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.

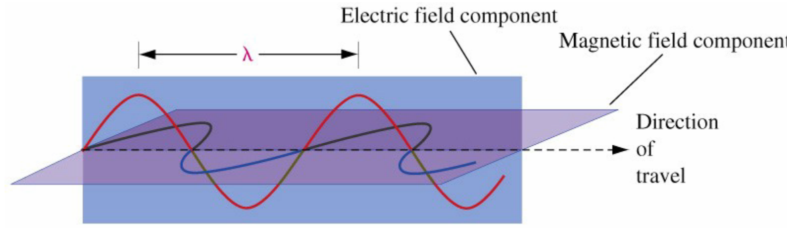
$$F = G \times \left(\frac{m_1 m_2}{r^2} \right)$$

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***



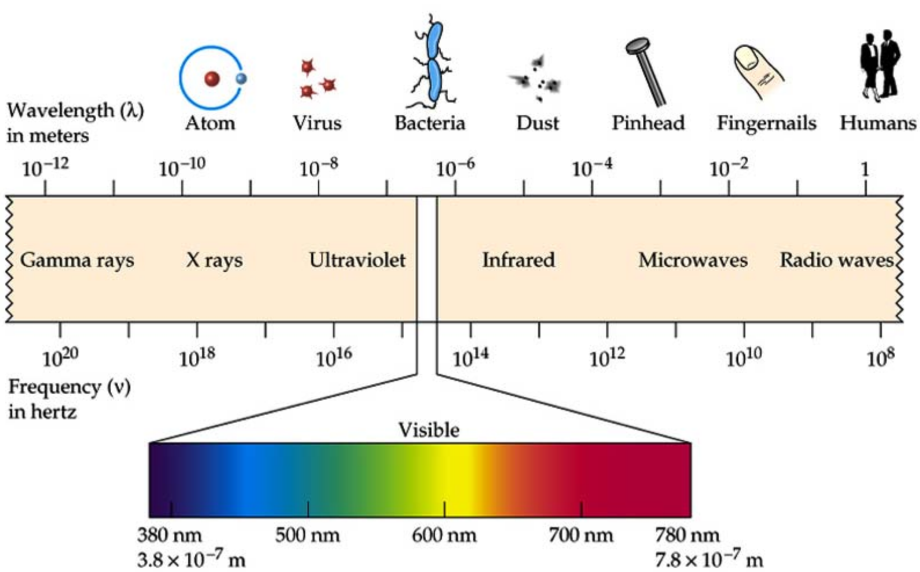
Light is composed of two perpendicular oscillating vectors waves:

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.

λ (m) $\times$ ν (s^{-1}) = c (m s^{-1}) $\qquad \nu = \dfrac{c}{\lambda}$

The Electromagnetic Spectrum:



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…

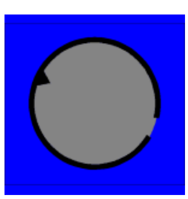
184 kJ/mol

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

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



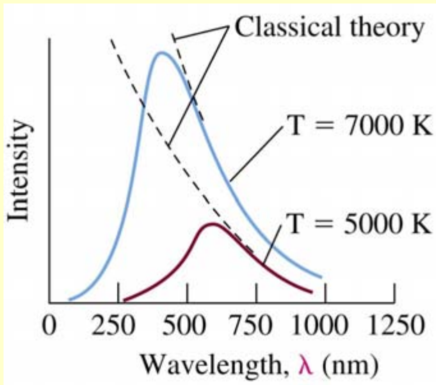
When light enters the cavity it is reflected throughout the internal surface.

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 "***Ultraviolet Catastrophe***".

Classically, the intensity of the light increases to infinity as the temperature increases.



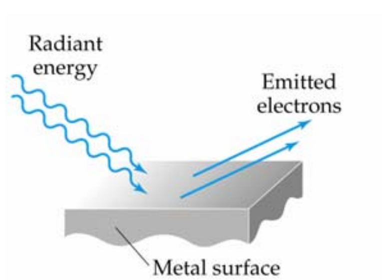
Experimentally, the maximum intensity shifts to the blue as temperature increases.

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

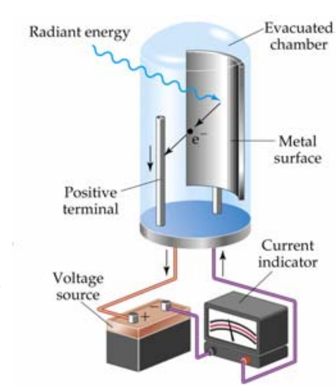
$$\rho(v)dv = \frac{8\pi h}{c^3} v^3 \frac{1}{e^{hv/kT} - 1} dv$$

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

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



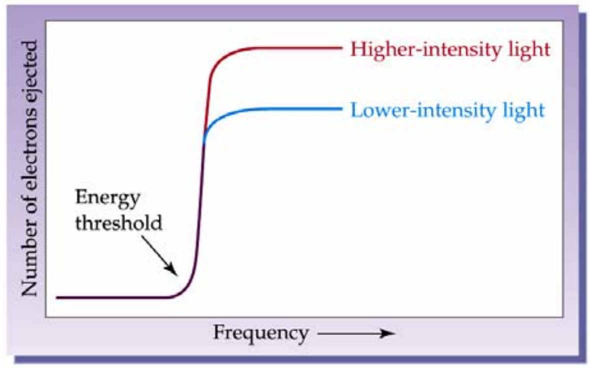
The ejected electrons produce a current that proportional to their number.



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 $(n\text{-}1)h\nu$ emit radiation of frequency ν and energy $h\nu$ (photon). If the photons energy is more than Φ then an electron is ejected:



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

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.

$$E = mc^2$$

$$h\nu = mc^2$$

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

since $$\frac{\nu}{c} = \frac{1}{\lambda}$$

$$\frac{h}{\lambda} = p \quad \text{or} \quad \lambda = \frac{h}{p}$$

Conclusion:

Light waves have mass,

particles have a wavelength.

Dude, you gotta wavelength!!

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

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

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

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

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

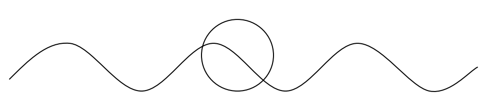
$m_e = 9.1\text{x}10^{-31}$ kg

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

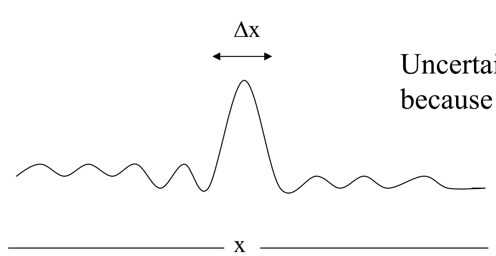
(on the order of atomic dimensions)

The particle and the wave:

The electron looks like a wave superimposed on a particle:



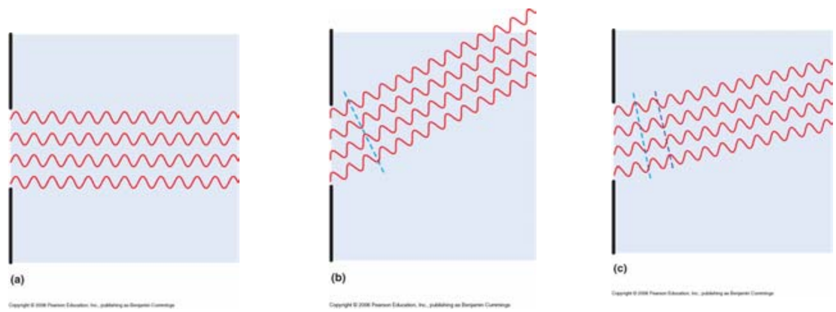
The electron appears as a build up of amplitude in the wave at position x:



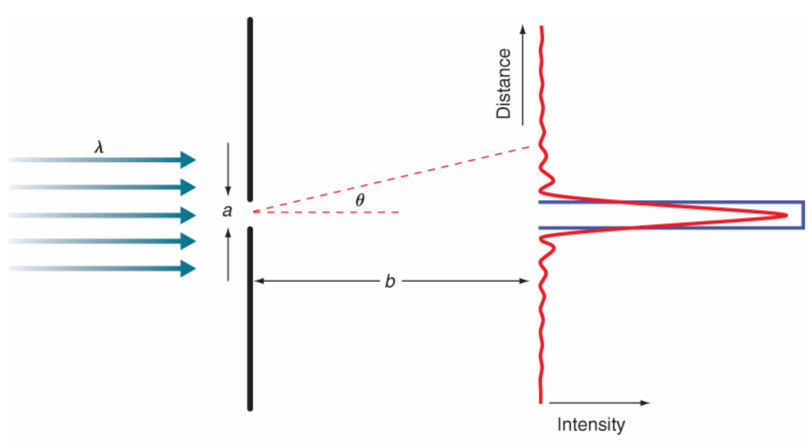
Uncertainty arises because of the width at x.

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), whereas those at acute angles pass with interference that is related to the angle of incidence. (b) and (c)



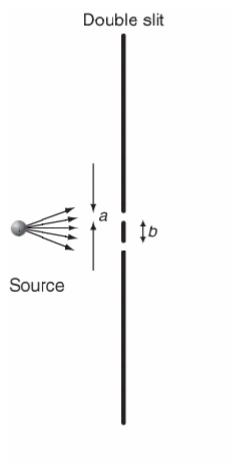
The result of wave transmission amplitude build up is a diffraction pattern.

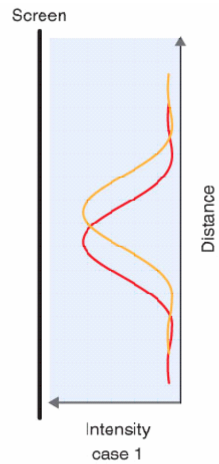


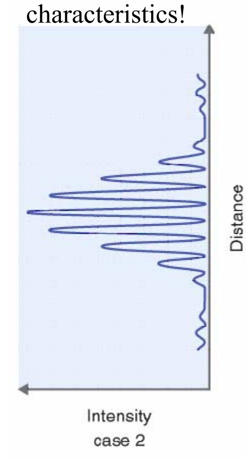
A source of electrons are directed toward the slits.

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

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

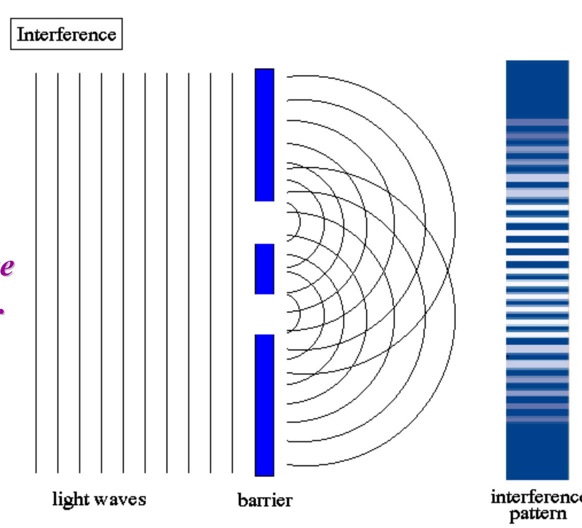






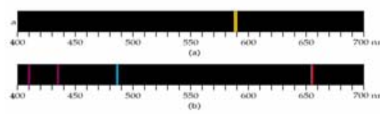
Such a pattern can only occur if the particle passes through both slits simultaneously!

The particle must have wavelike properties to do so.



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.

The Bohr Atom:

When an electron jumps form a lower state to a higher state, Energy (light) is absorbed.
When an electron jumps form a higher state to a lower state, Energy is (light) emitted.

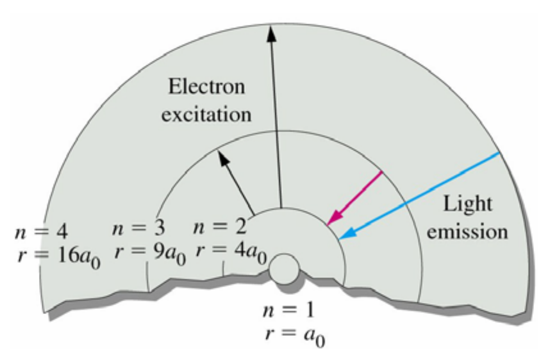
The Bohr Model:

$$r_n = n^2 a_o$$

n = 1, 2, 3, 4…

The Energy Levels:

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

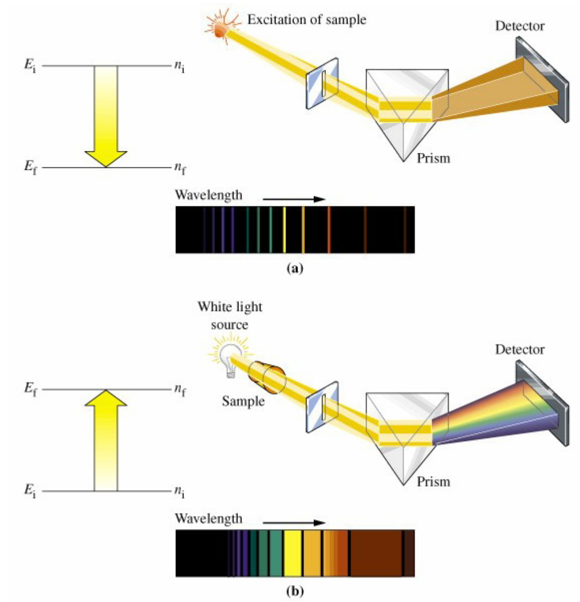


Emission of Light:

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:

$$E_n = \frac{-Z^2Rhc}{n^2}$$

The spacing between adjacent levels is given by:

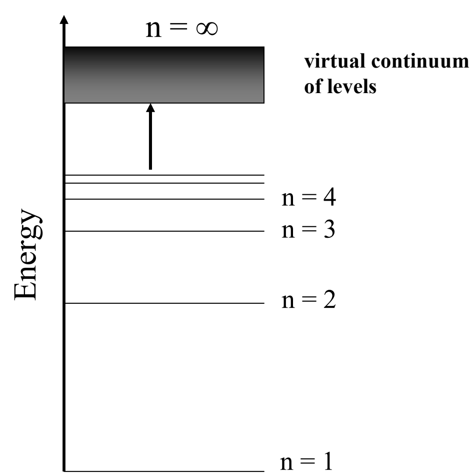
$$\Delta E = E_{n+1} - E_n$$

between n = 1 and 2:

$$\Delta E = \frac{3Z^2Rhc}{4} = 0.75 \times Z^2Rhc$$

between n = 2 and 3:

$$\Delta E = \frac{5Z^2Rhc}{36} = 0.139 \times Rhc$$



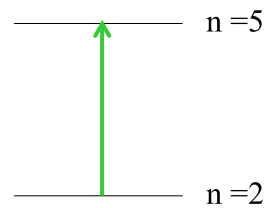
(as n increases, the levels get closer together)

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.

$$|\Delta E| = \frac{h\times c}{\lambda_{photon}} = 4.576\times10^{-19}\,J$$

$$\lambda_{photon}\,(\text{meters}) = \frac{h\times c}{|\Delta E|} = \frac{6.626\times10^{-34}\,Js \times 2.997\times10^{8}\,m/s}{4.576\times10^{-19}\,J}$$

$$\lambda_{photon} = 4.340\times10^{-7}\,m \times\frac{10^9\,nm}{1m} = $$ **434.0 nm**