{x}\ {}_0\langle \mathbf{x}t| \tag{3.104} $$

$$ \mathbf{p}(t)\, |\mathbf{p}t'\rangle_0 = |\mathbf{p}t'\rangle_0\, \mathbf{p} \tag{3.105} $$

We can see that

$$ \begin{aligned} \langle \mathbf{x}t|\, \mathbf{x}(\tau)\, |\mathbf{p}t'\rangle_{\lambda=0} &= \langle \mathbf{x}t|\, \mathbf{x}(\tau)\, |\mathbf{p}t'\rangle_0 \\ &= \langle \mathbf{x}t|\, \mathbf{x}(t) - \int_{t'}^{t} \mathrm{d}\tau'\ \Theta(\tau-\tau')\mathbf{S}(\tau')\, |\mathbf{p}t'\rangle_0 \\ &= \langle \mathbf{x}t|\, \mathbf{x}(t)\, |\mathbf{p}t'\rangle_0 - \langle \mathbf{x}t| \int_{t'}^{t} \mathrm{d}\tau'\ \Theta(\tau-\tau')\mathbf{S}(\tau')\, |\mathbf{p}t'\rangle_0 \\ &= \langle \mathbf{x}t|\, \mathbf{x}\, |\mathbf{p}t'\rangle_0 - \langle \mathbf{x}t| \int_{t'}^{t} \mathrm{d}\tau'\ \Theta(\tau-\tau')\mathbf{S}(\tau')\, |\mathbf{p}t'\rangle_0 \\ &= \left[\mathbf{x} - \int_{t'}^{t} \mathrm{d}\tau'\ \Theta(\tau-\tau')\mathbf{S}(\tau')\right] \langle \mathbf{x}t|\mathbf{p}t'\rangle_0 \end{aligned} \tag{3.106} $$

and similarly to $\mathbf{p}(\tau)$

$$ \begin{aligned} \langle \mathbf{x}t|\, \mathbf{p}(\tau)\, |\mathbf{p}t'\rangle_{\lambda=0} &= \langle \mathbf{x}t|\, \mathbf{p}(\tau)\, |\mathbf{p}t'\rangle_0 \\ &= \langle \mathbf{x}t|\, \mathbf{p}(t') + \int_{t'}^{t} \mathrm{d}\tau'\ \Theta(\tau'-\tau)\mathbf{F}(\tau')\, |\mathbf{p}t'\rangle_0 \\ &= \langle \mathbf{x}t|\, \mathbf{p}(t')\, |\mathbf{p}t'\rangle_0 + \langle \mathbf{x}t| \int_{t'}^{t} \mathrm{d}\tau'\ \Theta(\tau'-\tau)\mathbf{F}(\tau')\, |\mathbf{p}t'\rangle_0 \\ &= \langle \mathbf{x}t|\, \mathbf{p}\, |\mathbf{p}t'\rangle_0 + \langle \mathbf{x}t| \int_{t'}^{t} \mathrm{d}\tau'\ \Theta(\tau'-\tau)\mathbf{F}(\tau')\, |\mathbf{p}t'\rangle_0 \\ &= \left[\mathbf{p} + \int_{t'}^{t} \mathrm{d}\tau'\ \Theta(\tau'-\tau)\mathbf{F}(\tau')\right] \langle \mathbf{x}t|\mathbf{p}t'\rangle_0 \,. \end{aligned} \tag{3.107} $$

As for $\lambda = 0$ at the coincident time or the same time, Eq.(3.106) and Eq.(3.107) can be rewritten as

$$-i\hbar\frac{\delta}{\delta\mathbf{F}\tau}\langle\mathbf{x}t|\mathbf{p}t\rangle_0 = \langle\mathbf{x}t|\,\mathbf{x}(\tau)\,|\mathbf{p}t'\rangle_0 = \left[\mathbf{x}-\int_{t'}^{t}\mathrm{d}\tau'\;\Theta(\tau-\tau')\mathbf{S}(\tau')\right]\langle\mathbf{x}t|\mathbf{p}t'\rangle_0 \tag{3.108}$$

and

$$-i\hbar\frac{\delta}{\delta\mathbf{S}\tau}\langle\mathbf{x}t|\mathbf{p}t\rangle_0 = \langle\mathbf{x}t|\,\mathbf{p}(\tau)\,|\mathbf{p}t'\rangle_0 = \left[\mathbf{p}+\int_{t'}^{t}\mathrm{d}\tau'\;\Theta(\tau'-\tau)\mathbf{F}(\tau')\right]\langle\mathbf{x}t|\mathbf{p}t'\rangle_0 \tag{3.109}$$

Now integrate equation Eq.(3.108) and Eq.(3.109) to

$$\int\frac{\mathrm{d}\,\langle\mathbf{x}t|\mathbf{p}t'\rangle}{\langle\mathbf{x}t|\mathbf{p}t'\rangle} = \frac{i}{\hbar}\int_{t'}^{t}\mathrm{d}\tau\mathbf{F}(\tau)\left[\mathbf{x}-\int_{t'}^{t}\mathrm{d}\tau'\;\mathbf{S}(\tau')\Theta(\tau'-\tau)\right] \tag{3.110}$$

$$\ln\left[\frac{\langle\mathbf{x}t|\mathbf{p}t'\rangle}{\langle\mathbf{x}t'|\mathbf{p}t'\rangle}\right] = \frac{i}{\hbar}\left[\int_{t'}^{t}\mathrm{d}\tau\mathbf{F}(\tau)\,\mathbf{x}-\int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\;\mathbf{S}(\tau')\Theta(\tau'-\tau)\mathbf{F}(\tau)\right] \tag{3.111}$$

To obtain

$$\begin{aligned}\langle\mathbf{x}t|\mathbf{p}t'\rangle &= \langle\mathbf{x}t'|\mathbf{p}t'\rangle_0\exp\left(\frac{i}{\hbar}\left[\int_{t'}^{t}\mathrm{d}\tau\mathbf{F}(\tau)\,\mathbf{x}-\int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\;\mathbf{S}(\tau')\Theta(\tau'-\tau)\mathbf{F}(\tau)\right]\right)\\ &= \exp\Big(\frac{i}{\hbar}\mathbf{x}\mathbf{p}\Big)\exp\left(\frac{i}{\hbar}\left[\int_{t'}^{t}\mathrm{d}\tau\mathbf{F}(\tau)\,\mathbf{x}-\int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\;\mathbf{S}(\tau')\Theta(\tau'-\tau)\mathbf{F}(\tau)\right]\right)\\ &= \exp\Big(\frac{i}{\hbar}\mathbf{x}\mathbf{p}\Big)\exp\left(\frac{i}{\hbar}\int_{t'}^{t}\mathrm{d}\tau\mathbf{F}(\tau)\,\mathbf{x}\right)\exp\left(-\frac{i}{\hbar}\int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\;\mathbf{S}(\tau')\Theta(\tau'-\tau)\mathbf{F}(\tau)\right)\end{aligned} \tag{3.112}$$

and for $\mathbf{p}$ also

$$\int\frac{\mathrm{d}\,\langle\mathbf{x}t|\mathbf{p}t'\rangle}{\langle\mathbf{x}t|\mathbf{p}t'\rangle} = -\frac{i}{\hbar}\int_{t'}^{t}\mathrm{d}\tau\mathbf{S}(\tau)\left[\mathbf{p}+\int_{t'}^{t}\mathrm{d}\tau'\;\Theta(\tau-\tau')\mathbf{F}(\tau')\right] \tag{3.113}$$

$$\ln\left[\frac{\langle\mathbf{x}t|\mathbf{p}t'\rangle}{\langle\mathbf{x}t'|\mathbf{p}t'\rangle}\right] = -\frac{i}{\hbar}\left[\int_{t'}^{t}\mathrm{d}\tau\mathbf{S}(\tau)\,\mathbf{p}+\int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\;\mathbf{S}(\tau)\Theta(\tau-\tau')\mathbf{S}(\tau')\right] \tag{3.114}$$

To obtain

$$\begin{aligned}\langle \mathbf{x}t|\mathbf{p}t'\rangle &= \langle \mathbf{x}t'|\mathbf{p}t'\rangle_0 \exp\left(-\frac{i}{\hbar}\left[\int_{t'}^{t}\mathrm{d}\tau\mathbf{S}(\tau)\,\mathbf{p} + \int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\;\mathbf{S}(\tau)\Theta(\tau-\tau')\mathbf{F}(\tau')\right]\right)\\ &= \exp\!\left(\frac{i}{\hbar}\mathbf{x}\mathbf{p}\right)\exp\left(-\frac{i}{\hbar}\left[\int_{t'}^{t}\mathrm{d}\tau\mathbf{S}(\tau)\,\mathbf{p} + \int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\;\mathbf{S}(\tau)\Theta(\tau-\tau')\mathbf{F}(\tau')\right]\right)\\ &= \exp\!\left(\frac{i}{\hbar}\mathbf{x}\mathbf{p}\right)\exp\left(-\frac{i}{\hbar}\int_{t'}^{t}\mathrm{d}\tau\mathbf{S}(\tau)\,\mathbf{x}\right)\exp\left(-\frac{i}{\hbar}\int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\;\mathbf{S}(\tau)\Theta(\tau-\tau')\mathbf{F}(\tau')\right)\end{aligned} \tag{3.115}$$

Look at the expectation of pure source Hamiltonian

$$H(\mathbf{x},\mathbf{p},\tau) = H\left(-i\hbar\frac{\delta}{\delta\mathbf{F}(\tau)}, i\hbar\frac{\delta}{\delta\mathbf{S}(\tau)}\right) \tag{3.116}$$

$$\langle \mathbf{x}t|\,\hat{H}'\,|\mathbf{p}t'\rangle\Big|_{\lambda=0} = \langle \mathbf{x}t| - \mathbf{x}(\tau)\cdot\mathbf{F}(\tau) + \mathbf{p}(\tau)\cdot\mathbf{S}(\tau)\,|\mathbf{p}t'\rangle \tag{3.117}$$

$$= \langle \mathbf{x}t| - i\hbar\frac{\delta}{\delta\mathbf{F}(\tau)} + i\hbar\frac{\delta}{\delta\mathbf{S}(\tau)}\,|\mathbf{p}t'\rangle\Bigg|_{\substack{\lambda=0\\ \mathbf{F},\mathbf{S}=0}}. \tag{3.118}$$

From the time-dependent Schrödinger's equation, we obtain

$$\begin{aligned} i\hbar\frac{\mathrm{d}}{\mathrm{d}\tau}\langle \mathbf{x}t|\mathbf{p}t'\rangle_0 &= \langle \mathbf{x}t|\,\hat{H}'\,|\mathbf{p}t'\rangle\Big|_{\lambda=0} && (3.119)\\ &= \langle \mathbf{x}t| - i\hbar\frac{\delta}{\delta\mathbf{F}(\tau)} + i\hbar\frac{\delta}{\delta\mathbf{S}(\tau)}\,|\mathbf{p}t'\rangle\Bigg|_{\substack{\lambda=0\\ \mathbf{F},\mathbf{S}=0}}. && (3.120)\end{aligned}$$

Devided by $i\hbar$

$$\frac{\mathrm{d}}{\mathrm{d}\tau}\langle \mathbf{x}t|\mathbf{p}t'\rangle_0 = \langle \mathbf{x}t| - \frac{\delta}{\delta\mathbf{F}(\tau)} + \frac{\delta}{\delta\mathbf{S}(\tau)}\,|\mathbf{p}t'\rangle\Bigg|_{\substack{\lambda=0\\ \mathbf{F},\mathbf{S}=0}} \tag{3.121}$$

substitute Eq.(3.97) and Eq.(3.103) into above equation

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}\tau}\langle \mathbf{x}t|\mathbf{p}t'\rangle_0 &= \langle \mathbf{x}t| - \frac{i}{\hbar}\left[\mathbf{x}(t) - \int_{t'}^{t}\mathrm{d}\tau'\;\Theta(\tau'-\tau)\mathbf{S}(\tau')\right]\\ &\quad + \frac{i}{\hbar}\left[\mathbf{p}(t') + \int_{t'}^{t}\mathrm{d}\tau'\;\Theta(\tau'-\tau)\mathbf{F}(\tau')\right]|\mathbf{p}t'\rangle|_{\substack{\lambda=0\\ \mathbf{F},\mathbf{S}=0}} && (3.122)\\ &= \left[\frac{i}{\hbar}\left(\mathbf{x} - \int_{t'}^{t}\mathrm{d}\tau'\Theta(\tau'-\tau)\mathbf{S}(\tau')\right) - \frac{i}{\hbar}\left(\mathbf{p} + \int_{t'}^{t}\mathrm{d}\tau'\Theta(\tau-\tau')\mathbf{F}(\tau')\right)\right]\langle \mathbf{x}t|\mathbf{p}t'\rangle|_{\lambda=0}. && (3.123)\end{aligned}$$

We integrate along time $t = (t', t)$, we already have

$$\begin{aligned}\int \frac{\mathrm{d}\,\langle \mathbf{x}t|\mathbf{p}t'\rangle_0}{\langle \mathbf{x}t|\mathbf{p}t'\rangle_0} &= \frac{i}{\hbar}\int_{t'}^{t} \mathrm{d}\tau\;\mathbf{x} - \frac{i}{\hbar}\int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\Theta(\tau'-\tau)\mathbf{S}(\tau') \\ &\quad - \frac{i}{\hbar}\int_{t'}^{t} \mathrm{d}\tau\;\mathbf{p} - \frac{i}{\hbar}\int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\Theta(\tau-\tau')\mathbf{F}(\tau') \qquad (3.124)\\ \ln\left[\frac{\langle \mathbf{x}t|\mathbf{p}t'\rangle_0}{\langle \mathbf{x}t'|\mathbf{p}t'\rangle_0}\right] &= \frac{i}{\hbar}\int_{t'}^{t} \mathrm{d}\tau\;\mathbf{x} - \frac{i}{\hbar}\int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\Theta(\tau'-\tau)\mathbf{S}(\tau') \\ &\quad - \frac{i}{\hbar}\int_{t'}^{t} \mathrm{d}\tau\;\mathbf{p} - \frac{i}{\hbar}\int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\Theta(\tau-\tau')\mathbf{F}(\tau'). \qquad (3.125)\end{aligned}$$

The result show as in below

$$\begin{aligned}\langle \mathbf{x}t|\mathbf{p}t'\rangle_0 &= \langle \mathbf{x}t'|\mathbf{p}t'\rangle_0 \exp\left[-\frac{i}{\hbar}\int_{t'}^{t} \mathrm{d}\tau\;\mathbf{p} - \frac{i}{\hbar}\int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\Theta(\tau-\tau')\mathbf{F}(\tau')\right] \qquad (3.126)\\ &= \langle \mathbf{x}|\mathbf{p}\rangle_0 \exp\left[-\frac{i}{\hbar}\int_{t'}^{t} \mathrm{d}\tau\;\mathbf{p} - \frac{i}{\hbar}\int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\Theta(\tau-\tau')\mathbf{F}(\tau')\right] \qquad (3.127)\\ &= \exp\left(\frac{i}{\hbar}\mathbf{x}\mathbf{p}\right) \qquad (3.128)\\ &\times \exp\left[\frac{i}{\hbar}\int_{t'}^{t} \mathrm{d}\tau\;\mathbf{x} - \frac{i}{\hbar}\int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\Theta(\tau'-\tau)\mathbf{S}(\tau')\right] \qquad (3.129)\\ &\times \exp\left[-\frac{i}{\hbar}\int_{t'}^{t} \mathrm{d}\tau\;\mathbf{p} - \frac{i}{\hbar}\int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\Theta(\tau-\tau')\mathbf{F}(\tau')\right] \qquad (3.130)\end{aligned}$$

Consider the variational of our transformation, we have

$$\frac{\delta}{\delta\mathbf{F}(\tau)}\,\langle \mathbf{x}t|\mathbf{p}t'\rangle_0 = \frac{i}{\hbar}\left[\mathbf{x} - \int_{t'}^{t}\mathrm{d}\tau'\;\Theta(\tau'-\tau')\mathbf{S}(\tau')\right]\langle \mathbf{x}t|\mathbf{p}t'\rangle_0 \qquad (3.131)$$

and

$$\frac{\delta}{\delta\mathbf{S}(\tau)}\,\langle \mathbf{x}t|\mathbf{p}t'\rangle_0 = -\frac{i}{\hbar}\left[\mathbf{p} + \int_{t'}^{t}\mathrm{d}\tau'\;\Theta(\tau-\tau')\mathbf{F}(\tau')\right]\langle \mathbf{x}t|\mathbf{p}t'\rangle_0 \qquad (3.132)$$

Solve the solution of transformation function by integrating Eq.(3.132) as

$$\begin{aligned}\frac{\delta\,\langle \mathbf{x}t|\mathbf{p}t'\rangle_0}{\langle \mathbf{x}t|\mathbf{p}t'\rangle_0} &= -\frac{i}{\hbar}\left[\mathbf{p} + \int_{t'}^{t}\mathrm{d}\tau'\Theta(\tau-\tau')\mathbf{F}(\tau')\right]\;\delta\mathbf{S}(\tau) \qquad (3.133)\\ \int\frac{\mathrm{d}\,\langle \mathbf{x}t|\mathbf{p}t'\rangle_0}{\langle \mathbf{x}t|\mathbf{p}t'\rangle_0} &= -\frac{i}{\hbar}\int\left[\mathbf{p} + \int_{t'}^{t}\mathrm{d}\tau'\Theta(\tau-\tau')\mathbf{F}(\tau')\right]\;\mathrm{d}\tau\mathbf{S}(\tau) \qquad (3.134)\\ &= -\frac{i}{\hbar}\left[\mathbf{p}\;\int_{t'}^{t}\mathrm{d}\tau\mathbf{S}(\tau) + \int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\mathbf{S}(\tau)\Theta(\tau-\tau')\mathbf{F}(\tau')\right] \qquad (3.135)\\ \ln\left[\frac{\langle \mathbf{x}t|\mathbf{p}t\rangle_0}{\langle \mathbf{x}t'|\mathbf{p}t\rangle_0}\right] &= -\frac{i}{\hbar}\left[\mathbf{p}\int_{t'}^{t}\mathrm{d}\tau\mathbf{S}(\tau) + \int_{t'}^{t}\mathrm{d}\tau\int_{t'}^{t}\mathrm{d}\tau'\mathbf{S}(\tau)\Theta(\tau-\tau')\mathbf{F}(\tau')\right] \qquad (3.136)\end{aligned}$$

The result show as in below

$$\langle \mathbf{x}t|\mathbf{p}t\rangle_0 = \langle \mathbf{x}t'|\mathbf{p}t'\rangle_0 \exp\left[-\frac{i}{\hbar}\int_{t'}^{t} \mathrm{d}\tau\ \mathbf{p} - \frac{i}{\hbar}\int_{t'}^{t} \mathrm{d}\tau \int_{t'}^{t} \mathrm{d}\tau'\Theta(\tau-\tau')\mathbf{F}(\tau')\right] \tag{3.137}$$

$$= \langle \mathbf{x}|\mathbf{p}\rangle_0 \exp\left[-\frac{i}{\hbar}\int_{t'}^{t} \mathrm{d}\tau\ \mathbf{p} - \frac{i}{\hbar}\int_{t'}^{t} \mathrm{d}\tau \int_{t'}^{t} \mathrm{d}\tau'\Theta(\tau-\tau')\mathbf{F}(\tau')\right] \tag{3.138}$$

$$= \exp\left(\frac{i}{\hbar}\mathbf{x}\mathbf{p}\right) \tag{3.139}$$

$$\times \exp\left[-\frac{i}{\hbar}\int_{t'}^{t} \mathrm{d}\tau\ \mathbf{p} - \frac{i}{\hbar}\int_{t'}^{t} \mathrm{d}\tau \int_{t'}^{t} \mathrm{d}\tau'\Theta(\tau-\tau')\mathbf{F}(\tau')\right] \tag{3.140}$$

CHAPTER IV

ATOMIC LAYER DEPOSITION

Atomic layer deposition is one of several processes in material science of growth or deposition the thin film (this mean that the thickness less than 5 micrometers) on the surface of substrate.

This method allows to deposit thin film of a variety of materials by taking advantages of sequential chemical processes that occur in a specially designed ALD reactor. The most important components of ALD reactor, that uses gas phase chemicals are shown in this simplified model.

The chemical, that are used for the deposition, are called precursors and enter the reaction chamber along with the carrier gas. A vacuum pump is used to ensure a low pressure and that the reaction by products and precursor leftover are removed. The precursors enter the reaction chamber one at a time and react with

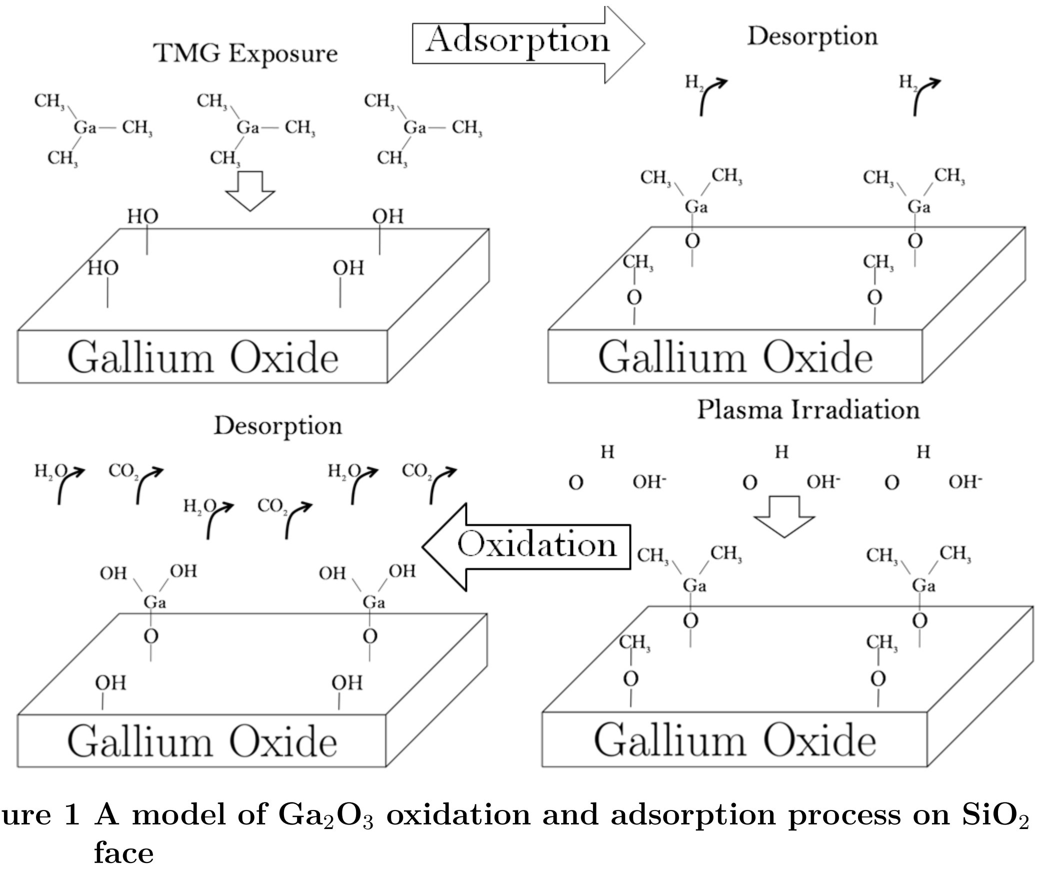


Figure 1 A model of Ga_2O_3 oxidation and adsorption process on SiO_2 surface

the substrate in a self limiting manner. As the substrate is repeatedly exposed to different precursors a thin film of desired material is deposited in each cycle. The thickness of a thin film depends on the number of the cycles.

As an example would be the deposition of gallium oxide Ga_2O_3 on a silicon substrate by using trimethylgallium (TMG) or $Ga(CH_3)_3$ and water vapor as precursors and oxide OH^- as carrier gas[1, 2]. In this process the deposition cycle consists of four steps.

In the first step, gallium oxide Ga_2O_3 is inserted into the chamber and that reacts or purges with the hydroxyl group i.e. hydrogen chloride of hydrochloric acid (HCl) on the substrate surface, forming the first layer. As a result, hydrogen chloride is produced as some hydrogen gases are removed from the galluim oxide and hydrogen from the hydroxyl group. The excess trimethylgallium (TMG) and hydrogen chloride are then removed from the chamber in the second step by purging with the carrier gas be hydrogen gas. In the third step, the second precursors, water vapor (at the plasma state), is inserted into the chamber and that reacted with the gallium oxide on the surface. As a result, methyl CH_3 is replaced with hydroxide and gallium dioxide is formed[1].

Finally, in the fourth step, the excess water vapor is purged from the chamber with carbondioxide CO_2, leaving behind the first layer of gallium dioxide. By repeating this cycle, a film with desired thickness can be deposited.

The structure of the deposited film depends upon the substrate temperatures. For example, amorphous film scan be obtained at lower temperatures and crystallized films at higher temperatures. The substrate material and the thickness of the deposited layer.

The advantages of atomic layer deposition process is easy to control the thickness of the thin film. The deposition of multilayer is straightforward because the thickness depend on the number of repeat cycle. Moreover, ALD can be used for complicated surface material even high complexity.

CHAPTER V

CONCLUSION:ON THE INTERACTION OF ADSORPTION PROCESS

The study of adsorption is importance in the field of surface science. Often there are many important step in the preparation of a device such as in the growth of semiconductor devices. But adsorption can also be of significant importance in industrially relevant processes such as in the production of coating car or house glass and coating surface of jewelry to make the hard surface. The most significant example is chemical catalysis since the reactants have to adsorb on the clean surface before they can react. But also from a fundamental point of view the physical and chemical factors determining adsorption processes are most interesting.

In this chapter, we will show the behavior of atomic adsorption on the surface and introduce the basic quantities necessary to explain the adsorption. After classifying the different ways of adsorption process the necessary theoretical tools can use to treat these systems will be shown.

We can accord an article from W. Kohn 1994, which describes the potential for atomic adsorption via adsorption coefficient[10, 11] approaches to square root of energy, $s(E) \rightarrow E^{1/2}$. For the propagator which can be describes the behavior of quantum system by using the quantum dynamical principle. According to this paper, author prefer the behavior of adsorbed atom on surface to be the same with a step-potential and the energy of atom is the eigenvalue from Schrödinger equation with Bloch theorem, we suppose the potential geometry is the periodic function, $u(x)$ in one-dimensional, for modeling the behavior of clean surface.

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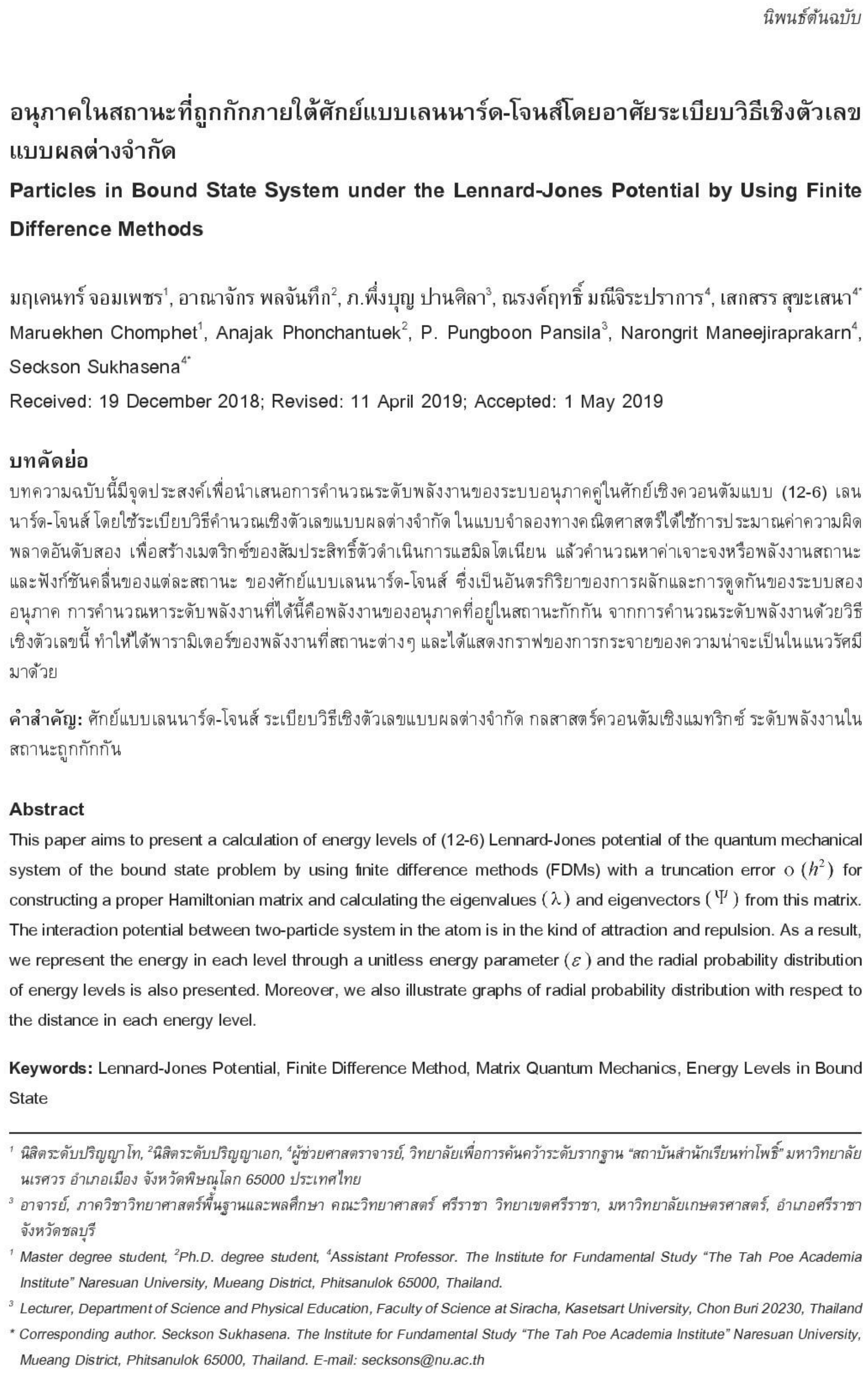

นิพนธ์ต้นฉบับ

อนุภาคในสถานะที่ถูกกักภายใต้ศักย์แบบเลนนาร์ด-โจนส์โดยอาศัยระเบียบวิธีเชิงตัวเลขแบบผลต่างจำกัด

Particles in Bound State System under the Lennard-Jones Potential by Using Finite Difference Methods

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บทคัดย่อ

บทความฉบับนี้มีจุดประสงค์เพื่อนำเสนอการคำนวณระดับพลังงานของระบบอนุภาคคู่ในศักย์เชิงควอนตัมแบบ (12-6) เลนนาร์ด-โจนส์ โดยใช้ระเบียบวิธีคำนวณเชิงตัวเลขแบบผลต่างจำกัด ในแบบจำลองทางคณิตศาสตร์ได้ใช้การประมาณค่าความผิดพลาดอันดับสอง เพื่อสร้างเมตริกซ์ของสัมประสิทธิ์ตัวดำเนินการแฮมิลโตเนียน แล้วคำนวณหาค่าเจาะจงหรือพลังงานสถานะและฟังก์ชันคลื่นของแต่ละสถานะ ของศักย์แบบเลนนาร์ด-โจนส์ ซึ่งเป็นอันตรกิริยาของการผลักและการดูดกันของระบบสองอนุภาค การคำนวณหาระดับพลังงานที่ได้นี้คือพลังงานของอนุภาคที่อยู่ในสถานะกักกัน จากการคำนวณระดับพลังงานด้วยวิธีเชิงตัวเลขนี้ ทำให้ได้พารามิเตอร์ของพลังงานที่สถานะต่างๆ และได้แสดงกราฟของการกระจายของความน่าจะเป็นในแนวรัศมีมาด้วย

คำสำคัญ: ศักย์แบบเลนนาร์ด-โจนส์ ระเบียบวิธีเชิงตัวเลขแบบผลต่างจำกัด กลสาสตร์ควอนตัมเชิงแมทริกซ์ ระดับพลังงานในสถานะถูกกักกัน

Abstract

This paper aims to present a calculation of energy levels of (12-6) Lennard-Jones potential of the quantum mechanical system of the bound state problem by using finite difference methods (FDMs) with a truncation error $\mathrm{o}\,(h^2)$ for constructing a proper Hamiltonian matrix and calculating the eigenvalues (λ) and eigenvectors (Ψ) from this matrix. The interaction potential between two-particle system in the atom is in the kind of attraction and repulsion. As a result, we represent the energy in each level through a unitless energy parameter (ε) and the radial probability distribution of energy levels is also presented. Moreover, we also illustrate graphs of radial probability distribution with respect to the distance in each energy level.

Keywords: Lennard-Jones Potential, Finite Difference Method, Matrix Quantum Mechanics, Energy Levels in Bound State

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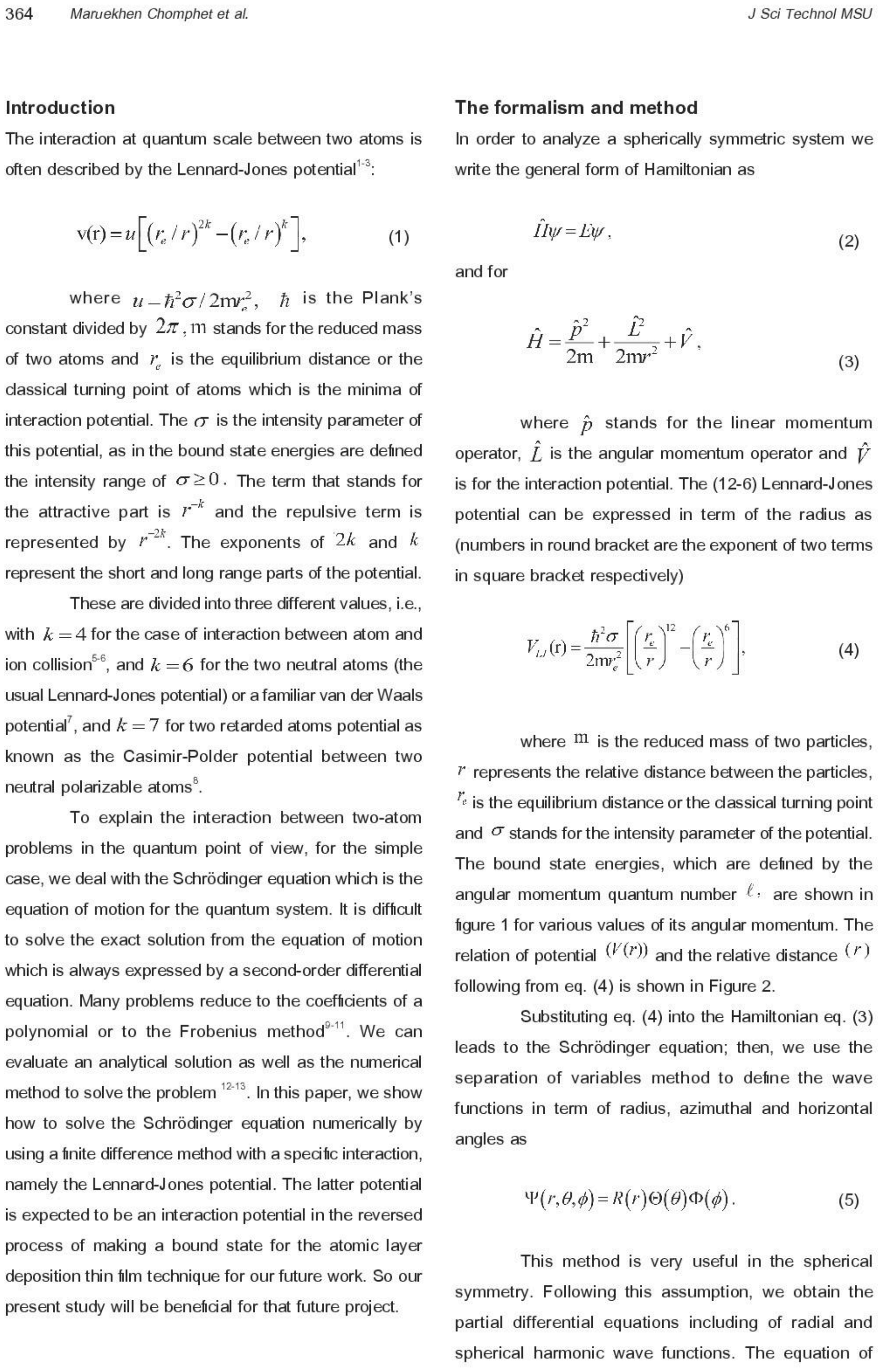
Figure 1 M. Chomphet , A. Phonchantuek , P. P. Pansila , N. Maneejiraprakarn ,S. Sukhasena *Journal of Science & Technology MSU. 2019 Jul 1*;38(4).



Introduction

The interaction at quantum scale between two atoms is often described by the Lennard-Jones potential[1-3]:

$$\mathrm{v(r)} = u\left[\left(r_e / r\right)^{2k} - \left(r_e / r\right)^{k}\right], \qquad (1)$$

where $u - \hbar^2\sigma / 2\mathrm{m}r_e^2$, $\hbar$ is the Plank's constant divided by 2π, m stands for the reduced mass of two atoms and r_e is the equilibrium distance or the classical turning point of atoms which is the minima of interaction potential. The σ is the intensity parameter of this potential, as in the bound state energies are defined the intensity range of $\sigma \geq 0$. The term that stands for the attractive part is r^{-k} and the repulsive term is represented by r^{-2k}. The exponents of $2k$ and k represent the short and long range parts of the potential.

These are divided into three different values, i.e., with $k = 4$ for the case of interaction between atom and ion collision[5-6], and $k = 6$ for the two neutral atoms (the usual Lennard-Jones potential) or a familiar van der Waals potential[7], and $k = 7$ for two retarded atoms potential as known as the Casimir-Polder potential between two neutral polarizable atoms[8].

To explain the interaction between two-atom problems in the quantum point of view, for the simple case, we deal with the Schrödinger equation which is the equation of motion for the quantum system. It is difficult to solve the exact solution from the equation of motion which is always expressed by a second-order differential equation. Many problems reduce to the coefficients of a polynomial or to the Frobenius method[9-11]. We can evaluate an analytical solution as well as the numerical method to solve the problem [12-13]. In this paper, we show how to solve the Schrödinger equation numerically by using a finite difference method with a specific interaction, namely the Lennard-Jones potential. The latter potential is expected to be an interaction potential in the reversed process of making a bound state for the atomic layer deposition thin film technique for our future work. So our present study will be beneficial for that future project.

The formalism and method

In order to analyze a spherically symmetric system we write the general form of Hamiltonian as

$$\hat{H}\psi = E\psi, \qquad (2)$$

and for

$$\hat{H} = \frac{\hat{p}^2}{2\mathrm{m}} + \frac{\hat{L}^2}{2\mathrm{m}r^2} + \hat{V}, \qquad (3)$$

where $\hat{p}$ stands for the linear momentum operator, $\hat{L}$ is the angular momentum operator and $\hat{V}$ is for the interaction potential. The (12-6) Lennard-Jones potential can be expressed in term of the radius as (numbers in round bracket are the exponent of two terms in square bracket respectively)

$$V_{LJ}(\mathrm{r}) = \frac{\hbar^2\sigma}{2\mathrm{m}r_e^2}\left[\left(\frac{r_e}{r}\right)^{12} - \left(\frac{r_e}{r}\right)^{6}\right], \qquad (4)$$

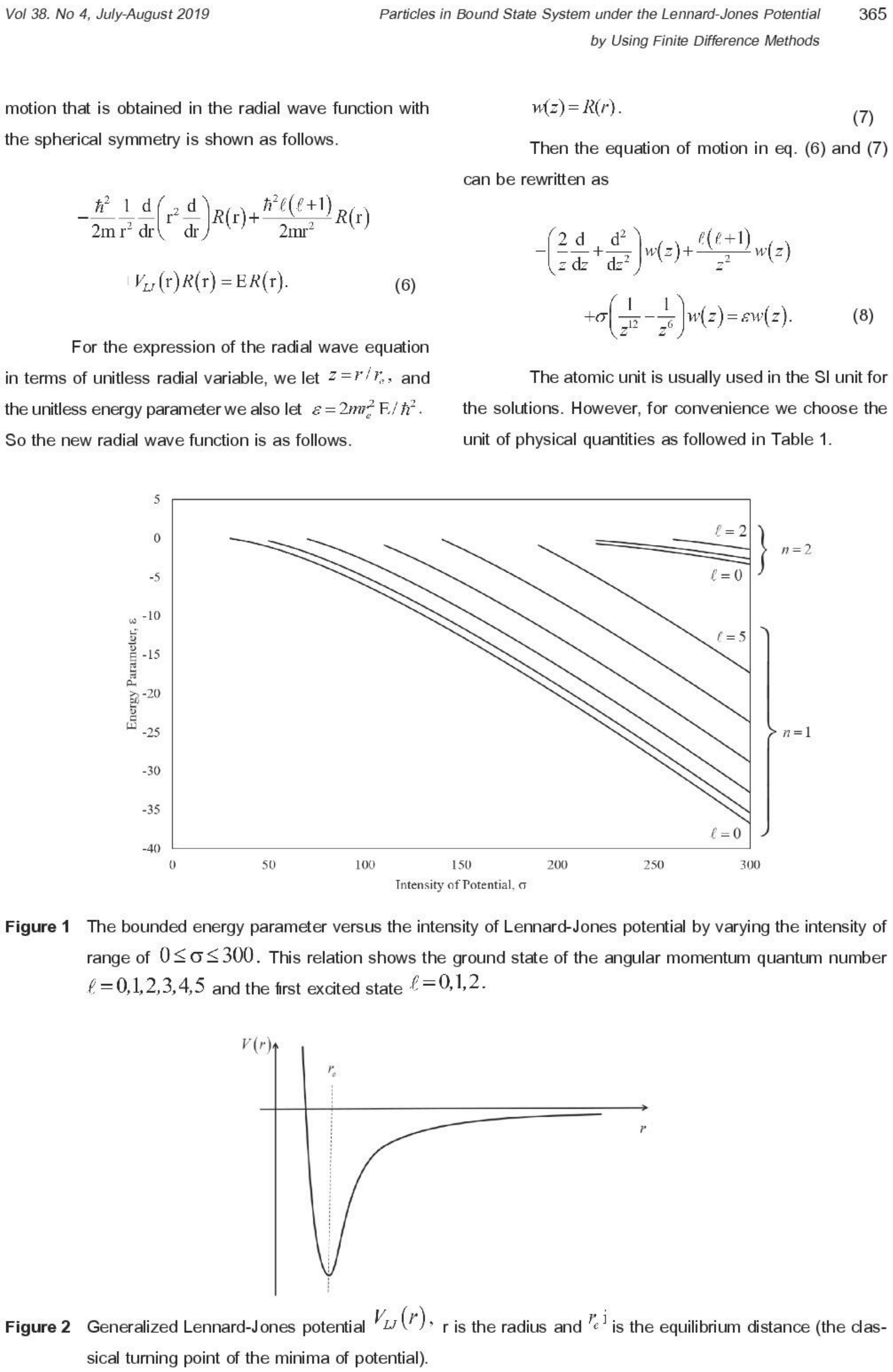
where m is the reduced mass of two particles, r represents the relative distance between the particles, r_e is the equilibrium distance or the classical turning point and σ stands for the intensity parameter of the potential. The bound state energies, which are defined by the angular momentum quantum number ℓ, are shown in figure 1 for various values of its angular momentum. The relation of potential $(V(r))$ and the relative distance (r) following from eq. (4) is shown in Figure 2.

Substituting eq. (4) into the Hamiltonian eq. (3) leads to the Schrödinger equation; then, we use the separation of variables method to define the wave functions in term of radius, azimuthal and horizontal angles as

$$\Psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi). \qquad (5)$$

This method is very useful in the spherical symmetry. Following this assumption, we obtain the partial differential equations including of radial and spherical harmonic wave functions. The equation of

Figure 2 M. Chomphet , A. Phonchantuek , P. P. Pansila , N. Maneejiraprakarn ,S. Sukhasena *Journal of Science & Technology MSU. 2019 Jul 1*;38(4).



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motion that is obtained in the radial wave function with the spherical symmetry is shown as follows.

$$-\frac{\hbar^2}{2\mathrm{m}}\frac{1}{\mathrm{r}^2}\frac{\mathrm{d}}{\mathrm{dr}}\left(\mathrm{r}^2\frac{\mathrm{d}}{\mathrm{dr}}\right)R(\mathrm{r})+\frac{\hbar^2\ell(\ell+1)}{2\mathrm{mr}^2}R(\mathrm{r})$$

$$+V_{LJ}(\mathrm{r})R(\mathrm{r})=\mathrm{E}R(\mathrm{r}). \qquad (6)$$

For the expression of the radial wave equation in terms of unitless radial variable, we let $z=r/r_e$, and the unitless energy parameter we also let $\varepsilon=2mr_e^2\,\mathrm{E}/\hbar^2$. So the new radial wave function is as follows.

$$w(z)=R(r). \qquad (7)$$

Then the equation of motion in eq. (6) and (7) can be rewritten as

$$-\left(\frac{2}{z}\frac{\mathrm{d}}{\mathrm{d}z}+\frac{\mathrm{d}^2}{\mathrm{d}z^2}\right)w(z)+\frac{\ell(\ell+1)}{z^2}w(z)$$

$$+\sigma\left(\frac{1}{z^{12}}-\frac{1}{z^6}\right)w(z)=\varepsilon w(z). \qquad (8)$$

The atomic unit is usually used in the SI unit for the solutions. However, for convenience we choose the unit of physical quantities as followed in Table 1.

Figure 1 The bounded energy parameter versus the intensity of Lennard-Jones potential by varying the intensity of range of $0\leq\sigma\leq300$. This relation shows the ground state of the angular momentum quantum number $\ell=0,1,2,3,4,5$ and the first excited state $\ell=0,1,2$.

Figure 2 Generalized Lennard-Jones potential $V_{LJ}(r)$, r is the radius and r_e is the equilibrium distance (the classical turning point of the minima of potential).

Figure 3 M. Chomphet , A. Phonchantuek , P. P. Pansila , N. Maneejiraprakarn ,S. Sukhasena ***Journal of Science & Technology MSU. 2019 Jul 1***;38(4).

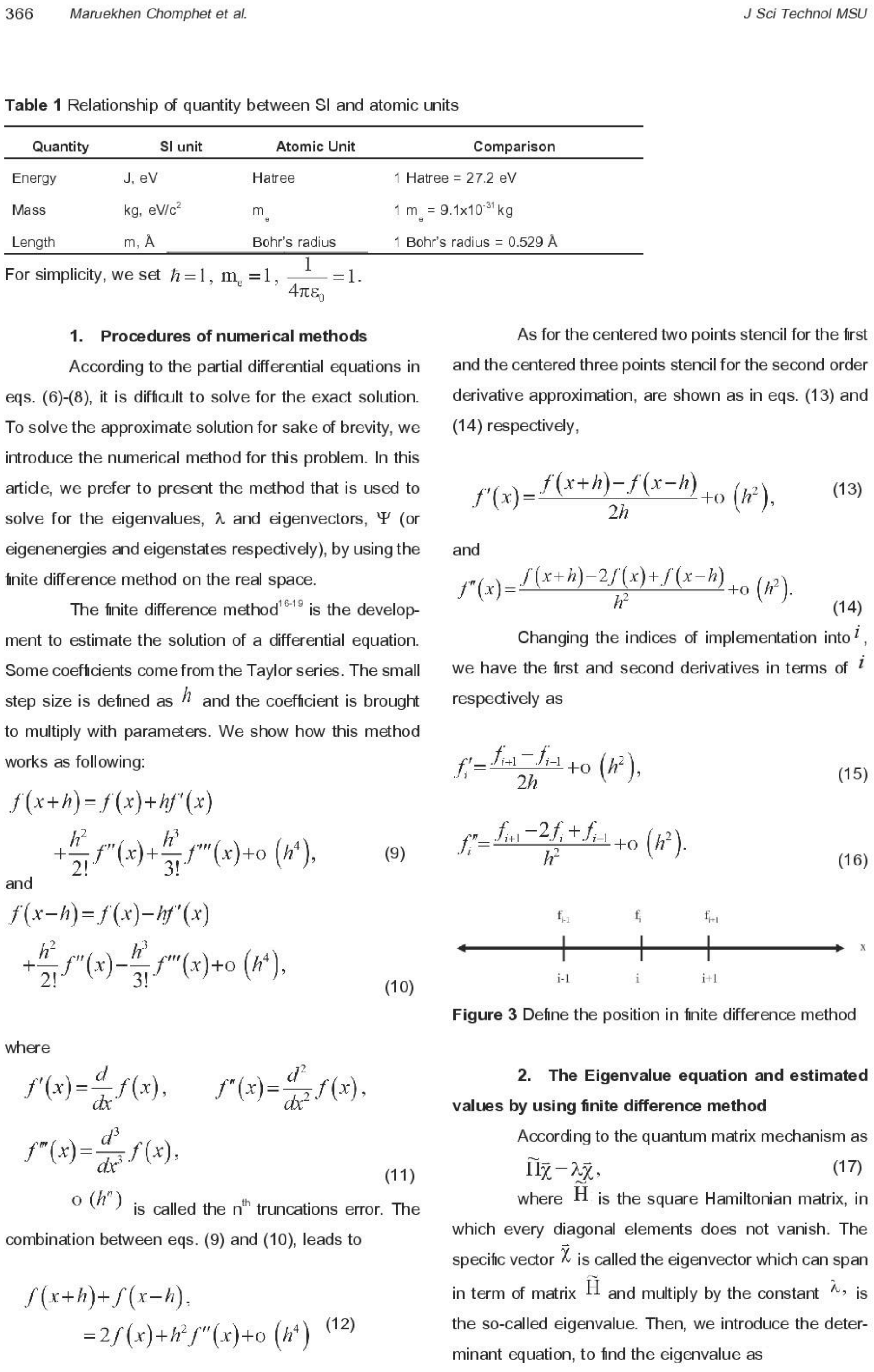


Table 1 Relationship of quantity between SI and atomic units

Quantity	SI unit	Atomic Unit	Comparison
Energy	J, eV	Hatree	1 Hatree = 27.2 eV
Mass	kg, eV/c^2	m$_e$	1 m$_e$ = 9.1x10^{-31} kg
Length	m, Å	Bohr's radius	1 Bohr's radius = 0.529 Å

For simplicity, we set $\hbar=1$, $m_e=1$, $\frac{1}{4\pi\varepsilon_0}=1$.

1. Procedures of numerical methods

According to the partial differential equations in eqs. (6)-(8), it is difficult to solve for the exact solution. To solve the approximate solution for sake of brevity, we introduce the numerical method for this problem. In this article, we prefer to present the method that is used to solve for the eigenvalues, λ and eigenvectors, Ψ (or eigenenergies and eigenstates respectively), by using the finite difference method on the real space.

The finite difference method[16-19] is the development to estimate the solution of a differential equation. Some coefficients come from the Taylor series. The small step size is defined as h and the coefficient is brought to multiply with parameters. We show how this method works as following:

$$f(x+h)=f(x)+hf'(x) +\frac{h^2}{2!}f''(x)+\frac{h^3}{3!}f'''(x)+o\left(h^4\right), \quad (9)$$

and

$$f(x-h)=f(x)-hf'(x) +\frac{h^2}{2!}f''(x)-\frac{h^3}{3!}f'''(x)+o\left(h^4\right), \quad (10)$$

where

$$f'(x)=\frac{d}{dx}f(x), \qquad f''(x)=\frac{d^2}{dx^2}f(x), \qquad f'''(x)=\frac{d^3}{dx^3}f(x), \quad (11)$$

$o\left(h^n\right)$ is called the nth truncations error. The combination between eqs. (9) and (10), leads to

$$f(x+h)+f(x-h), =2f(x)+h^2f''(x)+o\left(h^4\right) \quad (12)$$

As for the centered two points stencil for the first and the centered three points stencil for the second order derivative approximation, are shown as in eqs. (13) and (14) respectively,

$$f'(x)=\frac{f(x+h)-f(x-h)}{2h}+o\left(h^2\right), \quad (13)$$

and

$$f''(x)=\frac{f(x+h)-2f(x)+f(x-h)}{h^2}+o\left(h^2\right). \quad (14)$$

Changing the indices of implementation into i, we have the first and second derivatives in terms of i respectively as

$$f_i'=\frac{f_{i+1}-f_{i-1}}{2h}+o\left(h^2\right), \quad (15)$$

$$f_i''=\frac{f_{i+1}-2f_i+f_{i-1}}{h^2}+o\left(h^2\right). \quad (16)$$

Figure 3 Define the position in finite difference method

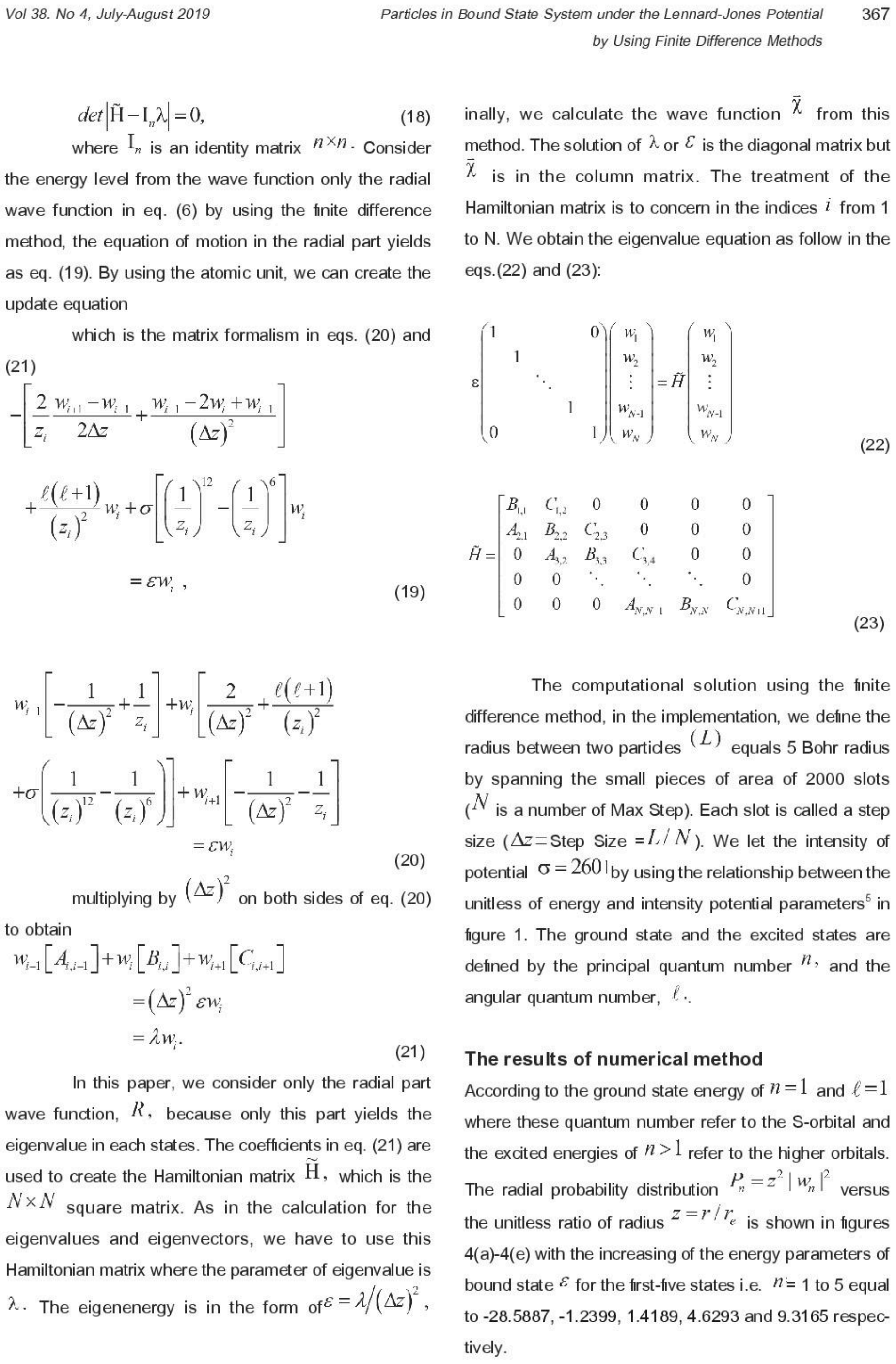
2. The Eigenvalue equation and estimated values by using finite difference method

According to the quantum matrix mechanism as

$$\widetilde{\Pi}\bar{\chi}-\lambda\bar{\chi}, \quad (17)$$

where $\widetilde{\mathrm{H}}$ is the square Hamiltonian matrix, in which every diagonal elements does not vanish. The specific vector $\bar{\chi}$ is called the eigenvector which can span in term of matrix $\widetilde{\Pi}$ and multiply by the constant λ, is the so-called eigenvalue. Then, we introduce the determinant equation, to find the eigenvalue as

Figure 4 M. Chomphet , A. Phonchantuek , P. P. Pansila , N. Maneejiraprakarn ,S. Sukhasena *Journal of Science & Technology MSU. 2019 Jul 1*;38(4).



$$det\left|\tilde{\mathrm{H}}-\mathrm{I}_n\lambda\right|=0, \qquad (18)$$

where I_n is an identity matrix $n\times n$. Consider the energy level from the wave function only the radial wave function in eq. (6) by using the finite difference method, the equation of motion in the radial part yields as eq. (19). By using the atomic unit, we can create the update equation

which is the matrix formalism in eqs. (20) and (21)

$$-\left[\frac{2}{z_i}\frac{w_{i\ 1}-w_{i\ 1}}{2\Delta z}+\frac{w_{i\ 1}-2w_i+w_{i\ 1}}{(\Delta z)^2}\right]$$

$$+\frac{\ell(\ell+1)}{(z_i)^2}w_i+\sigma\left[\left(\frac{1}{z_i}\right)^{12}-\left(\frac{1}{z_i}\right)^{6}\right]w_i$$

$$=\varepsilon w_i\ , \qquad (19)$$

$$w_{i\ 1}\left[-\frac{1}{(\Delta z)^2}+\frac{1}{z_i}\right]+w_i\left[\frac{2}{(\Delta z)^2}+\frac{\ell(\ell+1)}{(z_i)^2}\right.$$

$$\left.+\sigma\left(\frac{1}{(z_i)^{12}}-\frac{1}{(z_i)^{6}}\right)\right]+w_{i+1}\left[-\frac{1}{(\Delta z)^2}-\frac{1}{z_i}\right]$$

$$=\varepsilon w_i \qquad (20)$$

multiplying by $(\Delta z)^2$ on both sides of eq. (20) to obtain

$$w_{i-1}\left[A_{i,i-1}\right]+w_i\left[B_{i,i}\right]+w_{i+1}\left[C_{i,i+1}\right]$$

$$=(\Delta z)^2\varepsilon w_i$$

$$=\lambda w_i. \qquad (21)$$

In this paper, we consider only the radial part wave function, R, because only this part yields the eigenvalue in each states. The coefficients in eq. (21) are used to create the Hamiltonian matrix $\widetilde{\mathrm{H}}$, which is the $N\times N$ square matrix. As in the calculation for the eigenvalues and eigenvectors, we have to use this Hamiltonian matrix where the parameter of eigenvalue is λ. The eigenenergy is in the form of $\varepsilon=\lambda/(\Delta z)^2$, inally, we calculate the wave function $\bar{\chi}$ from this method. The solution of λ or ε is the diagonal matrix but $\bar{\chi}$ is in the column matrix. The treatment of the Hamiltonian matrix is to concern in the indices i from 1 to N. We obtain the eigenvalue equation as follow in the eqs.(22) and (23):

$$\varepsilon\begin{pmatrix}1 & & & & 0\\ & 1 & & & \\ & & \ddots & & \\ & & & 1 & \\ 0 & & & & 1\end{pmatrix}\begin{pmatrix}w_1\\ w_2\\ \vdots\\ w_{N-1}\\ w_N\end{pmatrix}=\tilde{H}\begin{pmatrix}w_1\\ w_2\\ \vdots\\ w_{N-1}\\ w_N\end{pmatrix} \qquad (22)$$

$$\tilde{H}=\begin{bmatrix}B_{1,1} & C_{1,2} & 0 & 0 & 0 & 0\\ A_{2,1} & B_{2,2} & C_{2,3} & 0 & 0 & 0\\ 0 & A_{3,2} & B_{3,3} & C_{3,4} & 0 & 0\\ 0 & 0 & \ddots & \ddots & \ddots & 0\\ 0 & 0 & 0 & A_{N,N\ 1} & B_{N,N} & C_{N,N\ 1}\end{bmatrix} \qquad (23)$$

The computational solution using the finite difference method, in the implementation, we define the radius between two particles (L) equals 5 Bohr radius by spanning the small pieces of area of 2000 slots (N is a number of Max Step). Each slot is called a step size (Δz = Step Size = L/N). We let the intensity of potential $\sigma=260$ by using the relationship between the unitless of energy and intensity potential parameters[5] in figure 1. The ground state and the excited states are defined by the principal quantum number n, and the angular quantum number, ℓ.

The results of numerical method

According to the ground state energy of $n=1$ and $\ell=1$ where these quantum number refer to the S-orbital and the excited energies of $n>1$ refer to the higher orbitals. The radial probability distribution $P_n=z^2\,|\,w_n|^2$ versus the unitless ratio of radius $z=r/r_e$ is shown in figures 4(a)-4(e) with the increasing of the energy parameters of bound state ε for the first-five states i.e. n= 1 to 5 equal to -28.5887, -1.2399, 1.4189, 4.6293 and 9.3165 respectively.

Figure 5 **M. Chomphet , A. Phonchantuek , P. P. Pansila , N. Maneejiraprakarn ,S. Sukhasena *Journal of Science & Technology MSU. 2019 Jul 1*;38(4).**

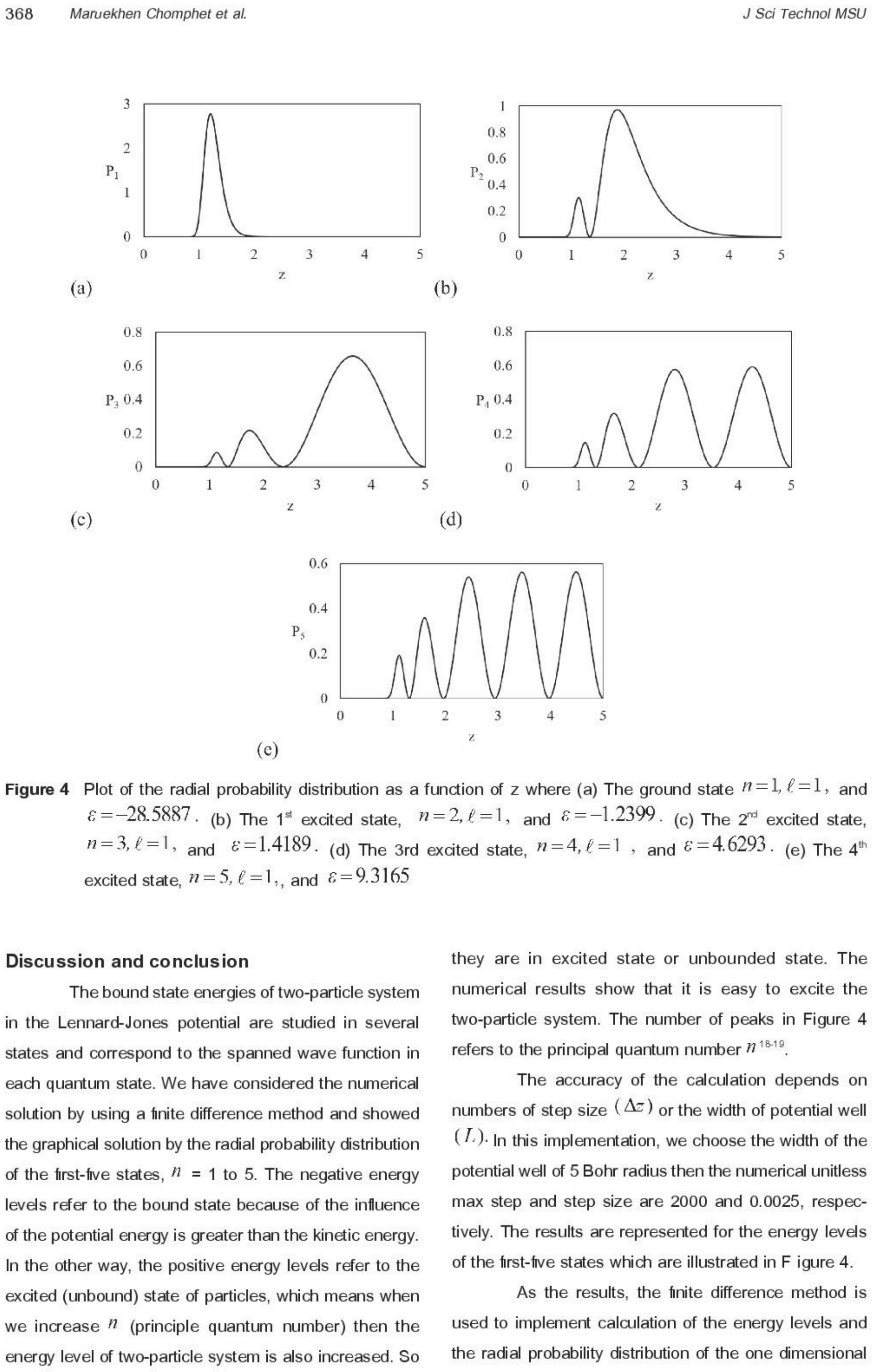


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Figure 4 Plot of the radial probability distribution as a function of z where (a) The ground state $n=1, \ell=1$, and $\varepsilon=-28.5887$. (b) The 1st excited state, $n=2, \ell=1$, and $\varepsilon=-1.2399$. (c) The 2nd excited state, $n=3, \ell=1$, and $\varepsilon=1.4189$. (d) The 3rd excited state, $n=4, \ell=1$, and $\varepsilon=4.6293$. (e) The 4th excited state, $n=5, \ell=1,$, and $\varepsilon=9.3165$

Discussion and conclusion

The bound state energies of two-particle system in the Lennard-Jones potential are studied in several states and correspond to the spanned wave function in each quantum state. We have considered the numerical solution by using a finite difference method and showed the graphical solution by the radial probability distribution of the first-five states, n = 1 to 5. The negative energy levels refer to the bound state because of the influence of the potential energy is greater than the kinetic energy. In the other way, the positive energy levels refer to the excited (unbound) state of particles, which means when we increase n (principle quantum number) then the energy level of two-particle system is also increased. So they are in excited state or unbounded state. The numerical results show that it is easy to excite the two-particle system. The number of peaks in Figure 4 refers to the principal quantum number n[18-19].

The accuracy of the calculation depends on numbers of step size (Δz) or the width of potential well (L). In this implementation, we choose the width of the potential well of 5 Bohr radius then the numerical unitless max step and step size are 2000 and 0.0025, respectively. The results are represented for the energy levels of the first-five states which are illustrated in F igure 4.

As the results, the finite difference method is used to implement calculation of the energy levels and the radial probability distribution of the one dimensional

Figure 6 M. Chomphet , A. Phonchantuek , P. P. Pansila , N. Maneejiraprakarn ,S. Sukhasena *Journal of Science & Technology MSU. 2019 Jul 1*;38(4).

Schrödinger equation with the Lennard-Jones potential. This proposed method is highly useful, efficient and easy to implement.

The finite difference scheme is wildly used in several research problems even referred to the differential equation with the truncation error of $O\left(h^2\right)$ for a centered three points stencil for a second derivative.

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Figure 7 M. Chomphet , A. Phonchantuek , P. P. Pansila , N. Maneejiraprakarn ,S. Sukhasena ***Journal of Science & Technology MSU. 2019 Jul 1***;38(4).