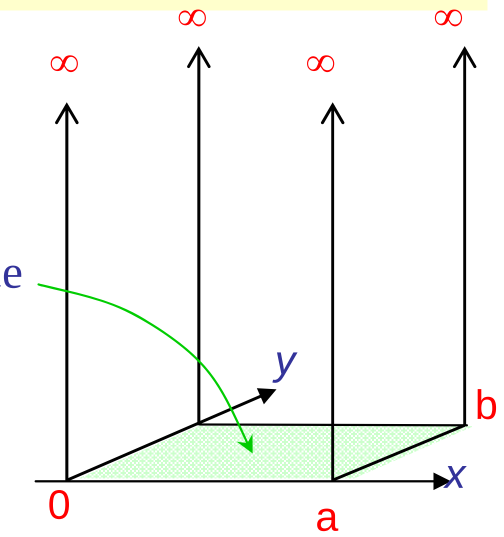
The Particle in a 2-D Box

$$\hat{H}\psi = E\psi \quad \text{where} \quad \hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + V(x,y)$$

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

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



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

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

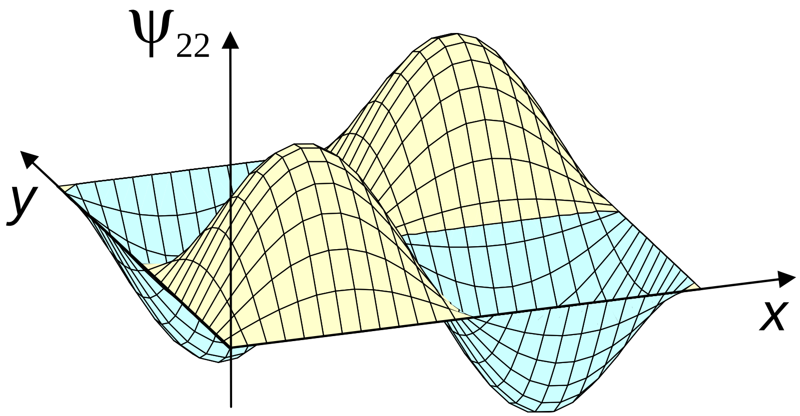
then
$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} + \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} = -\frac{2m}{\hbar^2}E_{n1,n2} = -\frac{2m}{\hbar^2}(E_{n1} + E_{n2})$$

i.e.
$$\frac{\partial^2 X_{n1}}{\partial x^2} = -\frac{2mE_{n1}}{\hbar^2}X_{n1} \quad \text{and} \quad \frac{\partial^2 Y_{n2}}{\partial y^2} = -\frac{2mE_{n2}}{\hbar^2}Y_{n2}$$

and from 1-D solutions:
$$\psi_{n1,n2} = \frac{2}{\sqrt{ab}}\sin\left(n_1\frac{\pi x}{a}\right)\sin\left(n_2\frac{\pi y}{b}\right)$$

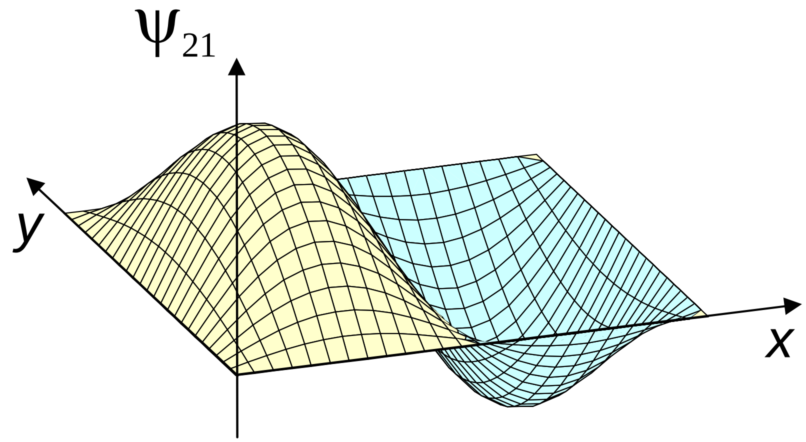
$$E_{n1,n2} = \left(\frac{\pi^2\hbar^2}{2m}\right)\left(\frac{n_1^{\,2}}{a^2} + \frac{n_2^{\,2}}{b^2}\right)$$

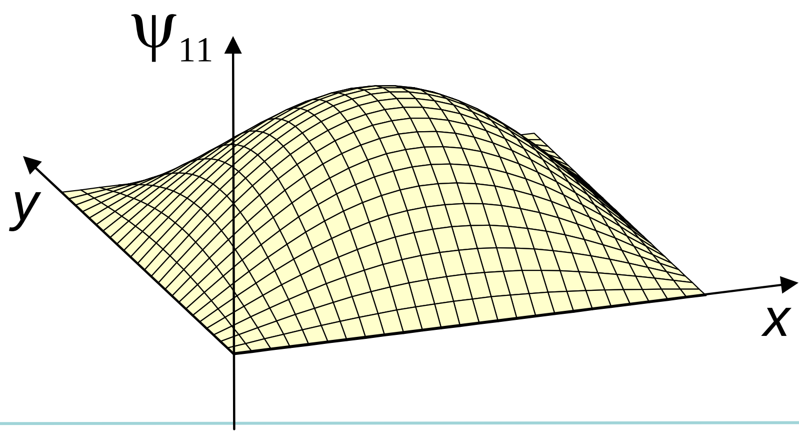
The Particle in a 2-D Box – Solutions



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

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



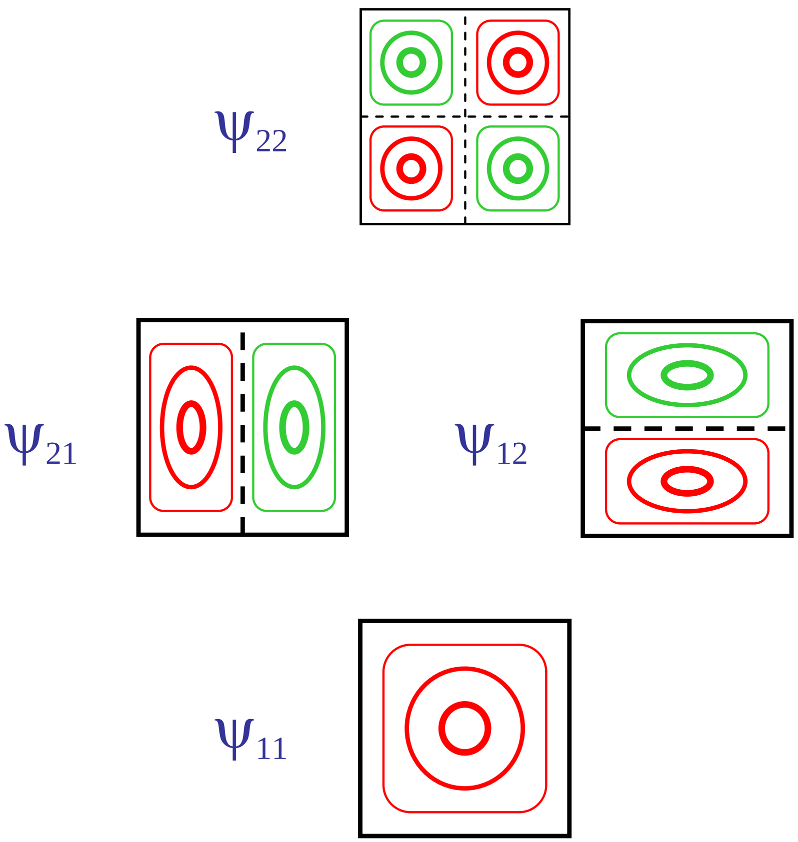


$$E_{11} = \left(\frac{\pi^2\hbar^2}{2m}\right)\left(\frac{1}{a^2} + \frac{1}{b^2}\right)$$

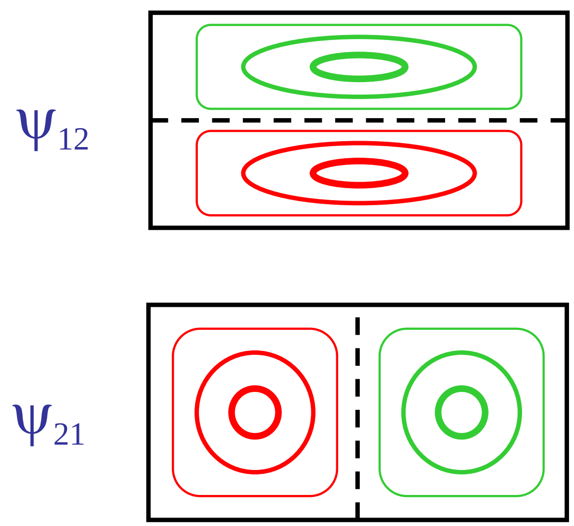
The Particle in a 2-D Box – Degeneracy

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

For the square well ($a = b$) $\quad \psi_{n1,n2} \neq \psi_{n2,n1}$ but $E_{n1,n2} = E_{n2,n1} = \dfrac{\pi^2\hbar^2}{2m}\left(\dfrac{n_1^{\,2} + n_2^{\,2}}{a^2}\right)$



Not so for $a \neq b$!



$$\frac{1}{a^2} + \frac{4}{b^2} \neq \frac{4}{a^2} + \frac{1}{b^2} \quad \text{unless} \quad a = b$$

Operators

An operator changes a function into another in a specific manner: $\hat{\Omega} f = g$

e.g. Suppose $f = f(x) = x^2 + 2x + 1$

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

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

Not all the usual rules of algebra apply to operators!

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

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

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

} 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 $\hat{A} = x,\ \hat{B} = \mathrm{d}/\mathrm{d}x$

$$\hat{A}\hat{B} f = 2x^2 + 2x,$$

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

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

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 $\frac{\hbar}{i}\frac{\partial}{\partial q}$.
- The operator for the total energy is $-\frac{\hbar}{i}\frac{\partial}{\partial t}$.
- All other properties (observables) can be expressed as some combination of the above.

For example, because the dipole moment depends on coordinates, the operator looks just like the classical expression: $d = \sum_i q_i \vec{r}_i$

Examples of Q.M. Operators

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

Expectation Values

The expectation value of the operator Ω is defined by

$$\langle\Omega\rangle = \int \psi^* \hat{\Omega}\psi \; d\tau$$

Ψ is assumed to be normalized:

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

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

$\Rightarrow$ 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 set 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 $\qquad \delta(p_q)\delta(q) \geqslant \hbar/2$

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

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.

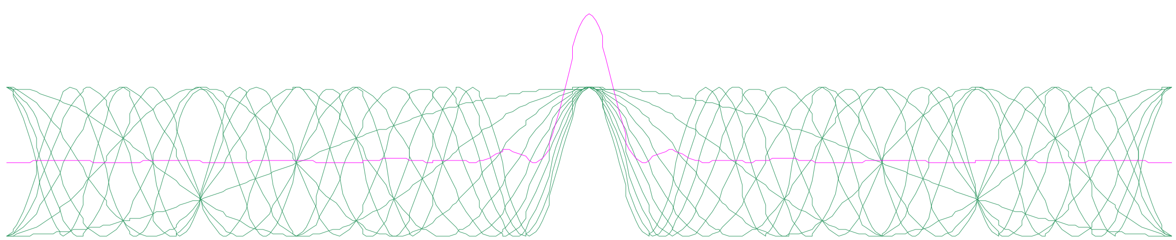
Suppose the momentum of a particle is known exactly:

$$\psi = \exp(ipx/\hbar) \qquad \frac{\hbar}{i}\frac{\partial\psi}{\partial x} = p\psi$$

p is an eigenvalue, but

$\psi^*\psi = 1$ is 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.



Commutation of Operators

Enrichment

If observables A and B can be precisely determined simultaneously, then the operators $\hat{A}$ and $\hat{B}$ must commute.

If the state function is simultaneously an eigenfunction of $\hat{A}$ and $\hat{B}$, then $\left[\hat{A},\hat{B}\right]=0$

Proof $$\left[\hat{A},\hat{B}\right]\psi=\hat{A}\hat{B}\psi-\hat{B}\hat{A}\psi=b\hat{A}\psi-a\hat{B}\psi=ab\psi-ab\psi=0$$

If $\hat{A}$ and $\hat{B}$ commute, A and B can be determined simultaneously.

Proof Start with $\hat{A}\psi=a\psi$ and $\left[\hat{A},\hat{B}\right]=0$

$$\hat{A}\hat{B}\psi=\hat{B}\hat{A}\psi=a\hat{B}\psi,\ \text{i.e.}\ \hat{A}\left(\hat{B}\psi\right)=a\left(\hat{B}\psi\right)$$

Evidently $\left(\hat{B}\psi\right)$ is proportional to ψ assuming ψ is non-degenerate

Therefore $\hat{B}\psi=b\psi$

For degenerate wave functions it is necessary to prove that any linear combination is also an eigenfunction.

$$\hat{A}\psi_m=a\psi_m$$
$$\hat{A}\psi_n=a\psi_n$$

$$\hat{A}\left(c_m\psi_m+c_n\psi_n\right)=ac_m\psi_m+ac_n\psi_n=a\left(c_m\psi_m+c_n\psi_n\right)$$

and that the coefficients can always be chosen to produce mutually orthogonal linear combinations

The Uncertainty Principle

Enrichment

Take a pair of non-commuting operators $\hat{A}$ and $\hat{B}$ whose experimental observables are

$$\langle A \rangle = \langle \;|\hat{A}|\; \rangle, \quad \langle B \rangle = \langle \;|\hat{B}|\; \rangle$$

Define $\hat{C} = -i\left[\hat{A},\hat{B}\right] \neq 0$ and error operators $\hat{\Delta}_A = \hat{A} - \langle A \rangle, \quad \hat{\Delta}_B = \hat{B} - \langle B \rangle$

Then
$$\left[\hat{\Delta}_A, \hat{\Delta}_B\right] = \hat{A}\hat{B} - \langle A \rangle \hat{B} - \langle B \rangle \hat{A} + \langle A \rangle \langle B \rangle - \hat{B}\hat{A} + \langle B \rangle \hat{A} + \langle A \rangle \hat{B} - \langle A \rangle \langle B \rangle$$
$$= \left[\hat{A},\hat{B}\right] = i\hat{C}$$

Let $I(\alpha) = \int \left| \left(\alpha \hat{\Delta}_A - i\hat{\Delta}_B\right)\psi \right|^2 d\tau \quad \geq 0$ where α is an arbitrary real parameter

Then
$$I(\alpha) = \alpha^2 \langle \hat{\Delta}_A^2 \rangle - \left\langle i\alpha\left(\hat{\Delta}_A\hat{\Delta}_B - \hat{\Delta}_B\hat{\Delta}_A\right)\right\rangle + \langle \hat{\Delta}_B^2 \rangle = \alpha^2 \langle \hat{\Delta}_A^2 \rangle - \alpha \langle \hat{C} \rangle + \langle \hat{\Delta}_B^2 \rangle$$

Rearranging,
$$\langle \hat{\Delta}_A^2 \rangle \left[\alpha - \frac{1}{2}\frac{\langle \hat{C} \rangle}{\langle \hat{\Delta}_A^2 \rangle}\right]^2 - \frac{1}{4}\frac{\langle \hat{C} \rangle^2}{\langle \hat{\Delta}_A^2 \rangle} + \langle \hat{\Delta}_B^2 \rangle \geq 0$$

which has a minimum at $\alpha = \dfrac{1}{2}\dfrac{\langle \hat{C} \rangle}{\langle \hat{\Delta}_A^2 \rangle}$ for which $-\tfrac{1}{4}\langle \hat{C} \rangle^2 + \langle \hat{\Delta}_A^2 \rangle \langle \hat{\Delta}_B^2 \rangle \geq 0$

Taking square roots $\langle \hat{\Delta}_A^2 \rangle^{1/2} \langle \hat{\Delta}_B^2 \rangle^{1/2} \geq \tfrac{1}{2}\langle \hat{C} \rangle$ or $\sigma_A \sigma_B \geq \dfrac{1}{2i}\left[\hat{A},\hat{B}\right]$

Solutions for the Particle in a Finite Box

Enrichment

The energy levels are given by $E = \varepsilon V_0$ where ε is a dimensionless parameter which satisfies the equation

$$(2\varepsilon - 1)\sin\left(b\varepsilon^{1/2}\right) - 2\left(\varepsilon - \varepsilon^2\right)^{1/2}\cos\left(b\varepsilon^{1/2}\right) = 0 \qquad \text{where} \qquad b = (2mV_0)^{1/2}\, a/\hbar$$

best solved numerically

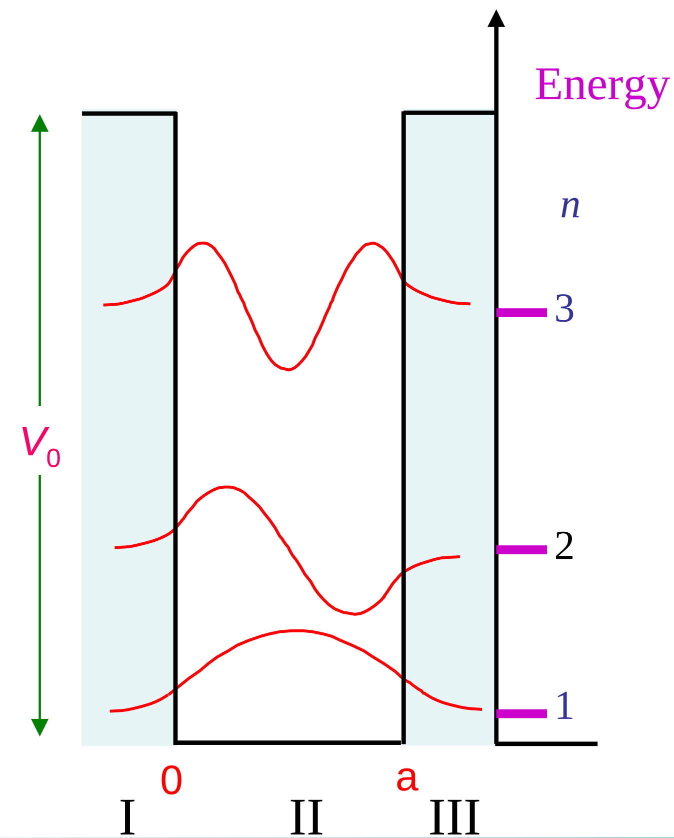
The number of bound states is given by $N - 1 < b/\pi \leqslant N$

The wave functions are

$$\psi_{\mathrm{I}} = A\exp\{\kappa x\} \qquad \kappa = \left[2m(V_0 - E)/\hbar^2\right]^{1/2} \qquad x < 0$$

$$\psi_{\mathrm{II}} = A\cos\left[(2mE)^{1/2}\, x/\hbar\right] + B\sin\left[(2mE)^{1/2}\, x/\hbar\right]$$

$$\psi_{\mathrm{III}} = G\exp\{-\kappa x\} \qquad \kappa = \left[2m(V_0 - E)/\hbar^2\right]^{1/2} \qquad x > 0$$



- Inside the box the functions look like those of the infinite well.
- The wave functions penetrate the walls and decay exponentially.

Tunnelling

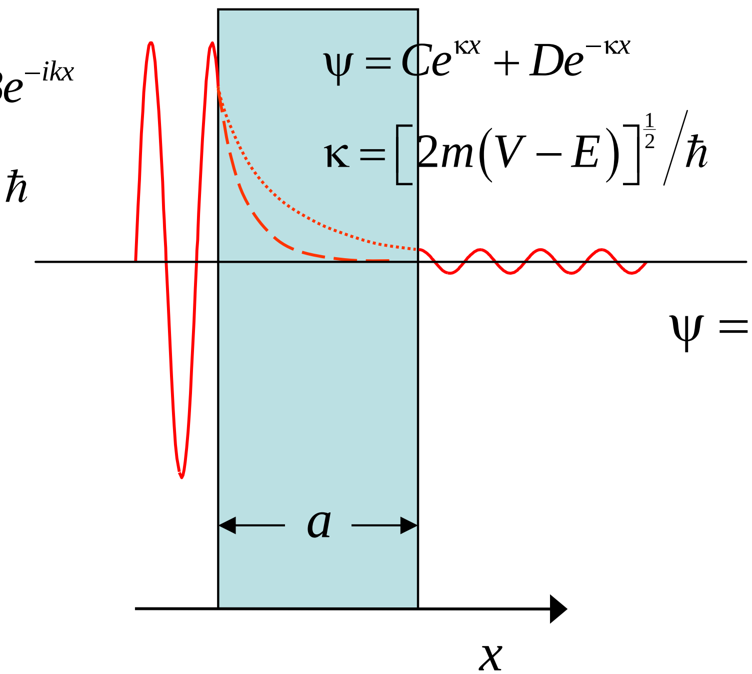
Consider a particle of energy E striking a potential barrier of height V.

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

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

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

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



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

Application of boundary conditions gives the transmission probability:

$$G = \frac{A'^2}{A^2} = \left\{ 1 + \frac{\left(e^{\kappa a} - e^{-\kappa a}\right)^2}{16\frac{E}{V}\left(1 - \frac{E}{V}\right)} \right\}^{-1}$$

Tunnelling depends on:

- the mass of the particle
- its energy (compared to the barrier)
- the width of the barrier