Chapter 3

Formalism of Quantum Mechanics

3.1 Quantum Systems

In this course, only non-relativistic quantum mechanics is considered. Clearly, the case of photons is excluded since $E = pc$. Thus, by quantum system, one means one of the following cases.

1. A single structureless particle moving in a force field. The source of the force field is not included in the system.
2. A collection of structureless particles (identical or otherwise, distinguishable or otherwise) interacting with each other and a force field.
3. A collection of the particles with internal degrees of freedom (like spin) where there is no classical discription.

Classical mechanics treats the first two cases. In these cases, the description of the quantum system is based on the classical description. The third case will be handled separately, later.

3.2 Postulates of Quantum Mechanics

Before the working postulates of the quantum mechanics are presented, note the following:

- ▷ The mathematical rigour is not followed strictly, thus making the postulates incomplete. However, in introductory course, these are enough.
- ▷ The aim is to present a operational quantum mechanics for describing observed world.

The following table gives the postulates as compared to those of classical mechanics given for a case of a single particle in external force field in 1D. Generalization to 3D or many particles is immediate.

	Classical Mechanics	Quantum Mechanics
I	A state of a classical system is given by a pair of real numbers (x, p), with x being position and p being momentum of the particle.	A state of the quantum system is given by a vector Ψ in some Hilbert space $\mathcal{H}$.
II	An observable or a dynamical variable Ω is a real valued function of x and p, denoted by $\omega(x, p)$.	Let $\hat{X}$ and $\hat{P}$ be two operators on $\mathcal{H}$, such that $$\left[\hat{X}, \hat{P}\right] = i\hbar.$$ $\hat{X}$ is called position operator and $\hat{P}$ is called momentum operator. An observable Ω is represented by a hermitian operator $$\hat{\Omega} = \omega\left(x \to \hat{X}, p \to \hat{P}\right)$$ obtained by substituting the operators in place of x and p in classical expression.
III	A measurement of an observable Ω is $\omega(x, p)$. The act of measurement does not disturb the state of the system.	A measurement of an observable Ω yields a value from the set of eigenvalues of $\hat{\Omega}$. If ϕ is an eigenvector of $\hat{\Omega}$ with eigenvalue λ, then the probability of obtaining λ as a result of measurement on system in state Ψ is given by $$P_\Omega(\lambda) \propto \left|\langle \phi, \Psi \rangle\right|^2.$$ As a result of measurement the state of the system suddenly changes from Ψ to ϕ.
IV	The time evolution of the state is given by Newton's laws. $$\begin{aligned} \frac{d}{dt}x(t) &= \frac{p}{m} \\ \frac{d}{dt}p(t) &= F(x, p, t) \end{aligned}$$	The time evolution of the state of the system is given by Schrödinger equation: $$i\hbar\frac{d}{dt}\Psi(t) = \hat{H}\Psi(t).$$ Where $\hat{H}$ is the operator corresponding to the classical Hamiltonian of the system.

Discussion

- ▷ The first three postulates are about the state of the system and computing the value of the measurement of dynamical variables at some instant.
- ▷ Postulate I defines the state of the system. To begin with, the choice of the Hilbert space is arbitrary. Any Hilbert space will do! In the table given below, the most common choice is given.
- ▷ Note that since Ψ is an element of a Hilbert space, superposition principle is automatic.
- ▷ Postulate II is a correspondance between the classical dynamical variables with the operators on $\mathcal{H}$. Again, choice of position operator and momentum operator is arbitrary, except the commutator relationship between the two.
- ▷ The postulate is fuzzy on the issue of order of operation, that is, it is unclear whether the classical variable xp will be $\hat{X}\hat{P}$ or $\hat{P}\hat{X}$ or $\left(\hat{X}\hat{P}+\hat{P}\hat{X}\right)/2$. The last choice is appealing since the operator is hermitian.
- ▷ Postulate III contains lot of information. One can organize this information in following steps:

  1. Given $\hat{\Omega}$, find all eigenvalues (must be real since $\hat{\Omega}$ is hermitian). Suppose the set of eigenvalues is discrete and is given by $\Lambda_\Omega = \{\omega_i \,|\, i = 1, 2, \ldots\}$. Let $B_\Omega = \{\phi_i \,|\, i = 1, 2, \ldots\}$ be the set of corresponding eigenvectors. B_Ω is an orthonormal basis of $\mathcal{H}$.
  2. Now expand the state Ψ of the system in terms of ϕ_i,

     $$\Psi = \sum_i C_i \phi_i$$

     where $C_i = \langle \phi_i, \Psi \rangle$.
  3. The sample space of measurement of Ω is Λ_Ω. Probability of getting ω_i as a result of measurement is given by

     $$P_\Omega(\omega_i) = |\langle \phi_i, \Psi \rangle|^2 .$$

- ▷ If the eigenvalues of $\hat{\Omega}$ are continuous, procedure is still the same:

  1. Given $\hat{\Omega}$, find all eigenvalues (must be real since $\hat{\Omega}$ is hermitian). In this case, the set of eigenvalues is some subset of $\mathbb{R}$ say, $\Lambda_\Omega \subset \mathbb{R}$. Let $B_\Omega = \{\phi_\omega \,|\, \omega \in \Lambda_\Omega\}$ be the set of corresponding eigenvectors. B_Ω is an orthonormal basis of $\mathcal{H}$.
  2. Now expand the state Ψ of the system in terms of ϕ_i,

     $$\Psi = \int_{\Lambda_\Omega} C(\omega)\phi_\omega d\omega$$

     where $C(\omega) = \langle \phi_\omega, \Psi \rangle$.

3. The sample space of measurement of Ω is Λ_Ω. Probability density function for getting ω as a result of measurement is given by

$$P_\Omega(\omega) = |\langle \phi_\omega, \Psi \rangle|^2 .$$

▷ One can define a projection operator as follows: Let $B = \{\phi_i \,|\, i = 1, 2, \ldots\}$ be an orthonormal basis of $\mathcal{H}$. Then any state Ψ can be expanded in terms of ϕ_i,

$$\Psi = \sum_i C_i \phi_i$$

where $C_i = \langle \phi_i, \Psi \rangle$. Let P_i be an operator such that

$$P_i \Psi = \langle \phi_i, \Psi \rangle \, \phi_i.$$

Note this projection operator has the same geometric interpretation as that of projection on coordinate axes in plane geometry. Clearly,

$$\Psi = \sum_i P_i \Psi \implies \sum_i P_i = I$$

where I is the identity operator.

▷ Note that the Postulate III also mentions that a measurement will abruptly change the state of the system. Suppose measurement is done and yields a result ω_i. Then the new state will be ϕ_i. This is called as the *collapse of the wavevector.*

▷ The probabilities given in Postulate III are to be interpreted in *frequency* or *ensemble* sense (See Math Primer.).

3.3 Wave Mechanics

In chapter 2, the QM was introduced using wavefunctions. That is a free particle was associated with a wavefunction $\Psi(x, t)$, and probability density function of its location with $|\Psi(x, t)|^2$. When the Hilbert space is chosen to be $L_2(\mathbb{R})$, the quantum mechnics is more popularly known as wave mechanics.

	Quantum Mechanics	Wave Mechanics
I	A state of the quantum system is given by a vector Ψ in some Hilbert space $\mathcal{H}$.	Let $\mathcal{H} = L_2(\mathbb{R})$. The state of the system is given by a square integrable function $\Psi(x)$.
II	Let $\hat{X}$ and $\hat{P}$ be two operators on $\mathcal{H}$, such that $$\left[\hat{X}, \hat{P}\right] = i\hbar.$$ $\hat{X}$ is called position operator and $\hat{P}$ is called momentum operator. An observable Ω is represented by a hermitian operator $$\hat{\Omega} = \omega\left(x \to \hat{X}, p \to \hat{P}\right)$$ obtained by substituting the operators in place of x and p in classical expression.	Choose $\hat{X}$ and $\hat{P}$ $$\begin{aligned} \hat{X}f(x) &= xf(x) \\ \hat{P}f(x) &= -i\hbar\frac{d}{dx}f(x). \end{aligned}$$ Check that $$\left[\hat{X}, \hat{P}\right] = i\hbar$$ holds.
III	A measurement of an observable Ω yields a value from the set of eigenvalues of $\hat{\Omega}$. If ϕ is an eigenvector of $\hat{\Omega}$ with eigenvalue λ, then the probability of obtaining λ as a result of measurement on system in state Ψ is given by $$P_\Omega(\lambda) \propto \lvert\langle\phi, \Psi\rangle\rvert^2 .$$ As a result of measurement the state of the system suddenly changes from Ψ to ϕ.	
IV	The time evolution of the state of the system is given by Schrödinger equation: $$i\hbar\frac{d}{dt}\Psi(t) = \hat{H}\Psi(t).$$ Where $\hat{H}$ is the operator corresponding to the classical Hamiltonian of the system.	Classical Hamiltonian in case of conservative force field is just the total energy, that is $$\begin{aligned} H &= \frac{P^2}{2m} + V(x) \\ \hat{H} &= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \hat{V}\left(\hat{X}\right) \end{aligned}$$ The Schrödinger equation becomes $$i\hbar\frac{\partial}{\partial t}\Psi(x,t) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi(x,t) + V(x)\Psi(x,t).$$

Here are some features of wave mechanics:

▷ The choice of the position operator and momentum operator are not unique. Here is an alternate choice:

$$\begin{aligned}\hat{X}f(p) &= i\hbar\frac{d}{dp}f(p)\\ \hat{P}f(p) &= pf(p).\end{aligned}$$

This choice is as good since $\left[\hat{X},\hat{P}\right] = i\hbar$ holds. This assignment is called *momentum space representation* as opposite to the earlier choice, which is called *real space representation.*(The choice of p as a dummy variable is only due to its popularity.)

▷ The eigenvalues of $\hat{X}$ on $L_2(\mathbb{R})$ are continuous. The set of eigenvalues is just $\Lambda_{\hat{X}} = \mathbb{R}$! That is every real number is an eigenvalue of $\hat{X}$. The eigenvector ϕ_λ corresponding to an eigenvalue λ is $\phi_\lambda(x) = \delta(x-\lambda)$. Thus the set of eigenvectors is

$$B_{\hat{X}} = \{\phi_\lambda \,|\, \lambda \in \mathbb{R}\}.$$

Check:

- $B_{\hat{X}}$ is orthonormal, that is

$$\langle \phi_\lambda, \phi_{\lambda'}\rangle = \delta(\lambda - \lambda').$$

- $B_{\hat{X}}$ is complete, that is every function can be written as

$$f(x) = \int_{\mathbb{R}} f(\lambda)\delta(x-\lambda)d\lambda = \int_{\mathbb{R}} f(\lambda)\phi_\lambda(x)d\lambda$$

Probability density function for finding particle at λ as a result of measurement on a system which is in state Ψ at an instant t , is given by

$$\begin{aligned}P_{\hat{X}}(\lambda,t) &= |\langle\phi_\lambda,\Psi\rangle|^2\\ &= \left|\int_{-\infty}^{\infty}\delta(x-\lambda)\Psi(x,t)dx\right|^2\\ &= |\Psi(\lambda,t)|^2\end{aligned}$$

▷ Now, what are the eigenvalues and eigenvectors of the momentum operator on $L_2(\mathbb{R})$? Again $\Lambda_{\hat{P}} = \mathbb{R}$. For any real number p, let $\xi_p(x) = \exp(ipx/\hbar)/\sqrt{2\pi\hbar}$. Now

$$\hat{P}\xi_p(x) = \left(-i\hbar\frac{d}{dx}\right)\left[\frac{1}{\sqrt{2\pi\hbar}}\exp\left(\frac{ipx}{\hbar}\right)\right] = p\xi_p(x)$$

Thus, the set of eigenvectors are

$$B_{\hat{P}} = \{\xi_p(x)\,|\, p\in\mathbb{R}\}.$$

Again Check:

– $B_{\hat{P}}$ is orthonormal, that is

$$\langle \xi_p, \xi_{p'} \rangle = \delta(p - p').$$

(See tutorial problem 1.4)

– $B_{\hat{P}}$ is complete. Remember, every square integrable function admits a fourier transform, that is every function can be written as

$$\begin{aligned} f(x) &= \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} g(p) \exp\left(\frac{ipx}{\hbar}\right) dp \\ &= \int_{\mathbb{R}} g(p)\xi_p(x) dp \end{aligned}$$

Probability density function for the particle to have momentum p as a result of measurement on a system which is in state Ψ at an instant t , is given by

$$\begin{aligned} P_{\hat{P}}(p) &= |\langle \xi_p, \Psi \rangle|^2 \\ &= \left| \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \exp\left(-\frac{ipx}{\hbar}\right) \Psi(x) dx \right|^2 \\ &= |(\mathcal{F}\Psi)(p)|^2 \end{aligned}$$

Where $\mathcal{F}\Psi$ is the fourier transform of Ψ. This formula is identical to the one given in case of a free particle in previous chapter.

▷ Neither the eigenfunctions of $\hat{X}$ nor the eigenfunctions of $\hat{P}$ belong to $L_2(\mathbb{R})$. However, these are orthonormal set of functions that span $L_2(\mathbb{R})$, thus these will be used without worrying about mathematical difficulty.

3.4 Schrödinger Equation

In classical mechanics, if a single particle is moving in a conservative force field then the total energy is a constant of motion. In most parts of this course, only conservative force fields are considered. The hamiltonian function (that is total energy) is then independent of time.

Assume, that the hamiltonian operator $\hat{H}$ on hilbert space $\mathcal{H}$ is independent of time (that is there is no explicit dependence on t). Let the set of eigenvalues of $\hat{H}$ be given by

$$\Lambda_{\hat{H}} = \{E_1, E_2, \ldots\}$$

with correpsonding set of eigenvectors

$$B_{\hat{H}} = \{\psi_1, \psi_2, \ldots\}.$$

That is, for each i,

$$\hat{H}\psi_i = E_i\psi_i.$$

This equation is called *time independent Schrodinger equation.* And the eigenvectors ψ_i are *stationary states.* The eigenvalues E_i are called *energy eigenvalues.* The set $\Lambda_{\hat{H}}$ is called the *energy spectrum.*

Remeber $B_{\hat{H}}$ is an orthonormal basis of $\mathcal{H}$. Let $\Psi(t)$ be the state of the system at some time t. Then,

$$\Psi(t) = \sum_i c_i(t)\psi_i$$

Putting this in Schrodinger equation we get

$$\begin{aligned} \sum_i \left(i\hbar \frac{d}{dt} c_i(t) \right) \psi_i &= \sum_i c_i(t) \hat{H} \psi_i \\ \therefore \quad \sum_i \left(i\hbar \frac{d}{dt} c_i(t) \right) \psi_i &= \sum_i \left(E_i c_i(t) \right) \psi_i \end{aligned}$$

Equating the coefficients on either side

$$i\hbar \frac{d}{dt} c_i(t) = E_i c_i(t)$$

Solving this differential equation,

$$c_i(t) = c_i(0) e^{-iE_i t/\hbar}$$

Thus[1]

$$\begin{aligned} \Psi(t) &= \sum_i c_i(0) e^{-iE_i t/\hbar} \psi_i \\ &= e^{-i\hat{H}t/\hbar} \sum_i c_i(0)\psi_i = e^{-i\hat{H}t/\hbar}\Psi(0) \end{aligned}$$

The operator $\hat{U}(t) = \exp\left[-i\hat{H}t/\hbar\right]$ is called as time evolution operator. Check

Now, if $t = 0$, the state of the system is one of the stationary states, say $\Psi(t = 0) = \psi_i$ for some i, the time evolution of the state of the system is given

$$\Psi(t) = e^{-iE_i t/\hbar}\Psi(0)$$

[1] For given operator A, define

$$\exp\left[A\right] = 1 + A + \frac{1}{2!}A^2 + \cdots + \frac{1}{n!}A^n + \cdots$$

If the series on rhs converges, e^A is a well defined operator. Now, check by brute force method, that if $Au = \lambda u$ then

$$e^A u = e^\lambda u$$

Now consider an observable Ω with eigenvectors ϕ with eigenvalue ω . The probability that measurement of Ω will yield ω, at a time t is

$$\begin{aligned} P_\Omega(\omega,t) &= |\langle\phi,\Psi(t)\rangle|^2 \\ &= \left|e^{-iE_it/\hbar}\langle\phi,\Psi(0)\rangle\right|^2 \\ &= |\langle\phi,\Psi(0)\rangle|^2 \\ &= P_\Omega(\omega,0) \end{aligned}$$

Thus, if system is in a stationary state then all properties of the system are independent of time.

3.5 Uncertainty Principle

Expectation Value

Theorem 6. *An observable Ω is represented by an operator $\hat{\Omega}$. If the quantum system is in state (normalized) Ψ, then the average (expectation) value of Ω, denoted by $\langle\Omega\rangle$, is given by*

$$\langle\Omega\rangle_\Psi = \left\langle\Psi,\hat{\Omega}\Psi\right\rangle.$$

Proof. Let the spectrum of $\hat{\Omega}$ be $\Lambda_\Omega = \{\omega_i\,|\,i=1,2,\ldots\}$. Let $B_\Omega = \{\phi_i\,|\,i=1,2,\ldots\}$ be the set of corresponding normalized eigenvectors. Let

$$\Psi = \sum_i C_i\phi_i$$

where $C_i = \langle\phi_i,\Psi\rangle$. If$\Psi$ is normalized. Then

$$\begin{aligned} \langle\Psi,\Psi\rangle &= \sum_i\sum_j C_i^*C_j\langle\phi_i,\phi_j\rangle \\ 1 &= \sum_i\sum_j C_i^*C_j\delta_{i,j} = \sum_i |C_i|^2. \end{aligned}$$

By postulate III, the probability of getting ω_i as a result of measurement is given by

$$P_\Omega(\omega_i) = |\langle\phi_i,\Psi\rangle|^2 = |C_i|^2$$

if Ψ is normalized. Clearly

$$\sum_i P_\Omega(\omega_i) = 1.$$

The expectation value of the observable Ω is then

$$\langle\Omega\rangle_\Psi = \sum_i \omega_i P_\Omega(\omega_i) = \sum_i \omega_i |C_i|^2$$

Now,

$$\begin{aligned}\left\langle \Psi, \hat{\Omega}\Psi \right\rangle &= \sum_i \sum_j C_i^* C_j \left\langle \phi_i, \hat{\Omega}\phi_j \right\rangle \\ &= \sum_i \sum_j C_i^* C_j \omega_j \delta_{i,j} \\ &= \sum_i \omega_i \left|C_i\right|^2\end{aligned}$$

□

Definition 7. The uncertainty in the measurement of an observable Ω in a system that is in state Ψ is defined as

$$\Delta\Omega = \sqrt{\left\langle \left(\hat{\Omega} - \left\langle \hat{\Omega} \right\rangle_\Psi \right)^2 \right\rangle_\Psi}.$$

Theorem 8. *If A and B are two observables of a system which is in state Ψ, then*

$$(\Delta A)^2 (\Delta B)^2 \geq \left(\frac{1}{2i} \left\langle \left[\hat{A}, \hat{B}\right] \right\rangle_\Psi \right)^2.$$

Proof. Let $f = \left(\hat{A} - \left\langle \hat{A} \right\rangle\right)\Psi$ and $g = \left(\hat{B} - \left\langle \hat{B} \right\rangle\right)\Psi$. (Note the subscript in $\langle\rangle_\Psi$ has been dropped for brevity.) Now $(\Delta A)^2 = \langle f, f\rangle$ and $(\Delta B)^2 = \langle g, g\rangle$. Then by Schrwarz inequality,

$$(\Delta A)^2 (\Delta B)^2 = \langle f, f\rangle \langle g, g\rangle \geq \left|\langle f, g\rangle\right|^2$$

And,

$$\begin{aligned}\langle f, g\rangle &= \left\langle \left(\hat{A} - \left\langle \hat{A} \right\rangle\right)\Psi, \left(\hat{B} - \left\langle \hat{B} \right\rangle\right)\Psi \right\rangle \\ &= \left\langle \hat{A}\hat{B} \right\rangle - \left\langle \hat{A} \right\rangle \left\langle \hat{B} \right\rangle\end{aligned}$$

Simillarly,

$$\langle g, f\rangle = \left\langle \hat{B}\hat{A} \right\rangle - \left\langle \hat{A} \right\rangle \left\langle \hat{B} \right\rangle.$$

Now for any complex number z

$$|z|^2 = (\text{Re } z)^2 + (\text{Im } z)^2 \geq (\text{Im } z)^2 = \left[\frac{1}{2i}\left(z - z^*\right)\right]^2.$$

Now let $z = \langle f, g\rangle$. Then

$$\begin{aligned}\left|\langle f, g\rangle\right|^2 &\geq \left[\frac{1}{2i}\left(\langle f, g\rangle - \langle g, f\rangle\right)\right]^2 \\ &= \left[\frac{1}{2i}\left(\left\langle \hat{A}\hat{B} \right\rangle - \left\langle \hat{B}\hat{A} \right\rangle\right)\right]^2.\end{aligned}$$

Putting everything together

$$(\Delta A)^2 (\Delta B)^2 \geq \left[\frac{1}{2i}\left(\left\langle\left[\hat{A},\hat{B}\right]\right\rangle\right)\right]^2.$$

$\square$

Apply this to $\hat{X}$ and $\hat{P}$, then

$$\begin{aligned}(\Delta X)^2 (\Delta P)^2 &\geq \left[\frac{1}{2i}\left(\left\langle\left[\hat{X},\hat{P}\right]\right\rangle\right)\right]^2 \\ &= \left(\frac{\hbar}{2}\right)^2.\end{aligned}$$

This is Heisenberg's Uncertainty Principle. Minimal Interpretation of the uncertainty principle is ensemble interpretation. That is, a large number of copies of the system are made and set in state Ψ. Make measurement of X on half of them. Make measurement of P on the other half. Now from the samples compute uncertainties, that is standard deviation σ_X and σ_P. Uncertainty principle says that

$$\sigma_X \sigma_P \geq \frac{\hbar}{2}.$$