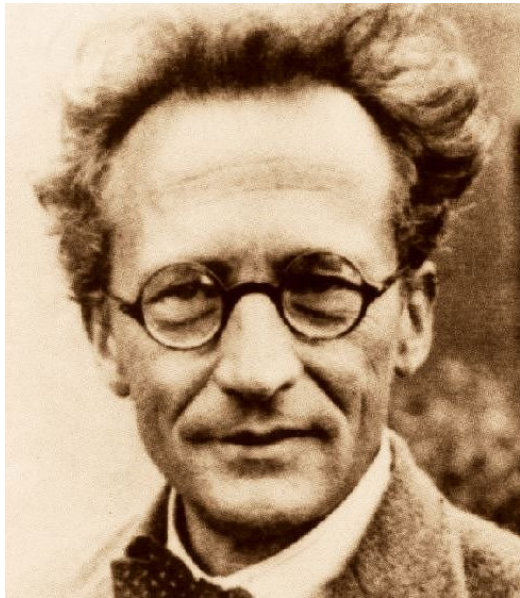


# 15. Wavefunction formulation of Schrodinger's equation



$$\psi(t)$$

# Recap: Schrodinger's equation

The form of the Schrodinger equation is

$$\boxed{\text{vector}} \quad |\psi(t)\rangle = \boxed{\text{matrix}} \quad \exp\left(-\frac{it}{\hbar} H\right) \boxed{\text{vector}} \quad |\psi(0)\rangle$$

The operator (i.e. matrix)  $U = \exp\left(-\frac{it}{\hbar} H\right)$  takes the state and time evolves it forward.

The Hamiltonian is a Hermitian matrix, and this makes U always a “unitary matrix”

$$U^{-1} = U^+$$

Generally it is not a simple task to find the explicit unitary matrix from a Hamiltonian, except in certain simple cases. Solving the Schrodinger's equation is a difficult task.

Hamiltonian=The physical process changing the state

t=The amount of time the process is applied for

U=The effect this has on the state

# Wavefunction formulation

Actually the way we showed the Schrodinger equation is not the usual way it is written. Usually it is written as a differential equation

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

Here:

$m$  = mass of particle

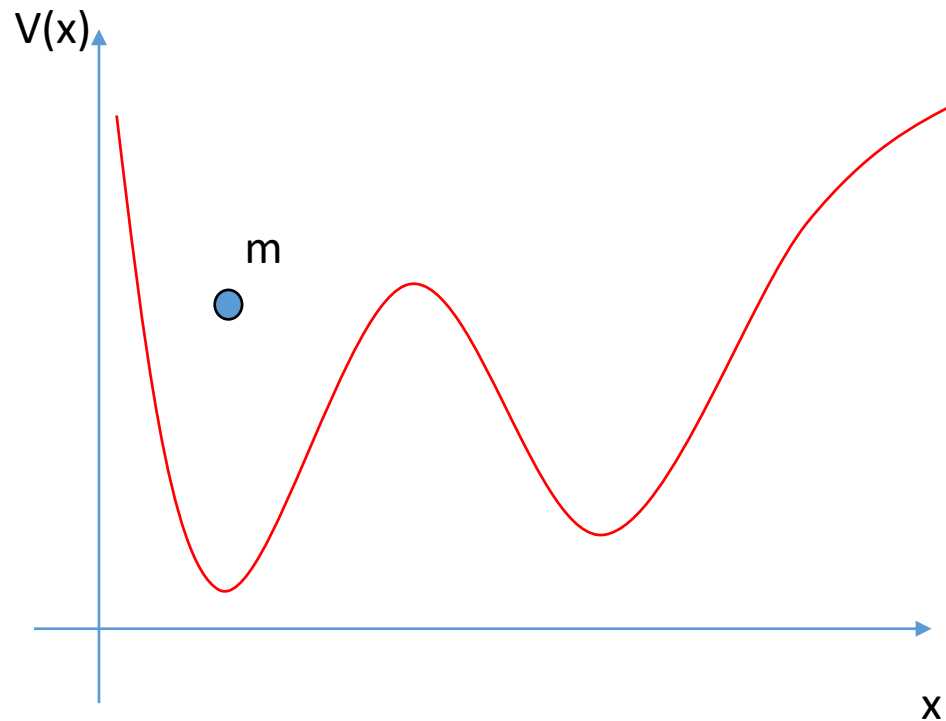
$x$  = position of particle

$V(x)$  = potential energy of particle

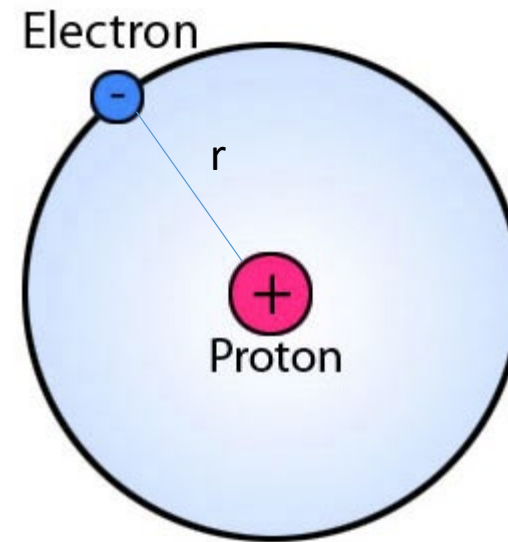
This looks quite different to the matrix formulation that we saw before. Yet it is actually equivalent (a special case actually) to the previous version. How is this possible?

# The problem setting

We have a particle of mass  $m$  in some potential energy landscape such as that below:



Example: electron in an atom

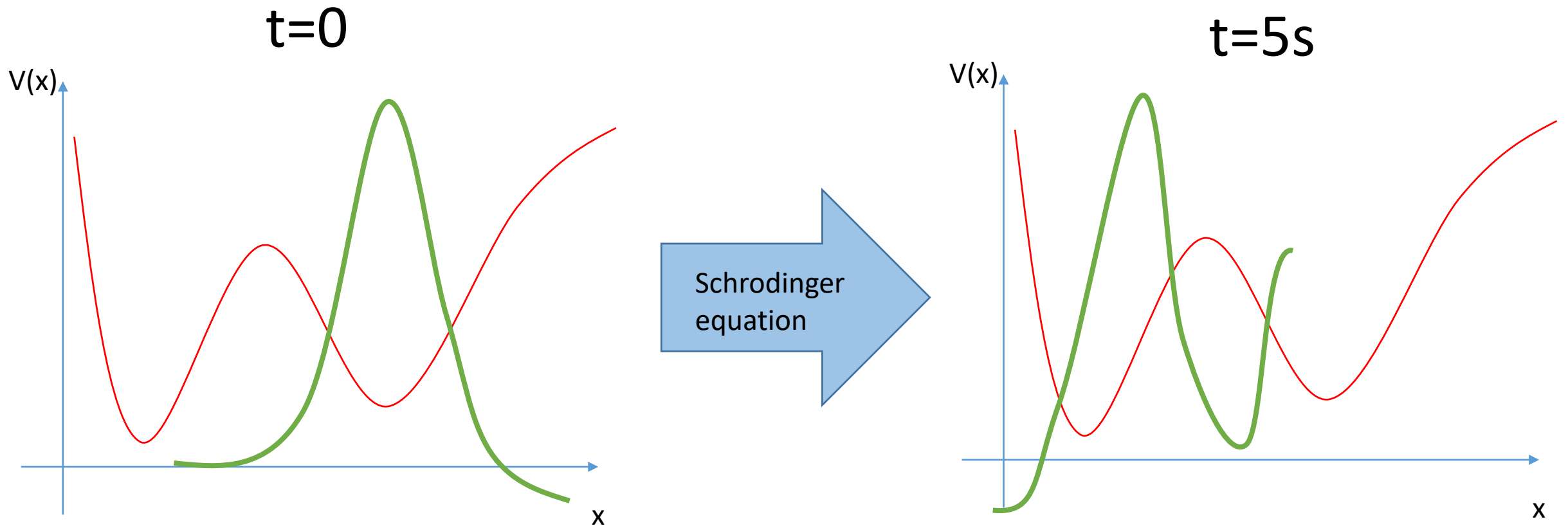


$$m = 9.1 \times 10^{-31} \text{ kg}$$

$$V(r) = -\frac{e^2}{4\pi\epsilon r}$$

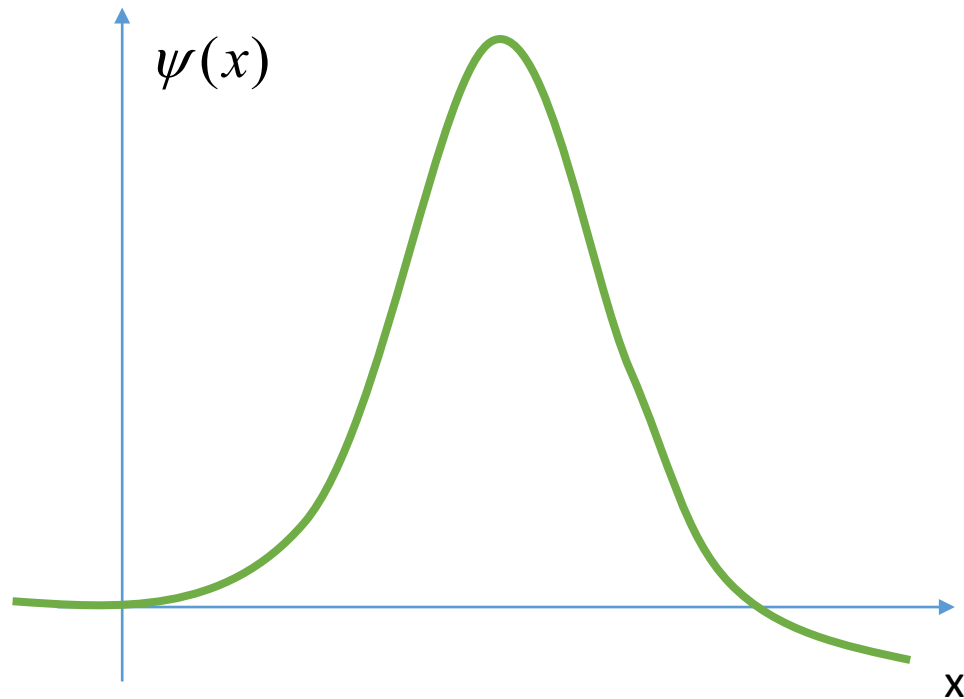
# Time evolution of the wavefunction

Then what the Schrodinger equation does is to predict how the wavefunction evolves in time.



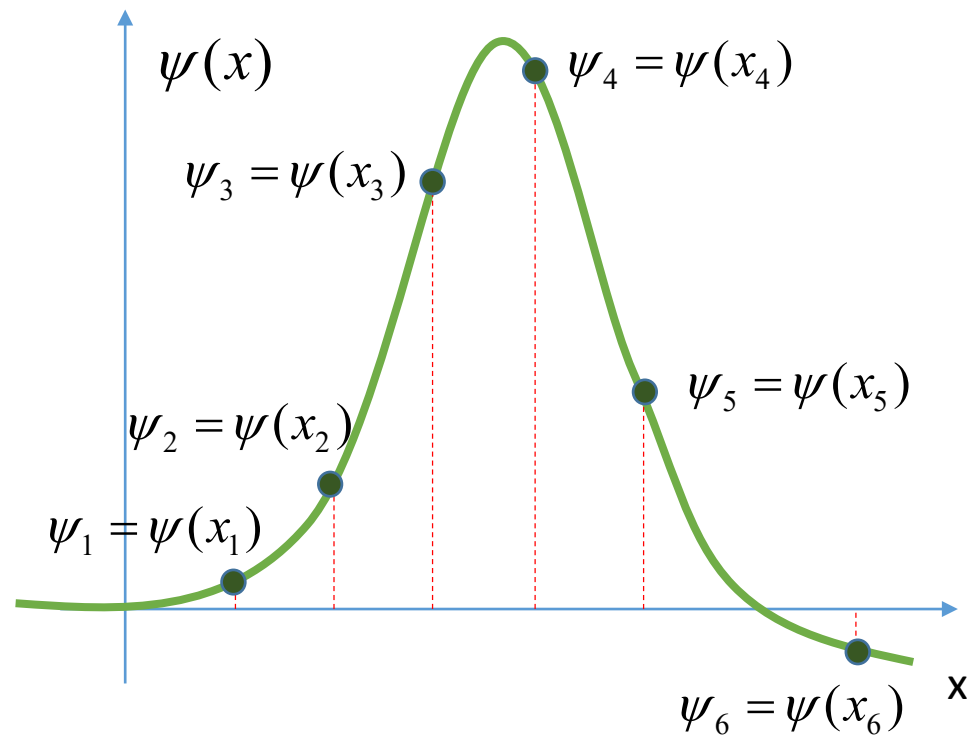
# Continuous wavefunctions

One obvious difference here is that the wavefunction is a function  $\psi(x)$  and not a vector  $|\psi\rangle$ .



# Continuous wavefunctions

One obvious difference here is that the wavefunction is a function  $\psi(x)$  and not a vector  $|\psi\rangle$ .



$$|\psi\rangle = \begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \vdots \end{pmatrix}$$

We can always turn a continuous wavefunction into a vector by taking a discrete sample of points. Then by taking the points very close we can represent the function in the same way. Actually we can do this in other ways such as Fourier analysis or Bessel functions, or any other set of orthogonal functions.

# The kinetic energy term

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

What is this weird looking term here?

If we define the momentum operator as  $\hat{p} = -i\hbar \frac{d}{dx}$

Then we can equally write  $-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} = \frac{\hat{p}^2}{2m}$  which is the kinetic energy

So the Schrodinger equation is  $i\hbar \frac{d\psi}{dt} = H\psi$

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

Or equivalently  $\psi(t) = \exp(-\frac{it}{\hbar} H)\psi(0)$

Kinetic energy

Potential energy



# The momentum operator

But why is the momentum operator like  $\hat{p} = -i\hbar \frac{d}{dx}$  ?

Recall that de Broglie's relation said that  $p = \frac{h}{\lambda}$

Say we have a wavefunction like a plane wave

$$\psi(x) = e^{ikx} = e^{2\pi ix/\lambda}$$

Then

$$\hat{p}\psi(x) = -i\hbar \frac{d}{dx} (e^{2\pi ix/\lambda}) = -\frac{i\hbar 2\pi i}{\lambda} e^{2\pi ix/\lambda} = \frac{h}{\lambda} e^{2\pi ix/\lambda}$$

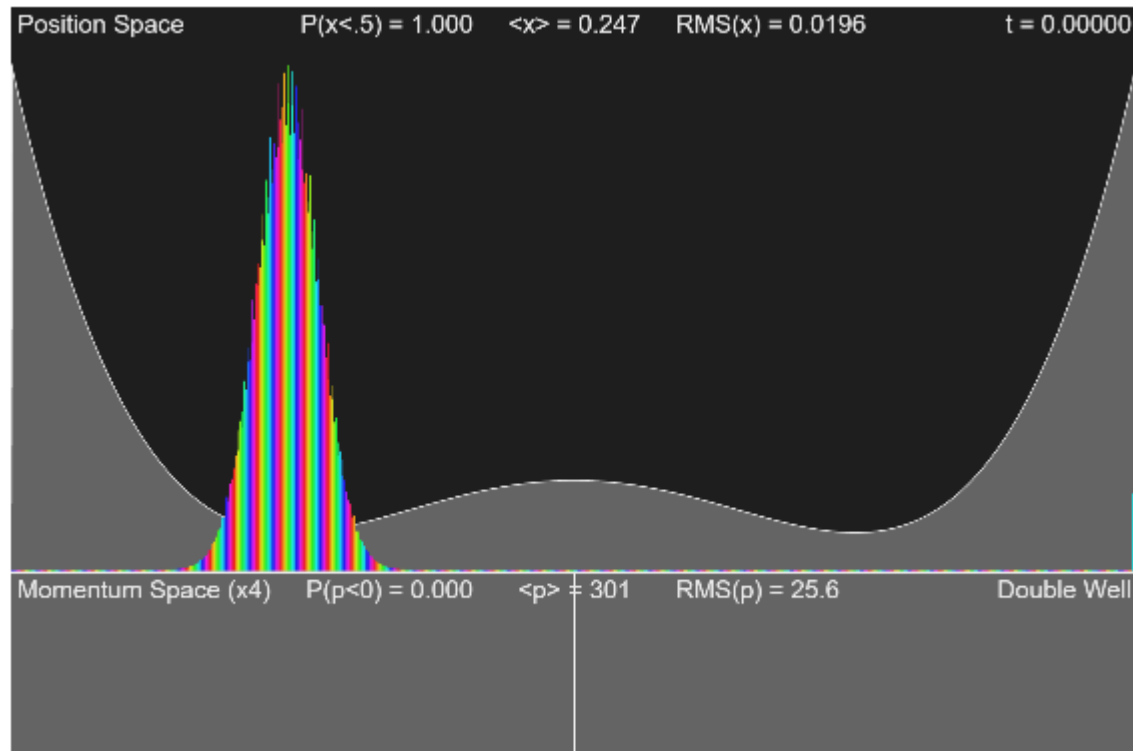
De Broglie momentum is the eigenvalue (so expectation value is too).

# Numerical time evolution

The best way to understand how the Schrodinger equation work is to play with the equation.

Look at <http://schrodingerequation.online/> for a numerical solver.

$$V(x)$$



Potential:

☐ Harmonic ☒ Double well ☐ Infinite square well ☐ Barrier ☐ Step ☐ Customized

Potential parameters:

Potential height:

Custom potential function:

Initial state:

☒ Gaussian pulse ☐ Harmonic ground state ☐ Harmonic potential 1st excited ☐ Infinite well nth excited state ☐ Customized

Initial state parameters:

Level n:

Position:

Velocity:

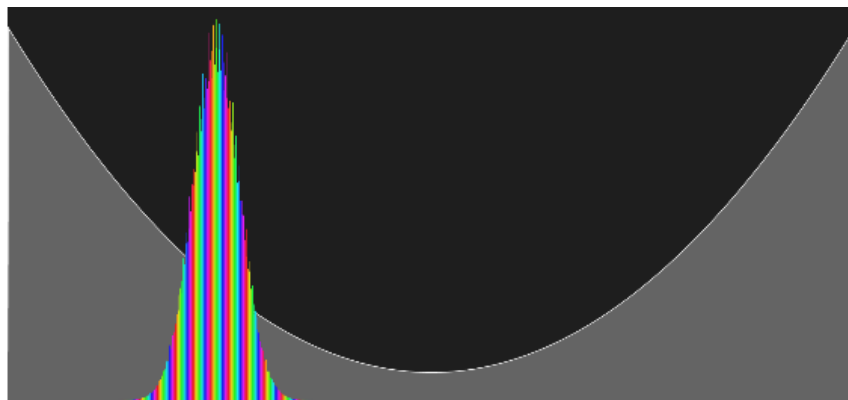
Variance:

Custom wavefunction:

Controls

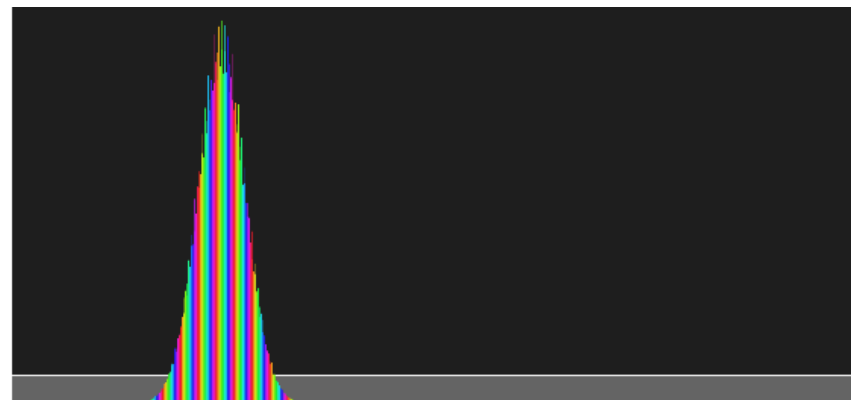
$$\psi(x, t = 0)$$

# Potential shapes



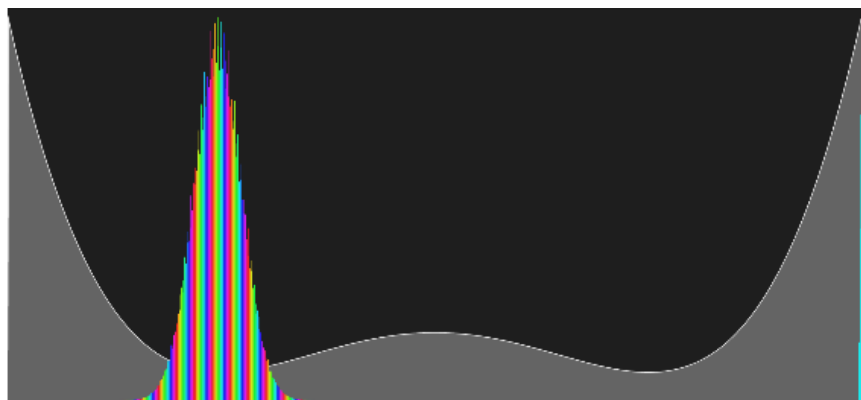
Harmonic

$$V(x) = \frac{1}{2}x^2$$



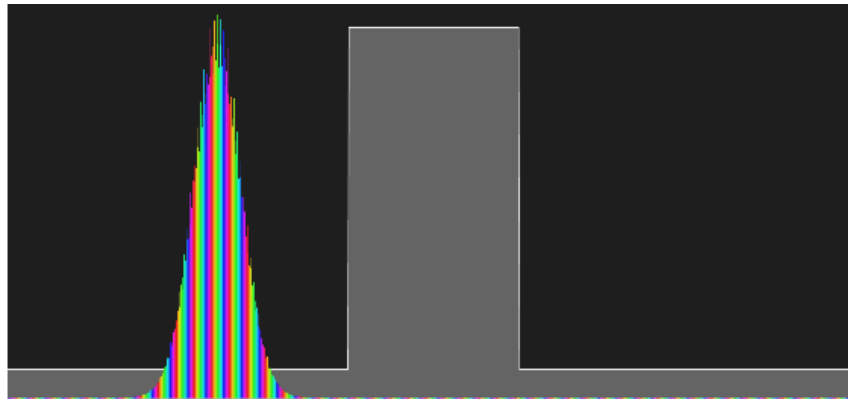
Infinite square well

$$V(x) = \begin{cases} 0 & 0 < x < 1 \\ \infty & \text{otherwise} \end{cases}$$

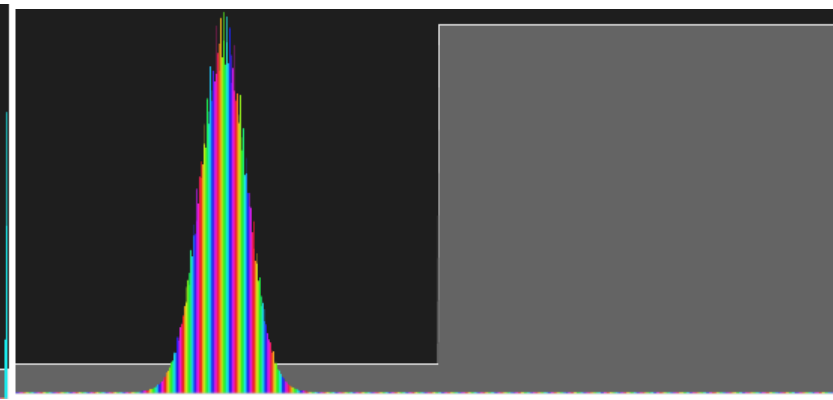


Double well

$$V(x) = (x - 1/4)^2 (x - 3/4)^2$$

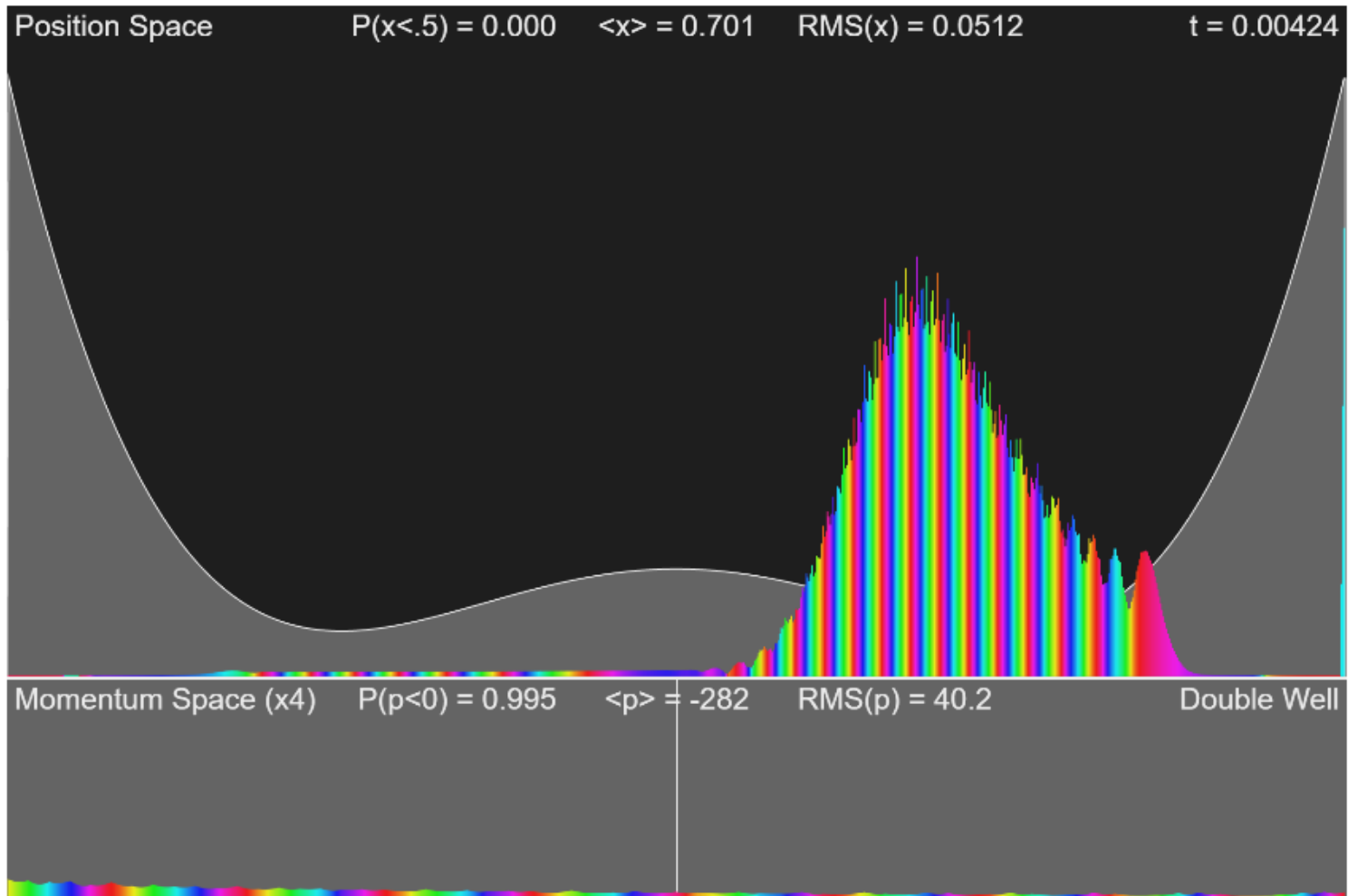


Barrier



Step

# Wavefunction



Plotted is the magnitude of the wavefunction  $|\psi(x)|$

The phase of the wavefunction

$$\arg(\psi(x))$$

Is shown as the colour



# Stationary states

Using the preset initial states for the harmonic oscillator and infinite square well

These are special wavefunctions that do not evolve in time, except for the phase.

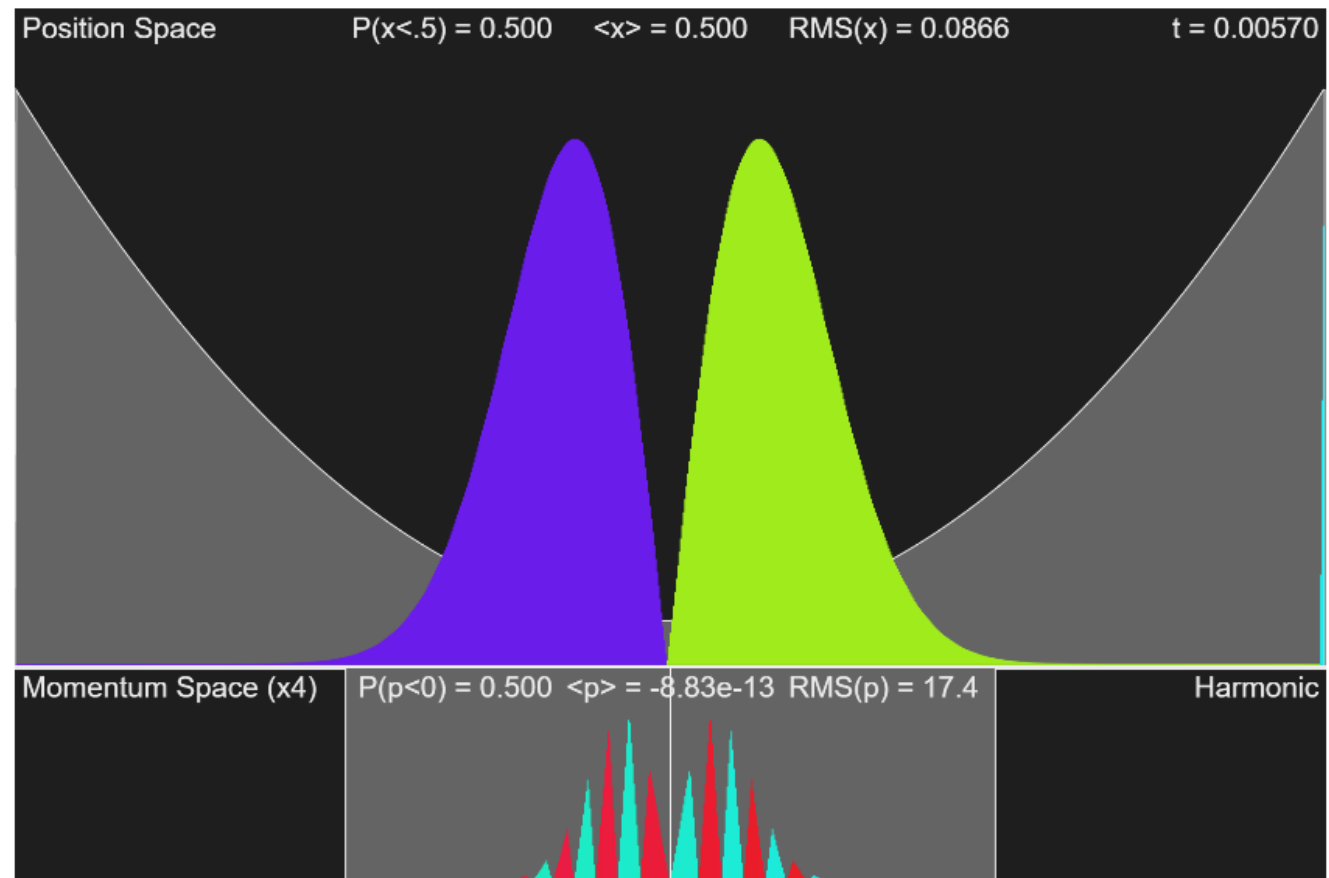
These states satisfy

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

Then

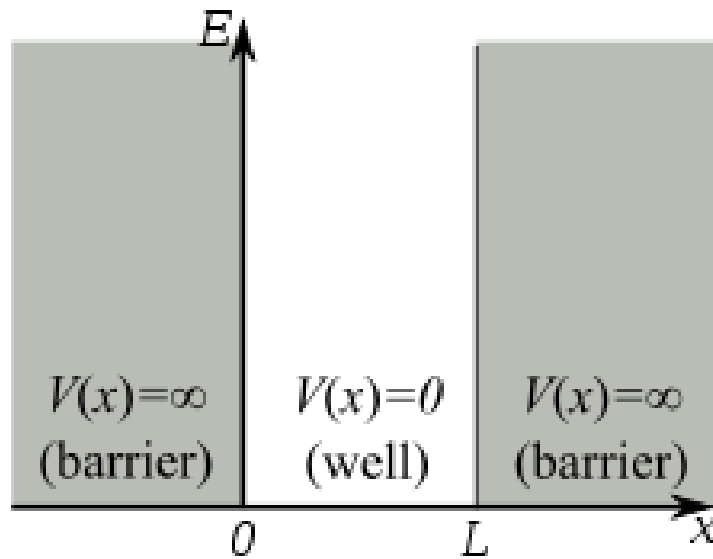
$$\psi(t) = \exp\left(-\frac{it}{\hbar} H\right) \psi(0) = e^{-itE/\hbar} \psi(0)$$

Only the phase changes. These are stable states in the evolution.



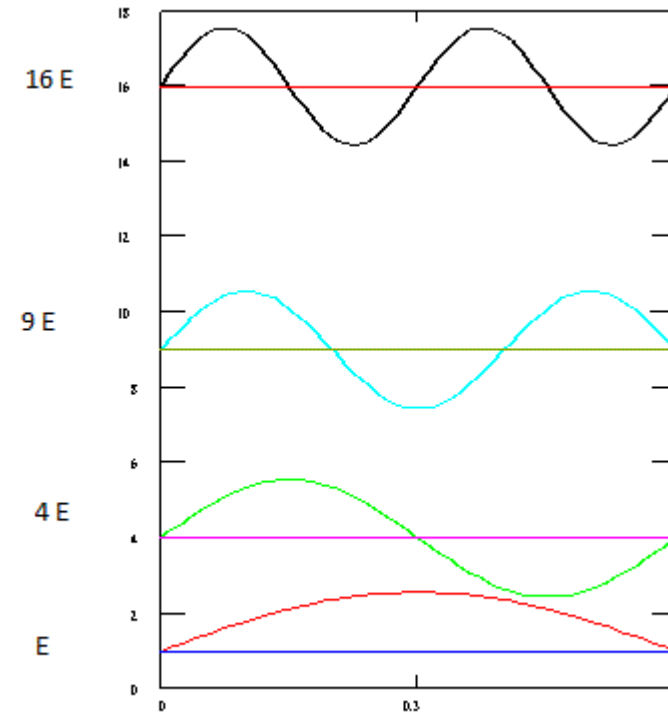
# Infinite square well

The potential  $V(x)$



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

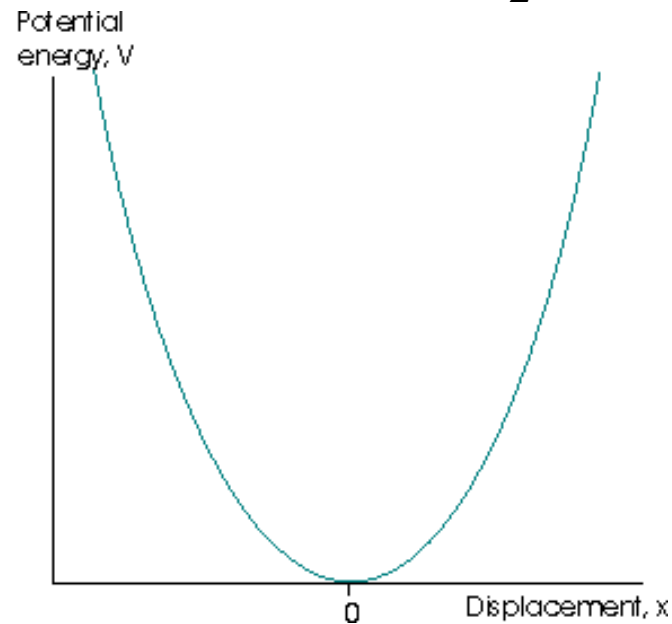
Wavefunction  $\psi(x)$



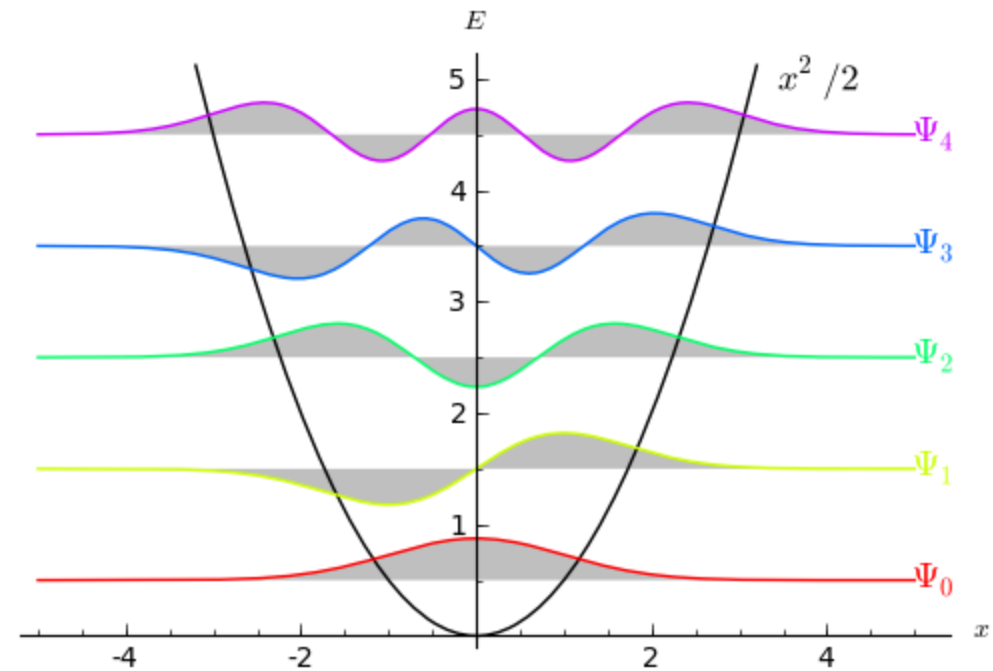
$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

# Harmonic oscillator

The potential  $V(x) = \frac{1}{2}m\omega^2 x^2$



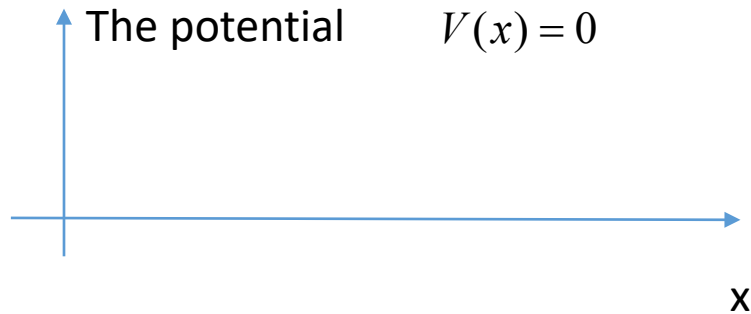
$$E_n = \hbar\omega \left( n + \frac{1}{2} \right)$$



$$\psi_n(x) = \frac{1}{\sqrt{2^n n!}} \cdot \left( \frac{m\omega}{\pi\hbar} \right)^{1/4} \cdot e^{-\frac{m\omega x^2}{2\hbar}} \cdot H_n \left( \sqrt{\frac{m\omega}{\hbar}} x \right), \quad n = 0, 1, 2, \dots$$

Hermite  
polynomials

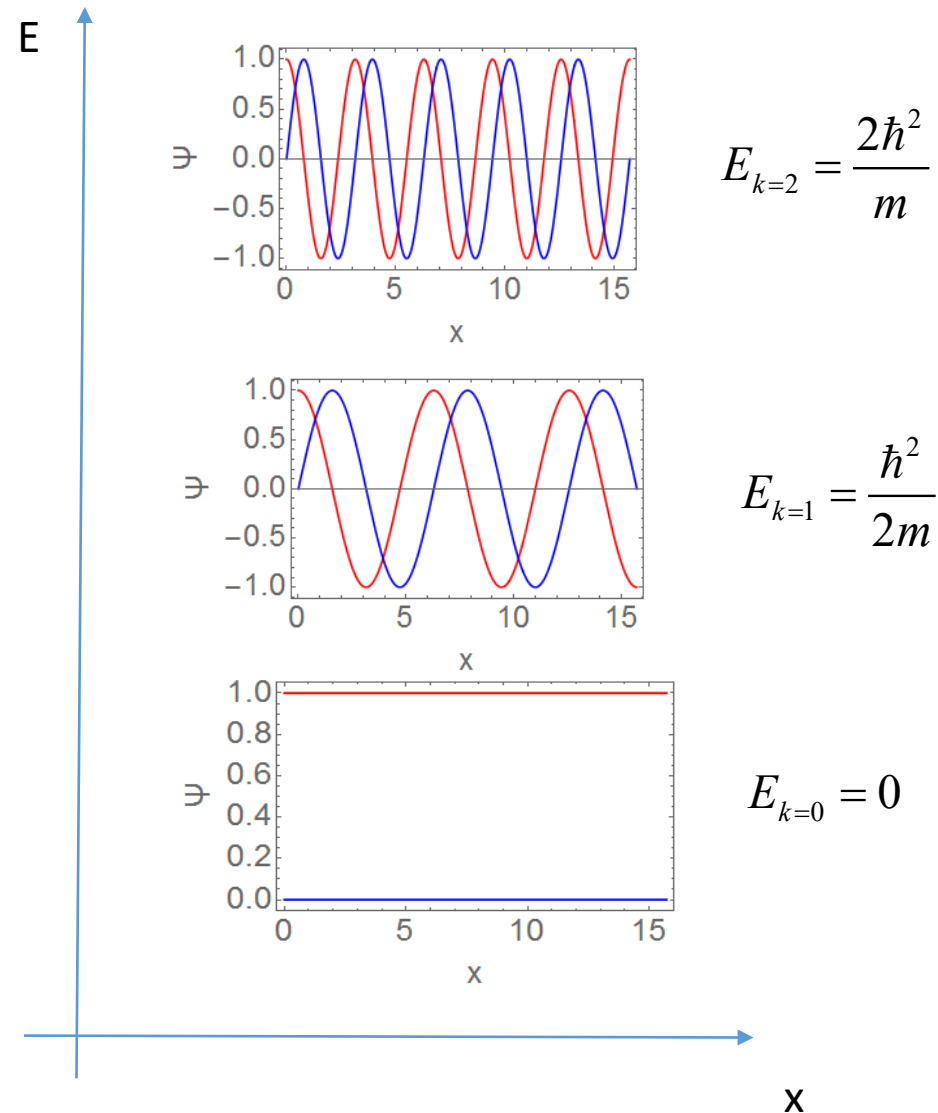
# Free particle



$$E_k = \frac{\hbar^2 k^2}{2m}$$

$$k = \frac{2\pi}{\lambda}$$

Consistent with de Broglie:  $p = h / \lambda$

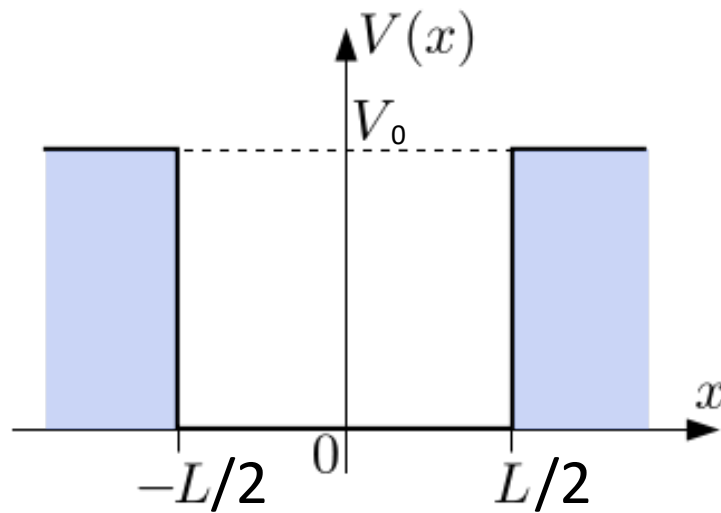


$k$  is NOT discrete!

$$\psi_k(x) = e^{ikx}$$



# Finite square well

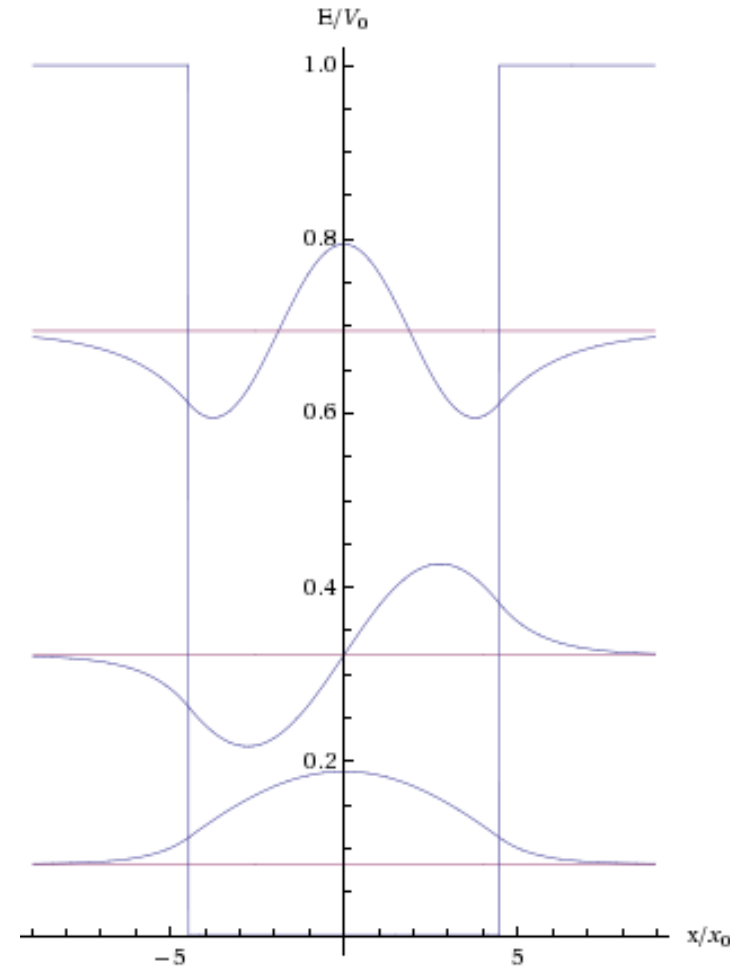


$$E_n = \frac{2\hbar^2 v_n^2}{mL^2}$$

Where  $v_n$  solutions of

$$\sqrt{u_0^2 - v^2} = \begin{cases} v \tan v, & \text{(symmetric case)} \\ -v \cot v, & \text{(antisymmetric case)} \end{cases}$$

$$u_0^2 = mL^2 V_0 / 2\hbar^2$$



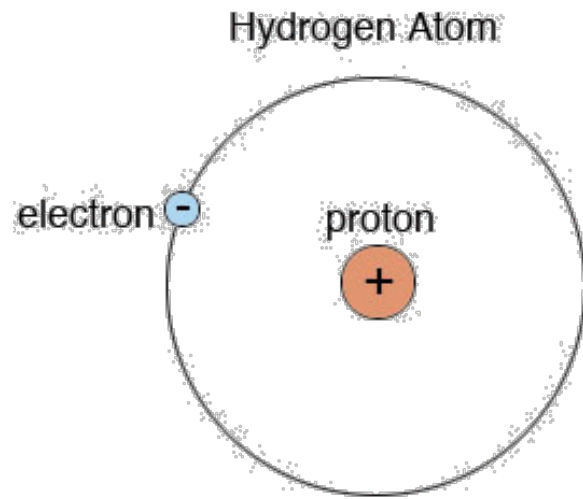
$$\psi_1 = Fe^{-\alpha x} + Ge^{\alpha x}$$

$$\psi_2 = A \sin(kx) + B \cos(kx)$$

$$\psi_3 = He^{-\alpha x} + Ie^{\alpha x}$$

A,B,F,G,H,I =  
coefficients such  
that the  
wavefunction is  
smooth

# Hydrogen atom



Coulomb law

$$V(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

$$E_n = -\frac{e^4 m}{32\hbar^2 \pi^2 \epsilon_0^2 n^2} \quad \begin{aligned} n &= 1, 2, 3, \dots \\ \ell &= 0, 1, 2, \dots, n-1 \\ m &= -\ell, \dots, \ell. \end{aligned}$$

$$\rho = \frac{2r}{na_0},$$

$a_0$  is the [Bohr radius](#),

$L_{n-\ell-1}^{2\ell+1}(\rho)$  is a [generalized Laguerre polynomial](#) of degree  $n - \ell - 1$ ,

$Y_\ell^m(\vartheta, \varphi)$  is a [spherical harmonic](#) function of degree  $\ell$  and order  $m$ .

## Hydrogen Wave Function

Probability density plots.

$$\psi_{nlm}(r, \vartheta, \varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]}} e^{-\rho/2} \rho^\ell L_{n-\ell-1}^{2\ell+1}(\rho) \cdot Y_{lm}(\vartheta, \varphi)$$

