From Last Time...

• Hydrogen atom:
  - One electron orbiting around one proton (nucleus)
  - Electron can be in different “quantum states”
  - Quantum states labeled by integer $n$
  - In each different quantum state, electron has
    • Different orbital radius
    • Different energy
    • Different wavelength
  - $n=1$ is lowest energy state, energy depends on state as $-\frac{13.6}{n^2} \text{ eV}$
Emitting and absorbing light

Photon is emitted when electron drops from one quantum state to another.

Absorbing a photon of correct energy makes electron jump to higher quantum state.

Zero energy

\[
\begin{align*}
E_1 &= -\frac{13.6}{1^2} \text{ eV} \\
E_2 &= -\frac{13.6}{2^2} \text{ eV} \\
E_3 &= -\frac{13.6}{3^2} \text{ eV}
\end{align*}
\]

Photon emitted
\[ hf = E_2 - E_1 \]

Photon absorbed
\[ hf = E_2 - E_1 \]
Line spectra

- This says that gases such as Hydrogen emit light only at certain frequencies, wavelengths.
- The photon energies correspond to separations between the energy levels.
The wavefunction

- Our explanation of the hydrogen atom originated from wave nature of electron.

- The electron wave is a standing wave around the circumference of the orbit.

- For each quantum state, there is a wavefunction associated with the electron.

- This is not unique to the hydrogen.
General aspects of Quantum Systems

- System exists only in discrete quantum states
- Usually labeled by an integer
- Each quantum state has an energy associated with it.
Example: ‘Particle in a box’

Particle confined to a fixed region of space e.g. ball in a tube- ball moves only along length $L$

- Classically, ball bounces back and forth in tube.
  - No friction, so ball continues to bounce back and forth, retaining its initial speed.
  - These are different ‘classical states’ of the ball.
  - Could label each state with a speed, momentum=$(mass)\times(speed)$, or kinetic energy.
  - Any momentum, energy is possible. Can increase momentum in arbitrarily small increments.
Quantum Particle in a Box

- In Quantum Mechanics, ball represented by wave
  - Wave reflects back and forth from the walls.
  - Reflections cancel unless wavelength meets the standing wave condition:
    integer number of half-wavelengths fit in the tube.

\[ \lambda = L \]
Two half-wavelengths

\[ \lambda = 2L \]
One half-wavelength

momentum

\[ p = \frac{h}{\lambda} = \frac{h}{L} \]

\[ p = \frac{h}{\lambda} = \frac{h}{2L} \]
The ‘Ground State’

- This is the lowest energy state
- It is the lowest energy (longest wavelength) standing wave that fits in the tube.
- It is the superposition of two waves (reflections)
  - One wave traveling to the right
  - One wave traveling to the left
- Energy of motion: \( E_{kinetic} = \frac{1}{2} m v^2 = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} \)
Quantized energy levels

- Standing wave condition says tube contains integer number of half-wavelengths:

\[ n \frac{\lambda}{2} = L \Rightarrow \lambda = \frac{2L}{n} \]

- And energy depends on wavelength as so

\[ E = \frac{h^2}{2m\lambda^2} \]

\[ E = \frac{h^2}{8mL^2} n^2 \]

- Or Quantized Energy =

\[ E_n = n^2 E_o \]
The wavefunction of a particle

• We use a probabilistic interpretation
  - The wavefunction $\Psi(x)$ (psi) of a particle describes the extended, wave-like properties.
  - The square magnitude of the wavefunction $|\Psi|^2$ gives the probability of finding the particle at a particular spatial location

• Similar to the interpretation used for light waves
  - Square of the electric field gives light intensity = number of photons / second.
Particle in a box: Wavefunctions

Wavefunction

Probability = (Wavefunction)$^2$

- Ground state wavefunction and probability.
- Height of probability curve represents likelihood of finding particle at that point.
Understanding Probability

![Coin](image1.png)

![Dice](image2.png)

**Heads vs. Tails**

- Heads: Probability = 0.5
- Tails: Probability = 0.5

**Dice Outcomes**

- Each number (1 to 6) has a probability of $\frac{1}{6}$. 

![Dice Outcomes Graph](image3.png)
Discrete vs continuous

- "Continuous" probability distribution
Using the probability

- Ground-state probability density for particle in a box - not uniform

\[ P(0 < x < L/4) = \text{probability to find particle between } x=0 \text{ and } x=L/4. \]

\[ P(5L/8) dx = \text{probability to find particle in narrow region } dx \text{ about } x=5L/8. \]
Particle in a box: Wavefunctions

Third state

Next higher state

Lowest energy state

Wavefunction

Probability
Probability of finding electron

- Classically, equally likely to find particle anywhere
- QM - true on average for high $n$

Zeroes in the probability!
Purely quantum, interference effect

$$P = \frac{1}{L} \quad 0 < x < L$$
Quantum Corral

- 48 Iron atoms assembled into a circular ring.
- The ripples inside the ring reflect the electron quantum states of a circular ring (interference effects).

D. Eigler (IBM)
Wavefunction of pendulum

\( n = 0 \)  
ground state

\( n = 1 \)

\( n = 2 \)
Classical vs quantum

Low classical amplitude, low energy

Higher classical amplitude, higher energy
Probability density of oscillator

Moves fast here, low prob of finding in a 'blind' measurement

Moves slow here, high prob of finding

Classical prob
Wavefunctions in two dimensions

- Physical objects often can move in more than one direction (not just one-dimensional)
- Could be moving at one speed in \( x \)-direction, another speed in \( y \)-direction.
- From deBroglie relation, wavelength related to momentum in that direction
  \[
  \lambda = \frac{h}{p}
  \]
- So wavefunction could have different wavelengths in different directions.
Two-dimensional (2D) particle in box

Ground state: same wavelength (longest) in both $x$ and $y$

Need two quantum #’s, one for $x$-motion, one for $y$-motion

Use a pair $(n_x, n_y)$

Ground state: $(1,1)$

Wavefunction

Probability = $(\text{Wavefunction})^2$

One-dimensional (1D) case
2D excited states

\[(n_x, n_y) = (2,1)\]

\[(n_x, n_y) = (1,2)\]

\[(n_x, n_y) = (2,2)\]
Three dimensions

• Each point in 2- or 3D space has a probability associated with it.
• Can plot for 2D, not for 3D.
• For 3D
  - Probability along a particular radius
  - Surfaces of constant probability
3D particle in box

• Ground state surface of constant probability
  • \((n_x, n_y, n_z) = (1,1,1)\)
All these states have the same energy, but different probabilities
Hydrogen atom

- Hydrogen a little different, in that it has spherical symmetry
- Not square like particle in a box.
- Still need three quantum numbers, but they represent ‘spherical’ things like
  - Radial distance from nucleus
  - Azimuthal angle around nucleus
  - Polar angle around nucleus
- Quantum numbers are integers \((n, l, m_l)\)
Hydrogen atom: 
Lowest energy (ground) state

- Spherically symmetric.
- Probability decreases exponentially with radius.

\[ n = 1, \quad \ell = 0, \quad m_\ell = 0 \]
$n=2$: next highest energy

$\ell = 0, \ m_\ell = 0$

$\ell = 1, \ m_\ell = \pm 1$

Same energy, but different probabilities
$n=3$: two $s$-states, six $p$-states and...

$n = 3, \ell = 0, m_\ell = 0$

$n = 3, \ell = 1, m_\ell = 0$

$n = 3, \ell = 1, m_\ell = \pm 1$
...ten $d$-states

$n = 3, \ l = 2, \ m_l = 0$

$n = 3, \ l = 2, \ m_l = \pm 1$

$n = 3, \ l = 2, \ m_l = \pm 2$