The Quantum-Mechanical Model of the Atom

Chapter 7

"Anyone who is not shocked by quantum mechanics has not understood it."
– *Neils Bohr* (1885-1962)

Chapter 7 – The Quantum-Mechanical Model of the Atom Suggested Problems

- 39, 41, 43, 45, 51, 55, 59, 63, 65, and 67
- Also available at http://www.western.edu/faculty/dorth

The Quantum-Mechanical Model of the Atom

- Quantum Mechanics – brief history
- The nature of light
- Atomic Spectroscopy
- Quantum Mechanics
  - deBroglie wavelength, Uncertainty Principle, Indeterminacy, Schroedinger Equation
- Schroedinger Equation solutions for H
  - Atomic orbitals

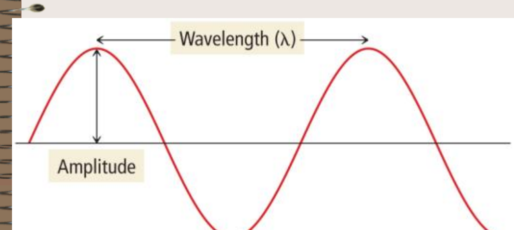
Need for Quantum Mechanics

- While "classical mechanics" was incredibly successful on scales from marbles to planets, there were problems at the atomic scale
- Solutions to seemingly unrelated problems of blackbody radiation, atomic line spectroscopy, and the photoelectric effect all ended up invoking $E = h\upsilon$ and contributed to development of Quantum Mechanics

Nature of light

- We now understand that light can exhibit both wave and particle properties
- Waves
  - Velocity, wavelength, frequency
  - Diffraction and Interference
  - Continuous distribution of energy
- Particles
  - Packets of energy

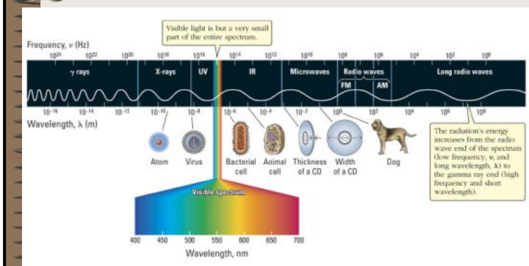
Wave Characteristics



Light is an Electromagnetic Wave

- It is our main tool in learning about nature
- It is a wave
  - wavelength, λ
  - frequency, ν
- velocity = (wavelength, λ)(frequency, υ)
- Speed of light, c = 3 x 10^8 m/s
- The oscillation is an oscillation of both an electric field and a magnetic field
  - oscillations are in phase and perpendicular to each other

The electromagnetic spectrum



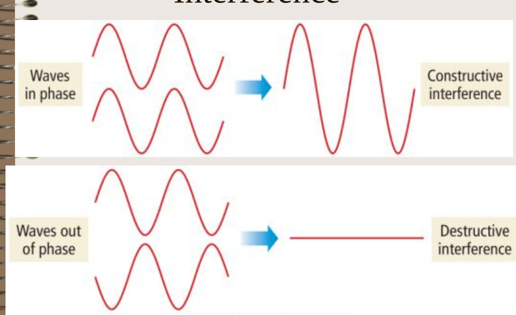
Wavelength and frequency relationships ($c = \lambda\nu$)

- Green light has a wavelength around 520 nm. What is its frequency?
- 5.77 x 10^{14} Hz

Interference – A wave Property

- the interaction between waves is called **interference**
- when waves interact so that they add to make a larger wave it is called **constructive interference**
  - waves are **in-phase**
- when waves interact so they cancel each other it is called **destructive interference**
  - waves are **out-of-phase**

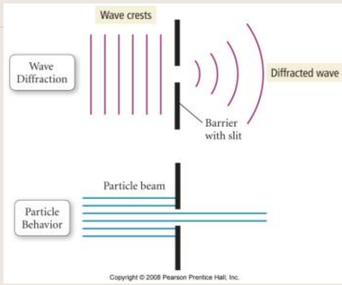
Interference



Diffraction – A wave Property

- when traveling waves encounter an obstacle or opening in a barrier that is about the same size as the wavelength, they bend around it – this is called **diffraction**
  - traveling **particles** do not diffract
- the diffraction of light through two slits separated by a distance comparable to the wavelength results in an interference pattern of the diffracted waves
- an interference pattern is a characteristic of all light waves

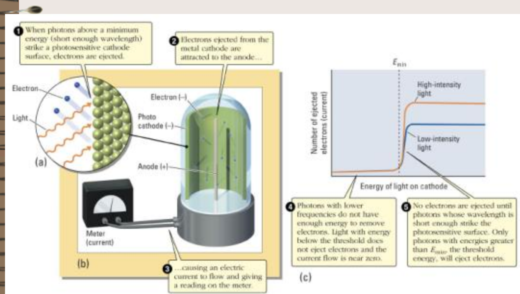
Diffraction



Photoelectric Effect – the data

- Shine light onto metal and electrons are ejected
  - you can measure both speed (kinetic energy) and number of electrons ejected
- Below some threshold frequency of light, no electrons are emitted, regardless of light intensity
- Above the threshold frequency, kinetic energy of emitted electrons increases linearly with frequency
- Above threshold frequency, number of ejected electrons increases with intensity

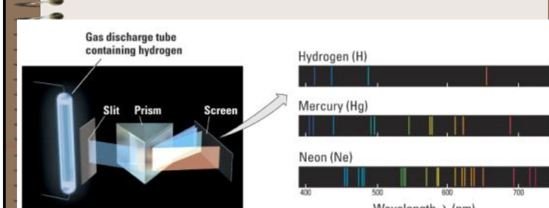
Photoelectric Effect



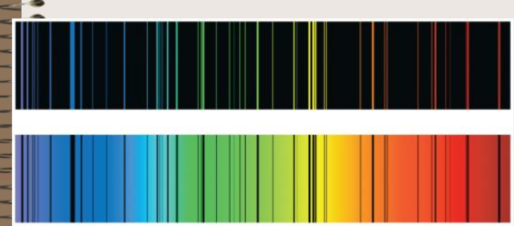
Photoelectric effect – explained by Einstein

- Light behaves as a set of particles (called photons) each with energy $E = h\nu$
- It takes a certain amount of energy, W to remove an electron from a metal surface
- An electron must be removed by a single photon
- Any leftover energy turns up as kinetic energy of the ejected electron

Atomic Spectroscopy Line Spectra



Emission vs. Absorption Spectra



Spectra of Mercury

Atomic Spectroscopy

- Hydrogen is simplest – look for a pattern in the wavelengths emitted
- Balmer-Rydberg Equation

$$\frac{1}{\lambda} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right)$$

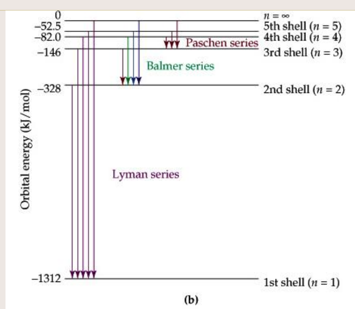
$R = 1.097x10^{-2}$ nm^{-1}

n and m integers, $n > m$

Balmer-Rydberg Equation

- Sets of lines (corresponding to various values of *m*) known as series
- Lyman Series (m = 1)
- Balmer Series (m = 2)
- Ritz-Paschen Series (m = 3)
- Brackett Series (m = 4)
- Pfund Series (m = 5)

Some of the Hydrogen series

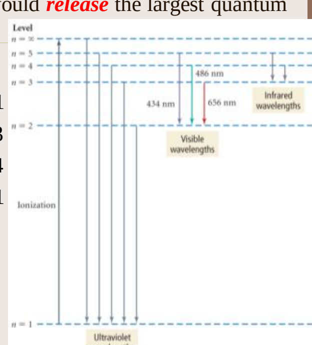


Bohr Theory of Hydrogen

- electrons move in orbits
- only particular radii are allowed
  - r = (52.9 pm) n^2, n = 1, 2, 3, etc.
- When an electron moves from one orbit to another energy is absorbed/emitted
  - E = hν ; h = 6.626 x 10^{-34} J s
- Since only particular radii are allowed, only particular energies are allowed
  - Energy is quantized

Which of the following transitions for an electron in a hydrogen atom would ***release*** the largest quantum of energy?

- A $n = 3 \rightarrow n = 1$
- B $n = 4 \rightarrow n = 3$
- C $n = 1 \rightarrow n = 4$
- D $n = 2 \rightarrow n = 1$



Problems with Bohr Theory

- It only works for hydrogen (or hydrogenic) species
  - hydrogenic = 1 electron
- It is unstable according to classical mechanics
  - as a charged species (electron) moves in circular orbit, it emits energy continuously and spirals towards the center of orbit

Key Points of Quantum Mechanics

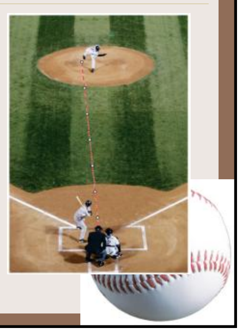
- Wave-particle duality
  - deBroglie wavelength
- Heisenberg Uncertainty Principle
- Indeterminancy
- Schroedinger's Equation

Particle-Wave Duality

- light has both wave properties (ν,λ) and particle properties (discrete energy/photon)
- "particles" have an associated wavelength, deBroglie wavelength $\lambda = h/(mv)$

A major league pitcher throws a 148.8 g baseball at a speed of 92.5 mph (41.4 m/s). What is the de Broglie wavelength of the baseball in meters?

- A 4.81×10^{-41}
- B 1.08×10^{-34}
- C 1.08×10^{-37}
- D 1.08×10^{-40}



Heisenberg Uncertainty Principle

- measuring one variable precisely (position, for example) can lead to increased uncertainty in another variable (in this case momentum)
- the role of observer is important in obtaining information from the wavefunction

$$(\text{uncertainty in position})(\text{uncertainty in momentum}) \geq \frac{h}{4\pi}$$

Determinacy vs. Indeterminacy

- according to classical physics, particles move in a path **determined** by the particle's velocity, position, and forces acting on it
  - determinacy = definite, predictable future
- because we cannot know both the position and velocity of an electron, we cannot predict the path it will follow
  - indeterminacy = indefinite future, can only predict probability
- the best we can do is to describe the probability an electron will be found in a particular region using statistical functions

Determinacy vs. Indeterminacy

Schroedinger's Equation

$$\hat{H}\Psi = E\Psi$$

- Its solution is a wavefunction, ψ, which contains all information about the system which can be known
- Wavefunction may return one or several values for experimental observables
- Results are not deterministic but part of statistical realm

Schroedinger's Equation

$$\hat{H}\Psi = E\Psi$$

$$\left(-\frac{h^2}{4\pi^2 m}\nabla^2 + V\right)\Psi = E\Psi$$

$$\left(-\frac{h^2}{4\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)-\frac{e^2}{4\pi\varepsilon_0\sqrt{x^2+y^2+z^2}}\right)\Psi = E\Psi$$

Hydrogen Atom solving H ψ= E ψ

- Solutions are indexed with integers: n, ℓ, m_l
- $E_n = -2.179 \times 10^{-18}/n^2$
- ψ depends upon all three integers, which have limits
  - principal quantum #, n = 1, 2, 3, etc.
  - angular momentum quantum # ℓ = 0, …, n-1
  - magnetic quantum #, m_l = - ℓ, - ℓ +1,…, 0, 1,…, ℓ

Orbitals

- Principal quantum number, n
  - determines Energy of orbital
  - determines number of orbitals (=n^2)
    - 1 orbital with n = 1
    - 9 orbitals with n = 3
  - Wavefunction contains (n-1) nodes
    - node is place where wavefunction (and hence the probability of finding an electron) is zero
  - Sometimes referred to as the shell number

Orbitals

- Angular momentum quantum number, ℓ
  - Determines the shape (and name) of the orbital
  - ℓ = 0 → s orbital, spherical shape
  - ℓ = 1 → p orbital, dumbbell shape
  - ℓ = 2 → d orbital, mostly clover shaped
  - ℓ = 3 → f orbital, multiple lobes in shape
- Magnetic quantum number, m_ℓ
  - Determines orientation of orbital in space
  - Affects energy when atom is placed in a magnetic field

Sets of quantum numbers

- What sets of quantum numbers (n, ℓ, m_l) are possible for n = 2?

n	ℓ	m_ℓ	name
2	0	0	2s
2	1	-1	$2p_x$
2	1	0	$2p_z$
2	1	1	$2p_y$

Which of the following is **NOT** an allowed set of quantum numbers?

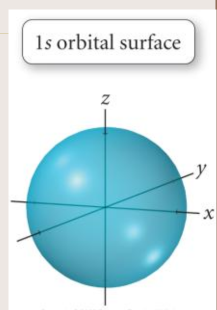
- A $n = 4$ $l = 3$ $m_l = 3$
- B $n = 1$ $l = 0$ $m_l = 0$
- C $n = 2$ $l = 1$ $m_l = 0$
- D $n = 3$ $l = 3$ $m_l = -2$

The Shapes of Atomic Orbitals

- the ***l*** quantum number primarily determines the shape of the orbital
- ***l*** can have integer values from 0 to (n – 1)
- each value of l is called by a particular letter that designates the shape of the orbital
  - ***s*** orbitals are spherical
  - ***p*** orbitals are like two balloons tied at the knots
  - ***d*** orbitals are mainly like 4 balloons tied at the knot
  - ***f*** orbitals are mainly like 8 balloons tied at the knot

l = 0, the *s* orbital

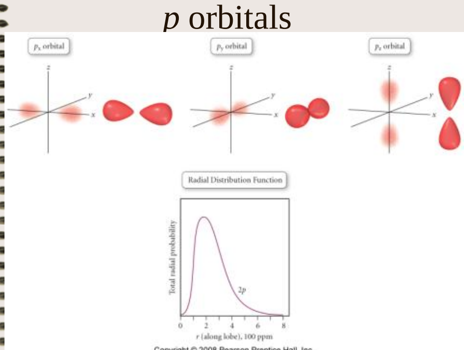
- spherical
- number of nodes = (n – 1)



l = 1, *p* orbitals

- each principal energy state above n = 1 has 3 ***p*** orbitals
  - m_l = -1, 0, +1
- each of the 3 orbitals point along a different axis
  - p_x, p_y, p_z
- two-lobed
- node at the nucleus, total of n nodes

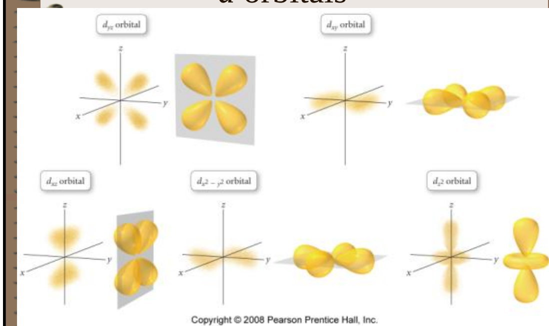
p orbitals



l = 2, *d* orbitals

- each principal energy state above n = 2 has 5 ***d*** orbitals
  - m_l = -2, -1, 0, +1, +2
- 4 of the 5 orbitals are aligned in a different plane
  - the fifth is aligned with the z axis, $d_{z\ squared}$
  - d_{xy}, d_{yz}, d_{xz}, $d_{x\ squared - y\ squared}$
- mainly 4-lobed
  - one is two-lobed with a toroid
- planar nodes
  - higher principal levels also have spherical nodes

d orbitals



l = 3, ***f*** orbitals

- each principal energy state above *n* = 3 has 7 ***d*** orbitals
  - m_l = -3, -2, -1, 0, +1, +2, +3
- mainly 8-lobed
  - some 2-lobed with a toroid
- planar nodes
  - higher principal levels also have spherical nodes

f orbitals