Quantum Physics PY1T20/PYU11P20

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Quantum Physics Lecture 10:

Eigenfunctions and eigenvalues: definition and significance.

Steady-state Schrodinger equation:
‘Stationary states’

Particle-in-a-box revisited
Wavefunctions for energy eigenstates
Normalisation
Probability density of position
Expectation values of position

Finite potential well

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Eigenfunctions and eigenvalues: definition

Last lecture, we defined the momentum operator: $\hat{p} = -i\hbar\frac{\partial}{\partial x}$

Operators like this play a crucial role in quantum mechanics.

In general they 'act' on functions to give other functions, e.g. $\hat{p}\psi = -i\hbar\frac{\partial\psi}{\partial x} = \phi$

But we saw that, if the function ψ was an infinite 1D wave, $\psi = Ae^{-iEt/\hbar}e^{ipx/\hbar}$

$$\hat{p}\psi = -i\hbar\frac{\partial\psi}{\partial x} = p\psi$$

This equation defines an 'eigenfunction' of the operator $\hat{p}$, with 'eigenvalue' p.

'The infinite 1D wave with momentum p is an eigenfunction of momentum, with eigenvalue p'.

Note 1: The factor of A and the exponential in time are irrelevant to this statement.
Note 2: The momentum operator has an infinite number of eigenfunctions, $\psi_p(x)$, corresponding to different eigenvalues p.

Eigenfunctions and eigenvalues: role in quantum mechanics

Operators, eigenfunctions, and eigenvalues, play a central role in quantum mechanics.

Every observable corresponds to an operator:

Momentum operator : $\hat{p} = -i\hbar\frac{\partial}{\partial x}$

Position operator: $\hat{x} = x$

Kinetic energy, potential energy, total energy, angular momentum, ...

The eigenfunctions of an operator are very special: no uncertainty in that observable. E.g. :

if you measure momentum, in a situation where the wavefunction is an infinite 1D wave – an eigenfunction of momentum with eigenvalue p – you will get one and only one result – p.

if you measure position, in a situation where the wavefunction is a 'spike' at some position x0 – an eigenfunction of position with eigenvalue x0 – you will get one and only one result – x0.

etc..

Eigenfunctions are special but scarce!

- Most of the time, the wavefunction of a physical system is not an eigenfunction of the thing you measure!

E.g. in electron diffraction, the wavefunction is a spread-out wave and not an eigenfunction of position.

- However, any wavefunction can be written as a sum of eigenfunctions of (any) observable. This describes a situation where, if we measure that observable, we get different values with some probabilities.

E.g. : state made of two waves, with momenta p and –p: $\psi = A\left(e^{ipx/\hbar} + e^{-ipx/\hbar}\right)$

If you measured the momentum of a particle in such a state, the probability of p is 0.5 and –p is 0.5. (1:1 odds).

Because probabilities are real and the prefactors in the superposition are complex, we must take the magnitude-squared to translate to probabilities. So $\psi = A\left(e^{ipx/\hbar} - e^{-ipx/\hbar}\right)$

also 1:1 odds,

but $\psi = A\left(\sqrt{3}e^{ipx/\hbar} - \sqrt{2}e^{-ipx/\hbar}\right)$

is 3:2 odds, i.e. 3/5 probability of p and 2/5 probability of –p.

Steady-state Schrodinger Equation

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E-U)\psi = 0}$$

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U\right)\psi = E\psi$$

Hamiltonian operator H
= Operator for energy

An eigenfunction equation.

“*eigen*” meaning “proper” or “characteristic”.

In general there is more than one solution ψ_n *(eigenfunction)*

Each solution corresponds to a specific value of energy
i.e. eigenfunctions ψ_n with corresponding eigenvalues E_n

- a re-statement of energy quantisation!

The eigenfunctions ψ_n are a complete orthogonal set (c.f. Fourier expansions to be seen in SF)

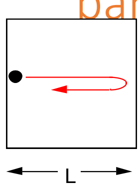
Stationary states?

$$\boxed{\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - U)\,\psi = 0} \qquad \underbrace{\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U\right)}_{Hamiltonian\ -\ \hat{H}}\psi = E\psi$$

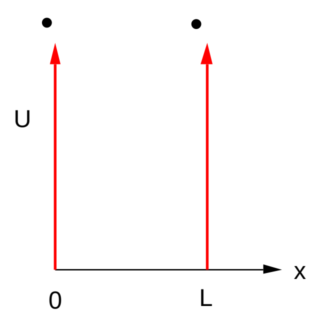
Solutions to the time-independent Schrodinger equation
= eigenfunctions of the Hamiltonian,
= states with a definite energy,
= 'stationary states'.
The probability density does not depend on time
- the full, time-dependent wavefunction for such a state is

$$\psi(x,t) = \psi(x)e^{-iEt/\hbar} \Rightarrow |\psi(x,t)|^2 = |\psi(x)|^2$$

"particle in a box" re-visited



$$\boxed{\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - U)\,\psi = 0}$$



described by "square well" potential
with infinitely high potential barriers :
(1) $U = 0$ for $0 < x < L$
(2) $U = \infty$ (and so $\psi = 0$) for $x \leq 0$ & $x \geq L$

Objective: find ψ for $0 < x < L$

Region (1) SSSE becomes $\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0$

'SHM' type equation: Oscillatory solutions e^{ikx}

“particle in a box” solution of SSSE

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0 \qquad \text{Try:} \quad \psi = Ce^{ikx} \Rightarrow k = \pm\sqrt{\frac{2mE}{\hbar^2}}$$

Recall free particle wavefunction $\quad \psi = C\exp(ipx/\hbar) = C\exp(ikx)$

Without time dependence. *C* is a constant

This is a free particle travelling in +ve *x*-direction (when p is +ve)
Wave travelling in -ve *x*-direction also possible
More general solution adds both *(making a standing wave!)*

General solution: $\quad \Psi = C\exp(ikx) + B\exp(-ikx)$

where *C* and *B* may be complex

Expand this using $\exp(i\theta) = \cos\theta + i\sin\theta$

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“particle in a box” solution of SSSE

$$\begin{aligned}\Psi &= C(\cos kx + i\sin kx) + B(\cos(-kx) + i\sin(-kx)) \\ &= C(\cos kx + i\sin kx) + B(\cos kx - i\sin kx) \\ &= (C + B)\cos kx + i(C - B)\sin kx\end{aligned}$$

Now apply boundary conditions at box walls…

At $x = 0$ must have $\psi = 0$

So $\psi(0) = C + B = 0$ and hence $C = -B$

Putting into equation for ψ *gives* $\Psi = 2iC\sin kx = A\sin kx$

A is another constant

Also $\psi = 0$ at $x = L$ so $\quad k = \frac{n\pi}{L} \quad n = 1, 2, 3\ldots.$

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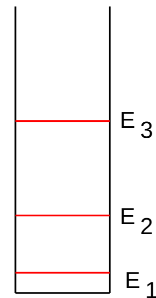
“particle in a box” energy levels

$$k = \frac{n\pi}{L} \qquad n = 1, 2, 3 \ldots.$$

$$\therefore \frac{p}{\hbar} L = n\pi \qquad \text{also} \qquad E = \frac{p^2}{2m}$$

$$\therefore E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = \frac{n^2 h^2}{8mL^2}$$



quantised energy, as before!

“particle in a box” wavefunctions

$$\psi_n = A \sin\left(px/\hbar\right) = A \sin\left(\frac{\sqrt{2mE_n}}{\hbar} x\right) = A \sin\left(\frac{n\pi}{L} x\right)$$

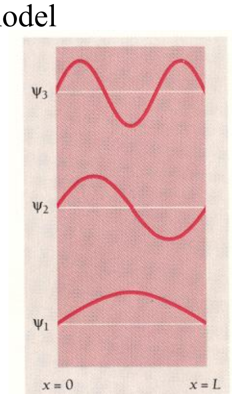
Same function form as “standing waves” of earlier model

Properties:

(1) ψ is single-valued and continuous

(2) likewise $d\psi/dx$

(with the <u>exception</u> that $d\psi/dx$
is non-continuous at $x = 0$, $x = L$)



(an unusual feature, occurs only when potential is infinite)

“particle in a box” wavefunctions

(3) ψ normalisable? $\psi_n = A \sin\left(\frac{n\pi}{L} x\right)$

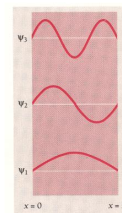
$$\int_{-\infty}^{+\infty} |\psi_n|^2 \, dx = \int_0^L |\psi_n|^2 \, dx = 1$$

$$\sin^2\theta = \tfrac{1}{2}(1 - \cos 2\theta)$$

$$= A^2 \int_0^L \sin^2\left(\frac{n\pi}{L} x\right) dx$$

$$= \frac{A^2}{2}\left[\int_0^L dx - \int_0^L \cos\left(\frac{2n\pi}{L} x\right) dx\right]$$

$$= \frac{A^2}{2}\left[x - \frac{L}{2n\pi} \sin\left(\frac{2n\pi}{L} x\right)\right]_0^L = \frac{A^2}{2} L = 1$$



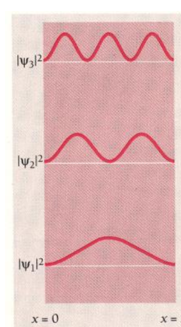
$$\therefore A = \sqrt{\frac{2}{L}}$$

$$\boxed{\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right)}$$

Probability density

$$\boxed{\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L} x\right)}$$

$$\boxed{|\psi_n|^2 = \frac{2}{L} \sin^2\left(\frac{n\pi}{L} x\right)}$$



From plot, for $n = 1$, $|\psi|^2 = 2/L$ (max value) at $x = L/2$
but for $n = 2$, $|\psi|^2 = 0$ at $x = L/2$
depends dramatically on the quantum number!

(This is also in contrast to classical view of equal probability everywhere throughout the box!)

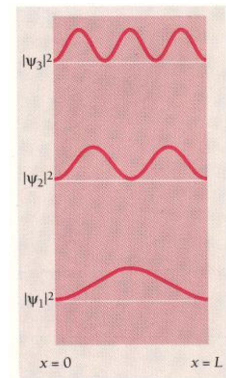
But consider **expectation value** of position……..

Expectation value of position

$$\langle x \rangle = \int_{-\infty}^{+\infty} x|\psi|^2\,dx = \frac{2}{L}\int_0^L x\sin^2\left(\frac{n\pi}{L}x\right)dx$$

$$= \frac{2}{L}\left[\frac{x^2}{4} - \frac{x\sin\left(\frac{2n\pi}{L}x\right)}{2\left(\frac{2n\pi}{L}\right)} - \frac{\cos\left(\frac{2n\pi}{L}x\right)}{8\left(\frac{2n\pi}{L}\right)^2}\right]_0^L$$

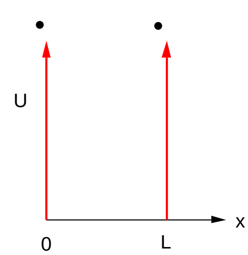
$$= \frac{2}{L}\left(\frac{L^2}{4}\right) = \frac{L}{2}$$

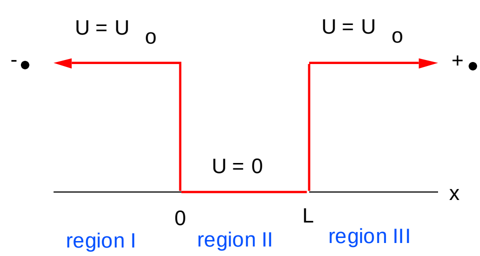


Average position is <u>the middle</u> of the box, irrespective of n!

(Same as classical…) *N.B. Classical view (uniform probability across box) is equivalent to very large n*

Finite Square Potential Well





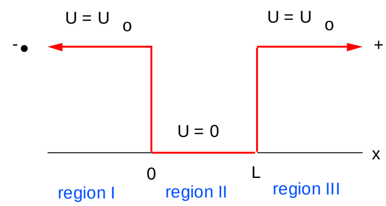
Comparison with infinite case (left):
(1) potential is finite at edges of well
(2) <u>three</u> regions: I ($x < 0$), II ($0 \le x \le L$) and III ($x > L$)
(3) specify that regions I and III extend to infinite distance
(4) consider **only** case of $\boldsymbol{E \le U_o}$

Classical view: infinite and finite well cases are equivalent
Quantum view: E_n *values differ & "particle <u>in</u> the walls"*

Apply SSSE to region I

Since $U = U_o \geq E$, SSSE becomes

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - U_0)\,\psi = 0$$



where quantity (E - U_o) is <u>negative</u>, expect different solution!
Re-write as:

$$\frac{d^2\psi}{dx^2} - a^2\psi = 0 \qquad \text{where } a = \frac{\sqrt{2m(U_0 - E)}}{\hbar}$$

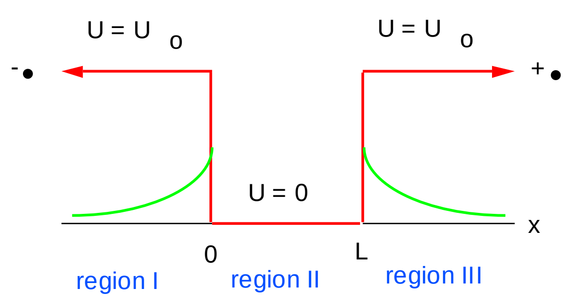
Solutions are <u>real</u> exponentials:

$$\psi_I = Ae^{ax} + Be^{-ax}$$

For ψ_I to be finite as x approaches -∞ : must have $B = 0$
As x is -ve, hence exponential <u>decay</u>
Finite ψ_I means that particle exists in the wall!

$$\boxed{\psi_I = Ae^{ax}}$$

Other regions?



In region I, the wavefunction is exponential decay (green),
likewise in region III
(use same arguments, think of boundary x = L as $x' = 0$)

Region II is different because $U = 0$ so (E - U) is <u>positive</u>,
expect complex 'wave' solutions, as previous infinite well case?
Yes, but with important <u>difference</u>…..

Region II solution

For infinite wall case had $\psi = A\sin(px/\hbar) + B\cos(px/\hbar)$

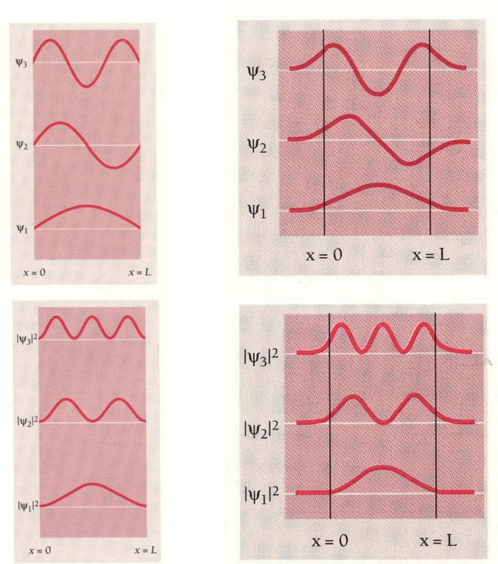
where $B = 0$ because $\psi = 0$ at $x = 0$; this is not a requirement in finite case (as ψ is non-zero in regions I and III). Therefore, keep general solution as:

$$\psi = F\sin(px/\hbar) + G\cos(px/\hbar)$$

But expect G is small

In that case, the main effect of 2nd term is at the walls
When apply boundary conditions, ensuring that ψ and $d\,\psi/dx$ both match across wall (*more complicated maths*), find that the wavelengths are slightly longer (eg $\lambda_1 > 2L$) (effect of adding cos term!) and hence energies are slightly lower !

Illustrate the complete wavefunction



ψ plot shows:
longer wavelength,
or lower energies

$|\,\psi\,|^2$ plot shows:
particle can exist
in the walls