Lecture 2. The Development of Quantum mechanics

Summary. Many important theoretical and experimental results would follow from the discovery of the particle nature of light.

Matter also has a wave particle duality. Turn about is fair play as deBroglie showed that matter, even people, have a wave-like nature. The deBroglie wave equation for matter is: λ = h / p where p = mv = momentum , λ = wavelength, m = mass, v = velocity amd h = Planck's constant.. Note the inverse relationship of m and λ. Which means that a 1g mass (very heavy) at 1m/s has $\lambda = 7 \times 10^{-33}$m, but 1 proton at speed of light has $\lambda = 1 \times 10^{-11}$m.

Uncertainty Principle: If photons are waves, then in the same way we can't say what the location of a wave is when we pluck a guitar string, we can't say where a photon (or an e^- for that matter) is.

The discrete lines in atomic spectra suggest a particle nature to radiation in which the emitted lines correspond to a transition of a photon between energy levels as an electron moves between upper and lower stability regions of an atom.

Quantum mechanics is developed by Schrodinger and Heisenberg who use it to explain the behavior of the fundamental particles that make up the atom. By describing electronic distributions around the nucleus, it becomes possible to develop the modern theory of chemical bonding.

Matter also has a wave particle duality.

If matter has a wave-particle duality there need to be examples of a wave nature of matter. deBrolgie generated an equation that would predict the sign of matter waves

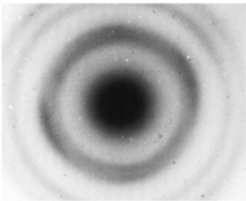
$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

where $\lambda \equiv$ wavelength, $m \equiv$ mass, $v \equiv$ velocity, and $mv \equiv p \equiv$ momentum
As expected, there is an inverse relationship between mass and wavelength. What are the magnitudes in the relationship between λ and m?

- An e^- with mass 10^{-31} kg can generate nm (nanometer) waves
- A proton with mass 10^{-27} kg can generate pm (picometer) waves
- A 1 g marble can generate 10^{-31} m waves

So only atomic particles generate appreciable, detectable waves.

An experimtal success proves deBroglie was right!! In 1925 Davisson and Germer see a diffraction pattern from electrons. Diffraction is solely a wave phenomenon but electrons are showing it.



electron diffraction becomes an extraordinary tool in analytical measurements of molecules

Uncertainty Principle

The wave particle duality of EMR and matter brings to an end the idea that classical physics can be used to precisely identify trajectories or locations.

Consider these notions.

- Where is a wave? Pluck a guitar string. Where is the wave it makes? Its location is not well identified.

- What about the continuum of mass and energy? Expected in classical physics, on the atomic level, atom by atom, matter is discrete.

It turns out that there are complementary pairs of physical parameters that allow us to quantify uncertainty. Here is a famous one from quantum mechanics

$$\Delta p \Delta x \geq \frac{1}{2}\hbar \qquad \hbar = \frac{h}{2\pi} \equiv 1.05 \times 10^{-34}\ \text{Js}$$

where Δp ≡ momentum and Δx ≡ location

Another famous one in spectroscopy is

$$\Delta v \Delta t \geq \frac{1}{2}\hbar \longleftarrow$$

says that the longer you look at something the narrower (more

where Δv ≡ frequency and Δt ≡ time

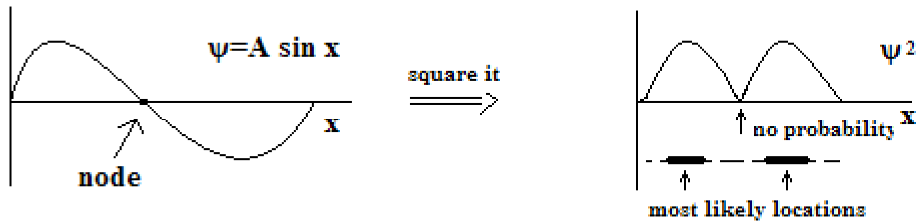
Wave Functions and Energy Levels

Schrödinger decided it would be a good idea to develop a method for generating wave function. This was the beginning of quantum mechanics.

ψ ≡ psi ≡ is the wave function he wanted to identify.

Why?

ψ^2 ≡ psi squared ≡ yields the probability that a particle will be in a certain volume



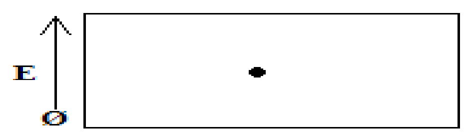
Schrödinger's method was to generate a differential equation

$$-\underbrace{\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2}}_{\text{2nd derivative of }\psi}+\underset{\substack{\uparrow\\ \text{potential energy}\\ \text{function}}}{V(x)}\Psi = \underset{\substack{\uparrow\\ \text{system energy}}}{E}\Psi$$

Taking a differential equations course would let you solve this, a great reason to become an engineer!!

Particle in a Box is solved with quantum mechanics.

As a first application of Schrödinger Equation, consider a **particle in a box.** Imagine having a box with an electron or proton in it. The potential in the box is V(x) = Ø everywhere so the

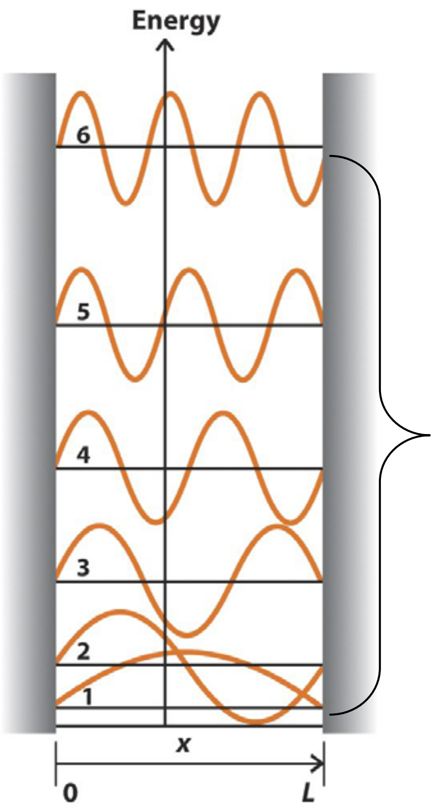


Schrödinger Equation is now simplified.

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} = E\Psi$$

solve this to find ψ

To better understand the particle in a box, think of a model system like this, a guitar string which is a standing wave in physics.



Note there are only specific λ that work. They are functions of L, the length of the box, just like standing waves in physics.

So solve like standing waves:

$$\Psi(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \qquad n=1,2,\ldots$$

is the wave function. Can we find E?

All kinetic, no potential in box $\longrightarrow E_k = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}$

Note that multiples of half λ work: λ=2L/n n=1,2,…
So, substituting:

$$E_n = \frac{n^2h^2}{8mL^2}$$

What do we see from this?

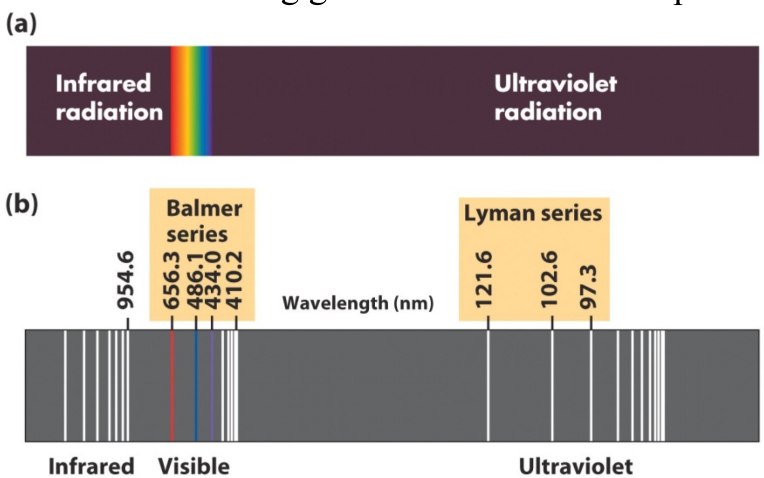
$$\Psi = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \qquad E = \frac{n^2h^2}{8mL^2} \qquad n=1,2,\ldots$$

- E can't be zero--makes sense, the uncertainty principle doesn't permit particle to lose all energy and become fixed.
- As L, length of box, increases, ΔE gets smaller which is why when L is macroscopic (we can see it) the energy levels are too small to distinguish.
- We have quantized energy levels!! n=1,2,3,…And this was done using a classical physics model of a standing wave.
- What made the quantized levels? Boundary conditions. At the edges of the box, the fixed points determine which ψ are possible.
- To find ΔE, stick in n=2 and n=1 for $E = \frac{n^2h^2}{8mL^2}$ and subtract.

$$\Delta E = h\nu = \frac{(2n+1)h^2}{8mL^2}$$

Atomic Spectra and Energy Levels

As if blackbodies and photoelectric effects weren't bad enough for classical physics, some school teacher named Balmer started electrocuting gases and the emission spectra he saw were not continuous, but rather discrete lines.



A guy named Rydberg came up with an empirical equation to describe the separation in frequency between the lines:

$$v = R\left(\frac{1}{n_1^2} - \frac{1}{n_u^2}\right) \quad \text{with} \quad R = 3.3\times10^{15}\,\text{Hz}$$

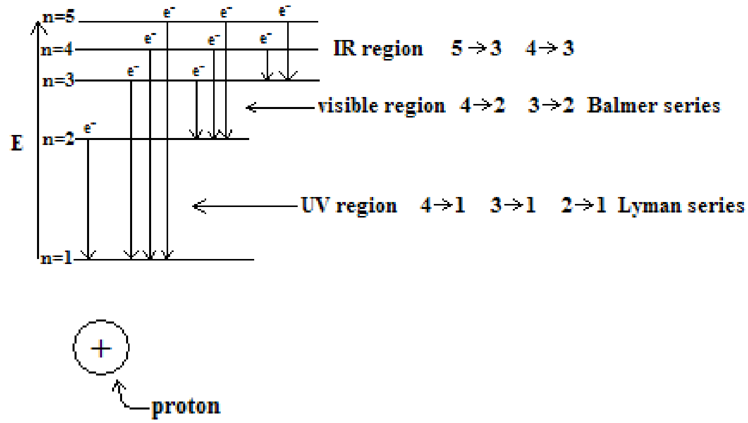
Believe it or not, he decided the constant should be the first letter of his last name!!

$n_\ell \equiv$ the lower energy level in hydrogen $\qquad n_u \equiv$ the upper energy level in hydrogen

If n_ℓ was n=1 the lines showed up in UV region

If n_ℓ was n=2 the lines showed up in visible region

If n_ℓ was n=3 the lines showed up in IR region



Using Rydberg's equation $\quad v = R\left(\frac{1}{n_l^2} - \frac{1}{n_u^2}\right)$

allows a quick calculation of discrete values of E, *v*, or λ for the hydrogen electron.

Principle Quantum Number, n, Describes the Energy Level and Distance from the Nucleus

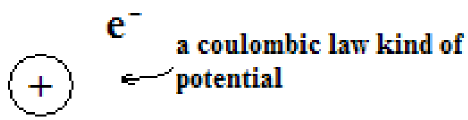
What a great chance for Schrödinger! He could try to mimic what Balmer and Rydberg saw. Can quantum mechanics yield

$v = 3.3 \times 10^{15}\left(\frac{1}{n^2}\right)$?

Solve

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

with V(x) for a H atom. Imagine:



So $V(x) = \dfrac{(-e)(+e)}{4\pi\varepsilon_o r}$ with $r \equiv$ radius of e^- $\quad\varepsilon_o \equiv$ vacuum permittivity

and the solution is:

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + \frac{e^2}{4\pi\varepsilon_o r}\Psi = E\Psi$$

solved

$$E_n = \frac{hR}{n^2} \text{ with } R = 3.29 \times 10^{15}\,\text{Hz}$$

Schrödinger did it!! He generated the same solution as Rydberg did experimentally. *n* turns out to be the principle quantum number and tells us size of atom as the distance of electrons from the nucleus.