Quantum Mechanics

Outline :

- Review of Previous Lecture.
- Single Particle Wavefunctions.
- Time-Independent Schrödinger equation.
- Particle in a Box.
- Quantum Superposition
- The Hydrogen Atom.

Review of Previous Lecture

• Wave-particle duality : all objects display both wave and particle properties

• The De Broglie equation relates wave and particle properties :

$$p = h/\lambda$$
 $p = momentum$
 $\lambda = wavelength$

• The Uncertainty Principle places fundamental limits on our measurements :

$$\Delta x \, \Delta p_x \ge \frac{\hbar}{2} \qquad \qquad \Delta E \, \Delta t \ge \frac{\hbar}{2}$$

• Quantum mechanical waves are "probability waves" :

Probability $\propto |\psi|^2$

 ψ is generally complex.

• We want to look at the equations governing these quantum mechanical probability waves.



Schrödinger Equation

• A lot of quantum mechanics consists in simply solving this equation for different potentials *V* :

Potential :	Physical significance :	
$\frac{1}{2}Kx^2$	Simple harmonic oscillator	
$\frac{q_1q_2}{4\pi\varepsilon_0 r}$	Coulomb potential : atoms	
Complicated crystal lattice	Solid state physics	

Particle in a Box

• We're going to start with something much simpler - a particle in a one dimensional box. The box is represented by an infinite potential well.



Particle in a Box

• For the region $0 \le x \le L$:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \qquad \qquad (1)$$

$$\Rightarrow \psi(x) = A\cos kx + B\sin kx$$

• Since $\psi(0) = \psi(L) = 0$ this leaves :

$$\psi(x) = N \sin\left(\frac{n\pi x}{L}\right) \qquad n = 1, 2, 3, \dots$$

Normalisation factor

• Substituting in (1) gives :

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

A discrete set of allowed energy levels : **quantisation** of energy.

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Particle in a Box







Quantum Superposition

• If ψ_1 and ψ_2 are both solutions to the Schrödinger equation, then so is :

$$\psi \propto A\psi_1 + B\psi_2$$

• The wavefunction must still be correctly *normalised* to give unit probability :

$$\psi \propto \frac{1}{\sqrt{A^2 + B^2}} (A\psi_1 + B\psi_2)$$

- ψ_1 and ψ_2 are solutions corresponding to energies E_1 and E_2 . What energy does a particle described by ψ have ?
 - → It does *not* have a well defined energy.
 - An energy measurement could yield E_1 with probability $\propto A^2$ or energy E_2 with probability $\propto B^2$.

<u>Note</u>: to show that this is the correct way to normalise the combined wavefunction, you will need to know that when both wavefunctions are real: $\int \psi_1 \times \psi_2 \, dx = 0$ 13

This is fairly easy to show for the wavefunctions describing a particle in a box that we have already seen.

Quantum Superposition

• The average energy obtained in an energy measurement is still well defined :

$$\langle E \rangle = \frac{1}{(A^2 + B^2)} (A^2 E_1 + B^2 E_2)$$

• One could also define the spread or standard deviation of a series of energy measurements on the same state ψ .

This is how one formally derives the quantum mechanical uncertainty relations.





Schrödinger's Cat

- We know that quantum superpositions exist on microscopic scales since we observe the resulting interference effects.
- Devise a scheme to transfer this microscopic superposition into a macroscopic one :



Before Opening the Box

Whole Alive + Decayed Dead

After Opening the Box

Whole Alive Buy Kitty + Decayed Dead Dead

?!?

The Hydrogen Atom

Classical electromagnetism does not predict a stable atom :



- Electron suffers centripetal acceleration and radiates energy in the form of electromagnetic waves.
- Eventually the electron would spiral into the nucleus.
- In general, quantum mechanical systems do not have a ground state corresponding to the classical energy minimum (e.g. particle in a box).
- In the case of the hydrogen atom, the quantum mechanical ground state corresponds to an electron at a radius of :

 $a_0 \approx 0.529 \times 10^{-10} \text{m}$ (Bohr radius)

Since there are no lower energy states to occupy, the electron *cannot* lose more energy through radiation ⇒ the hydrogen atom is stable !

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The Hydrogen Atom

• The quantum mechanical prescription for understanding the hydrogen atom is simple. We just find the solutions to the Schrödinger equation with the relevant potential :

$$\frac{-\hbar^{2}}{2m}\left(\frac{d^{2}\psi}{dx^{2}} + \frac{d^{2}\psi}{dy^{2}} + \frac{d^{2}\psi}{dz^{2}}\right) - \frac{e^{2}}{4\pi\varepsilon_{0}r}\psi = E\psi$$

$$\frac{\text{Coulomb potential}}{r = \sqrt{x^{2} + y^{2} + z^{2}}}\qquad \psi = \psi(x, y, z)$$

- The approach is exactly the same as for a simple 1-dimensional problem such as a particle in a box, but the algebra is a bit more complicated.
- Energy of electron defined by principal quantum number n = 1, 2, 3, ... (for a free atom in the absence of external magnetic fields etc.)



Hydrogen Atom Wavefunctions

pure **|6,4,1>** state :

equal superposition of |4,3,3> and |4,1,0> states :

equal superposition of |3,2,2> and |3,1,-1> states:







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Summary

- We have looked at some of the laws that dictate the behaviour of quantum mechanical "probability waves".
- Most non-relativistic quantum mechanical systems can be understood just by solving the Schrödinger equation for the relevant potential.
- It always emerges that bound states (e.g. a particle in a box or an electron in an atom) have a discrete energy spectrum → energy is quantised. Loosely speaking, this is because we have to fit a certain number of De Broglie wavelengths into the space available (like standing waves on a violin string).
- Different quantum states can be superposed on top of one another. In that case the energy of the system might not even be well defined. Superposition :
 - o exists for macroscopic systems ? (Schrödinger's Cat)
 - is what enables us to exploit quantum mechanics : quantum computing, quantum teleportation, etc.



- This is completely independent of *x*
 - This wavefunction contains no information about the location of the particle.
- But if Δx is infinite, then by the uncertainty relationship, the momentum is known perfectly.

Schrödinger Equation (more advanced derivation)

• So, the following wavefunction describes a particle of unique momentum :

$$\psi(x,t) = A e^{i(kx - \omega t)}$$

• This means that I expect the following two relations to be relevant :

De Broglie :

$$p = \hbar k$$

Kinetic energy :
 $E = \frac{p^2}{2m}$

• These are both satisfied if the above wavefunction is inserted into :

$$\frac{-\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} = E \psi(x) \qquad \text{(spatial part of the wavefunction only)}$$

• A slight generalisation takes into account the possibility that the particle has energy by virtue of being in a potential *V* as well as kinetic energy :

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V\psi(x) = E\psi(x) \qquad \frac{\text{Time-independent}}{\text{Schrödinger equation.}}$$

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Time Dependence

• Going back to the wavefunction describing free particles of fixed momentum :

$$\psi(x,t) = A e^{i(kx - \omega t)}$$

• We also expect particles described by this wavefunction to satisfy the second De Broglie relation :

$$E = \hbar \omega$$

• This suggests the equation :

$$i\hbar \frac{d\psi(t)}{dt} = E\psi(t)$$
 (temporal wavefunction only)

• Solutions to this are simply :

$$\psi(t) = Ae^{-iEt/\hbar}$$

Time Dependence

• Then the product wavefunction :

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

satisfies :

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

Schrödinger equation.

• For the energy states we have been considering, the time-dependent factor $e^{-iEt/\hbar}$ does not change $|\psi(x)|^2$, so it was safe to treat them in a time-independent way.

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The Hydrogen Atom (advanced)

Degeneracy :

- Hidden in the energy level diagram for hydrogen is a high level of *degeneracy* : different quantum states that happen to have the same energy.
- For the hydrogen atom (in fact, for any quantum mechanical system with a central potential), each energy level has a well defined angular momentum.

Quantum Numbers	Principal	Total Angular Momentum	z-component of Angular Momentum	
	n = 1	l = 0		
	<i>n</i> = 2	l = 0 $l = 1$	► <i>m</i> = −1,0,+1	
	<i>n</i> = 3	l = 0 l = 1 l = 2	 <i>m</i> = −1,0,+1 <i>m</i> = −2,−1,0,+1,+2 	
Angular Momentum = $\sqrt{l(l+1)}\hbar$				

