Chapter 2. Foundations of quantum mechanics

I. Basics

Each observable corresponds in quantum mechanics to an operator, which represents a mathematical operation.

Examples:

$$\hat{q} \to \hat{q}f(q) = q \times f(q)$$

$$\frac{d}{dq} \to \frac{d}{dq} f(q) = \frac{df(q)}{dq}$$

Some important operators in the coordinate representation:

Coordinate operator:

$$\hat{q} \to q \times$$

Linear momentum operator:

$$\hat{P}_q \to \frac{\hbar}{i}\frac{d}{dq} \qquad (\hbar = h/2\pi = 1.055 \times 10^{-34}\, Js)$$

Hamiltonian (energy) operator:

$$\hat{H} = \frac{\hat{p}_q^2}{2m} + V(q) \to -\frac{\hbar^2}{2m}\frac{d^2}{dq^2} + V(q)$$

The form of an operator depends on the representation. For example, the coordinate and momentum operators in the momentum representation become:

$$\hat{q} \to \frac{\hbar}{i}\frac{d}{dp_q}, \qquad\qquad \hat{p}_q \to p_q \times$$

Later, we will see that transformations exist between different representations.

Two operators commute if

$$[\hat{\Omega}_1, \hat{\Omega}_2] = \hat{\Omega}_1\hat{\Omega}_2 - \hat{\Omega}_2\hat{\Omega}_1 = 0$$

For example, $\hat{q}$ and $\hat{p}_q$ do not commute:

$$\hat{q}\hat{p}_q f(q) = \frac{\hbar}{i} q \frac{df(q)}{dq} \qquad (f(q) \text{ is an arbitrary function})$$

$$\hat{p}_q\hat{q} f(q) = \frac{\hbar}{i}\left[q\frac{df(q)}{dq} + f(q) \right]$$

so

$$[\hat{q}, \hat{p}_q] f(q) = \frac{\hbar}{i} q \frac{df(q)}{dq} - \frac{\hbar}{i}\left[q\frac{df(q)}{dq} + f(q) \right] = i\hbar f(q)$$

$$[\hat{q}, \hat{p}_q] = i\hbar \neq 0$$

If a function $\phi(q)$ that satisfies the following eigenequation

$$\hat{\Omega}\phi(q) = \omega\phi(q),$$

it is called an eigenfunction of the operator $\hat{\Omega}$ with the constant ω as its eigenvalue.

Example:

$$\frac{d^2}{dq^2}\sin(kq) = -k^2\sin(kq)$$

So, $\sin(kq)$ is said to be an eigenfunction of the operator d^2/dq^2 with $-k^2$ as the eigenvalue.

If the eigenvalues of two eigenfunctions are the same, these two eigenstates are called degenerate (example: $\sin kq$ and $\cos kq$).

In quantum mechanics, we only deal with Hermitian operators.

$$\int\varphi^*(\hat{\Omega}\psi)d\tau = [\int\psi^*(\hat{\Omega}\varphi)d\tau]^* = \int\psi(\hat{\Omega}\varphi)^*d\tau$$

Example, $\hat{p}$ is Hermitian

$$\int\varphi^*\left(-i\hbar\frac{d}{dq}\right)\psi dq = -i\hbar\int\varphi^* d\psi = -i\hbar\left[\varphi^*\psi\Big|_{q=-\infty}^{q=\infty} - \int\psi d\varphi^*\right]$$

$$= \int\psi\left(i\hbar\frac{d}{dq}\right)\varphi^* dq = \left[\int\psi^*\left(-i\hbar\frac{d}{dq}\right)\varphi dq\right]^*$$

i. Eigenvalues of Hermitian operators are always real.

ii. Eigenfunctions of a Hermitian operator are orthogonal:

$$\int \psi_n^* \psi_m d\tau = 0 \quad \text{if } n \neq m$$

and can be normalized

$$\int \psi_n^* \psi_n d\tau = \int |\psi_n|^2 d\tau = 1$$

Combining the two, the eigenfunctions are orthonormal:

$$\int \psi_n^* \psi_m d\tau = \delta_{nm}$$

where $\delta_{nm} (= 0 \text{ if } n \neq m \text{ and } 1 \text{ if } n = m)$ is the Kronecker delta.

iii. Eigenfunctions of a Hermitian operator form a complete set, namely, an arbitrary wavefunction can be expressed as a linear combination of the eigenfunctions:

$$\Psi = \sum_n c_n \psi_n$$

with $\hat{\Omega}\psi_n = \omega_n \psi_n$. The expansion coefficients, c_n, determines the chance of the system to be in a particular eigenstate (the superposition principle).

II. The postulates of quantum mechanics

Quantum mechanics can be established from a small number of postulates. They cannot be derived or proven. Their validity is established by the confirmation of their predictions.

Postulate I: The state of a bound quantum system is completely described by a wavefunction $\Psi(\mathbf{q},t)$, where $\{\mathbf{q}=q_1,q_2,...\}$ are the (spatial + spin) coordinates of the particles in the system. All observables are determined by $\Psi(\mathbf{q},t)$.

Example: ground state wave function of a 1D harmonic oscillator: $\Psi_0(q) = Ne^{-\alpha q^2}$

Postulate II: Every observable corresponds to a Hermitian operator. In the coordinate representation, such an operator can be constructed by expressing

$$\hat{q} \to q\times, \quad \hat{p}_q \to \frac{\hbar}{i}\frac{\partial}{\partial q}$$

Example: angular momentum operator:

$$\hat{l}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$$

<u>Postulate III (Born's interpretation)</u>: The probability for finding the system in the volume element $d\tau$ at point $\mathbf{q}$ is proportional to $|\Psi(\mathbf{q})|^2 d\tau$.

The <u>probability density</u> $|\Psi(\mathbf{q})|^2$ is always real and non-negative, although the <u>probability amplitude</u> $\Psi(\mathbf{q})$ can be complex.

The statistical interpretation of the wavefunction requires that it be single valued, continuous, and <u>square-integratable</u>:

$$\int |\Psi|^2 d\tau < \infty$$

In fact, wavefunction can be normalized such that $\int |\Psi|^2 d\tau = 1$.

Example. The wavefunction of H atom is $\Psi = e^{-r/a_0}$ where a_0 = 52.9 pm. Calculate the probability to find the electron inside a small box of 1.0 pm^3 at $r = 0$ and $r = a_0$.

Normalization:

$$C = \int |\Psi|^2 d\tau = \int_0^\infty e^{-2r/a_0} r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi$$

$$= \frac{a_0^3}{4} 4\pi = \pi a_0^3$$

where we have used spherical coordinates:

$$x = r\sin\theta\cos\phi, \qquad y = r\sin\theta\sin\phi, \qquad z = r\cos\theta$$
$$d\tau = dx\,dy\,dz = r^2\sin\theta\,dr\,d\theta\,d\phi$$

and

$$\int_0^\infty e^{-ax}x^n dx = \frac{n!}{a^{n+1}}$$

The normalized wavefunction:

$$\Psi = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}, \text{ and} \qquad |\Psi|^2 = \left(\frac{1}{\pi a_0^3}\right) e^{-2r/a_0}$$

The probability at $r = 0$:

$$P = |\Psi|^2 d\tau = (2.15\times10^{-6}\ pm^{-3})\times(1.0\ pm^3) = 2.15\times10^{-6}$$

and at $r = a_0$:

$$P' = (2.15\times10^{-6}\ pm^{-3}\,e^{-2})\times(1.0\ pm^3) = 2.91\times10^{-7}$$

Postulate IV (Schrödinger equation): The wavefunction evolves in time according to the equation:

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

For time-independent Hamiltonian, the time-dependent Schrödinger equation (TDSE) can be reduced to a time-independent form:

$$\Psi(\mathbf{q},t) = \psi(\mathbf{q})\varphi(t)$$

The TDSE becomes:

$$i\hbar\psi(\mathbf{q})\frac{\partial\varphi(t)}{\partial t} = \varphi(t)\hat{H}\psi(\mathbf{q})$$

Divide both sides by Ψ, we have

$$i\hbar\varphi(t)^{-1}\frac{\partial\varphi(t)}{\partial t} = \psi(\mathbf{q})^{-1}\hat{H}\psi(\mathbf{q})$$

Since two sides depend on different variables, they have to be constant (E). Hence, the equation can be separated into two:

$$i\hbar\frac{\partial\varphi(t)}{\partial t} = E\varphi(t), \quad \hat{H}\psi(\mathbf{q}) = E\psi(\mathbf{q}),$$

The first has a solution: $\varphi(t) \propto e^{-iEt/\hbar}$, and the second one is called the time-independent Schrödinger equation (TISE).

Notice that the norm of both Ψ and ψ is the same because:

$$\Psi^*\Psi = (\psi^* e^{iEt/\hbar})(\psi e^{-iEt/\hbar}) = \psi^*\psi$$

They are called stationary states and $e^{-iEt/\hbar}$ is the phase.

Postulate V: If a system is described by the wavefunction Ψ, the mean value of the observable Ω in a series measurements is given by the expectation value of the corresponding operator:

$$\left\langle \hat{\Omega} \right\rangle = \frac{\int \Psi^* \hat{\Omega} \Psi d\tau}{\int \Psi^* \Psi d\tau}$$

where the wavefunction can always be normalized $\int \Psi^* \Psi d\tau$=1.

If Ψ is an eigenfunction of $\hat{\Omega}$ ($\hat{\Omega}\Psi = \omega\Psi$), each measurement yields the same eigenvalue ω and $\left\langle \hat{\Omega} \right\rangle = \omega$.

If Ψ is not an eigenfunction, it can always be expressed as a linear combination of the eigenfunctions:

$$\Psi = \sum_n c_n \psi_n \qquad \text{(with } \hat{\Omega}\psi_n = \omega_n \psi_n\text{)}$$

so,

$$\left\langle \hat{\Omega} \right\rangle = \int \left(\sum_n c_n \psi_n \right)^* \hat{\Omega} \left(\sum_m c_m \psi_m \right) d\tau$$

$$= \int \left(\sum_n c_n \psi_n \right)^* \left(\sum_m c_m \omega_m \psi_m \right) d\tau \qquad \left(\int \psi_n^* \psi_m d\tau = \delta_{nm} \right)$$

$$= \sum_n \sum_m c_n^* c_m \omega_m \delta_{nm} = \sum_n \left| c_n \right|^2 \omega_n$$

Each measurement always yields one of the eigenvalues, the chance for a particular eigenvalue (ω_n) to appear in a measurement is given by $\left| c_n \right|^2$.

Summary

Quantum mechanics		Mathematics
Measurement	⇔	Operation
Measuring equipment	⇔	Operator
Observable	⇔	Eigenvalue
State of the system	⇔	Wavefunction

III. Bra and ket notation

It is often more convenient to express wavefunctions in bra and ket notation.

bra: $\langle\varphi| = \varphi^*$,

ket: $|\psi\rangle = \psi$,

transpose: $[\langle\varphi|]^T = |\varphi\rangle$

overlap: $\langle\varphi|\psi\rangle = \int \varphi^* \psi d\tau$, $\langle\varphi|\psi\rangle = \langle\psi|\phi\rangle^*$

density: $\varphi^*\psi = |\psi\rangle\langle\varphi|$

integral with operator: $\langle\varphi|\hat{\Omega}|\psi\rangle = \int \varphi^* \hat{\Omega} \psi d\tau$

Eigenequation: $\hat{\Omega}|\phi_n\rangle = \omega_n|\phi_n\rangle$

Orthonormality: $\langle\psi_n|\psi_m\rangle = \delta_{nm}$

Expectation value: $\langle\hat{\Omega}\rangle = \dfrac{\langle\psi|\hat{\Omega}|\psi\rangle}{\langle\psi|\psi\rangle}$

Linear combination: $|\Psi\rangle = \sum_n c_n|\psi_n\rangle$

IV. Heisenberg's uncertainty principle

If two operators commute:

$$[\hat{\Omega}_1, \hat{\Omega}_2] = 0$$

one can always find simultaneous eigenfunctions for both operators. This means that the corresponding observables can be simultaneously measured with arbitrary accuracy.

Example, 1D free particle ($V = 0$)

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dq^2} = E\Psi, \quad \text{or} \quad \frac{d^2\Psi}{dq^2} = -\frac{2mE}{\hbar^2}\Psi$$

$\hat{p}_q$ and $\hat{H}$ commute for a free particle:

$$\left[\hat{p}_q, \frac{\hat{p}_q^2}{2m}\right] = 0$$

So common eigenfunctions can be found and they can be measured simultaneously and accurately!

Solution of Schrödinger equation:

$$\Psi(q) = \exp(\pm ikq) = \cos kq \pm i \sin kq, \qquad \text{(plane wave)}$$

where the wave vector is $k = (2mE)^{1/2}/\hbar$.

Action of momentum and Hamiltonian:

$$\hat{p}_q \Psi = \frac{\hbar}{i}\frac{d}{dq}(e^{ikq}) = \frac{\hbar}{i}(ik)e^{ikq} = \hbar k e^{ikq} = \hbar k \Psi$$

$$\hat{H}\Psi = -\frac{\hbar^2}{2m}\frac{d^2}{dq^2}(e^{ikq}) = -\frac{\hbar^2}{2m}(ik)^2 e^{ikq} = \frac{\hbar^2 k^2}{2m}\Psi$$

Ψ is eigenfunction of both $\hat{p}_q$ and $\hat{H}$, the eigenvalues are

$$p_q = \hbar k, \qquad E = \frac{\hbar^2 k^2}{2m}$$

de Broglie’s relation:

$$p = k\hbar = \frac{2\pi}{\lambda}\frac{h}{2\pi} = \frac{h}{\lambda} \qquad (\lambda = \frac{2\pi}{k})$$

It is impossible to specify simultaneously, with arbitrary precision, both the momentum and position of a particle, because $[\hat{q}, \hat{p}] = i\hbar$. The constraint

$$\Delta p \, \Delta q \geq \hbar/2$$

is Heisenberg’s uncertainty principle, and *p* and *q* are complementary observables.

Time and energy is another pair of complementary observables:

$$\Delta E \, \Delta t \geq \hbar/2$$

Example: Calc. the position uncertainty of a 1.0 kg particle with a speed uncertainty of 10^{-6} m/s. What if the mass is 1.0×10^{-31} kg?

$$\Delta q \;=\; \hbar/(2\Delta p) \;=\; \hbar/(2m\Delta v)$$

$$\;=\; 1.05\times10^{-34}\,Js/(2\times1.0\;kg\times1.0\times10^{-6}\;m/s)$$

$$\;=\; 5.25\times10^{-29}\;m$$

However, for a particle with the electronic size

$$\Delta q = 525\;m$$

<u>Classical - quantum correspondence:</u>

	Classical	Quantum
State	$q + p$	$\Psi(q)$
Eq. of motion	Newton	Schrödinger
Wave nature	no	yes
Interference	no	yes
Uncertainty	no	yes
Energy	arbitrary	often quantized
Applicability	1 m, 1 kg	1 pm, 10^{-25} kg