Chapter 7
Quantum Theory of the Atom

I) Light Waves

A) Nature of Light

Electromagnetic radiation (or electromagnetic energy or radiant energy)

Types
visible light
x-rays
microwaves
radiowaves

Travel as waves
electromagnetic radiation is a result of oscillating electric and magnetic fields moving simultaneously through space.

B) Wave Nature of Light

Characterize a wave by its

1) Wavelength (λ, Greek lambda)

- distance between any point on the wave and the corresponding point on the next wave.
- distance between successive crests (high points) or troughs (low points)
- units - meters (m) or nanometers (1 nm = 10^{-9} m)

2) Frequency (ν, Greek nu)

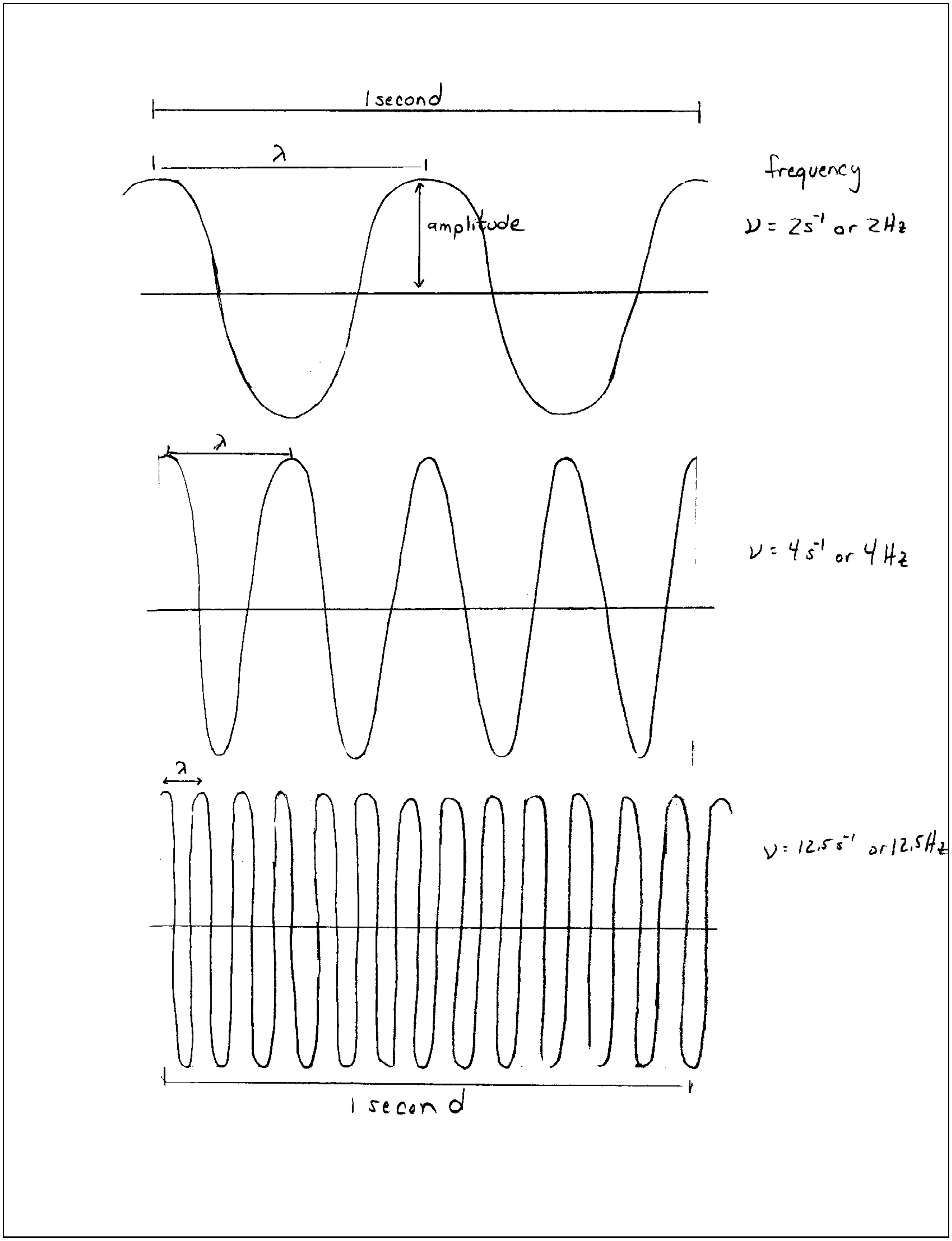
- number of cycles a wave undergoes a second
- units - 1/sec (s^{-1}) or hertz (Hz = s^{-1})

3) Amplitude

- height of the crest (depth of the crest)
- measures the strength of its electric and magnetic fields
- related to the intensity of the radiation (how dim or bright)

Notes: frequency and wavelength are inversely related
as the frequency (ν) increases the wavelength (λ) decreases

Examples of Frequency, Wavelength, and Amplitude



C) Speed of wavelength

distance traveled per unit time
units - meters per second (m/s)

speed of light = $\nu\lambda$
$c = \nu\lambda$

speed depends on the medium in which it travels
1) in a vacuum
$c = 2.99792458 \times 10^8$ m/s

2) in air
c is slightly less than in a vacuum

D) Electromagnetic Spectrum

the electromagnetic spectrum is the range of frequencies and wavelengths of electromagnetic radiation

- the regions on the spectrum are named after instruments used to produce or receive them.
- visible spectrum is a small region
  red ($\lambda \approx 750$ nm) to violet ($\lambda \approx 400$ nm)
  visible light waves are produced by the motions of an e- within atoms and molecules
- Gamma Rays
  shortest wavelength with the highest frequency
- Radiowaves
  has the longest wavelength and the lowest frequencies
- Waves in the electromagnetic spectrum travel at the same speed but differ in the frequency and wavelength
- An example of the electromagnetic spectrum can be found in Figure 7.5 in the fifth edition of General Chemistry by Ebbing.

II) Quantum Effects

Explaining the nature of light using:
1) wave properties
2) both wave and particle properties

A) Planck's quantization of Energy

Research problem:
When solids are heated, they emit visible light

Temp.	Light	Example
~1000 K	soft red	glow of coal
1500 K	brighter and more orange	heating coil of a toaster
>2000K	brighter and whiter	filament of a light bulb

This phenomenon is known as Blackbody radiation
the changing intensity and λ of light emitted as a dense object is heated.

Attempts to use classical physics to predict l of emitted light failed
classical physics predicted as an object got hotter and acquired more energy color shift to blue - violet - beyond.

Max Planck (1900)
Explanation for the spectrum of a heated solid
His Assumption:
A hot, glowing object could emit (or absorb) only certain amounts of energy,

$E = nh\nu$

E - energy
n - positive integer (1, 2, 3, ...)
h - plank's constant = 6.63×10^{-34} J·s
ν - frequency

B) Photoelectric Effect

Research problem:
Monochromic light of sufficient energy shines on a metal plate causing an electric current to flow. (See figure 7.6 in the fifth edition of General Chemistry by Ebbing)

Albert Einstein (1905)
Used Plank's theory to explain this phenomenon.

Experiments so far demonstrated:
1) e^- are ejected from the surface only if light of a minimum frequency is used.
2) The number of e^- ejected is directly proportional to the intensity of light.
3) Wave theory alone could not explain this phenomenon.

Einstein's explanation included:
- Planck's idea of quantized energy
- light being described by both
  - wave-like properties
  - particle-like properties

Planck's idea of quantized energy assumed
a beam of light is a stream of particles called photons

Energy of a photon: $E = h\nu$ h = Planck's constant = 6.63×10^{-34} J·s
ν = frequency

In summary: for the photoelectric effect, an e^- is ejected only if some minimum amount of energy is used.

Example:
A compact disc player uses lasers that emit red light with a wavelength of 685 nm.
a) What is the energy of one photon of this light?
b) What is the energy of a mole of photons of this light?

convert nm to m

$$685\text{ nm}\left(\frac{10^{-9}\text{ m}}{1\text{ nm}}\right) = 6.85 \times 10^{-7}\text{ m}$$

convert λ to ν $c = \nu\lambda$ $\nu = c/\lambda$

$$\nu = \frac{2.998 \times 10^{8}\text{ m/s}}{6.85 \times 10^{-7}\text{ m}} = 4.38 \times 10^{14}\text{ s}^{-1} = 4.38 \times 10^{14}\text{ Hz}$$

E of 1 photon, $E = h\nu$

$$E = \left(6.626 \times 10^{-34} \ \frac{J \bullet s}{photon}\right)(4.38 \times 10^{14} \ s^{-1}) = 2.90 \times 10^{-9} \frac{J}{photon}$$

E of 1 mole of photons

$$2.90 \times 10^{-9} \frac{J}{photon}\left(\frac{6.02 \times 10^{23} \ photons}{1 \ mol \ photons}\right) = 1.75 \times 10^{5} \ \frac{J}{mol}$$

III) Bohr Theory

A) Atomic line spectra

Line Spectrum is a spectrum containing radiation of only certain wavelengths

For example, the hydrogen line spectrum is

visible light	wavelength
red	656 nm
green	486 nm
blue	434 nm
violet	410 nm

A Swiss school teacher, Johann Balmer, in 1885 derived a formula to fit the four lines in the hydrogen line spectrum.

$$\frac{1}{\lambda} = 1.097 \times 10^{7}/\text{m}\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad n = 3, 4, 5, 6$$

B) Bohr's model of the hydrogen atom

His model accounts for

1) stability of the hydrogen atom
   e^- exist, they do not continually radiant energy

2) line spectrum of the atom
   uses Planck's quantum theory

Postulates of Bohr's Model

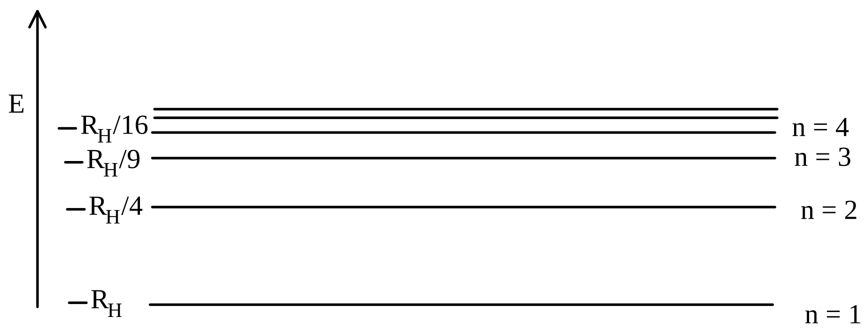
which is the first connection between spectra of excited atoms and quantum ideas of Planck and Einstein

1) Energy level Postulate

H atom has only certain allowable Energy Levels

$E = -\frac{R_H}{n^2}$ where n - principle quantum number = 1, 2, 3, . . . ∞

R_H - Rydberg's constant = 2.18×10^{-18} J



2) Transition between Energy Levels Postulate

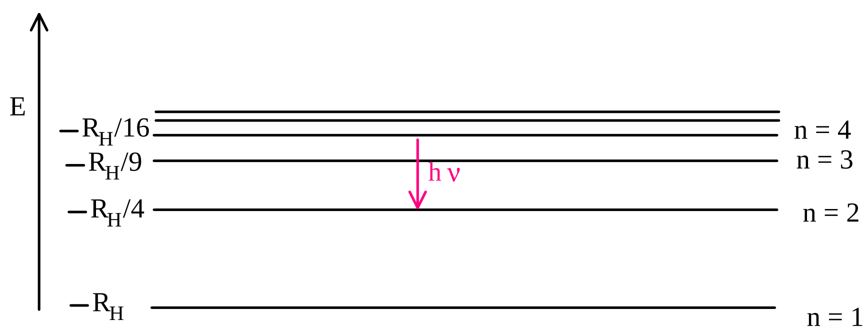
e^- can move between energy levels

- by absorbing or emitting a photon
- Energy of a photon is the difference in energy between the energy levels

Emission of light during a transition

- gives the line spectrum of the element
- results from an e^- moving from a higher energy level to a lower energy level

Energy of an emitted photon $h\nu = E_i - E_f$



C) Predicting the Line Spectrum of the Hydrogen Atom

Bohr used Einstein's photon concept to derive a formula (Balmer's Formula) to predict the lines in the emission spectrum.

Derivation:

Energy of a photon $h\nu = E_i - E_f$

energy of each energy level E_i and E_f

$$E_i = -\frac{R_H}{n_i^2} \qquad E_f = -\frac{R_H}{n_f^2}$$

Substitute energy of energy levels into the energy of a photon equation.

$$h\nu = -\frac{R_H}{n_i^2} + \left(+\frac{R_H}{n_v^2}\right)$$

simplify $h\nu = R_H\left(\frac{1}{n_v^2} - \frac{1}{n_i^2}\right)$

recall $c = \nu\lambda$ or $\nu = c/\lambda$

substitute for frequency

$$\frac{hc}{\lambda} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

solve for $1/\lambda$

$$\frac{1}{\lambda} = \frac{R_H}{hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

where $R_H = 2.180 \times 10^{-18}$ J

$h = 6.626 \times 10^{-24}$ J•s

$c = 2.998 \times 10^{8}$ m/s

Bohr's equation for predicting the emission line spectrum of an element gives Balmer's Formula for the hydrogen's emission line spectrum.

Note: $\frac{R_H}{hc} = 1.097 \times 10^7/\text{m}$

recall Balmer's Formula $\frac{1}{\lambda} = 1.097 \times 10^7/\text{m}\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \quad n = 3, 4, 5, 6$

Example:
Calculate the wavelength of light emitted from a hydrogen atom when an electron undergoes a transition from level n = 3 to n = 1.

$$\frac{1}{\lambda} = \frac{R_H}{hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

$$\frac{1}{\lambda} = \frac{2.18\times10^{-18}\,\text{J}}{(6.626\times10^{-34}\,\text{J}\bullet\text{s})(2.998\times10^{8}\,\text{m/s})}\left(\frac{1}{1^2} - \frac{1}{3^2}\right)$$

$$\frac{1}{\lambda} = 9742472\ \text{m}^{-1}$$

$$\lambda = 1.03\times10^{-7}\,\text{m} = 103\ \text{nm}$$

D) Miscellaneous Notes

1) an e^- in the n = 1 energy level is in the ground state
an e^- in n = 2 or higher energy level is in the excited state

2) Bohr's model is only good for the H atom or species with only one electron
H, He^+ or Li^{2+} for example.

3) Energy is quantized

4) Light behavior is describe by both wave-like properties and particle-like properties which is called Wave-Particle Duality

$$E = h\nu$$

ν: frequency of the associated wave

E: energy of a photon (particle)

IV) Quantum Mechanics

A) Wave nature of an electron

(1920's) de Broglie combined
1) mass-energy equivalence $E = mc^2$
2) energy of a photon $E = h\nu = hc/\lambda$

equate the two equations

$$mc^2 = \frac{hc}{\lambda}$$

$$mc = \frac{h}{\lambda}$$

solve for λ

$$\lambda = \frac{h}{mc}$$

substitute v - speed for c - speed of light

$$\lambda = \frac{h}{mv}$$ de Broglie relationship

m - mass
v - speed
h - Planck's constant

de Broglie shows through this relationship that matter behaves as though it were moving as a wave.
(the larger the mass, the smaller the wavelength)

Example:
a) the fastest serve in tennis is ~130 miles/hr (58 m/s). Calculate the wavelength assoicated with a 6.0×10^{-2} kg tennis ball at this speed.

$$\lambda = \frac{h}{mv} = \frac{(6.63 \times 10^{-34} \text{J} \bullet \text{s})}{(6.0 \times 10^{-2}\text{kg})(58\ \text{m/s})} = 1.9 \times 10^{-34}$$

units: $$\frac{\text{J} \bullet \text{s}}{(\text{kg})(\frac{\text{m}}{\text{s}})} = \frac{\left(\text{kg}\frac{\text{m}^2}{\text{s}^2}\right)\text{s}}{(\text{kg})(\frac{\text{m}}{\text{s}})} = \text{m}$$

b) Calculate the wavelength assoicated with an e^- moving at 58 m/s.
$m_e = 9.1095 \times 10^{-31}$ kg

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} \frac{\text{kg m}^2}{\text{s}^2}\text{s}}{(9.1095 \times 10^{-31}\text{kg})(58\ \frac{\text{m}}{\text{s}})} = 1.3 \times 10^{-5}\ \text{m} = 1.3 \times 10^{4}\ \text{nm}$$ infrared region

B) Wave Functions

If an e^- has properties of both a particle and a wave, how is the position of an e^- in an atom determined?

1) (1927) Werner Heisenberg

Uncertainy Principle
It is impossible to know simultaneously the exact position and velocity of a particle.

$(\Delta x)(m\Delta v_x) \geq \frac{h}{4\pi}$

Δx - uncertainty of position

Δv_x - uncertainty in speed

- Can not prescribe the exact path of an e^- (no circular orbits - Bohr's Model)
- Can predict the probablity of finding an e^- within a given volume and given energy

2) (1926) Erwin Schrodinger
formulated an equation to describe the behavior and energies of submicroscopic particles

Schrodiner equation incorporates both
a) particle behavior: terms of mass (m)
b) wave behavior: terms of wave function (Ψ, psi)
a more useful term is Ψ^2 - the probability of finding the e^- in a certain region in space

Schrodinger's equation lets us calculate the probability that an electron is at a particular point in space.

The region of space an e^- is most likely to be found is called an atomic orbital. The atomic orbital is often represented as an electron density cloud around the nucleus. The density cloud is the probability that an e^- will be found in a particular region of an atom.

The atomic orbitals have various shapes, which are classified into four main types

atomic orbital	name	shape
s-orbital	*s*harp	sherical cloud
p-orbital	*p*rincipal	dumbell cloud - two lobes on opposite sides of the nucleus
d-orbital	*d*iffuse	complicated shapes
f-orbital	*f*undamental	complicated shapes

V) Quantum Numbers

Schrodinger found that an atomic orbital is identified by three numbers called quantum numbers

A) Principal Quantum Number (n)

- determines the energy of the e^-
- measure of the most probable distance from the nucleus
  (the larger the number, the further from the nucleus)
- known as a shell of e^-

n	letter designation
1	K
2	L
3	M
4	N
. . .	
∞	

B) Angular Momentum Quantum Number (l)

- orbital shape is given by l
- within a shell of electron exist subhells (l)
- number of subshells possible in a shell is limited by the value of n

l = 0, 1, 2, 3, . . . n-1

l	subshell label
0	s
1	p
2	d
3	f

C) Magnetic Quantum Number (m_l)

- within subshells exist orbitals
- m_l value designates the number of orbtials within a subshell
- orbtials differ in orientation and not shape
- number of orbitals within a given subshell = $2l + 1$

m_l = $-l$, ... , 0, ... , $+l$

i.e. if $l = 3$, $m_l = -3, -2, -1, 0, +1, +2, +3$ (a total of 7 orbital within the subshell f)
Table showing possible values of the three quantum numbers

n	l	subshell	m_l	no. of orbitals
1	0	1s	0	1
2	0	2s	0	1
	1	2p	-1, 0, +1	3
3	0	3s	0	1
	1	3p	-1, 0, +1	3
	2	3d	-2, -1, 0, +1, +2	5
4	0	4s	0	1
	1	4p	-1, 0, +1	3
	2	4d	-2, -1, 0, +1, +2	5
	3	4f	-3, -2, -1, 0, +1, +2, +3	7