From Last Time...

- Particle can exist in different quantum states, having
  - Different energy
  - Different momentum
  - Different wavelength
- The quantum wavefunction describes wave nature of particle.
- Square of the wavefunction gives probability of finding particle.
- Zero’s in probability arise from interference of the particle wave with itself.

Probability of finding electron

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

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).

Wavefunction of pendulum

Here are quantum wavefunctions of a pendulum. Which has the lowest energy?

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
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
  \[ \lambda = \frac{\hbar}{p} \]
- 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 \( \ell \)'s, one for x-motion, one for y-motion
Use a pair \((n_x, n_y)\)
Ground state: \((1,1)\)

Two-D excited states

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

These have exactly the same energy, but the probabilities look different.  
The different states correspond to ball bouncing in x or in y direction.

The classical version

Same velocity (energy), but details of motion are different.

Particle in a box

What quantum state could this be?
A. \(n_x=2, n_y=2\)  
B. \(n_x=3, n_y=2\)  
C. \(n_x=1, n_y=2\)

Next higher energy state

- The ball now has same bouncing motion in both x and y.  
- This is higher energy that having motion only in x or only in y.

\((n_x, n_y) = (2,2)\)
Three dimensions
- Object can have different velocity (hence wavelength) in x, y, or z directions.
  - Need three quantum numbers to label state
  - \((n_x, n_y, n_z)\) labels each quantum state (a triplet of integers)
  - Each point in three-dimensional space has a probability associated with it.
  - Not enough dimensions to plot probability
  - But can plot a surface 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
- Lowest energy state is same in all directions.
  - Surface of constant probability is surface of a sphere.
  - \(n = 1, \ell = 0, m = 0\)
\( n = 2: \) next highest energy

\( n = 2, \ell = 0, m_\ell = 0 \)
\( n = 2, \ell = 1, m_\ell = \pm 1 \)
\( n = 2, \ell = 1, m_\ell = \pm 1 \)

Same energy, but different probabilities

\( n = 2, \ell = 0, m_\ell = 0 \)
\( n = 2, \ell = 1, m_\ell = \pm 1 \)
\( n = 2, \ell = 1, m_\ell = 0 \)

\( n = 3: \) two \( s \)-states, six \( p \)-states and...

\( n = 3, \ell = 0, m_\ell = 0 \)
\( n = 3, \ell = 1, m_\ell = 0 \)
\( n = 3, \ell = 1, m_\ell = \pm 1 \)

\( n = 3, \ell = 2, m_\ell = 0 \)
\( n = 3, \ell = 2, m_\ell = \pm 1 \)
\( n = 3, \ell = 2, m_\ell = \pm 2 \)

...ten \( d \)-states

\( n = 3, \ell = 2, m_\ell = 0 \)
\( n = 3, \ell = 2, m_\ell = \pm 1 \)
\( n = 3, \ell = 2, m_\ell = \pm 2 \)

Back to the particle in a box

Wavefunction

Probability = (Wavefunction)^2

• Here is the probability of finding the particle along the length of the box.
• Can we answer the question: Where is the particle?

Where is the particle?

• Can say that the particle is inside the box, (since the probability is zero outside the box), but that’s about it.
• The wavefunction extends throughout the box, so particle can be found anywhere inside.
• Can’t say exactly where the particle is, but I can tell you how likely you are to find at a particular location.

How fast is it moving?

• Box is stationary, so average speed is zero.
• But remember the classical version

\[ \vec{v} = \frac{\vec{p}}{m} \]

Particle bounces back and forth.
- On average, velocity is zero.
- But not instantaneously
- Sometimes velocity is to left, sometimes to right
Quantum momentum

- Quantum version is similar. Both contributions
  - Wave traveling right (positive momentum +\(\frac{h}{\lambda}\))
  - Wave traveling left (negative momentum -\(\frac{h}{\lambda}\))

Ground state is a standing wave, made equally of

\[ \text{One half-wavelength} \]
\[ \lambda = 2L \]

momentum \[ \frac{h}{\lambda} \]

Particle in a box

\[ \lambda = 2L \]

One half-wavelength

momentum \[ \frac{h}{\lambda} \]

What is the uncertainty of the momentum in the ground state?

A. Zero
B. \(\frac{h}{2L}\)
C. \(\frac{h}{L}\)

Uncertainty in Quantum Mechanics

Position uncertainty = \(L\)  
(Momentum uncertainty from \(\frac{h}{\lambda}\))

\[ \lambda = 2L \]

One half-wavelength

Reducing the box size reduces position uncertainty, but the momentum uncertainty goes up!

The product is constant:

(position uncertainty) \(\times\) (momentum uncertainty) \(\sim\) \(h\)

Heisenberg Uncertainty Principle

- Using
  - \(\Delta x\) = position uncertainty
  - \(\Delta p\) = momentum uncertainty
- Heisenberg showed that the product
  \[(\Delta x) \times (\Delta p)\] is always greater than \(\frac{h}{4\pi}\)

In this case we found:

(position uncertainty) \(\times\) (momentum uncertainty) \(\sim\) \(h\)

Zero-point energy

- In all cases, wave represents the quantum-mechanical nature of the particle.
- In all cases, the lowest energy state represented a particle with some motion.
- The particle can NEVER sit still.
- This also comes from the uncertainty principle
  - If the particle were sitting still, it’s momentum would be accurately zero.
  - Means that position is completely uncertain.

Unusual wave effects

- Classically, pendulum with particular energy never swings beyond maximum point.
- This region is ‘classically forbidden’
- Quantum wave function extends into classically forbidden region.

Classically forbidden region

End of swing
Quantum mechanics predicts some probability of the pendulum being found beyond the limits of its swing!

This is a common effect in quantum mechanics, arising from wave nature of particle.

**Particle in a box, again**

Particle contained entirely within closed tube.

Open top: particle can escape if we shake hard enough. But at low energies, particle stays entirely within box. Like an electron in metal (remember photoelectric effect)

Quantum mechanics says something different!

In quantum mechanics, there is some probability of the particle penetrating through the walls of the box.

Nonzero probability of being outside the box!

Two neighboring boxes

- When another box is brought nearby, the electron may disappear from one well, and appear in the other!
- The reverse then happens, and the electron oscillates back and forth, without 'traversing' the intervening distance.

The tunneling distance

- 'High' probability
- Low probability

Example: Ammonia molecule

- NH$_3$
- Nitrogen (N) has two equivalent 'stable' positions.
- It quantum-mechanically tunnels between 2.4x10$^{11}$ times per second (24 GHz)
- Was basis of first 'atomic' clock (1949)
Atomic clock question

Suppose we changed the ammonia molecule so that the distance between the two stable positions of the nitrogen atom INCREASED.
The frequency of the clock would

A. decrease.
B. increase.
C. stay the same.

Tunneling between conductors

- If one well is a little deeper than the other, the particle tunnels and then stays in the other well.
- The well can be made lower by applying an electric field.
- This is the principle of quantum-mechanical tunneling.

Scanning Tunneling Microscopy

- Over the last 20 yrs, technology developed to controllably position tip and sample 1-2 nm apart.
- Is a very useful microscope!

Can we see atoms?

STM image analysis

- The tip is scanned across the sample, recording the z-position at each point.
A closer look at a silicon circuit

Silicon

- 7x7 surface reconstruction
- These 10 nm scans show the individual atomic positions

Surface steps on Si

7x7 + steps

- 7x7 unit cell structure on the terraces

Atomic wires from Si steps

CaF grown uniquely at step edges

Molecular wires, 3 nm diameter from ferrocene precursor

Will atomic wires/particles be the next generation storage media?

Images courtesy M. Lagally, Univ. Wisconsin

Images courtesy F. Himpsel, Univ. Wisconsin
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Manipulation of atoms

- Take advantage of tip-atom interactions to physically move atoms around on the surface
  - This shows the assembly of a circular ‘corral’ by moving individual iron atoms on the surface of copper (111).
  - The (111) orientation supports an electron surface state which can be ‘trapped’ in the corral

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).

The Stadium Corral

- Again iron on copper. This was assembled to investigate quantum chaos.
  - The electron wavefunction leaked out beyond the stadium too much to observe expected effects.

Some fun!

Kanji for atom (lit. original child)
Iron on copper (111)
Carbon Monoxide man
Carbon Monoxide on Pt (111)