Chem. 140B

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Introduction to Quantum Chemistry

Why as a chemist, do you need to learn this material?

Without Quantum Mechanics, how would you explain:

- Periodic trends in properties of the elements
- Structure of compounds
  e.g. Tetrahedral carbon in ethane, planar ethylene, etc.
- Bond lengths/strengths
- Discrete spectral lines (IR, NMR, Atomic Absorption, etc.)
- Electron Microscopy & surface science

Without Quantum Mechanics, chemistry would be a purely empirical science.

(We would be no better than biologists…)

Classical Physics

On the basis of experiments, in particular those performed by Galileo, Newton came up with his laws of motion:

1. A body moves with a constant velocity (possibly zero) unless it is acted upon by a force.
2. The "rate of change of motion", i.e. the rate of change of momentum, is proportional to the impressed force and occurs in the direction of the applied force.
3. To every action there is an equal and opposite reaction.
4. The gravitational force of attraction between two bodies is proportional to the product of their masses and inversely proportional to the square of the distance between them.

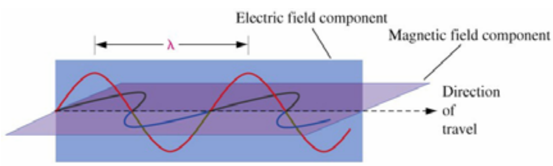
$$F = G \times \left(\frac{m_1 m_2}{r^2}\right)$$

The Failures of Classical Mechanics

1. Black Body Radiation: ***The Ultraviolet Catastrophe***
2. The Photoelectric Effect: ***Einstein's belt buckle***
3. The de Broglie relationship: ***Dude you have a wavelength!***
4. The double-slit experiment: ***More wave/particle duality***
5. Atomic Line Spectra: ***The 1st observation of quantum levels***

Black Body Radiation

Light Waves: ***Electromagnetic Radiation***



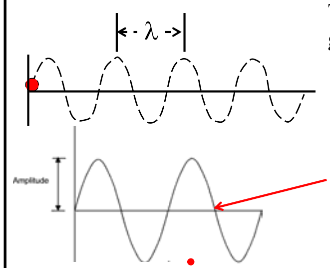
Light is composed of two perpendicular oscillating vectors waves:

A magnetic field & an electric field

As the light wave passes through a substance, the oscillating fields can stimulate the movement of electrons in a substance.

$$\lambda\ (\text{m}) \times \nu\ (\text{s}^{-1}) = c\ (\text{m s}^{-1}) \qquad \nu = \frac{c}{\lambda}$$

Light is characterized by a ***wavelength*** and ***frequency***:



The wavelength is given the symbol λ *(lambda)*

λ can be measured from crest to crest or trough to trough.

a node is a point of zero amplitude

The *amplitude* measures the crest height of a wave.

The frequency of light ν (*nu*) measures the number of crests that pass through a point in space per second.

Wavelength has units of length: m… cm… µm… nm… pm

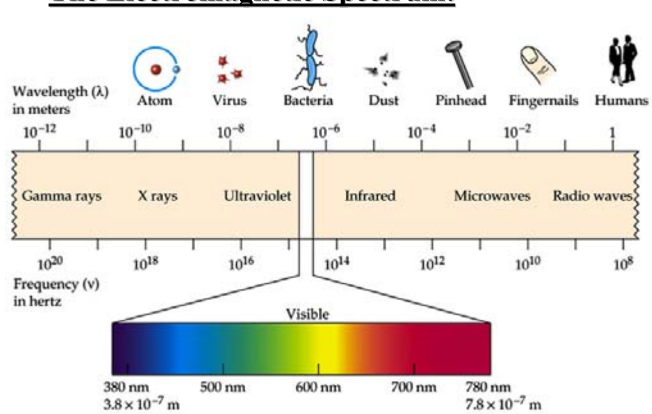
Frequency has units of inverse time: s^{-1} or Hz (hertz)

$$\lambda\ (\text{m}) \times \nu\ (\text{s}^{-1}) = c\ (\text{m s}^{-1})$$

"***C***", the speed of electromagnetic radiation (light) moving through a vacuum is: 2.99792458×10^8 m/s

$$\nu = \frac{c}{\lambda} \qquad \lambda = \frac{c}{\nu}$$

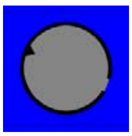
The Electromagnetic Spectrum:



Quantized Energy and Photons

1900: Max Planck explained the phenomenon "Black Body Radiation" by concluding that light must be ***quantized***.

Cavity with a small opening

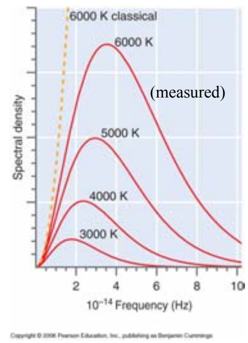


When light enters the cavity it is reflected throughout the internal surface.

The light that escapes is representative of the internal temperature of the the cavity.

Classical theory predicts that the intensity of the light that escapes increases with the frequency of the light.

This leads to what is called the "***Ultraviolet Catastrophe***".



Experimentally, the wavelength of maximum intensity shifts to the blue as temperature increases for a BBR.

Classically, the intensity (spectral density) of the light emitted by a black body radiator is predicted to increase infinity as the temperature increases (as λ decreases).

Rayleigh-Jeans Law

$$f(\lambda) = \frac{2\pi ckT}{\lambda^4}$$

Based on this classical interpretation, for a given temperature, as λ approaches zero (more to the UV) the intensity approaches infinity.

Plank's equation corrected for classical failure by stating that energy can only be transferred in a finite minimum quantity.

h = Planck's constant (6.626×10^{-34} J·s)

As λ decreases:

$$f(\lambda) = \frac{2\pi ckT}{\lambda^5}\left(\frac{h}{e^{\frac{hc}{\lambda kT}} - 1}\right)$$

Planck's correction avoids the Ultraviolet Catastrophe by reducing the intensity as λ decreases:

Planck's Law

$$E = h \times \nu$$

As the *frequency* of light increases, the energy of the photon increases

combining: $\nu = \frac{c}{\lambda}$ ***yields:*** $E = \frac{h \times c}{\lambda}$

As the *wavelength* of light increases, the energy of the photon decreases

Blue Light, (higher frequency)

has more energy than

Red Light, with a longer wavelength.

As the frequency of light increases, the energy ***increases***.
As the wavelength of light increases, the energy ***decreases***.

$$E_{photon} = h \cdot \nu = \frac{hc}{\lambda}$$

Red Light (650 nm)

$$E_{photon} = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\,\text{Js}\times3.00\times10^{8}\,\text{m/s}}{650\ \text{nm}\times\frac{1\ \text{m}}{10^{9}\ \text{nm}}} = 3.06\times10^{-19}\ \frac{\text{J}}{\text{photon}}$$

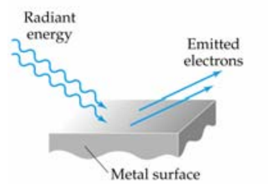
This doesn't seem like much, but when you consider a mole of photons…

184 kJ/mol

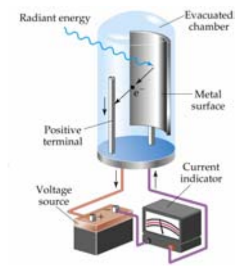
Now that's what I'm talkin' about!

In 1905 Albert Einstein used Planck's Law to explain the ***Photoelectric Effect***.

When light strikes the surface of certain metals, electrons are ejected.



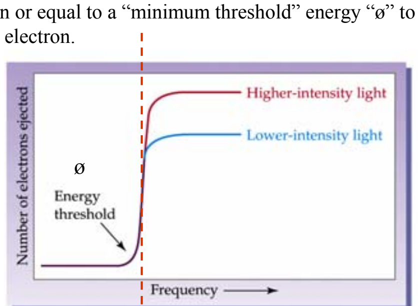
The ejected electrons produce a current that proportional to their number.



It is found that the current produced follows the light intensity.

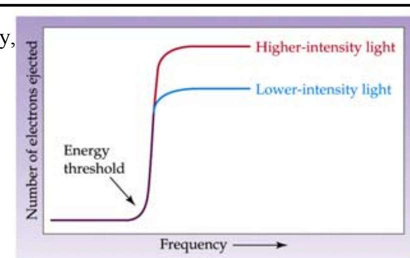
And there is a frequency dependence, below which, no electros are ejected.

•1905 – Einstein: Oscillators in light source can only have quantized energies $nh\nu$ $(n = 0,1,2,3,\ldots)$.
•As oscillators change their energy from $nh\nu$ to $(n-1)h\nu$ they emit radiation of frequency ν and energy $h\nu$ (photon).
•Therefore, if an oscillator is to absorb a photon, the photon's energy must be greater then or equal to a "minimum threshold" energy "ø" to stimulate ejection of an electron.



Below the threshold energy, no ejection of electrons occur.

Above that, any excess energy supplied by the photon is manifested in the kinetic energy of the ejected electron.



At the threshold, the electrons are ejected with zero KE.

$$\text{KE (electron)} = \text{E (photon)} - \Phi = \tfrac{1}{2} m_e v^2$$

$$E(\text{photon}) = h\nu = \frac{hc}{\lambda}$$

Example: A certain metal has a threshold Energy (ø) of 146.0 kJ/mol.

Will 532 nm light cause electrons to be ejected?

if E (photon) > ø then electrons are ejected

i.e. the energy of the photon must be greater then the threshold.

Solution: Calculate the energy of a mole of 532 nm photons

$$E_{photon} = h\nu = \frac{hc}{\lambda} =$$

$$E_{photon} = \frac{6.626\times10^{-34}\,\text{Js} \times 3.00\times10^{8}\,\frac{\text{m}}{\text{s}}}{532\text{ nm} \times \frac{\text{m}}{10^{9}\text{ nm}}} = 3.74\times10^{-19}\text{J}$$

Example: A certain metal has a threshold Energy (Φ) of 146.0 kJ/mol.

Will 532 nm light cause electrons to be ejected?

if E (photon) > Φ then electrons are ejected

i.e. the energy of the photon must be greater then the threshold.

$$3.74\times10^{-19}\,\frac{\text{J}}{\text{photon}} \times \frac{\text{kJ}}{10^{3}\,\text{J}} \times \frac{6.022\times10^{23}\,\text{photons}}{\text{mol}} = 225\text{ kJ/mol}$$

E(photon) > Φ ∴ Electron are ejected

The Wave-like Nature of a Particle

Louis de Broglie in response to Planck & Einstein's assertion that light was "particle-like" (photon) stated that small particles moving fast could exhibit a characteristic wavelength.

$$E = mc^2$$

$$h\nu = mc^2$$

$$\frac{h\nu}{c} = mc = p \text{ (momentum)}$$

Conclusion:

Light waves have mass, particles have a wavelength.

since $\frac{\nu}{c} = \frac{1}{\lambda}$ $\quad \frac{h}{\lambda} = p$ or $\lambda = \frac{h}{p}$

What is the de Broglie wavelength of a 1 gram marble traveling at 10 cm/s

$h = 6.63 \times 10^{-34}$ J s

$\lambda = 6.6 \times 10^{-30}$ m $= 6.6 \times 10^{-20}$ Å (insignificant)

What is the de Broglie wavelength of an electron traveling at 0.1 c (c=speed of light)?

$c = 3.00 \times 10^{8}$ m/s

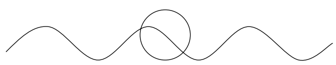
$m_e = 9.1 \times 10^{-31}$ kg

$\lambda = 2.4 \times 10^{-11}$ m $= 0.24$ Å

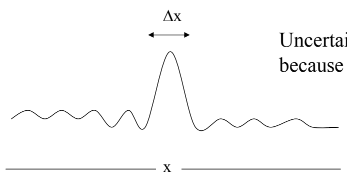
(on the order of atomic dimensions)

The particle and the wave:

The electron looks like a wave superimposed on a particle:



The electron appears as a build up of amplitude in the wave at position x:

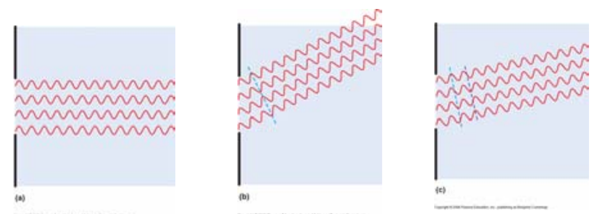


Uncertainty arises because of the width at x.

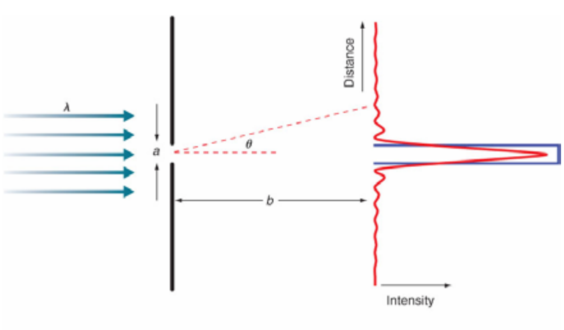
The Double-slit experiment

When light waves impinge upon a single slit, they may pass such that those incident clear with no destructive interference (a).

When light waves at acute angles, they do so with interference that is related to the angle of incidence. (b) and (c)



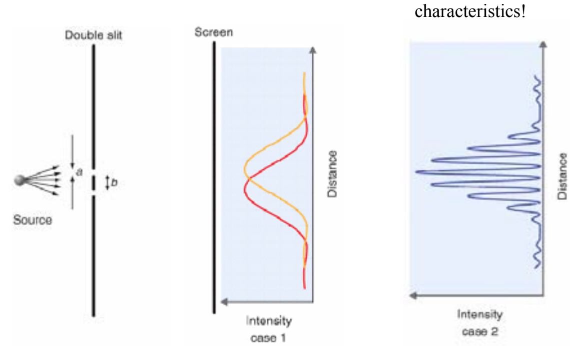
The result of wave transmission amplitude build up is a diffraction pattern.



A source of electrons are directed toward the slits.

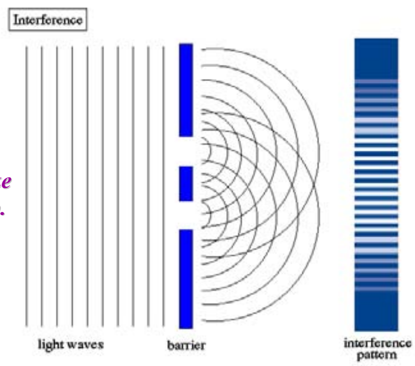
With one slit closed, we see the expected build up of intensity.

With both slits open, we see a diffraction pattern that is fits wavelike characteristics!



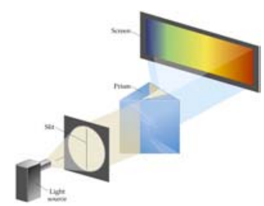
Such a pattern can only occur if the particle passes through both slits simultaneously!

The particle must have wavelike properties to do so.

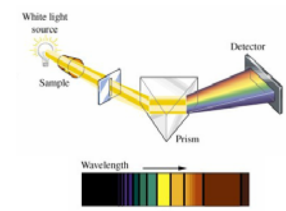


Line Spectra and the Bohr Model

1860: Robert Wilhelm Bunsen and Gustav Kirchoff noted the presence of dark lines arising from absorption of light when observing the spectrum of a bright light source through the flame seeded with alkali metals.



Normal spectrum of white light.



Gaps due to absorption by atoms in the flame

Atomic Line Spectra

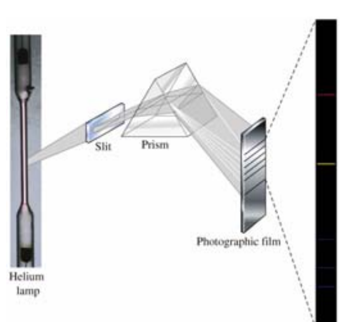
When a discharge lamp of He is passed through a prism,

Zap!

He(g) + ⚡ ⟶ He*(g)

The He(g) is excited.

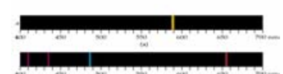
The excited state relaxes through collisions, producing light only at certain frequencies (colors).



He*(g) ⟶ He(g) + $h\nu$

Atomic Line Spectra:

Pre-1900 – Numerous researchers produced atomic spectra by heating up atoms of a material to high temperature and collecting the emitted energy in the form of an atomic spectrum.



1911 – Rutherford proposes model of the atom. Positive central nucleus surrounded by many electrons.

1913 – Bohr's laws of the Hydrogen atom structure:

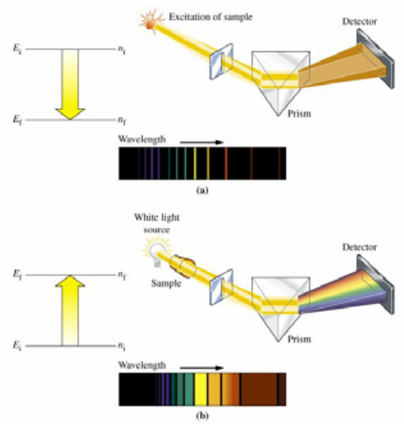
1. Electron orbits nucleus (like a planet around the sun)
2. Of the possible orbits only those for which the orbital angular momentum of the electron is an integral multiple of $h/2\pi$ are allowed.
3. Electrons in these orbits don't radiate energy.
4. When an electron changes its orbit a quantum of energy (photon) is emitted with energy $\Delta E = h\nu$, where ΔE is the energy difference between the two orbits.

Emission of Light:

Electrons move from a higher level (state) to a lower level (state)

Absorption of Light:

Electrons move from a lower level (state) to a higher level (state)



Energy Levels in the Bohr Atom:

$$E_n = -\frac{R_H}{n^2}$$

The spacing between adjacent levels is given by:

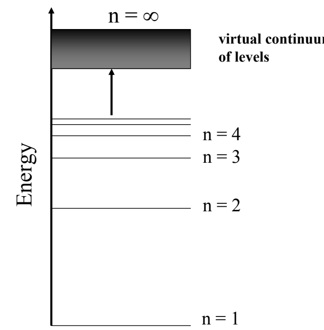
$$\Delta E = E_{n+1} - E_n$$

between n = 1 and 2:

$$\Delta E = \frac{3R_H}{4} = 0.75 \times R_H$$

between n = 2 and 3:

$$\Delta E = \frac{5R_H}{36} = 0.139 \times R_H$$



(as n increases, the levels get closer together)

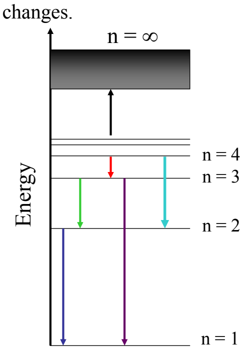
The energies of different transitions:

Since the gaps between states gets closer and closer together with increasing n, the frequency of the light emitted changes.

2→1 > 3→2 > 4→3

And

3→1 > 4→2

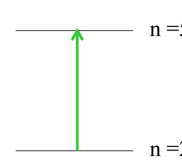


Determine the wavelength (in nm) associated with an electron jumping from n = 2 to n = 5 in a hydrogen atom.

$$\Delta E = -Rhc\left(\frac{1}{n_{final}^2} - \frac{1}{n_{initial}^2}\right) \qquad n_{final} = 5 \qquad n_{initial} = 2$$

$$\Delta E = -2.179\times10^{-18}\,J \times\left(\frac{1}{5^2} - \frac{1}{2^2}\right)$$

$$\Delta E = 4.576\times10^{-19}\,J$$



The value of ΔE is positive because this is an absorption.

Determine the wavelength (in nm) associated with an electron jumping from n = 2 to n = 5 in a hydrogen atom.

$$|\Delta E| = \frac{h \times c}{\lambda_{photon}} \quad = 4.576 \times 10^{-19}\,J$$

$$\lambda_{photon}\,(meters) = \frac{h \times c}{|\Delta E|} \quad = \frac{6.626 \times 10^{-34}\,Js \;\times\; 2.997 \times 10^{8}\,m/s}{4.576 \times 10^{-19}\,J}$$

$$\lambda_{photon} = 4.340 \times 10^{-7}\,m \;\times \frac{10^{9}\,nm}{1m} = \quad 434.0\ nm$$

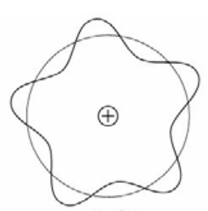
Schrödinger Wave Equations and the Origins of Orbitals

Taking on the ideas of Bohr, de Broglie and Heisenberg, Irwin Schrödinger proposed that matter can be described as a wave.

In this theory, the electron is treated as both a wave and a particle.

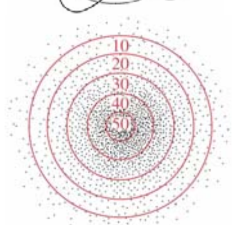
An electron is described by a ***Wave Function*** **"Ψ"** that completely defines a system of matter.

The ***mental picture*** of an electron corresponds to a wave superimposed upon the radial trajectory of a particle orbiting the nucleus.



The position of an electron is best described by the image of a dart board:

As the ***Schrödinger Wave Equation*** is solved time and time again, the position of an electron is found such that each "hit" builds up a pattern.



Probability Distributions