The Particle in a 2-D Box
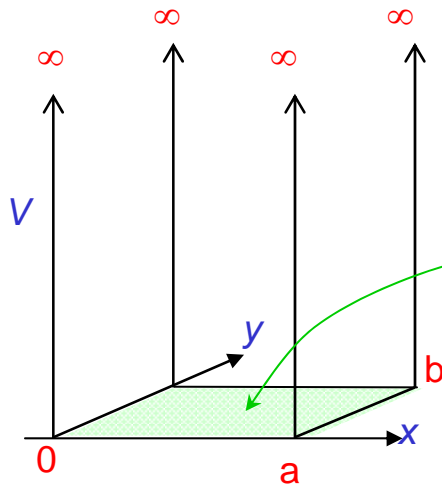
$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + V(x,y)$$

particle confined to surface

$$V(x,y) = \infty \qquad 0 > x > a;\ 0 > y > b$$

$$V(x,y) = 0 \qquad 0 \leqslant x \leqslant a \ \text{ and } \ 0 \leqslant y \leqslant b$$

$$\frac{\partial^2}{\partial x^2}\psi_{n1,n2}(x,y) + \frac{\partial^2}{\partial y^2}\psi_{n1,n2}(x,y) = -\frac{2m}{\hbar^2}E_{n1,n2}\psi_{n1,n2}(x,y)$$

Separation of Variables: suppose $\psi_{n1n2} = X_{n1}(x)\,Y_{n2}(y)$

then $\qquad \dfrac{1}{X}\dfrac{\partial^2 X}{\partial x^2} + \dfrac{1}{Y}\dfrac{\partial^2 Y}{\partial y^2} = -\dfrac{2m}{\hbar^2}E_{n1,n2} = -\dfrac{2m}{\hbar^2}(E_{n1} + E_{n2})$
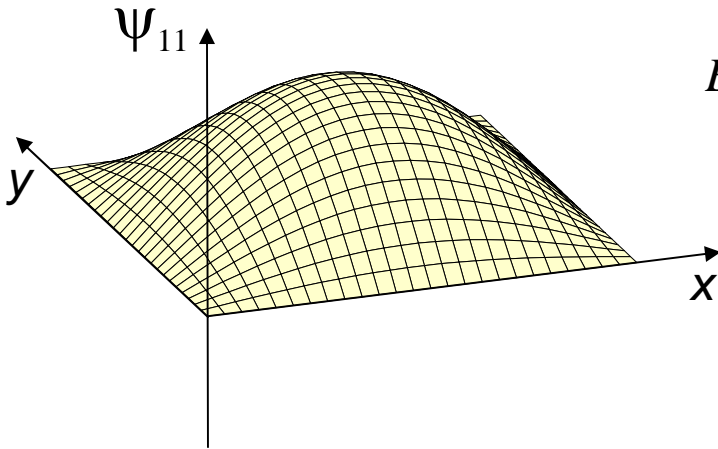
i.e. $\qquad \dfrac{\partial^2 X_{n1}}{\partial x^2} = -\dfrac{2mE_{n1}}{\hbar^2}X_{n1}$ and $\quad \dfrac{\partial^2 Y_{n2}}{\partial y^2} = -\dfrac{2mE_{n2}}{\hbar^2}Y_{n2}$
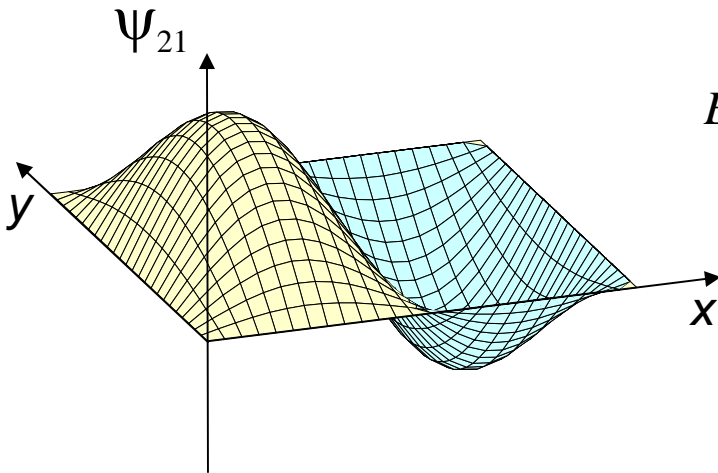
and from 1-D solutions:

$$\psi_{n1,n2} = \frac{2}{\sqrt{ab}}\sin\left(n_1\frac{\pi x}{a}\right)\sin\left(n_2\frac{\pi y}{b}\right)$$

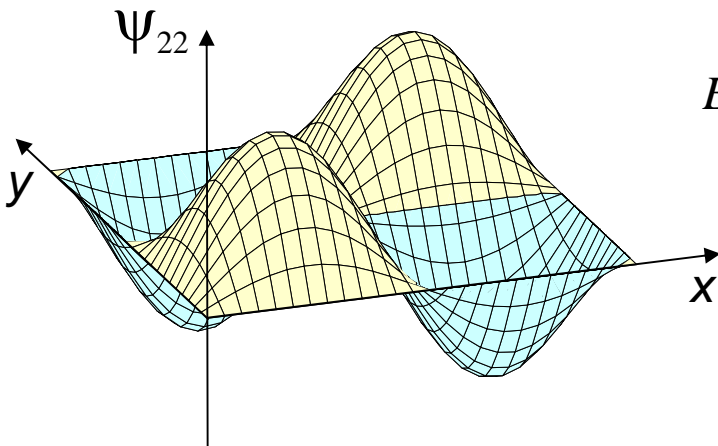$$E_{n1,n2} = \left(\frac{\pi^2\hbar^2}{2m}\right)\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2}\right)$$

The Particle in a 2-D Box – Solutions

Ψ_{11}

$$E_{11} = \left(\frac{\pi^2 \hbar^2}{2m} \right) \left(\frac{1}{a^2} + \frac{1}{b^2} \right)$$

Ψ_{21}

$$E_{21} = \left(\frac{\pi^2 \hbar^2}{2m} \right) \left(\frac{4}{a^2} + \frac{1}{b^2} \right)$$

Ψ_{22}

$$E_{22} = \left(\frac{\pi^2 \hbar^2}{2m} \right) \left(\frac{4}{a^2} + \frac{4}{b^2} \right)$$

The Particle in a 2-D Box – Degeneracy

Degeneracy   occurs whenever one function can be changed into another by a symmetry transformation of the system.

Consider the square well (a = b).
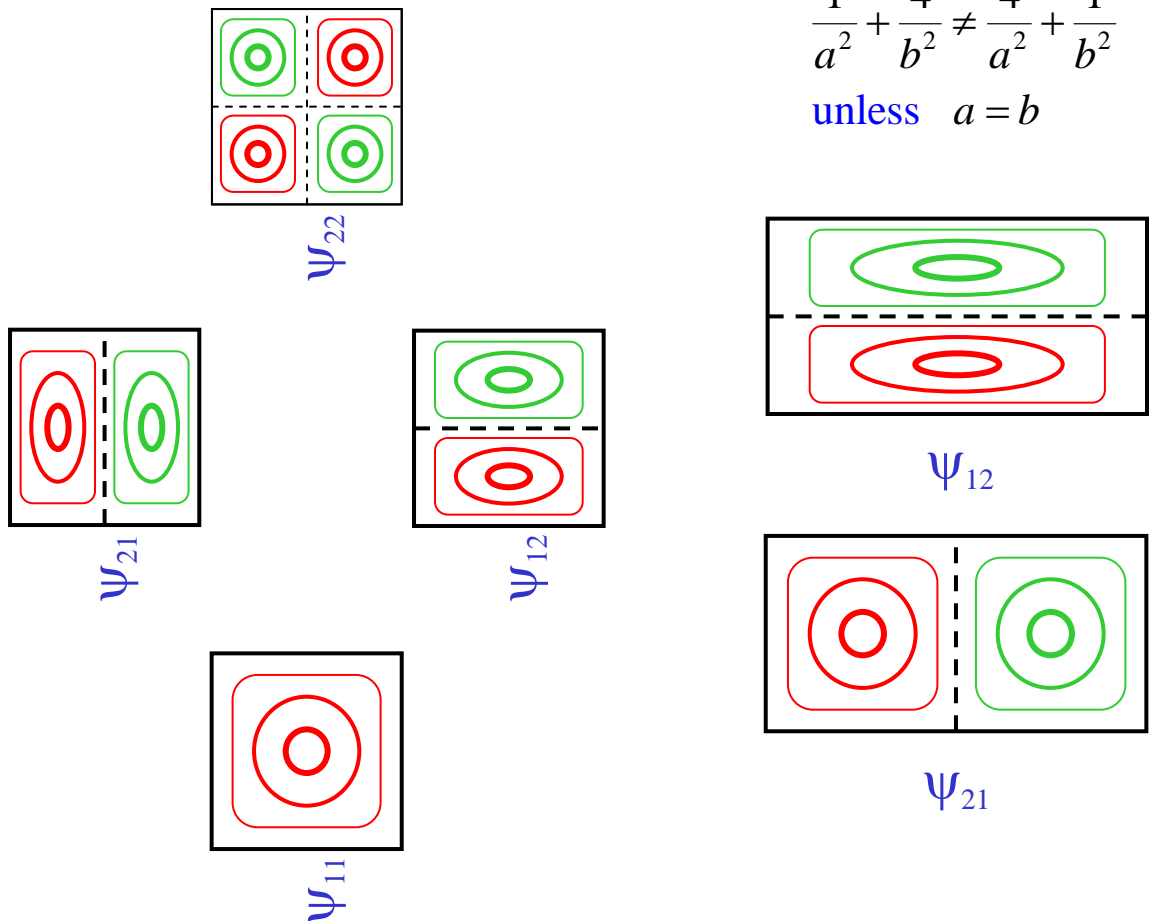
$$\psi_{n1,n2}(x, y) \neq \psi_{n2,n1}(x, y)$$

but

$$E_{n1,n2} = E_{n2,n1} = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_1^2 + n_2^2}{a^2}\right)$$

$$\frac{1}{a^2} + \frac{4}{b^2} \neq \frac{4}{a^2} + \frac{1}{b^2}$$

unless $a = b$

ψ_{22}

ψ_{21}

ψ_{12}

ψ_{12}

ψ_{21}

ψ_{11}

Operators

An operator changes a function into another in a specific manner:

$$\hat{\Omega} f = g$$

e.g. suppose $\qquad f = f(x) = x^2 + 2x + 1$

then if $\quad \hat{\Omega}_1 = d/dx, \quad \hat{\Omega}_1 f = 2x + 2$

or if $\quad \hat{\Omega}_2 = \sqrt{\ }, \quad \hat{\Omega}_2 f = x + 1$

Not all the usual rules of algebra apply to operators!

$$(\hat{A} + \hat{B})f = \hat{A}f + \hat{B}f$$

$$\hat{A}(f + g) = \hat{A}f + \hat{A}g$$

$$\hat{A}cf = c\hat{A}f, \quad c \text{ is a constant}$$

linear operators only

$$\hat{A}\hat{B}f = \hat{A}(\hat{B}f)$$

But $\hat{A}\hat{B}f \neq \hat{B}\hat{A}f$ in general

e.g. suppose $\quad \hat{A} = x, \ \hat{B} = d/dx$

$$\hat{A}\hat{B}f = 2x^2 + 2x, \quad \text{but} \quad \hat{B}\hat{A}f = 3x^2 + 4x + 1$$

Eigenvalue equation $\qquad \hat{\Omega} f = \omega f$

f is an eigenfunction (eigenvector) of $\hat{\Omega}$

ω is the corresponding eigenvalue

Construction of Q.M. Operators

- Write the classical expression for the observable of interest in terms of space coordinates, linear momenta and time.

- Linear coordinates and time are unchanged.

- Replace linear momentum p_q by $\dfrac{\hbar}{i}\dfrac{\partial}{\partial q}$.

- The operator for the total energy is $-\dfrac{\hbar}{i}\dfrac{\partial}{\partial t}$.

observable	classical expression	operator
position	x	x
momentum	$p_x = m\dot{x}$	$(\hbar/i)\partial/\partial x$
kinetic energy	$T = p^2/2m$ $= \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$	$-\dfrac{\hbar^2}{2m}\left(\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}\right)$
potential energy	$V(x,y,z)$	$V(x,y,z)$
total energy	$H = T+V$	$\widehat{H} = \hat{T} + V = -(\hbar/i)\partial/\partial t$
dipole moment	$d = \sum_i q_i \vec{r}_i$	$d = \sum_i q_i \vec{r}_i$
angular momentum	$\vec{L} = \vec{r} \wedge \vec{p}$	$\dfrac{\hbar}{i}\begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ x & y & z \\ \partial/\partial x & \partial/\partial y & \partial/\partial z \end{vmatrix}$
e.g. x component	$L_x = yp_z - zp_y$	$\hat{L}_x = \left(\dfrac{\hbar}{i}\right)\left(y\dfrac{\partial}{\partial z} - z\dfrac{\partial}{\partial y}\right)$

Expectation Values

The expectation value of the operator Ω is defined by

$$\langle \Omega \rangle = \int \psi^* \hat{\Omega} \psi \, d\tau \qquad \qquad \Psi \text{ is assumed to be normalized:}$$

If Ψ is an eigenfunction of Ω: $\qquad \hat{\Omega}\psi = \omega\psi$

$$\langle \Omega \rangle = \int \psi^* \omega\psi \, d\tau = \omega \int \psi^* \psi \, d\tau = \omega$$

Every measurement of the property Ω gives the eigenvalue ω.

Suppose Ψ is *not* an eigenfunction of Ω.
It can be expressed as a linear combination of eigenfunctions, e.g.:

$$\Psi = c_1\psi_1 + c_2\psi_2$$

Then
$$\langle \Omega \rangle = \int (c_1\psi_1 + c_2\psi_2)^* \hat{\Omega} (c_1\psi_1 + c_2\psi_2) \, d\tau$$

$$= \int (c_1\psi_1 + c_2\psi_2)^* (c_1\omega_1\psi_1 + c_2\omega_2\psi_2) \, d\tau$$

$$= c_1^* c_1 \omega_1 \int \psi_1^* \psi_1 \, d\tau + c_2^* c_2 \omega_2 \int \psi_2^* \psi_2 \, d\tau$$

$$+ c_1^* c_2 \omega_2 \int \psi_1^* \psi_2 \, d\tau + c_2^* c_1 \omega_1 \int \psi_2^* \psi_1 \, d\tau$$

$$= c_1^* c_1 \omega_1 + c_2^* c_2 \omega_2 = |c_1|^2 \omega_1 + |c_2|^2 \omega_2$$

A *single* measurement gives ω_1 or ω_2.
A series of measurements gives the *weighted average*.

Heisenberg Uncertainty Principle

There exist pairs of observables whose values may not be known simultaneously to better precision than a certain constant.

e.g. position q and linear momentum p_q $\delta(p_q)\delta(q) \geqslant \hbar/2$

energy and lifetime $\delta(E)\delta(t) \geqslant \hbar/2$

The Uncertainty Principle is a consequence of the probabilistic interpretation of ψ. Even if ψ is known exactly it is only possible to calculate the probability of finding it in a given region of space.
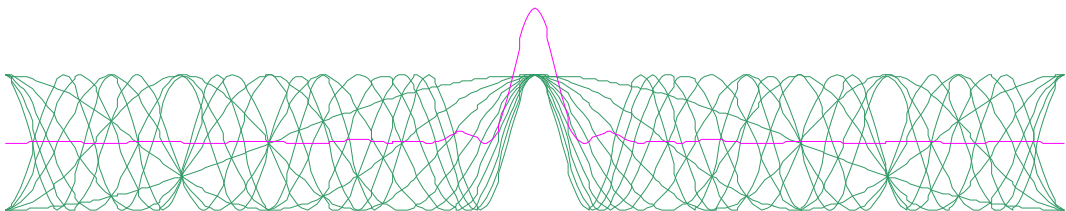
Suppose the momentum of a moving particle is known exactly:

$\psi = \exp(ipx/\hbar)$ $\dfrac{\hbar}{i}\dfrac{\partial \psi}{\partial x} = p\psi$ p is an eigenvalue
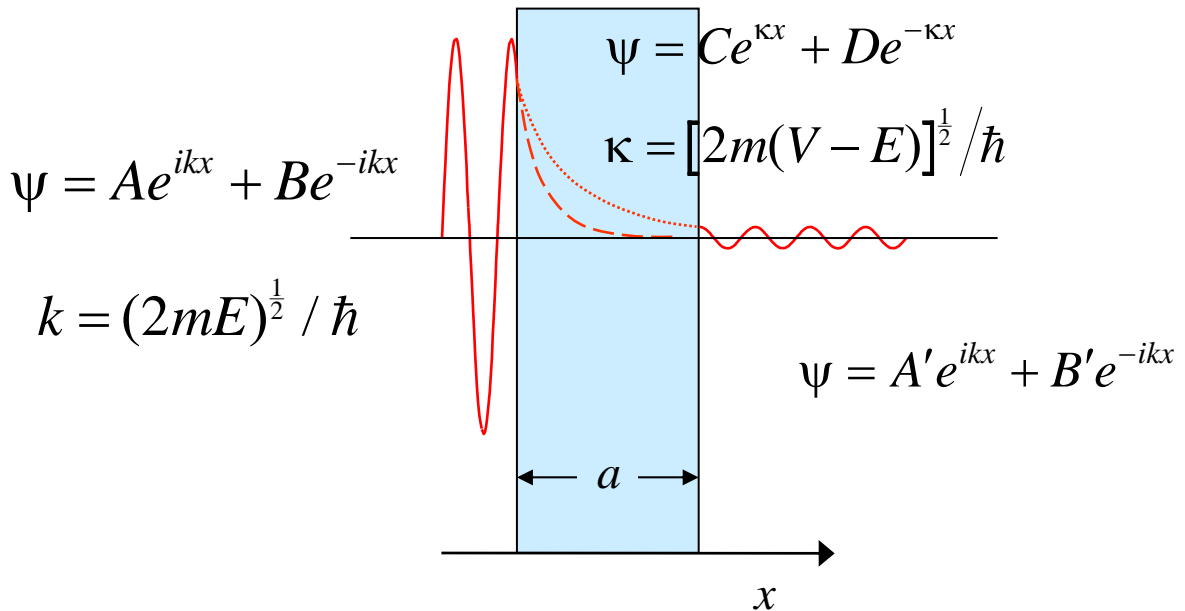
but $\psi^*\psi = 1$ constant everywhere!

Suppose the position of the particle is known precisely, i.e. the probability density peaks at a point.

Such localization is described by a wave packet formed by the superposition of many waves with a large spread of frequencies.

Tunnelling

Consider a particle of energy E striking a potential barrier of height V.

$$\psi = Ce^{\kappa x} + De^{-\kappa x}$$

$$\kappa = \left[2m(V-E)\right]^{\frac{1}{2}} \big/ \hbar$$

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

$$k = (2mE)^{\frac{1}{2}} / \hbar$$

$$\psi = A'e^{ikx} + B'e^{-ikx}$$

a

x

Application of boundary conditions gives the transmission probability:
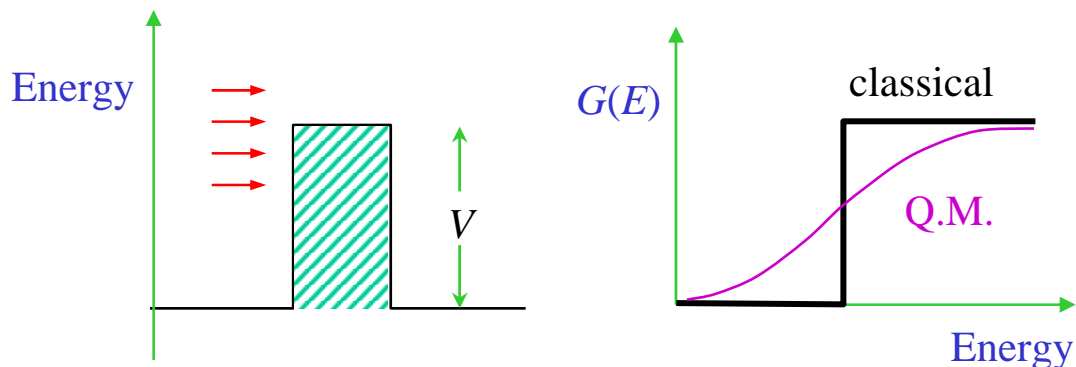
$$T = \frac{A'^2}{A^2} = \left\{ 1 + \frac{\left(e^{\kappa a} - e^{-\kappa a}\right)^2}{16\frac{E}{V}\left(1 - \frac{E}{V}\right)} \right\}^{-1}$$

Tunnelling depends on the mass of the particle, its energy (compared to the barrier), and the width of the barrier.

Tunnelling in Chemical Reactions

Sometimes reactions occur even if the reactants have $E < E_{act}$.

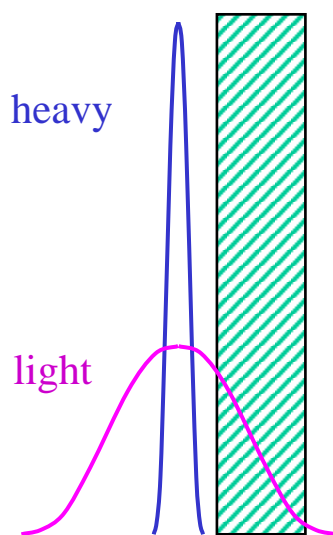This is tunnelling, a consequence of the wave nature of matter.

Energy

V

$G(E)$

classical

Q.M.

Energy

The transmission coefficient G depends on E-V, the barrier width, and the particle mass.

Tunnelling is only important for light particles (H, Mu, e$^-$).

This is because they have a large spread in their wave packets.

heavy

light

Tunnelling occurs if the wave packet width $\gtrsim$ barrier width.