Quantum Mechanics

October 27, 2016

Contents

1 Wave Functions and Operators

We introduce some of the mathematical structure of quantum mechanics (QM) by considering a particle in one dimension.

1.1 Wave Function and States

A classical point particle in one dimension has a position x at each time. In QM a particle has a *state* at each time given by a complex *wave function* $\psi(x)$.

Postulate. A measurement of position gives a result x with probability density $|\psi(x)|^2$, i.e.

$$|\psi(x)|^2 \delta x$$

will be the probability that particle is found between x and $x + \delta x$, or

$$\int_a^b |\psi(x)|^2 dx$$

is the probability that the particle is found in the interval $a \leq x \leq b$. This obviously requires

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$$

We say ψ is *normalised* if it satisfies this condition.

Example. (Gaussian wave function) Let

$$\psi(x) = Ce^{-\frac{(x-x_0)^2}{2\alpha}}$$

For some real $\alpha > 0$.
If α is small, $|\psi|^2$ will be sharply peaked around $x = x_0$.
If α is large, $|\psi|^2$ is more spread out.

Since ψ needs to be normalised,

$$\begin{aligned}\int_{-\infty}^{\infty} |\psi(x)|^2 dx &= |C|^2 \int_{-\infty}^{\infty} e^{-\frac{(x-x_0)^2}{\alpha}} dx \\ &= |C|^2 (2\pi)^{1/2} \\ &= 1\end{aligned}$$

So ψ is normalised if

$$C = \left(\frac{1}{2\pi}\right)^{1/4}$$

It is convenient to deal more generally with *normalisable* wave functions that are *not* identically zero, and satisfy

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx < \infty$$

In fact, $\psi(x)$ and $\phi(x) = \lambda\psi(x)$ contain the same physical information for any complex $\lambda \neq 0$.

If $\psi(x)$ is normalisable, we can choose λ to ensure $\psi(x)$ is normalised. Note also $\psi(x)$ and $e^{i\alpha}\psi(x)$ are physically equivalent for any real α, and when ψ is normalised,

$$|\psi(x)|^2 = |e^{i\alpha}\psi(x)|^2$$

i.e. they have the same probability distribution.

In general we will consider normalisable wave functions $\psi, \phi, \chi, \ldots$ that are *smooth* (differentiable any number of times) except at isolated points (see examples below). Also, $\psi, \psi', \ldots \to 0$ as $|x| \to \infty$.

Given states $\psi_1(x)$ and $\psi_2(x)$ can form new state

$$\psi(x) = \psi_1(x) + \psi_2(x)$$

which is called superposition.

Example. Take

$$\psi(x) = B\left(e^{-\frac{x^2}{2\alpha}} + e^{-\frac{(x-x_0)^2}{2\alpha}}\right)$$

i.e. the superposition of Gaussian wave function and itself at different positions.

By drawing the image of $|\psi(x)|^2$ we can get the probability distribution for single particle, with appropriate choice of B.

1.2 Operators and Observables

A quantum state contains information about other physical quantities *observables*, for example, momentum and energy, in addition to position. In QM, each observable is represented by an *operator* acting on wave functions:

Position:

$$\hat{x} = x$$

$$(\hat{x}\psi)(x) = x\psi(x)$$

Momentum:

$$\hat{p} = -i\hbar\frac{d}{dx}$$

$$(\hat{p}\psi)(x) = -i\hbar\frac{d\psi}{dx} = -i\hbar\psi'(x)$$

Energy, or *Hamiltonian*, for a particle of mass m moving at potential $V(x)$:

$$\begin{aligned} H &= \frac{\hat{p}^2}{2m} + V(\hat{x}) \\ &= -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) \end{aligned}$$

If an observable Q is measured when the system is in a state ψ, we would like to know:

(i) what results are possible;

(ii) what is the probability for each result.

1.2.1 Expectation values

For any normalisable $\psi(x)$ and $\phi(x)$, define

$$(\psi, \phi) = \int_{-\infty}^{\infty} \psi(x)^* \phi(x)\, dx$$

For normalised $\psi(x)$, define the *expectation value* of Q (some operator) in this state to be

$$\langle Q \rangle_\psi = (\psi, Q\psi) = \int_{-\infty}^{\infty} \psi^* Q \psi dx$$

Note for $Q = \hat{x}$,

$$\langle \hat{x} \rangle_\psi = (\psi, \hat{x}\psi) = \int_{-\infty}^{\infty} x |\psi(x)|^2 dx$$

standard expression for mean or expectation of x, and for $Q = \hat{p}$,

$$\langle \hat{p} \rangle_\psi = (\psi, \hat{p}\psi) = \int_{-\infty}^{\infty} -i\hbar \psi^* \psi' dx$$

Postulate. For any observable, $\langle Q \rangle_\psi$ is the mean result of measuring Q when the system is in state ψ.

Now consider ϕ and ψ (normalised) with

$$\phi(x) = \psi(x) e^{ikx}$$

for real k. Then $|\phi(x)|^2 = |\psi(x)|^2$. As a result, $\langle \hat{x} \rangle_\phi = \langle \hat{x} \rangle_\psi$, but

$$\begin{aligned}
\langle \hat{p} \rangle_\phi &= \int_{-\infty}^{\infty} -i\hbar \phi^* \phi' dx \\
&= \int_{-\infty}^{\infty} -i\hbar \psi^* \psi' + \int_{-\infty}^{\infty} \hbar k \psi^* \psi \\
&= \langle \hat{p} \rangle_\psi + \hbar k
\end{aligned}$$

So additional factor of e^{ikx} changes momentum by hk.

Example. Let

$$\psi = Ce^{-\frac{x^2}{2\alpha}}$$

as in the last subsection but with $x_0 = 0$.
Then $\langle \hat{p} \rangle_\psi = 0$,

$$\phi = Ce^{-\frac{x^2}{2\alpha}} e^{ikx}$$

with $\langle \hat{p} \rangle_\phi = \hbar k$.

1.2.2 Eigenvalues and Eigenstates

Consider an operator corresponding to an observable, Q, with

$$Q\psi = q\psi$$

for some number q. Then $\psi(x)$ is called an *eigenfunction*, or *eigenstate* of Q with eigenvalue q.

Postulate. If Q is measured when the system is in an eigenstate ψ, then the result is the eigenvalue q with probability 1.

Example. $Q = \hat{x}$. This has no normalisable eigenfunctions, since if

$$\hat{x}\psi(x) = x\psi(x) = q\psi(x)$$

for some q, then $\psi(x) = 0$ for all $x \neq q$.

Example. Set $Q = \hat{p} = -ih\frac{d}{dx}$, and $q = p$. Then $\psi = Ce^{ikx}$ is an eigenfunction with $p = \hbar k$. However, this is not normalisable on the real line (we'll return to this later).

Example. Set $Q = H$ with $V(x) = \frac{1}{2}kx^2$ with $k > 0$, a harmonic oscillator, and $q = E$. Then the eigenvalue equation

$$H\psi = -\frac{\hbar^2}{2m}\psi'' + \frac{1}{2}kx^2\psi = E\psi$$

is satisfied by

$$\psi = Ce^{-x^2/2\alpha}$$

(where C is chosen to normalise ψ) for $\alpha^2 = \hbar^2/km$ and $E = \frac{\hbar}{2}\sqrt{\frac{k}{m}}$.

In general, the energy eigenvalue equation

$$H_\psi = E_\psi$$

or

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

for particle in potential $V(x)$ is called the *time-independent Schrödinger Equation*(SE). Solving this determines all states of definite energy.

1.2.3 Additional comments

Remark. If ψ is any normalised state, then $\langle\hat{p}\rangle_\psi$ and $\langle H\rangle_\psi$ are real. This follows from definitions using integration by parts, e.g.

$$\begin{aligned}
\langle\hat{p}\rangle^* &= \left(\int_{-\infty}^{\infty} -i\hbar\psi^*\psi' dx\right)^* \\
&= \left(\int_{-\infty}^{\infty} i\hbar\psi(\psi^*)' dx\right) \\
&= i\hbar[\psi\psi^*]_{\infty}^{\infty}(=0) - i\hbar\int_{-\infty}^{\infty}\psi'\psi^* dx \\
&= \langle\hat{p}\rangle_\psi
\end{aligned}$$

Similarly we can check

$$\langle H \rangle_\psi = \int_{-\infty}^{\infty} \left(-\frac{\hbar^2}{2m} \psi^* \psi'' + \psi^* V \psi \right) dx$$

is real, integrate first term by parts twice after taking complex conjugate (assume V real).

Remark. Postulate 3 is consistent with Postulate 2 since

$$\begin{aligned} & H\psi = E\psi \\ \implies & \langle H \rangle_\psi = \int_{-\infty}^{\infty} \psi^* H \psi dx = \int_{-\infty}^{\infty} E \psi^* \psi dx = E \end{aligned}$$

for ψ normalised.

Remark. From the previous two remarks, the energy eigenvalue for a normalised eigenstate ψ is always real.

1.3 Infinite well or particle in a box

Let

$$V(x) = \begin{cases} 0 & |x| \leq a \\ \infty & |x| > a \end{cases}$$

assume $\psi(\pm a) = 0$ and justify at end and $\psi(x) = 0$ for $|x| > a$.

Consider SE for $-a \leq x \leq a$

$$-\frac{\hbar^2}{2m} \psi'' = E\psi$$

for $E > 0$, set $E = \frac{\hbar^2 k^2}{2m}$ where $k > 0$ so that SE becomes

$$\psi'' + k^2 \psi = 0$$

So

$$\psi = A \cos kx + B \sin kx$$

But $A \cos ka \pm B \sin ka = 0$ from boundary condition. That implies either

$$B = 0,\ ka = \frac{n\pi}{2}\ n = 1, 3, ...$$

or

$$A = 0,\ ka = \frac{n\pi}{2}\ n = 2, 4, ...$$

Solutions:

$$\psi_n(x) = \left(\frac{1}{a} \right)^{1/2} \left\{ \begin{array}{c} \cos \\ \sin \end{array} \right\} \frac{n\pi}{2a} x \text{ for } n > 0 \left\{ \begin{array}{c} \text{odd} \\ \text{even} \end{array} \right\}$$

energy eigenfunctions and discrete set of energy eigenvalues

$$E_n = \frac{\hbar^2 \pi^2 n^2}{8ma^2}$$

For $E < 0$, set

$$E = -\frac{\hbar^2 k^2}{2m}$$

with $k > 0$ so that SE becomes

$$\psi'' - k^2 \psi = 0$$

Solutions are

$$\psi = Ae^{kx} + Be^{-kx}$$

and cannot satisfy boundary conditions, except by $A = B = 0$.

To justify boundary conditions, consider potential with $V(x) = U \gg E$ for $|x| > a$. Setting

$$U - E = \frac{\hbar^2 k^2}{2m}$$

and SE is

$$\psi'' - k^2 \psi = 0$$

for $|x| > a$. So for normalisable solutions, we need

$$\psi = \begin{cases} Ae^{-kx} & x > a \\ Be^{+kx} & x < -a \end{cases}$$

Taking $U \to \infty$ with E fixed, $k \to \infty$, and $\psi \to 0$ for $|x| > a$.

2 The Schrödinger Equation

To continue our development of QM (in one dimension), we need to consider how things evolve in time.

Classical dynamics of a particle can be specified by the potential $V(x)$ (Force $f(x) = -V'(x)$). Quantum dynamics is also specified by Hamiltonian

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

also determined by potential.

Evolution of a quantum state in time is described by a t-dependent wave function $\Psi(x,t)$ which satisfies

$$i\hbar \frac{\partial}{\partial t}\Psi = H\Psi \tag{1}$$

the *time-dependent Schrödinger Equation.*

The operators $\hat{x}$ and $\hat{p}$ do not change in time, and (1) is

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V(x)\psi$$

a PDE linear in Ψ and first order in t, so specify $\Psi(x,0)$ and $\Psi(x,t)$ can be determined uniquely.

2.1 Stationary states

Consider a wave function of definite frequency:

$$\Psi(x,t) = \psi(x)\, e^{-i\omega t}$$

Substituting in (1) gives

$$\psi \hbar \omega e^{-i\omega t} = (H\psi)\, e^{-i\omega t}$$

This holds if and only if

$$H\psi = E\psi$$

with $E = \hbar\omega$.

Alternatively, look for a separable solution

$$\Psi(x,t) = f(t)\,\psi(x)$$

and find

$$\frac{1}{\psi}H\psi = \frac{i\hbar}{f}\dot{f} = E$$

which is a separation constant. This implies $H\psi = E\psi$ and $f(t) = f(0)\, e^{-iEt/\hbar}$.

A solution of this special form is called a *stationary state.* Special properties of stationary states:
(i)

$$|\Psi(x,t)|^2 = |\psi(x)|^2$$

So probability density does not change with time;
(ii)

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

is the unique solution with $\Psi(x,0) = \psi(x)$ and $H\psi = E\psi$. Then $H\Psi = E\Psi$ implies that the measurement of energy gives result E with certainty (probability 1) for all t.

Example. Consider particle in a box in chapter 1.3: found energy eigenstates $\psi_n(s) \begin{pmatrix} \sin \\ \cos \end{pmatrix}$ with

$$E_n = \frac{\hbar^2\pi^2}{8ma^2}n^2$$

for $n = 1, 2, ...$
Stationary state solutions of time dependent SE:

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

Note however $\psi_1 + \psi_2$ is *not* an energy eigenstate:

$$H(\psi_1 + \psi_2) = E_1\psi_1 E_2\psi_2 \not\propto \psi_1 + \psi_2$$

2.2 Conservation of Probability

The probability density

$$P(x,t) = |\Psi(x,t)|^2$$

obeys a conservation equation

$$\frac{\partial P}{\partial t} = -\frac{\partial J}{\partial x}$$

where

$$J(x,t) = -\frac{i\hbar}{2m}\left(\Psi^*\Psi' - \Psi'^*\,\Psi\right)$$

which is real (here $' = \frac{\partial}{\partial x}$), and is called the *probability current.*

This follows from time dependent SE

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\Psi'' + V\Psi$$

and its conjugate

$$-i\hbar\frac{\partial\Psi^*}{\partial t} = -\frac{\hbar^2}{2m}\,\Psi^{*\prime\prime} + V\Psi^*$$

So

$$\begin{aligned}\frac{\partial P}{\partial t} &= \Psi^* \frac{\partial \Psi}{\partial t} + \frac{\partial \Psi^*}{\partial t} \Psi \\ &= \Psi^* \frac{i\hbar}{2m} \Psi'' - \frac{i\hbar}{2m} \ \Psi^{*\,\prime\prime}\ \Psi\end{aligned}$$

Since the potential terms (V) cancel each other. That is equal to

$$-\frac{\partial J}{\partial x}$$

as claimed.

The conservation equation implies

$$\begin{aligned}\frac{d}{dt} \int_a^b P(x,t)\, dx &= \int_a^b + \frac{\partial P}{\partial t}(x,t)\, dx \\ &= \int_a^b -\frac{\partial J}{\partial x}(x,t)\, dx \\ &= -J(b,t) + J(a,t)\end{aligned}$$

Then boundary conditions $\Psi, J \to 0$ as $x \to \pm\infty$ (for fixed t) gives

$$\int_{-\infty}^{\infty} |\Psi(x,t)|^2\, dx$$

which is independent of time.

Hence $\Psi(x,0)$ normalised $\implies$ $\Psi(x,t)$ normalised for all $t \geq 0$.

2.3 Wave packets and particles

Any wave function that represents a particle localised in space (about some point, on some scale) is called a *wave packet*.

For example, consider Gaussian

$$\psi(x) = A \frac{1}{\alpha^{1/2}} e^{-x^2/2\alpha}$$

where $A = (\alpha/\pi)^{1/4}$.
Wave packet localised around $x = 0$ on length scale $\sqrt{\alpha}$.

So the solution of time dependent SE with $V = 0$ (free particle) and $\Psi(x,0) = \psi(x)$. Then

$$\Psi(x,t) = A \frac{1}{\gamma(t)^{1/2}} e^{-x^2/2\gamma(t)}$$

with

$$\gamma(t) = \alpha + \frac{i\hbar t}{m}$$

(see example sheet 1).

Then the probability density is

$$\begin{aligned} P_\Psi (x,t) &= |\Psi (x,t)|^2 \\ &= \frac{|a|^2}{|\gamma (t)\,|} e^{-\alpha x^2/|\gamma(t)|^2} \end{aligned}$$

localised around $x=0$ but the length scale $|\gamma (t)\,/\sqrt{\alpha}$ spreads with t.

However it's easy to check

$$\langle \hat{x} \rangle_\Psi = \langle \hat{p} \rangle_\Psi = 0$$

for all t.

Previously noted $\phi(x) = \psi(x)\, e^{ikx}$ has expectation value $\hbar k$ for momentum. Solution to SE with $\Phi(x,0) = \phi(x)$ is

$$\Phi(x,t) = \Psi(x-ut,t)\, e^{ikx} e^{-i\left(\hbar k^2/2m\right)t}$$

with $mu = \hbar k$ (can be checked directly). We can also check

$$\langle \hat{x} \rangle_\Phi = ut$$

and

$$\langle \hat{p} \rangle_\Phi = \hbar k$$

Moreover,

$$P_\Phi = |\Phi(x,t)|^2 = |\Psi(x-ut,t)|^2 = P_\Psi(x-ut,t)$$

So Φ corresponds to the moving particle with $mu = \hbar k$ momentum.

Gaussian wave function spreads out on time-scale $\tau \sim \frac{m\alpha}{\hbar}$.

For example, consider an electron $m = m_e$ and $\sqrt{\alpha} = 10^{-12}$ meter. Then $\tau \sim 10^{-20}$ sec.

Now take $m = 10^{-6}$ kg and $\alpha = 10^{-6}$ meter. Then $\tau \sim 10^{16}$ sec.

3 Bound States in One Dimension

A bound state for a particle of mass m in a potential $V(x)$ is a normalisable energy eigenstate (or stationary state)

$$H\psi = -\frac{\hbar^2}{2m}\psi'' + V(x)\psi = E\psi$$

(time-independent SE). This corresponds to a bounded classical orbit.

If $V(x) \to 0$ as $|x| \to \infty$, need $E < 0$ (see section 3.2 below).

3.1 Potential Well

Consider a potential well

$$V(x) = \begin{cases} -U & |x| < a \\ 0 & |x| \geq a \end{cases}$$

Seek solutions of time-independent SE with $-U < E < 0$:

$$\begin{aligned} -\frac{\hbar^2}{2m}\psi'' &= (E+U)\psi \quad |x| < a \\ -\frac{\hbar^2}{2m}\psi'' &= E\psi \quad |x| > n \end{aligned}$$

Set $U + E = \frac{\hbar^2 k^2}{2m}$ and $E = -\frac{\hbar^2\kappa^2}{2m}$ for $k, \kappa \in \mathbb{R}^+$. Then

$$k^2 + \kappa^2 = \frac{2mU}{\hbar^2}$$

Then SE becomes

$$\begin{aligned} \psi'' + k^2\psi &= 0 \quad |x| < a \\ \psi'' - \kappa^2\psi &= 0 \quad |x| > a \end{aligned}$$

Need ψ, ψ' continuous but ψ'' discontinuous at $x = \pm a$.

Consider *even parity* solutions with $\psi(-x) = \psi(x)$:

$$\psi = \begin{cases} A\cos kx & |x| < a \\ Be^{-\kappa x} & |x| > a \end{cases}$$

Matching ψ and ψ' at $x = a$ ($x = -a$ automatic for ψ even):

$$\begin{aligned} A\cos ka &= Be^{-\kappa a} \\ -Ak\sin ka &= -B\kappa e^{-\kappa a} \end{aligned}$$

These give the same result for A/B if and only if

$$k\tan ka = \kappa$$

To see when solutions exists, convenient to set

$$\xi = ak, \eta = a\kappa$$

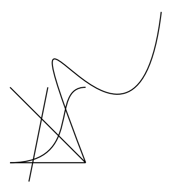
which are dimensionless (and positive), and consider

$$\eta = \xi \tan \xi,$$
$$\xi^2 + \eta^2 = \frac{2ma^2}{\hbar^2} U$$

For each point of intersection, we get one solution for ξ, η or k, κ and corresponding value of E.
Hence there is exactly one solution for $\frac{2ma^2}{\hbar^2} U < \pi^2$.

In general, there are n solutions for $(n-1)^2 \pi^2 < \frac{2ma^2 U}{h\hbar^2} < n^2 \pi^2$.

There are finite number of allowed energy eigenstates.



Note that now we have non-zero probability density $|\psi(x)|^2$ of measuring particle *outside* classically allowed region $|x| < a$ (for $E < 0$).

We can consider *odd parity* solutions $\psi(-x) = -\psi(x)$ similarly (see example sheet 1).

3.2 General Properties

3.2.1 Bound state energies

Consider time-independent SE with $V(x) \to 0$ as $x \to \pm\infty$. For 2nd order ODE, there are 2 complex constants in general solution.
But this is linear in ψ, so one complex constants corresponds to $\psi \to \lambda\psi$.

Now

$$-\frac{\hbar^2}{2m}\psi'' \sim E\psi$$

as $x \to \pm\infty$. So

$$\psi \sim A_\pm e^{ikx} + B_\pm e^{-ikx} \qquad E = \frac{\hbar^2 k^2}{2m} > 0$$
$$\psi \sim A_\pm e^{\kappa x} + B_\pm e^{-\kappa x} \quad E = -\frac{\hbar^2 \kappa^2}{2m} < 0$$

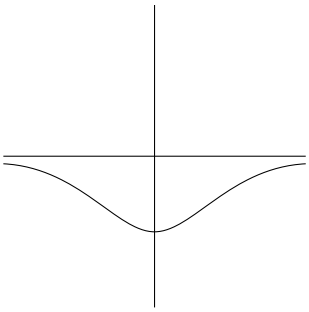
For $E > 0$ there is no normalisable solution.

For $E < 0$ we have normalisable solution if

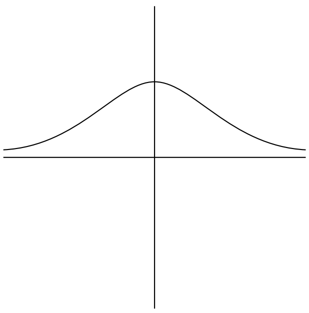
$$\psi \sim \begin{cases} B_+ e^{-\kappa x} & x \to +\infty \ \ (A_+ = 0) \\ A_- e^{\kappa x} & x \to -\infty \ \ (B_- = 0) \end{cases}$$

Only one complex constant left to choose, so specifying behaviour at both boundaries $\implies$ over-determined system, solutions exist for *particular* values of $E \implies$ bound state energies quantised.

We may have several bound states:



or none:



Furthermore, if $V(x) \geq V_0$ (constant), then for ψ normalisable,

$$\begin{aligned} H\psi = E\psi \implies E &= \langle H \rangle_\psi \\ &= \int_{-\infty}^{\infty} \left(-\frac{\hbar^2}{2m} \psi^* \psi'' + V(x) |\psi(x)|^2 \right) dx \\ &= \int_{-\infty}^{\infty} \left(\frac{\hbar^2}{2m} |\psi'|^2 + V(x) |\psi|^2 \right) dx \\ &\geq 0 + V_0 \end{aligned}$$

(integration by parts). So $0 > E > V_0$ for any bounded state.

4 Expectation and Uncertainty

4.1 Hermitian Operators

Recall earlier definition

$$(\phi, \psi) = \int_{-\infty}^{\infty} \phi(x)^* \psi(x)\, dx$$

with properties

$$(\psi, \alpha\psi) = \alpha(\phi, \psi) = (\alpha^* \phi, \psi)$$

and similarly

$$(\phi, \psi)^* = (\psi, \phi)$$

Regarding this as an inner product on wave functions, define the *norm* of *psi*, denoted $||\psi||$, by

$$||\psi||^2 = (\psi, \psi) = \int_{-\infty}^{\infty} |\psi(x)|^2 dx$$

which is real and positive, and $||\psi|| = 1$ is ψ is normalised.

An operator Q is *hermitian* if

$$(\phi, Q\psi) = (Q\phi, \psi)$$

for all normalisable ψ, ϕ. This implies

$$\begin{aligned} (\psi, Q\psi) = (Q\psi, \psi) &= (\psi, Q\psi)^* \\ \implies \langle Q \rangle_\psi &= \langle Q \rangle_\psi^* \end{aligned}$$

The operators $\hat{x}, \hat{p}$, and $H = \frac{\hat{p}^2}{2m} + V(\hat{x})$ are hermitian (for V real).

Check:

$$\begin{aligned} &(\phi, \hat{x}\psi) = (\hat{x}\phi, \psi) \\ \iff &\int_{-\infty}^{\infty} \phi(x)^* (x\psi(x))\, dx = \int_{-\infty}^{\infty} (x\phi(x))^* \psi(x)\, dx \end{aligned}$$

which is true (x is real).

$$\begin{aligned} &(\phi, \hat{p}\psi) = (\hat{p}\phi, \psi) \\ \iff &\int_{-\infty}^{\infty} \phi^* (-i\hbar\psi')\, dx = \int_{-\infty}^{\infty} (-ih\phi')^* \psi dx \end{aligned}$$

by parts and $[\phi^*\psi]_{-\infty}^{\infty} = 0$.

To show $(\phi, H\psi) = (H\phi, \psi)$, check KE and PE terms separately:
KE: $(\phi, \psi'') = -(\phi', \psi') = (\phi'', \psi)$;
PE: $(\phi, V(x)\psi) = (V(x)\phi, \psi)$ for V real.

(Later in chapter 6 we'll prove other general properties of hermitian operators, e.g. eigenvalues are real, eigenstates with distinct eigenvalues are orthogonal with respect to inner product.)

4.2 Ehrenfest's Theorem

Consider normalised $\Psi(x,t)$ satisfying SE

$$i\hbar\dot{\Psi} = H\Psi = \left(\frac{\hat{p}^2}{2m} + V(\hat{x})\right)\Psi = -\frac{\hbar^2}{2m}\Psi'' + V(x)\Psi$$

The expectation values

$$\langle \hat{x} \rangle_\Psi = (\Psi, \hat{x}\Psi)$$

and

$$\langle \hat{p} \rangle_\Psi = (\Psi, \hat{p}\Psi)$$

depend on t through Ψ. Ehrenfest's Theorem states

$$\frac{d}{dt}\langle \hat{x} \rangle_\Psi = \frac{1}{m}\langle \hat{p} \rangle_\Psi$$

and

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

which is the quantum counterparts to classical equations of motion (in first order form).

Proof.

$$\begin{aligned}\frac{d}{dt}\langle \hat{x} \rangle_\Psi &= \left(\dot{\Psi}, \hat{x}\Psi\right) + \left(\Psi, \hat{x}\dot{\Psi}\right) \\ &= \left(\frac{1}{i\hbar}H\Psi, \hat{x}\Psi\right) + \left(\Psi, \hat{x}\frac{1}{i\hbar}H\Psi\right)\end{aligned}$$

Since H is hermitian,

$$\begin{aligned}&-\frac{1}{i\hbar}(H\Psi, \hat{x}\Psi) + \frac{1}{i\hbar}(\Psi, \hat{x}H\Psi) \\ &= -\frac{1}{i\hbar}(\Psi, H\hat{x}\Psi) + \frac{1}{i\hbar}(\Psi, \hat{x}H\Psi) \\ &= \frac{1}{i\hbar}(\Psi, (\hat{x}H - H\hat{x})\Psi)\end{aligned}$$

But

$$\begin{aligned}(\hat{x}H - H\hat{x})\Psi &= \frac{-\hbar^2}{2m}\left(x\Psi'' - (x\Psi)''\right) + (xV - Vx)\Psi \\ &= +\frac{\hbar^2}{2m}2\Psi' \\ &= \frac{i\hbar}{m}\hat{p}\Psi\end{aligned}$$

as required.

Similarly,

$$\begin{aligned}\frac{d}{dt}\langle \hat{p} \rangle_\Psi &= \left(\dot{\Psi}, \hat{p}\Psi\right) + \left(\Psi, \hat{p}\dot{\Psi}\right) \\ &= \left(\frac{1}{i\hbar}H\Psi, \hat{p}\Psi\right) + \left(\Psi, \hat{p}\frac{1}{i\hbar}H\Psi\right) \\ &= \frac{1}{i\hbar}(\Psi, (\hat{p}H - H\hat{p})\Psi)\end{aligned}$$

But

$$\left(\hat{p}H - H\hat{p}\right)\Psi = -i\hbar\left(-\frac{\hbar^2}{2m}\right)\left(\left(\Psi''\right)' - \left(\Psi'\right)''\right)(=0) - i\hbar\left(\left(V\Psi\right)' - V\Psi'\right)$$
$$= -i\hbar V'(x)\,\Psi$$

as required.

4.3 The Uncertainty Principle

If ψ is any normalised state (at fixed time) define the *uncertainty* in position $(\Delta x)_\psi$ and momentum $(\Delta p)_\psi$ by

$$(\Delta x)^2_\psi = \left\langle\left(\hat{x} - \langle\hat{x}\rangle - \psi\right)^2\right\rangle_\psi \neq= \left\langle\hat{x}^2\right\rangle_\psi - \langle\hat{x}\rangle^2_\psi$$

and the same formula for $(\Delta p)_\psi$.

These quantify 'spread' of possible results of measurements.

Heisenberg's Uncertainty Principle states

$$(\Delta x)_\psi\,(\Delta p)_\psi \geq \frac{\hbar}{2}$$

Interpretation: we can never reduce combined uncertainty in measurements of position and momentum below this threshold.

Note: $X = \hat{x} - \alpha$ and $P = \hat{p} - \beta$ are both hermitian for any real α, β.

$$\left(\psi, X^2\psi\right) = (X\psi, X\psi) = ||X\psi||^2 \geq 0,\ \left(\psi, P^2\psi\right) = (P\psi, P\psi) = ||P\psi||^2 \geq 0$$

Choosing $\alpha = \langle\hat{x}\rangle_\psi$ and $\beta = \langle\hat{p}\rangle_\psi$, we deduce $(\Delta x)^2_\psi$ and $(\Delta p)^2_\psi$ are indeed real and positive, as required in our definition.

Example. For Gaussian

$$\psi(x) = \left(\frac{1}{\alpha\pi}\right)^{\frac{1}{4}} e^{-x^2/2\alpha}$$

find

$$\langle\hat{x}\rangle_\psi = \langle\hat{p}\rangle_\psi = 0$$

and

$$(\Delta x)^2_\psi = \alpha/2, (\Delta p)^2_\psi = \hbar^2/2\alpha$$

So

$$(\Delta x)_\psi\,(\Delta p)_\psi = \frac{\hbar}{2}$$

□