

POSTULATES OF QM

[Φ2.2, Φ7.1, H2.1]

We will now formulate the basic set of postulates upon which quantum mechanics is built.

A: THE OPERATOR POSTULATE

To each physical observable quantity F there corresponds in quantum-mechanical theory a linear operator \hat{F} .

For instance, in the position-space formulation

$$\begin{aligned} x &\rightarrow \hat{x} = x \\ p &\rightarrow \hat{p} = -i\hbar \frac{\partial}{\partial x} \end{aligned}$$

Observables must be real quantities

$\Rightarrow \hat{F}$ must be hermitian/self-adjoint.

B: THE WAVEFUNCTION POSTULATE

The state of a system is described, as completely as possible, by the wavefunction $\Psi(x, t)$. The time development of the wavefunction (and hence of the state) is determined by the Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi,$$

where \hat{H} is the Hamiltonian of the system. Usually the Hamiltonian is the total energy of the system.

This is an equation of motion, which uniquely determines $\mathcal{I}(q, t)$ given some initial condition $\mathcal{I}(q_0, t_0)$.

The concept of a Hamiltonian will become more familiar for those taking classical mechanics. See also Appendix A in Hemmer.

The postulate implies that it is not possible to obtain more information about a system than what is contained in $\mathcal{I}(q, t)$.

C: THE EXPECTATION VALUE POSTULATE

When a large number of measurements of an observable F is made on a system which is prepared in a state $\mathcal{I}(q_1, q_2, \dots, q_n, t)$ (before each measurement), the average \bar{F} of the measured values will approach the theoretical expectation value, which is postulated to be

$$\langle F \rangle = \int \mathcal{I}^* \bar{F} \mathcal{I} d\tau$$

where $d\tau = dq_1 dq_2 \dots dq_n$ and where the integration goes over the whole range of each of the variables.

q_n : generalized coordinate.

Example x, y, z for free particle in 3D.

We are supposing that the wavefunction is normalized,

$$\int d\tau |\tilde{\Psi}|^2 = 1.$$

D: THE MEASUREMENT POSTULATE

(i) The only possible result of a precise measurement of an observable F is one of the eigenvalues f_n of the corresponding linear operator \hat{F} .

(ii) Immediately after the measurement of the eigenvalue f_n , the system is in an eigenstate of \hat{F} , namely the eigenstate ψ_n corresponding to the measured eigenvalue f_n .

Which of the eigenvalues is measured, and the probability for each, depends on the state before the measurement.

EXAMPLE - INFINITE SQUARE WELL

We will use this example as a chance to recap from Intro to QM, and see how some of the postulates come into play.

The Hamiltonian is given by

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x),$$
$$= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x),$$

with potential energy function

$$V(x) = \begin{cases} 0, & \text{if } 0 \leq x \leq L \\ \infty, & \text{otherwise.} \end{cases}$$

This describes a particle in an infinite, square well. According to postulate B, the system is best described by a wavefunction $\Psi(x, t)$ which is a solution of

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi, \quad (1)$$

so this is our starting point. \hat{H} does not depend explicitly on t , so we will solve the Schrödinger equation (SE) using separation of variables. We assume

$$\Psi(x, t) = \psi(x) \phi(t).$$

Inserted into the SE, we get

$$\left[i\hbar \frac{d\psi}{dt} \right] \psi(x) = \left[-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi \right] \psi$$

or

$$i\hbar \frac{1}{\psi} \frac{d\psi}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + V.$$

depends only
on t

depends only on x

For this to always hold, both sides must be constant.

We therefore write:

$$i\hbar \frac{1}{\psi} \frac{d\psi}{dt} = E \rightarrow \psi(t) = \psi_0 e^{-iEt/\hbar}.$$

and

↑ can be absorbed
into ψ .

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi$$

This is often referred to as the time-independent Schrödinger equation. (TISE).

So far we have

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

We now need to find $\psi(x)$ and E .

For $x \leq 0$ and $x \geq L$ we must have

$\psi = 0$: a particle cannot be in an area with infinite potential, i.e. inside infinitely "hard walls". We therefore use the boundary conditions (BCs)

$$\psi(0) = \psi(L) = 0,$$

when solving the TISE

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi.$$

A general solution is

$$\psi(x) = C_1 \sin \sqrt{\frac{2mE}{\hbar^2}} x + C_2 \cos \sqrt{\frac{2mE}{\hbar^2}} x.$$

For simplicity we define

$$k = \frac{\sqrt{2mE}}{\hbar}.$$

From $\psi(0) = 0$ we get $C_2 = 0$. From $\psi(L) = 0$ we get the condition

$$\psi(L) = C_1 \sin kL = 0$$

$$\rightarrow kL = \pi \cdot n, \quad n=0 \text{ just the}$$

$$k = \frac{\pi \cdot n}{L} \quad n=1,2,3\dots \text{ trivial solution.}$$

Negative solutions \rightarrow

Hence, we have determined E :

$$E_n = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2 \cdot n^2}{2m L^2}, \quad n=1,2,3\dots$$

But what is C_1 ?

We said earlier that $|\Psi|^2$ is interpreted as a probability density. From postulate C we also connect Ψ to expectation values of operators. What if we use $\hat{F} = \hat{1}$?

$$\Rightarrow \langle 1 \rangle = \int dx \Psi^* \cdot 1 \cdot \Psi \cancel{\Psi} \\ = \int dx |\Psi|^2 = 1.$$

In other words, the total probability of finding a particle anywhere at all, must be 1. In our case:

$$1 = \int_0^L dx |\Psi|^2 = \int_0^L dx \left| \psi(x) e^{-iEt/\hbar} \right|^2 \\ = \int_0^L dx |\psi(x)|^2 = \int_0^L dx |C_1|^2 \sin^2 kx \\ = |C_1|^2 \frac{L}{2} \Rightarrow |C_1| = \sqrt{\frac{2}{L}}.$$

Choosing C_1 to be real, we therefore have

$$\underline{\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} \cdot x\right)}, \quad n=1,2,3\dots$$

Note:

The wavefunctions are orthonormal

$$\int_0^L dx \psi_n^*(x) \psi_m(x) = \delta_{nm}.$$

The set of wavefunctions is complete:

Any other function can be expressed as
a linear combination of them.

$$f(x) = \sum_{n=1}^{\infty} c_n \psi_n(x).$$

c_n complex number.

The general solution to the SE is

$$\Psi(x, t) = \sum_{n=1}^{\infty} c_n \bar{\psi}_n(x, t) = \sum_{n=1}^{\infty} c_n \psi_n(x) e^{-iE_n t/h}$$

Proof:

$$\begin{aligned} \textcircled{+} i \frac{\partial}{\partial t} \Psi(x, t) &= \sum_{n=1}^{\infty} c_n E_n \psi_n(x) e^{-iE_n t/h} \\ &\stackrel{!}{=} \hat{H} \Psi(x, t) \\ &= \sum_{n=1}^{\infty} \underbrace{\hat{H} c_n \psi_n(x)}_{= c_n E_n \psi_n(x)} e^{-iE_n t/h} \\ &= \sum_{n=1}^{\infty} c_n E_n \psi_n(x) e^{-iE_n t/h} \quad \text{OK.} \end{aligned}$$

Since the SE is linear, superposition
of solutions works. That makes life easy!

Normalization:

$$\begin{aligned} \int_0^L dx \bar{\Psi}(x, t) \Psi(x, t) &= \sum_{n,m=1}^{\infty} c_n^* c_m \left[\int_0^L dx \bar{\psi}_n(x) \psi_m(x) \right] \\ &= \sum_{n,m=1}^{\infty} c_n^* c_m e^{i(E_n - E_m)t/h} \delta_{nm} = \sum_n |c_n|^2 = 1. \end{aligned}$$

Expectation values

We now use postulate C to calculate some expectation values: we choose

$$\psi(x, t) = \psi_n(x) e^{-iE_n t/\hbar}$$

for simplicity, and calculate:

$$\begin{aligned} \langle E \rangle &= \int_0^L dx \psi_n^*(x) \hat{H} \psi_n(x) e^{-i(E_n - E_n)t/\hbar} \\ &= E_n \underbrace{\int_0^L dx |\psi_n|^2}_{} = E_n. \end{aligned}$$

$$\langle x \rangle = \int_0^L dx \psi_n^*(x) \hat{x} \psi_n(x) = \int_0^L dx x |\psi_n(x)|^2$$

$$= \frac{1}{2}$$

$$\langle p \rangle = 2 \int_0^L dx \sin \frac{n\pi x}{L} \left(-i\hbar \frac{d}{dx} \right) \sin \frac{n\pi x}{L}$$

$$= \frac{1}{L} \int_0^L dx \left(-i\hbar \frac{d}{dx} \right) \sin^2 \frac{n\pi x}{L}$$

$$= -\frac{i\hbar}{L} \sin \frac{n\pi x}{L} \Big|_0^L = 0.$$

No time-dependence, since $|\psi|^2 = |\psi_n|^2$ is time-independent. However, if we use a superposition of energy eigenstates

$$\psi(x, t) = C_1 \psi_1(x) e^{-iE_1 t/\hbar} + C_2 \psi_2(x) e^{-iE_2 t/\hbar}$$

we get

$$\begin{aligned} |\psi(x, t)|^2 &= |C_1|^2 |\psi_1|^2 + |C_2|^2 |\psi_2|^2 \\ &\quad + C_1 \psi_1^* C_2 \psi_2^* e^{-i(E_1 - E_2)t/\hbar} \\ &\quad + C_1^* \psi_1^* C_2 \psi_2 e^{+i(E_1 - E_2)t/\hbar} \end{aligned}$$

Assuming $c_1, c_2, \psi_1, \psi_2 \in \mathbb{R}$, we get

$$|\Psi(x,t)|^2 = |c_1|^2 |\psi_1(x)|^2 + |c_2|^2 |\psi_2(x)|^2 + 2 c_1 c_2 \psi_1(x) \psi_2(x) \cos\left(\frac{E_1 - E_2}{\hbar} t\right)$$

We have an oscillating probability density due to "interference" between the wavefunctions. This also leads to (potentially) time-dependent expectation values $\langle x \rangle(t)$ and $\langle p \rangle(t)$.
[See animation].

Measurements

If we measure the energy of the system described by the state

$$\Psi = c_1 \psi_1(x) e^{-i E_1 t / \hbar} + c_2 \psi_2(x) e^{-i E_2 t / \hbar}$$

what values can be got? We can only get E_1 , with a probability $|c_1|^2$, or E_2 , with probability $|c_2|^2$, according to postulate D. Furthermore, right after measurement, giving e.g. $E = E_1$, the system will be in the state

$$\Psi = \psi_1 e^{-i E_1 t / \hbar}$$

This is sometimes referred to as "wavefunction collapse".

if we instead measure the position, and find the particle at position x' , the state immediately after the measurement is a position eigenstate:

$$\psi_{x'}(x) = \delta(x - x')$$

This is clearly not an energy eigenstate. What energies could you get if you now measured the energy of the system?

TIME-DEPENDENCE OF EXPECTATION VALUE [H4.3]

From the simulation, we saw that the expectation values can have a time-dependence. In fact, we can find a general formula for the time-dependence of expectation values. Starting from

$$\langle F \rangle = \int \underline{Y}^* \hat{F} \underline{Y} d\underline{x},$$

we take the time-derivative of both sides:

$$\frac{d\langle F \rangle}{dt} = \int d\underline{x} \left[\frac{\partial \underline{Y}^*}{\partial t} \hat{F} \underline{Y} + \underline{Y}^* \frac{\partial \hat{F}}{\partial t} \underline{Y} + \underline{Y}^* \hat{F} \frac{\partial \underline{Y}}{\partial t} \right].$$

To proceed, we use the Schrödinger eq.

$$i\hbar \frac{\partial \underline{Y}}{\partial t} = \hat{H} \underline{Y} \rightarrow \frac{\partial \underline{Y}}{\partial t} = -i\frac{\hat{H}}{\hbar} \underline{Y},$$

hence, we get

$$\begin{aligned} \frac{d\langle F \rangle}{dt} &= \frac{i}{\hbar} \int d\underline{x} \left[(\hat{H} \underline{Y})^* \hat{F} \underline{Y} + \underline{Y}^* \hat{F} \hat{H} \underline{Y} \right] \\ &\quad + \int d\underline{x} \underline{Y}^* \frac{\partial \hat{F}}{\partial t} \underline{Y} \end{aligned}$$

We now use the fact that \hat{H} is hermitian,

$$\int d\underline{x} (\hat{H} \underline{Y})^* \underline{Y} = \int d\underline{x} \underline{Y}^* \hat{H} \underline{Y},$$

with $\underline{Y} = \hat{F} \underline{Y}$.

We then get

$$\begin{aligned}\frac{d\langle F \rangle}{dt} &= \frac{i}{\hbar} \int d\tau \overline{\Psi} (\hat{H}\hat{F} - \hat{F}\hat{H}) \Psi \\ &\quad + \int d\tau \overline{\Psi} \frac{\partial \hat{F}}{\partial t} \Psi \\ &= \frac{i}{\hbar} \langle [\hat{H}, \hat{F}] \rangle + \langle \frac{\partial \hat{F}}{\partial t} \rangle.\end{aligned}$$

We'll call this Ehrenfest's generalized theorem.

If we assume a system described by

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(x)$$

and use $\hat{F} = \hat{x}$ and \hat{p} , we get

$$\frac{d\langle x \rangle}{dt} = \frac{\langle p \rangle}{m}$$

$$\frac{d\langle p \rangle}{dt} = -\langle V'(x) \rangle$$

This is known as Ehrenfest's theorem.

This is analogous to the classical equations

$$\frac{dx}{dt} = \frac{p}{m}$$

$$\frac{dp}{dt} = -V'(x) = F.$$

The equations of motion for quantum mechanical expectation values of position, momentum and force coincide with the classical equations of (20)

motion - however, this does not mean generally
that the mean position of a wavepacket
follows the classical trajectory !

MEASUREMENT OF A DEGENERATE EIGENVALUE

Φ7-2

If we measure an observable \hat{F} , and the measured eigenvalue is non-degenerate, i.e.

$$\hat{F}|\psi_n\rangle = f_n |\psi_n\rangle$$

has only one solution $|\psi_n\rangle$ for the eigenvalue f_n , then from postulate D(ii), the system is in the state $|\psi_n\rangle$ immediately after the measurement.

However, if eigenvalue f_n is degenerate, with degeneracy g_n , the eigenvalue equation has g_n solutions $|\psi_{ni}\rangle$,

$$\hat{F}|\psi_{ni}\rangle = f_n |\psi_{ni}\rangle, \quad i = 1, 2, \dots, g_n.$$

In this case we must formulate D(ii) more precisely, as we shall now see.

Assume discrete set of eigenvalues f_n , and an orthonormalized set of eigenfunctions

$$\{|\psi_{ni}\rangle \mid n=1,2,\dots; i=1,2,\dots, g_n\}$$

The eigenfunctions form a complete set, meaning the state prior to the measurement can be expanded

$$|\Psi\rangle = \sum_n \sum_{i=1}^{g_n} c_{ni} |\psi_{ni}\rangle.$$

We find the expansion coefficients by projecting Ψ onto ψ_{ni} :

$$\begin{aligned}\langle \psi_{ni}, \Psi \rangle &= \left\langle \psi_{ni}, \sum_{n=1}^{g_n} \sum_{j=1}^{g_n} c_{nj} \psi_{nj} \right\rangle \\ &= \sum_{n=1}^{g_n} \sum_{j=1}^{g_n} S_{nj} S_{ji} c_{nj} = c_{ni}.\end{aligned}$$

$$\Rightarrow c_{ni} = \int d\tau \psi_{ni}^* \Psi.$$

Considering a series of measurements of F , on \mathbb{F}
the expectation value is

$$\langle F \rangle = \sum_n P_n f_n,$$

with P_n the probability of measuring f_n .

From the expectation value postulate, we have

$$\begin{aligned}\langle F \rangle_{\Psi} &= \int d\tau \Psi^* \hat{F} \Psi = \int d\tau (\hat{F} \Psi)^* \Psi \\ &= \int d\tau \left(\sum_{n=1}^{g_n} \sum_{i=1}^{g_n} c_{ni} \hat{F} \psi_{ni} \right)^* \Psi \\ &= \sum_{n=1}^{g_n} c_{ni} f_n \underbrace{\int d\tau \psi_{ni}^* \Psi}_{c_{ni}} = \sum_n \left(\sum_{i=1}^{g_n} |c_{ni}|^2 \right) f_n\end{aligned}$$

Both formulas valid for arbitrary state Ψ ;
Hence, the probability of measuring eigenvalue
 f_n when the system is in the state $\Psi = \sum_{n,i} c_{ni} \psi_{ni}$
is

$$P_n = \sum_{i=1}^{g_n} |c_{ni}|^2.$$

In the non-degenerate case the corresponding
relation is simply $P_n = |c_{ni}|^2$.

Notice that we may define

$$\mathcal{Y}_n = \sum_{i=1}^{g_n} c_{ni} \psi_{ni}$$

which has eigenvalue f_n , allowing us to write

$$\mathcal{E} = \sum_n \mathcal{Y}_n.$$

\mathcal{Y}_n is therefore the part of \mathcal{E} compatible with the eigenvalue f_n . Hence, D(ii) must be formulated:

Immediately after the measurement of the eigenvalue f_n the system is left in the normalized state

$$\frac{\mathcal{Y}_n}{\|\mathcal{Y}_n\|} = \frac{\sum_{i=1}^{g_n} c_{ni} \psi_{ni}}{\left\| \sum_{i=1}^{g_n} c_{ni} \psi_{ni} \right\|}.$$

The part of \mathcal{E} not compatible with f_n "is removed" by the measurement. "Wavefunction collapse".

$\|\mathcal{Y}_n\|$: norm of \mathcal{Y}_n .

EXAMPLE - 3D isotropic harmonic oscillator.

Recap: In 1D energies of harmonic oscillators is

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right), \quad n=0,1,2\dots$$

with eigenfunctions $\psi_n(x)$.

In 3D we have the orthonormal eigenfunction set

$$\psi_{n_x n_y n_z} = \psi_{n_x}(x) \psi_{n_y}(y) \psi_{n_z}(z)$$

and energy eigenvalues

$$\begin{aligned} E_{n_x n_y n_z} &= E_{n_x} + E_{n_y} + E_{n_z} = \hbar\omega\left(n_x + n_y + n_z + \frac{3}{2}\right) \\ &\equiv \hbar\omega\left(N + \frac{3}{2}\right) = E_N \end{aligned}$$

At $t=0$ the oscillator is prepared in the state

$$\begin{aligned} \Psi = & \underbrace{\sqrt{0.4} \psi_{000}}_{\mathcal{I}_0} + \underbrace{\sqrt{0.1} (\psi_{100} + \psi_{010} + \psi_{001})}_{\mathcal{I}_1} \\ & + \underbrace{\sqrt{0.1} (\psi_{200} + i\psi_{020} + \psi_{011})}_{\mathcal{I}_2} \end{aligned}$$

We see that we have

$$\|\Psi\| = \|\mathcal{I}_1\| + \|\mathcal{I}_2\| + \|\mathcal{I}_3\| = 0.4 + 3 \cdot 0.1 + 3 \cdot 0.1 = 1.$$

$\mathcal{I}_0, \mathcal{I}_1$, and \mathcal{I}_2 have $N=0, 1$ and 2 , respectively.

OK

The possible measured values for the energy are $E_0 = \frac{3}{2}\hbar\omega$, $E_1 = \frac{5}{2}\hbar\omega$ and $E_2 = \frac{7}{2}\hbar\omega$,

with probabilities $P_0 = 0.4$, $P_1 = 0.3$ and $P_2 = 0.3$, respectively. The corresponding normalized states after measurement are

$$\frac{\Psi_0}{\|\Psi_0\|} = |\psi_{000}\rangle$$

$$\frac{\Psi_1}{\|\Psi_1\|} = \frac{1}{\sqrt{3}} (\psi_{100} + \psi_{010} + \psi_{001})$$

$$\frac{\Psi_2}{\|\Psi_2\|} = \frac{1}{\sqrt{3}} (\psi_{200} + i\psi_{020} + \psi_{002})$$