Schrödinger's Cat

http://www.explosm.net/comics/949/

Wavefunctions

Wavefunctions are…

"Matter Waves"

From classical physics,

$$\psi(x) = e^{i2\pi x/\lambda} = \cos\left(\frac{2\pi x}{\lambda}\right) + i\sin\left(\frac{2\pi x}{\lambda}\right)$$

is a wave propagating in the positive *x* direction.

Using de Broglie's relation for a particle,

$$\psi(x) = \exp(ipx/\hbar) \qquad \hbar = h/2\pi$$

Solutions of the Schrödinger Equation

The wavefunction $\Psi(r,t)$ for a system is a solution of the Schrödinger equation, a differential equation for the spatial (r) and temporal (t) behaviour of de Broglie waves.

Ψ contains all information about the dynamical properties of the system. In principle, all observable properties may be deduced by performing the appropriate mathematical operation on Ψ.

$\Psi(r,t)$ is a function of time and all the coordinates of all the particles that make up the system.

$\Psi(r,t)$ can be interpreted as the amplitude of the probability density for the spatial description of the system.

Properties of Wavefunctions

For a single particle wavefunction, $\psi(r)$

the probability density of the particle at r is $|\psi|^2 = \psi^*\psi$

i.e. probability of finding the particle in region dx is $\psi^*(x)\psi(x)dx$

or in volume $d\tau$ is $\psi^*(\tau)\psi(\tau)d\tau$

An acceptable wavefunction is …

- continuous — usually also $\partial\psi / \partial q$
- single-valued — actually $\psi^*\psi$
- finite everywhere — $\int \psi^*\psi \, d\tau = 1$

These limitations force ψ to obey boundary conditions which result in quantization i.e. only some solutions of the Schrödinger equation survive.

A wavefunction is normalized if $\int \psi^*\psi \, d\tau = 1$

Two wavefunctions ψ_1 and ψ_2 are orthogonal if $\int \psi_1^*\psi_2 \, d\tau = 0$

The Schrödinger Equation

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\Psi + V\Psi = i\hbar\frac{\partial}{\partial t}\Psi \quad \text{or} \quad \hat{\mathrm{H}}\Psi = i\hbar\frac{\partial}{\partial t}\Psi$$

the Laplacian (del squared): $\nabla^2 = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$

Assume $\Psi(r,t) = \psi(r)\phi(t)$ and $V = V(r)$

then $$-\frac{\hbar^2}{2m}\nabla^2\psi(r)\phi(t) + V(r)\psi(r)\phi(t) = i\hbar\psi(r)\frac{\mathrm{d}\phi(t)}{\mathrm{d}t}$$

i.e. $$-\frac{\hbar^2}{2m\psi}\nabla^2\psi + V(r) = \frac{i\hbar}{\phi}\frac{\mathrm{d}\phi}{\mathrm{d}t}$$

This equation is separable in ψ and ϕ :

$$\left.\begin{aligned} -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi &= E\psi \\ i\hbar\frac{\mathrm{d}\phi}{\mathrm{d}t} &= E\phi \end{aligned}\right\}$$

The time-independent Schrödinger equation

$$\hat{\mathrm{H}}\psi = E\psi$$

$$\phi(t) = C\mathrm{e}^{-iEt/\hbar}$$

$\Psi(r,t) = C\psi(r)\mathrm{e}^{-\mathrm{i}Et/\hbar}$ is a stationary state, because $\Psi^*\Psi = C^2\psi^*\psi$ is independent of time

The Free Particle

The translational motion of a single free particle moving in 1 dimension is described by

$\hat{\mathrm{H}}\psi_n = E_n\psi_n$ where $\hat{\mathrm{H}} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$ is an operator.

and $V = 0$ for a free particle.

i.e. $\frac{\mathrm{d}^2\psi_n}{\mathrm{d}x^2} = \left(\frac{-2mE_n}{\hbar^2}\right)\psi_n$ a 2nd-order differential equation

Solutions: $\psi_n = C\mathrm{e}^{ikx}$, $k^2 = 2mE_n/\hbar^2 = p_n{}^2/\hbar^2$

i.e. $\psi_n = C\mathrm{e}^{\pm ip_n x/\hbar}$ *n* labels different solutions

In general, $\psi_n = A\mathrm{e}^{+ip_n x/\hbar} + B\mathrm{e}^{-ip_n x/\hbar}$

This represents an oscillation with wavelength *h*/*p*, since

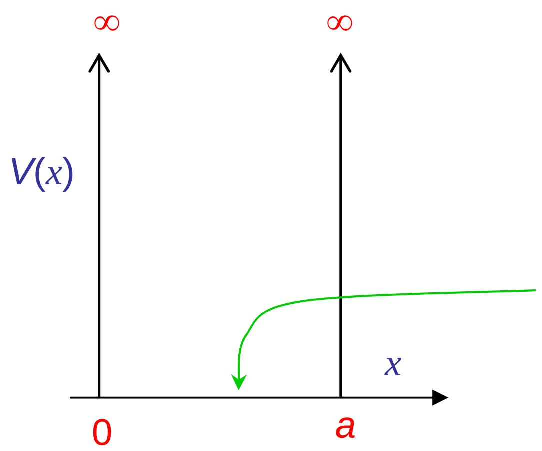
$$\exp\{\pm ipx/\hbar\} = \cos(2\pi x/\lambda) \pm i\sin(2\pi x/\lambda), \quad \lambda = h/p$$

Momentum, *p*, is associated with the first derivative of ψ

Kinetic energy, *E*, depends on the second derivative of ψ

For a given energy, E_n, $\psi^*\,\psi = C^2$ a constant.

The Particle in a 1-D Box



"box" = square well potential

$V(x) = \infty \qquad 0 > x \quad x > a$

$V(x) = 0 \qquad 0 \leqslant x \leqslant a$

particle somewhere on this line

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

By extrapolation from the free particle wavefunction,

$\psi = C\exp\left\{i\left[2m(E-V)\right]^{1/2} x/\hbar\right\}$ inside the box

$= C\exp\left\{-\left[2m(V-E)\right]^{1/2} x/\hbar\right\}$ for $V > E$ outside the box

$\rightarrow 0$ as $V \rightarrow \infty$ $\Rightarrow$ The particle is confined to the box (potential well).

Within the walls the situation is identical to the free particle...

i.e, $\psi_n = Ae^{+ip_n x/\hbar} + Be^{-ip_n x/\hbar}$ or $C\cos(p_n x/\hbar) + D\sin(p_n x/\hbar)$ … until boundary conditions are applied.

The Particle in a 1-D Box (continued)

$$\psi_n = C\cos(p_n x/\hbar) + D\sin(p_n x/\hbar)$$

Apply boundary conditions

At $x = 0,\ \psi = 0 \quad \Rightarrow \quad C = 0$

At $x = a,\ \psi = 0 \quad \Rightarrow \quad D\sin(p_n x/\hbar) = 0\ ;\ i.e.\ p_n a/\hbar = n\pi$

$\psi_n = D\sin(n\pi x/a) \qquad n = 1, 2, 3, \ldots \qquad$ n is called the quantum number

$$E_n = \frac{p_n{}^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2} \qquad n = 1, 2, 3, \ldots$$

Boundary conditions impose quantization.

The value of D is found by normalizing the wavefunction:

$$\int \psi_n{}^* \psi_n \, d\tau = 1$$

$$D^2 \int_0^a \sin^2(n\pi x/a)\,dx = \tfrac{1}{2} a D^2 = 1 \quad \Rightarrow \quad D = \left(\frac{2}{a}\right)^{1/2}$$

$$\psi_n = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right)$$

The Particle in a 1-D Box – Solutions

Energy Levels $E_n = \dfrac{n^2\pi^2\hbar^2}{2ma^2}$ $n = 1, 2, 3, \ldots$

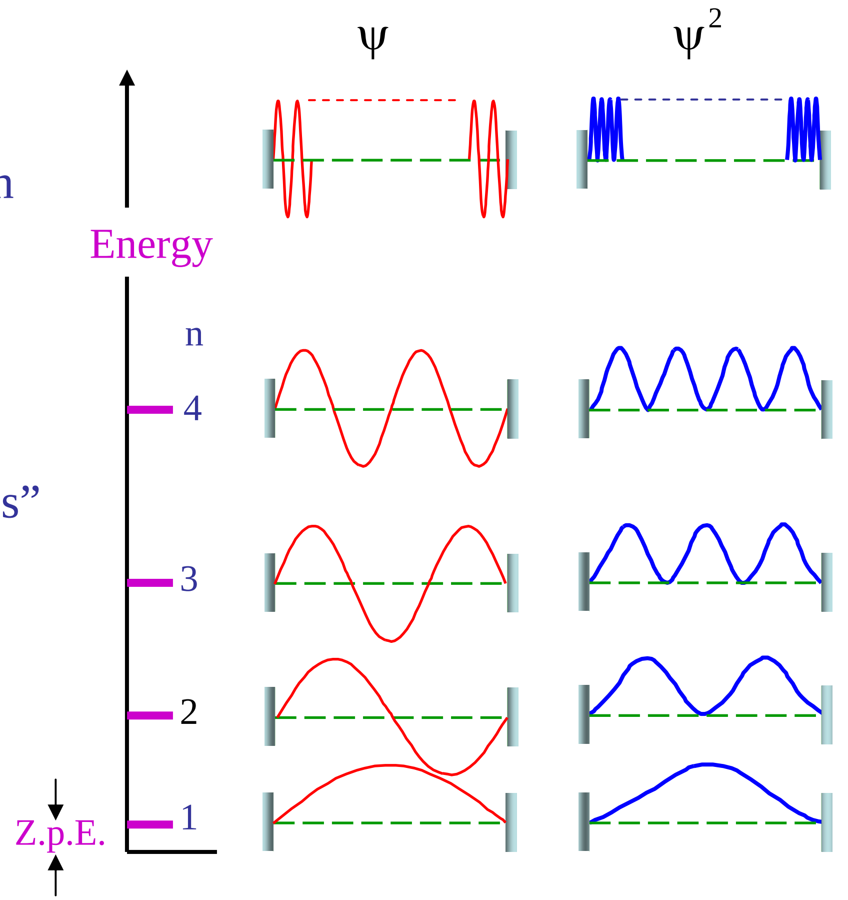
As $a \to \infty$, $\Delta E = E_{n+1} - E_n \to 0$, E becomes a continuous function

Wavefunctions $\psi_n = \left(\dfrac{2}{a}\right)^{1/2} \sin\left(\dfrac{n\pi x}{a}\right)$

Larger n and/or smaller a → sharper "wiggles"
⇒ higher momentum and kinetic energy.

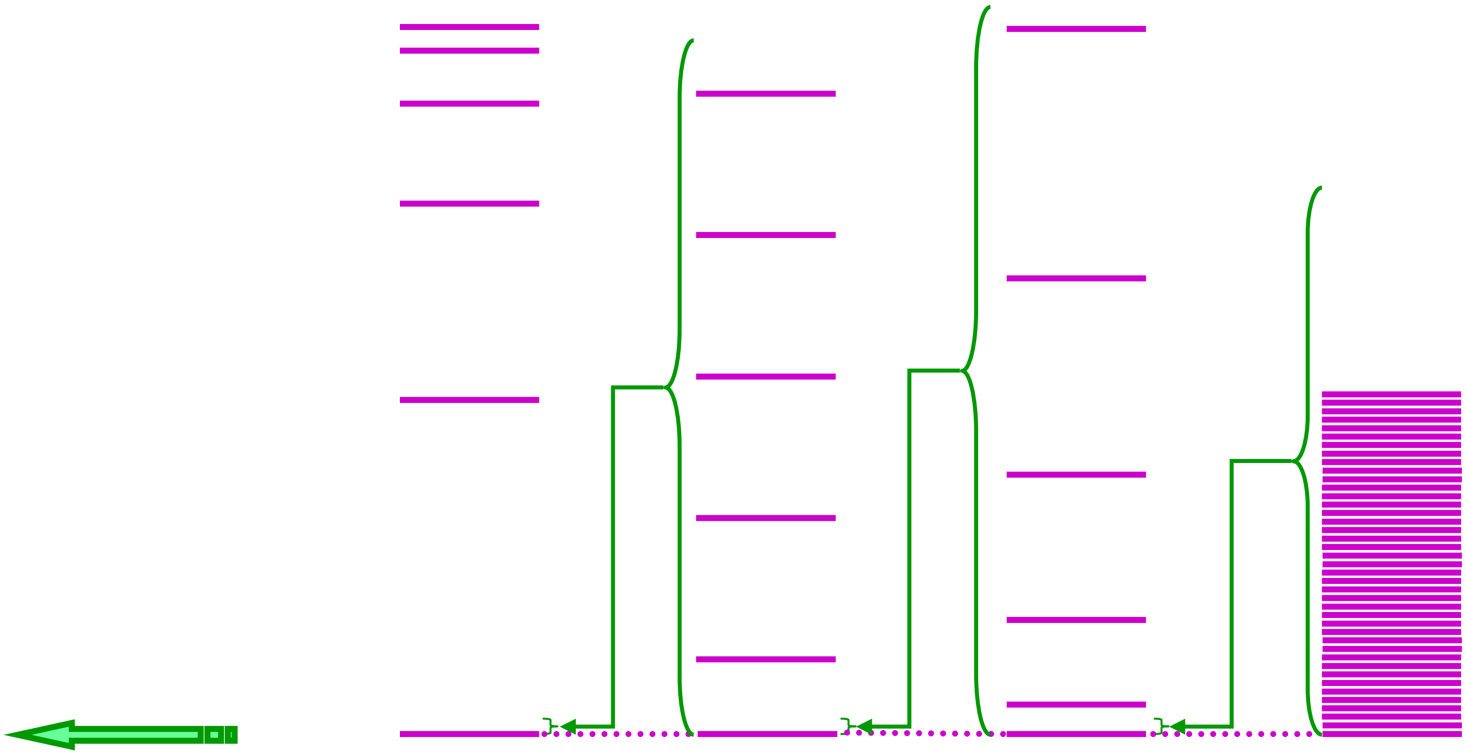
Wavefunctions of different energy (different n) are orthogonal.

$e.g.\ \int_0^a \psi_1\psi_2\, dx = \left(\dfrac{2}{a}\right)\int_0^a \sin\left(\dfrac{\pi x}{a}\right)\sin\left(\dfrac{2\pi x}{a}\right) dx = 0$



If a decreases, E and ΔE become larger

Molecular Energy Levels



very short λ gamma rays used to probe nuclear energy levels

Electronic	Vibrational	Rotational	Translational
UV + visible	IR	microwave	~0
λ: 10^{-9} - 10^{-6} m	10^{-6} - 10^{-4} m	10^{-4} - 10^{-2} m	$\rightarrow \infty$

very long λ used in radio frequency spectroscopy — NMR

Spectroscopy – Fundamentals

Frequency ν Hz (s^{-1}) $\omega = 2\pi\nu$ rad s^{-1}

Wavelength $\lambda = \frac{c}{\nu}$ m

1 micron = 1 μm= 10^{-6} m

1 Å = 0.1 nm = 10^{-10} m

Wavenumber $\bar{\nu} = 1/\lambda$ cm^{-1} $= \frac{\nu}{c}$ $\frac{(\text{Hz})}{(\text{cm s}^{-1})}$

$c = 2.998 \times 10^{10}$ cm s^{-1}

Emission and absorption spectroscopy are resonant processes.

$$\hbar\omega = h\nu = \Delta E$$

$h = 6.626 \times 10^{-34}$ J s

$\hbar = h/2\pi$

The intensities of spectral lines depend on…

population of states: Boltzmann distribution $\frac{N_{\text{upper}}}{N_{\text{lower}}} = \exp(-\Delta E / kT)$

transition probability: specific selection rules
often depend on symmetry

path length and concentration: Beer-Lambert Law $\frac{I}{I_0} = \exp(-\varepsilon[\text{M}]l)$

Statistical Interpretation of ψ

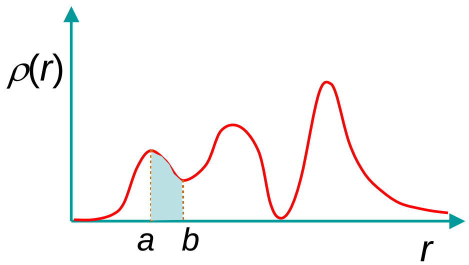
Born

The probability density of finding a particle at position *r*

$$\rho(r) = |\psi(r)|^2 = \psi^* \psi$$

The probability of finding the particle between a and b

$$P_{ab} = \int_a^b \rho(r) dr = \int_a^b |\psi(r)|^2 dr$$



N.B. The wave function may be complex, but a probability must be real and nonnegative.

The statistical interpretation implies indeterminacy: Until you measure the position you only know the probability of finding it at a particular position.

The Copenhagen interpretation says that the particle is not anywhere particular *until* we measure it. Measurement collapses the wave function.

Bohr

Measurements on a set of identical particles will generate different values (subject to the probability distribution ψψ*).

The *average* position is the expectation value: $\langle r \rangle = \int_{-\infty}^{\infty} r |\psi(r)|^2 dr = \int_{-\infty}^{\infty} \psi^* r \psi \, dr$

Schrödinger's Cat

Schrödinger

A closed box contains a small amount of radioactive material,
a Geiger counter hooked to a triggering device that can break
a vial of poison gas

…and a cat.

What is the state of the cat after a short time (during which one atom might decay)?

As long as the box is shut the cat's state is indeterminate:

$$\psi = \frac{1}{\sqrt{2}}\left(\psi_{\text{alive}} + \psi_{\text{dead}}\right)$$

Opening the box collapses the wave function to one state or the other.

Alternative (modern) explanation:

Triggering the Geiger counter is the measurement, *not* opening the box.