# Appendix B

# Non-relativistic Quantum Mechanics

The quantization has two kinds of the procedure, the first quantization and the second quantization. By the first quantization, we mean that the coordinate $\boldsymbol{r}$ and the momentum $\boldsymbol{p}$ of a point particle do not commute with each other. That is,

$$[x_i, p_j] = i\hbar\delta_{ij}.$$

In terms of this quantization procedure, we can obtain the Schrödinger equation by requiring that the particle Hamiltonian should be an operator and therefore the state $\psi$ should be introduced.

There is another quantization procedure, the second quantization, which is the quantization of fields. From the experimental observations of creations and annihilations of particle pairs or photons, one needs to quantize fields. The field quantization is closely connected to the relativistic field equations which inevitably includes anti-particle states (negative energy states in fermion field case). In this respect, one does not have to quantize the Schrödinger field in the non-relativistic quantum mechanics. Therefore, we discuss only the first quantization procedure and problems related to the quantization.

## B.1 Procedure of First Quantization

In the standard procedure of the first quantization, the energy $E$ and momentum $\boldsymbol{p}$ are regarded as operators, and the simplest expressions of $\hat{E}$ and $\hat{\boldsymbol{p}}$ are given as

$$\hat{E} \to i\frac{\partial}{\partial t}, \qquad \hat{\boldsymbol{p}} \to -i\boldsymbol{\nabla}. \tag{B.1.1}$$

For a free point particle with its mass $m$, the dispersion relation can be written as

$$E = \frac{\boldsymbol{p}^2}{2m}. \tag{B.1.2}$$

If one employs the quantization procedure of eq.($B$.1.1), then one should prepare some state which receives the operation of eq.($B$.1.1). This state is called wave function and is often denoted as $\psi(\boldsymbol{r},t)$. In this case, eq.($B$.1.2) becomes

$$i\frac{\partial}{\partial t}\psi(\boldsymbol{r},t) = -\frac{1}{2m}\boldsymbol{\nabla}^2\psi(\boldsymbol{r},t) \qquad (B.1.3)$$

which is the Schrödinger equation.

### New Picture of First Quantization

At a glance, one may feel that the procedure of eqs.($B$.1.1) and ($B$.1.2) are more fundamental than eq.($B$.1.3) itself. However, this is not so trivial. If one looks into the Maxwell equation, then one realizes that the Maxwell equation is already a quantized equation for classical electromagnetic fields. In this respect, the Maxwell equation does not have any corresponding classical equation of motions like the Newton equation. In this sense, eq.($B$.1.3) can be regarded as a fundamental equation for quantum mechanics as well, even though one can derive eq.($B$.1.3) from eqs.($B$.1.1) and ($B$.1.2).

In fact, in Appendix H, we treat the derivation of the Dirac equation from the Maxwell equation and the local gauge invariance, and there we see that the first quantization of eq.(B.1.1) is not needed and therefore it is not the fundamental principle any more. Instead, the Schrödinger equation is obtained from the non-relativistic reduction of the Dirac equation. In this respect, the derivation of the Schrödinger equation does not involve the first quantization.

## B.2 Mystery of Quantization or Hermiticity Problem ?

Here, we present a problem related to the quantization in box with the periodic boundary conditions. We restrict ourselves to the one dimensional case, but the result is easily generalized to three dimensions.

### B.2.1 Free Particle in Box

By denoting the wave function as

$$\psi(x) = e^{-iEt}u(x)$$

the static Schrödinger equation without interactions is written

$$-\frac{1}{2m}\frac{\partial^2 u(x)}{\partial x^2} = Eu(x). \qquad (B.2.1)$$

The solution can be obtained as

$$u(x) = \left\{\frac{1}{\sqrt{L}}e^{ikx}, \quad \frac{1}{\sqrt{L}}e^{-ikx}\right\}, \quad \text{with} \quad E = \frac{k^2}{2m} \qquad (B.2.2)$$

where one puts the particle into a box with its length $L$. Now, one requires that the wave function $u(x)$ should satisfy the periodic boundary conditions and should be the eigenstate of the momentum. In this case, one has

$$\hat{p}u_k(x) = ku_k(x), \qquad k = \frac{2\pi n}{L}, \qquad n = 0, \pm 1, \cdots.$$

Therefore, one can write the eigenstate wave function as

$$u_n(x) = \frac{1}{\sqrt{L}}e^{i\frac{2\pi n}{L}x}, \qquad n = 0, \pm 1, \cdots.$$

### B.2.2 Hermiticity Problem

Now, the quantization relation is written

$$\hat{p}x - x\hat{p} = -i \qquad (B.2.3)$$

and one takes the expectation value of the quantization relation with the wave function $u_n(x)$ and obtains

$$\langle u_n|\hat{p}x - x\hat{p}|u_m\rangle = -i\delta_{nm}. \qquad (B.2.4)$$

If one makes use of the hermiticity of $\hat{p}$, then one obtains

$$(n-m)\frac{2\pi}{L}\langle u_n|x|u_m\rangle = -i\delta_{nm}. \qquad (B.2.5)$$

However, the above equation does not hold for $n = m$ since the left hand side is zero while the right hand side is $-i$.

What is wrong with the calculation ? The answer is simple, and one should not make use of the hermiticity of the momentum $\hat{p}$ because the surface term at the boundary does not vanish for the periodic boundary condition. In fact, in the above evaluation, the surface term just gives the missing constant of $-i$ for $n = m$. In other words, one can easily show the following equation

$$\langle u_n|\hat{p}x|u_n\rangle = -i + \langle \hat{p}u_n|x|u_n\rangle. \qquad (B.2.6)$$

It should be noted that the hermiticity of the momentum in the following sense is valid

$$\langle u_n|\hat{p}|u_m\rangle = \langle \hat{p}u_n|u_m\rangle. \qquad (B.2.7)$$

From this exercise, one learns that the quantization condition of eq.($B$.2.3) should be all right, but the hermiticity of the momentum operator cannot necessarily be justified as long as one employs the periodic boundary conditions for the wave functions. Also, the periodic boundary conditions must be physically acceptable. Therefore, one should be careful for treating the momentum operator and it should be operated always on the right hand side as it is originally meant. In this case, one does not make any mistakes.

This argument must be valid even for a very large $L$ as long as one keeps the periodic boundary conditions. This may look slightly odd, but the free particle should be present anywhere in the physical space, and therefore one should give up the vanishing of the surface term in the plane wave case. The criteria of right physics must be given from the observation that physical observables should not depend on $L$. In other words, one should take the value of $L$ much larger than any other scales in the model, and this is called *thermodynamic limit.* In order to obtain any physical observables, one should always take the thermodynamic limit.

## B.3 Schrödinger Fields

The Schrödinger equation with a potential $U(\boldsymbol{r})$ is written as

$$i\frac{\partial\psi(\boldsymbol{r},t)}{\partial t} = \left(-\frac{1}{2m}\boldsymbol{\nabla}^2 + U(\boldsymbol{r})\right)\psi(\boldsymbol{r},t). \qquad (B.3.1)$$

From this equation, one can derive the vector current conservation

$$\frac{\partial\rho}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{j} = 0 \qquad (B.3.2)$$

where $\rho$ and $\boldsymbol{j}$ are defined as

$$\rho = \psi^\dagger\psi, \qquad \boldsymbol{j} = -\frac{i}{2m}\left(\psi^\dagger\boldsymbol{\nabla}\psi - (\boldsymbol{\nabla}\psi^\dagger)\psi\right). \qquad (B.3.3)$$

### B.3.1 Currents of Bound State

Now, it is interesting to observe how the currents from this Schrödinger field behave in the realistic physical situations. Since the time dependence of the Schrödinger field $\psi$ is factorized as

$$\psi(\boldsymbol{r},t) = e^{-iEt}u(\boldsymbol{r})$$

the basic properties of the field are represented by the field $u(\boldsymbol{r})$. When the field $u(\boldsymbol{r})$ represents a bound state, then $u(\boldsymbol{r})$ becomes a real field. In this case, the current density $\boldsymbol{j}$ vanishes to zero,

$$\boldsymbol{j} = -\frac{i}{2m}\left(u(\boldsymbol{r})\boldsymbol{\nabla}u(\boldsymbol{r}) - (\boldsymbol{\nabla}u(\boldsymbol{r}))u(\boldsymbol{r})\right) = 0. \qquad (B.3.4)$$

On the other hand, the probability density of $\rho \equiv |u(\boldsymbol{r})|^2$ is always time-independent, and since the bound state wave function is confined within a limited area of space, the $\rho$ is also limited within some area of space.

### B.3.2 Free Fields (Static)

When there is no potential, that is

$$U(\boldsymbol{r}) = 0$$

then the field can be described as a free particle solution. This solution is obtained when the theory is put into a box with its volume $V$,

$$\psi(\boldsymbol{r},t) = \frac{1}{\sqrt{V}}e^{-iEt}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}, \quad \frac{1}{\sqrt{V}}e^{-iEt}e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \qquad (B.3.5)$$

where $E$ is the energy of the particle and $\boldsymbol{k}$ denotes a quantum number which should correspond to the momentum of a particle. In this case, the probability density is finite and constant

$$\rho = \frac{1}{V} \tag{B.3.6}$$

while the current $\boldsymbol{j}$ is also a constant and can be written as

$$\boldsymbol{j} = \frac{\boldsymbol{k}}{m} \tag{B.3.7}$$

which just corresponds to the velocity of a particle.

### Real Field Condition

It is important to note that the Schrödinger field $\psi$ should be a complex function. If one imposes the condition that the field should be real,

$$\psi(\boldsymbol{r},t) = \psi^\dagger(\boldsymbol{r},t)$$

then one obtains from the Schrödinger equation eq.(B.1.3)

$$\frac{\partial\psi(\boldsymbol{r},t)}{\partial t} = 0.$$

Therefore, the Schrödinger field $\psi$ should be time independent. In this case, one sees immediately that the energy $E$ must be zero since

$$\left(-\frac{1}{2m}\boldsymbol{\nabla}^2 + U(\boldsymbol{r})\right)\psi(\boldsymbol{r},t) = 0.$$

Therefore, the real field condition of $\psi$ is too strong and it should not be imposed before solving the Schrödinger equation. This concept should always hold in the Schrödinger field, and therefore it is most likely true that the same concept should hold for relativistic boson fields as well. However, this statement may not be justified if the Klein-Gordon field should not have any correspondence with the Schrödinger field in the non-relativistic limit.

## B.3.3 Degree of Freedom of Schrödinger Field

The Schrödinger field is a complex field. However, the Schrödinger field $\psi$ itself should correspond to one particle. It is clear that one cannot make the following separation of the field into real and imaginary parts

$$\psi(\boldsymbol{r},t) = \rho(\boldsymbol{r},t)e^{i\xi(\boldsymbol{r},t)} \tag{B.3.8}$$

and claim that $\rho(\boldsymbol{r},t)$ and $\xi(\boldsymbol{r},t)$ describe two independent fields (particles). When $\psi$ is a complex field, it has right properties as a field, and the current density of the $\psi$ field has a finite value.

## B.4 Hydrogen-like Atoms

When the potential $U(\boldsymbol{r})$ is a Coulomb type,

$$U(\boldsymbol{r}) = -\frac{Ze^2}{r} \tag{B.4.1}$$

then the Schrödinger equation can be solved exactly and the Schrödinger field $\psi$ together with the energy eigenvalue $E$ can be obtained as

$$\psi(\boldsymbol{r}) = R_{n\ell}(r) Y_{\ell m}(\theta, \varphi) \tag{B.4.2}$$

$$E_n = -\frac{mZ^2e^4}{2n^2} = -\frac{m}{2n^2}\left(\frac{Z}{137}\right)^2 \tag{B.4.3}$$

where $R_{n\ell}(r)$ and $Y_{\ell m}$ denote the radial wave function and the spherical harmonics, respectively. The principal quantum number $n$ runs as $n = 1, 2, \cdots, \infty$, and $\ell$ runs as $\ell = 0, 1, 2, \cdots, \infty$, satisfying the condition

$$\ell \leq n - 1. \tag{B.4.4}$$

It should be worth writing the explicit shape of the wave functions for a few lowest states of $1s$, $2p$ and $2s$ with the Bohr radius $a_0 = \dfrac{1}{me^2}$.

$$1s-\text{state}: \quad R_{1s}(r) = \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} 2e^{-\frac{Zr}{a_0}}, \qquad Y_{00}(\theta, \varphi) = \frac{1}{\sqrt{4\pi}}$$

$$2p-\text{state}: \quad R_{2p}(r) = \left(\frac{Z}{2a_0}\right)^{\frac{3}{2}} \frac{Zr}{\sqrt{3}a_0} e^{-\frac{Zr}{2a_0}}$$

$$\begin{cases} Y_{11}(\theta, \varphi) = -\sqrt{\dfrac{3}{8\pi}} \sin\theta e^{i\varphi} \\ Y_{10}(\theta, \varphi) = \sqrt{\dfrac{3}{4\pi}} \cos\theta \\ Y_{1-1}(\theta, \varphi) = \sqrt{\dfrac{3}{8\pi}} \sin\theta e^{-i\varphi} \end{cases}$$

$$2s\text{–state}: \quad R_{2s}(r) = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(2 - \frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}}, \quad Y_{00}(\theta, \varphi) = \frac{1}{\sqrt{4\pi}}.$$

## B.5 Harmonic Oscillator Potential

The harmonic oscillator potential $U(x)$

$$U(x) = \frac{1}{2} m\omega^2 x^2$$

is a very special potential which is often used in quantum mechanics exercise problems since the Schrödinger equation with the harmonic oscillator potential can be solved exactly. However, the harmonic oscillator potential is not realistic since it does not have a free field-like solution. The Schrödinger field in the harmonic oscillator potential is always confined and there is no scattering state solution.

Nevertheless, it should be worth writing solutions of the Schrödinger field $\psi$ with its mass $m$ in the one dimensional harmonic oscillator potential. The Schrödinger equation can be written as

$$\left( -\frac{1}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} m\omega^2 x^2 \right) \psi(x) = E\psi(x). \tag{B.5.1}$$

In this case, the solution of the Schrödinger field $\psi$ together with the energy eigenvalue $E$ can be obtained as

$$\psi_n(x) = \left( \frac{\alpha^2}{4^n \pi (n!)^2} \right)^{\frac{1}{4}} H_n(\alpha x) e^{-\frac{1}{2}\alpha^2 x^2} \tag{B.5.2a}$$

$$E_n = \omega \left( n + \frac{1}{2} \right), \quad n = 0, 1, 2 \cdots \tag{B.5.2b}$$

where $\alpha$ is given as

$$\alpha = \sqrt{m\omega}. \tag{B.5.3}$$

$H_n(\xi)$ denotes the hermite polynomial and is given as

$$H_n(\xi) = (-)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2}$$

since $H_n(\xi)$ can be expressed in terms of the generating function as

$$e^{-x^2+2\xi x} = e^{-(x-\xi)^2+\xi^2} = \sum_{n=0}^{\infty} \frac{1}{n!} H_n(\xi) x^n.$$

Some of them are given below

$$H_0(\xi) = 1, \qquad H_1(\xi) = 2\xi, \qquad H_2(\xi) = 4\xi^2 - 2 \tag{B.5.4a}$$

$$H_3(\xi) = 8\xi^3 - 12\xi, \qquad H_4(\xi) = 16\xi^4 - 48\xi^2 + 12. \tag{B.5.4b}$$

### B.5.1 Creation and Annihilation Operators

The Hamiltonian of the one dimensional harmonic oscillator potential

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2 \qquad (B.5.5)$$

can be rewritten in terms of creation $a^\dagger$ and annihilation $a$ operators

$$a^\dagger = \sqrt{\frac{m\omega}{2}}x - \frac{i}{\sqrt{2m\omega}}\hat{p}, \qquad a = \sqrt{\frac{m\omega}{2}}x + \frac{i}{\sqrt{2m\omega}}\hat{p} \qquad (B.5.6)$$

as

$$\hat{H} = \omega\left(a^\dagger a + \frac{1}{2}\right). \qquad (B.5.7)$$

$a^\dagger$ and $a$ satisfies the following commutation relation

$$[a, a^\dagger] = 1 \qquad (B.5.8)$$

because of the definition of $a^\dagger$ and $a$ in eq.(B.5.6).

#### Number Operator $\hat{N}$

By introducing the number operator $\hat{N}$ as

$$\hat{N} = a^\dagger a \qquad (B.5.9)$$

one finds

$$[\hat{N}, a] = -a, \qquad [\hat{N}, a^\dagger] = a^\dagger. \qquad (B.5.10)$$

With the eigenstate $|\phi_n\rangle$ of the number operator $\hat{N}$ and its eigenvalue $n$

$$\hat{N}|\phi_n\rangle = n|\phi_n\rangle \qquad (B.5.11)$$

one can easily prove the following equations

$$a^\dagger|\phi_n\rangle = \sqrt{n+1}|\phi_{n+1}\rangle, \qquad a|\phi_n\rangle = \sqrt{n}|\phi_{n-1}\rangle. \qquad (B.5.12)$$

This indicates that $a^\dagger$ operator increases the quantum number $n$ by one unit while $a$ decreases it in the same way. Therefore, $a^\dagger$ and $a$ are called *creation* and *annihilation* operators, respectively. In addition, one can evaluate the expectation value of the number operator $\hat{N}$ with the state $|\phi_n\rangle$ as

$$n = \langle\phi_n|a^\dagger a|\phi_n\rangle = ||a\phi_n||^2 \geq 0$$

which shows that the $n$ must be a non-negative value. Therefore, one finds from eq.(B.5.12)

$$a|\phi_0\rangle = 0. \qquad (B.5.13)$$

Therefore, one sees that the smallest value of $n$ is $n = 0$. This leads to the constraint for $n$ as

$$n = 0, 1, 2 \cdots . \qquad (B.5.14)$$

Operating the Hamiltonian $\hat{H}$ on $|\phi_n\rangle$, one finds

$$\hat{H}|\phi_n\rangle = \omega\left(\hat{N} + \frac{1}{2}\right)|\phi_n\rangle = \omega\left(n + \frac{1}{2}\right)|\phi_n\rangle = E_n|\phi_n\rangle. \qquad (B.5.15)$$

Thus, the energy $E_n$ can be written as

$$E_n = \omega\left(n + \frac{1}{2}\right), \qquad n = 0, 1, 2 \cdots$$

which agrees with the result given in eq.(B.5.2). The state $|\phi_n\rangle$ can be easily constructed by operating $a^\dagger$ operator onto the $|\phi_0\rangle$

$$|\phi_n\rangle = \frac{1}{\sqrt{n!}}\left(a^\dagger\right)^n|\phi_0\rangle. \qquad (B.5.16)$$

It should be noted that the state $|\phi_n\rangle$ is specified by the quantum number $n$. If one wishes to obtain an explicit expression of the wave function, then one should project the state $|\phi_n\rangle$ onto the $|x\rangle$ or $|p\rangle$ representation as given below.

### Explicit Wave Function in $x$-representation

The wave function $\psi_n(x) \equiv \langle x|\phi_n\rangle$ in the $x-$representation can be obtained in the following way. First, one solves the differential equation from eq.(B.5.13)

$$\langle x|a|x\rangle\langle x|\phi_0\rangle = \left(\sqrt{\frac{m\omega}{2}}x + \frac{1}{\sqrt{2m\omega}}\frac{\partial}{\partial x}\right)\psi_0(x) = 0 \qquad (B.5.17)$$

which leads to the ground state wave function

$$\psi_0(x) = \left(\frac{\alpha^2}{\pi}\right)^{\frac{1}{4}} e^{-\frac{1}{2}\alpha^2 x^2}, \qquad \text{with} \quad \alpha = \sqrt{m\omega}. \qquad (B.5.18)$$

From eq.(B.5.16), one obtains the wave function for an arbitrary state $\psi_n(x)$

$$\psi_n(x) = \frac{1}{\sqrt{n!}}\langle x|\left(a^\dagger\right)^n|x\rangle\langle x|\phi_0\rangle = \frac{1}{\sqrt{n!}}\left(\frac{\alpha^2}{\pi}\right)^{\frac{1}{4}}\left(\sqrt{\frac{m\omega}{2}}x - \frac{1}{\sqrt{2m\omega}}\frac{\partial}{\partial x}\right)^n e^{-\frac{1}{2}\alpha^2 x^2}$$

which can be shown to be just identical to eq.(B.5.2a).