Chapter 1 – The Dawn of Quantum Theory

* By the Late 1900's
  - Chemists had
    -- generated a method for determining atomic masses
    -- generated the periodic table based on empirical observations
    -- resolved the structure of benzene
    -- elucidated the fundamentals of chemical reactions
  - Physicists had
    -- generated the relationship between heat and work
    -- developed the first two laws of thermodynamics
    -- demonstrated the wavelike nature of light
    -- applied statistical mechanics to chemical systems

* *Sounds great so what's the problem?*
  - The general scientific community believed:
    -- atoms are the basic constituents of matter
    -- Newton's Laws were universal
    -- all the phenomenon in the world is deterministic
  - There were several experiments which could not be explained based on this dogma:
    -- black body radiation
    -- the photoelectric effect
    -- discrete atomic spectra
  - What conclusions do these experiments lead to?
    -- atoms are not the smallest/most microscopic object
    -- we need something beside Newtonian physics to explain these experiments

* And then came quantum mechanics …
  - explains these unsolved issues
  - explains bonding, structure and reactivity
  - uses probability instead of determinism
  - generates rules for electrons in atoms and molecules

* Let's talk about these persnickety experiments
  - Black Body Radiation: if we apply heat to any object it will emit light
    red to white to blue
    -- classical physics assumed this emission of light was a result of oscillating e-'s
        which act as antennae and can oscillate equally well at any frequency, ν
    -- Rayleigh-Jeans Law: used classical physics to generate the relationship between
        spectral density, $\rho(\nu, T)$, and ν

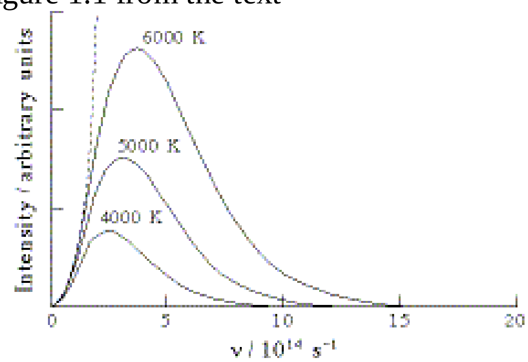
$$d\rho(\nu,T) = \rho_\nu(T)d\nu = \frac{8\pi k_B T}{c^3}\nu^2 d\nu \rightarrow \boxed{\rho_\nu(T) \propto \nu^2}$$

where $\rho_\nu(T)d\nu$ is the radiant energy density btwn ν and $\nu + d\nu$

$$k_B = R/N_A = \frac{8.314\ \frac{J}{mol\bullet K}}{6.022\times10^{23}\ \frac{particles}{mol}} = 1.380\times10^{-23}\ \tfrac{J}{K}\ \text{(Boltzmann constant)}$$

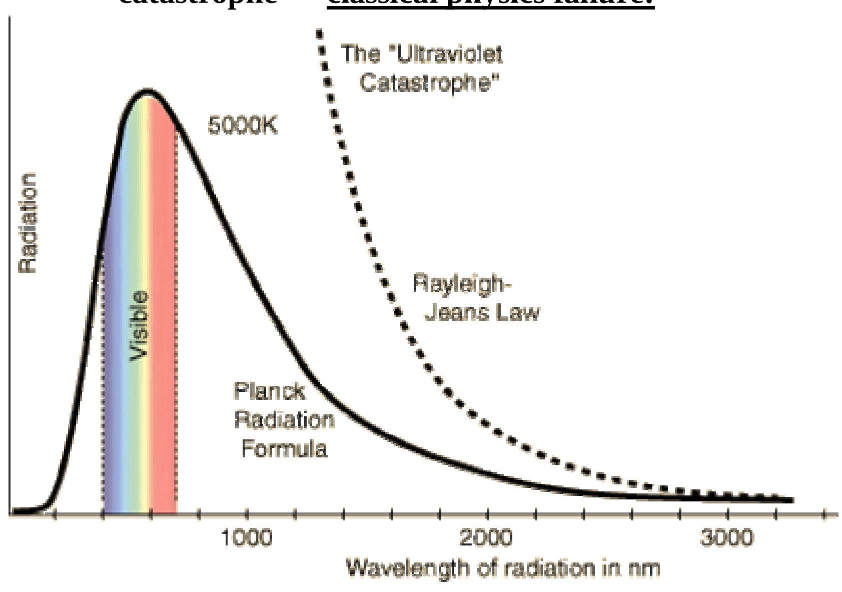
T = absolute temperature (K) $c = 2.998\times10^{8}\ \frac{m}{s}$ (speed of light)

--- Graphically: Figure 1.1 from the text



---- the dashed line is ν^2 and is consistent with the Rayleigh-Jeans Law at low T

---- this relationship does not work at high temperatures – called the **UV catastrophe** --- **<u>classical physics failure!</u>**



http://hyperphysics.phy-astr.gsu.edu/hbase/mod6.html#c4

--- So, how do we fix this? Planck to save the day

---- Planck proposed the energy of these oscillating electrons $\propto$ frequency or $E = nh\nu$ where $n = 1, 2, \ldots$ and h is proportionality constant

---- Blackbody radiation according to Planck

$$d\rho(\nu,T) = \rho_\nu(T)d\nu = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/k_BT}-1}d\nu$$

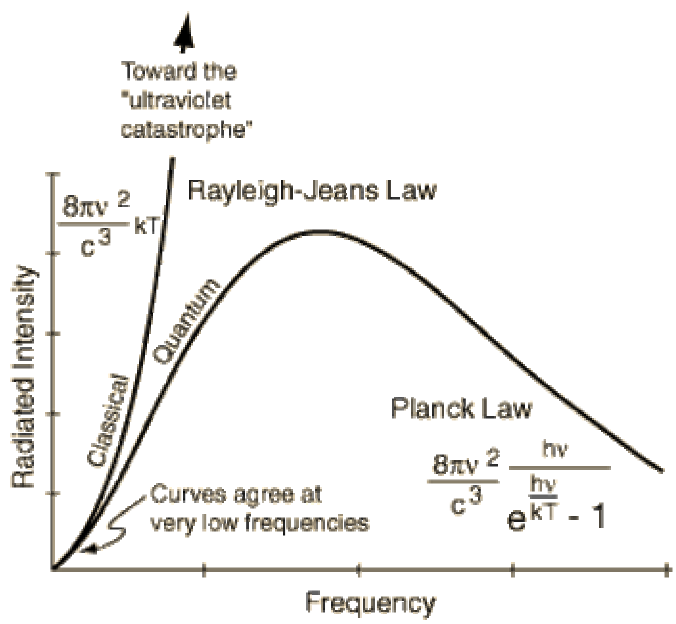
Recall the Taylor Series for $e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \ldots$ for $-\infty < x < \infty$

$$\therefore\ e^{h\nu/k_BT} - 1 = 1 + \frac{h\nu}{k_BT} + \left(\frac{h\nu}{k_BT}\right)^2\frac{1}{2!} + \ldots - 1$$

This expression can reproduce the classical description at low frequencies or for $h\nu << k_BT$

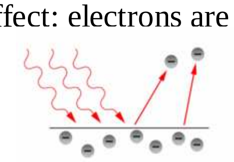
$$e^{h\nu/k_BT} - 1 = 1 + \frac{h\nu}{k_BT} + \left(\frac{h\nu}{k_BT}\right)^2\frac{1}{2!} + \ldots - 1 \sim \frac{h\nu}{k_BT} \text{ as } h\nu \to 0$$

$$\rho_\nu(T)d\nu = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/k_BT}-1}d\nu = \frac{8\pi \cancel{h}}{c^3}\frac{\nu^{\cancel{3}2}k_BT}{\cancel{h}\cancel{\nu}}d\nu = \frac{8\pi k_BT}{c^3}\nu^2 d\nu$$



http://hyperphysics.phy-astr.gsu.edu/hbase/mod6.html#c4

- Photoelectric Effect: electrons are emitted from a metallic surface when exposed to UV radiation



http://en.wikipedia.org/wiki/Photoelectric_effect

-- Classical physics states that light is an electric field, $\vec{E}$, oscillating perpendicular to its direction of propagation and the intensity of the radiation $\propto \vec{E}^2$

--- the e-'s should oscillate along with the field and as the intensity increases so should these oscillations which will eventually lead to the ejection of an e- from the surface of the metal – **WRONG!**

--- the photoelectric should occur for any frequency as long as the intensity of the incident radiation is sufficiently high – **WRONG!**

-- Experimentally:

--- the kinetic energy of the ejected e- is independent of the intensity of the incident radiation

--- there is a threshold frequency, ν_0, which is dependent upon the metal

---- below this threshold no e-'s will be ejected from the surface

---- above this threshold the K.E. of the e-'s varies linearly with ν

-- Einstein to the rescue, he proposed:

--- light is made up of energy packets aka photons aka quanta

--- the energy of a photon is proportional to the light frequency, E = hν

$$E = h\nu \rightarrow K.E. = \frac{1}{2} mv^2 = h\nu - \Phi$$

--- Φ is called the work function and is analogous to the ionization energy of an isolated metallic atom (remember we are taking away an e-)

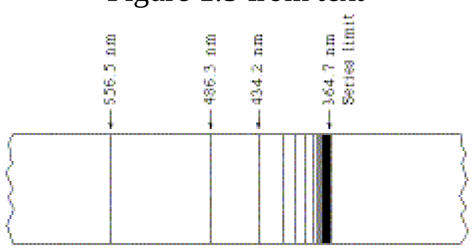
--- since $\frac{1}{2} mv^2$ must be ≥ 0, then $h\nu \geq \Phi$ or $h\nu_0 = \Phi$ hence $K.E. = h\nu - h\nu_0$

--- the constant h that Einstein predicted matched that of Planck's – **SUCCESS!**

- Hydrogen Atom Spectrum

-- In the 19th century scientists knew that each atom possessed a characteristic emission spectrum

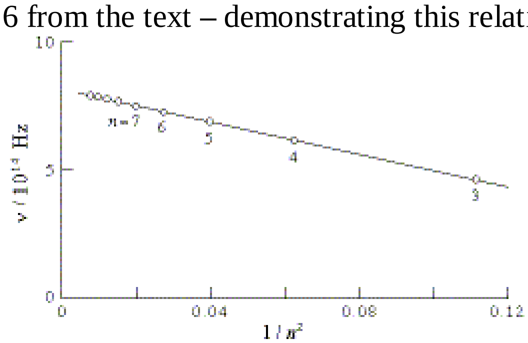
Figure 1.5 from text



--- these are called line spectra since they emit energy at a select number of frequencies – once again the spectrum is **not continuous** but **discrete -- quantized**

-- Balmer was the first one to show that these line spectra followed a particular pattern, $\nu \propto n^{-2}$ where n = 3, 4, 5, …

Figure 1.6 from the text – demonstrating this relationship



--- From this pattern he derived the relationship:

$$\nu = 8.2202 \times 10^{14} \left(1 - \frac{4}{n^2}\right) Hz \text{ and } \tilde{\nu} = 109680 \left(\frac{1}{2^2} - \frac{1}{n^2}\right) cm^{-1} \quad n = 3, 4, 5 \ldots$$

--- This relationship will give rise to all of the visible emissions for H, but what about the rest? Here comes Rydberg

-- Rydberg develops a formula which includes all of the possible emission lines of hydrogen

$$\tilde{\nu} = \frac{1}{\lambda} R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) cm^{-1} \text{ where } n_2 > n_1$$

- Wave-particle duality – here comes de Broglie
  -- classical optics supports the idea of light as a wave, e.g. refraction, etc.
  -- the photoelectric effect suggests that it can also be thought of as a particle
  -- enter de Broglie: he proposed that if light which is clearly a wave can act as particle than why can't a particle act as a wave
  -- Einstein proved that wavelength, λ, and momentum, p, are inversely proportional: $\lambda = \frac{h}{p}$
  -- de Broglie claimed matter would also follow this relationship
    --- for matter p = mv where m = mass and v = velocity
    --- therefore the de Broglie wavelength is given by $\lambda = \frac{h}{mv}$
    --- but if matter acts like a wave then why aren't we all oscillating?

    Example: What is the de Broglie wavelength of 75 kg boy and an electron each traveling at 10 mph?

$$\lambda_{boy} = \frac{h}{mv} = \frac{6.626\times10^{-34} J\bullet s}{75kg\times10\frac{miles}{hour}} = \frac{6.626\times10^{-34}\frac{kg\bullet m^2}{s}}{75kg\times10\frac{miles}{hour}\times\frac{1.6093km}{miles}\times\frac{hour}{3600s}\times\frac{1000m}{km}} = 1.98\times10^{-36} m$$

Too small to be detectable

$$\lambda_e = \frac{h}{mv} = \frac{6.626\times10^{-34} J\bullet s}{9.109\times10^{-31}kg\times10\frac{miles}{hour}} = \frac{6.626\times10^{-34}\frac{kg\bullet m^2}{s}}{9.109\times10^{-31}kg\times10\frac{miles}{hour}\times\frac{1.6093km}{miles}\times\frac{hour}{3600s}\times\frac{1000m}{km}} = 1.63\times10^{-7} m$$

On the order of UV

* Bohr, the hydrogen atom and Rydberg
  - the hydrogen atom
    -- consists of a massive positive nucleus and a smaller negative e- which is in a fixed orbit about the centrally located nucleus
    -- Coulomb's law: force of attraction btwn an e- and a proton (the nucleus of hydrogen)

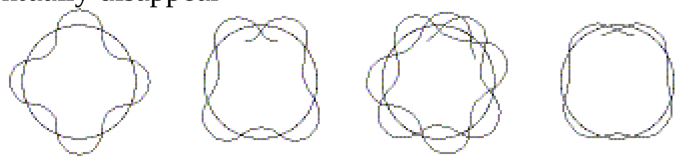
$$f = \frac{e^2}{4\pi\varepsilon_0 r^2}$$

where -e is the charge of an e-, e the charge of a proton, r is the radius and ε_0 is the permittivity $\approx 8.854\times10^{-12}\, C^2/J\bullet m$

    -- Centrifugal force: $f = \frac{m_e v^2}{r}$ where m_e is the mass of an e-
  - Bohr's Assumptions:
    -- there are stable atomic states in which atoms do not radiate
      --- these states are given by E_n with n = 1, 2, 3, … where n = 1 is the lowest energy state or ground state and is the most negative

-- angular momentum is quantized or these stationary orbits require an integer number of de Broglie wavelengths

-- Figure 1.9 from the text: (a) represents the Bohr assumption and (b) – (d) show what happens if the integer assumption is not in place – the wave will eventually disappear



(a) (b) (c) (d)

$2\pi r = n\lambda$ *where* $n = 1, 2, 3, \ldots$ since $\lambda = \frac{h}{p}$, then $2\pi r = n\frac{h}{p} = \frac{nh}{m_e v}$

$$v = \frac{nh}{2\pi m_e r} = \frac{n\hbar}{m_e r} \text{ where } \hbar = h/2\pi$$

back to centrifugal force: $f = \frac{m_e v^2}{r} = \frac{m_e}{r}\left(\frac{n\hbar}{m_e r}\right)^2 = \frac{n^2\hbar^2}{r^3 m_e}$

set this equal to Coulomb's Law and solve for r:

$\frac{n^2\hbar^2}{r^3 m_e} = \frac{e^2}{4\pi\varepsilon_0 r^2} \rightarrow r = \frac{4\pi\varepsilon_0 n^2\hbar^2}{m_e e^2}$ for n = 1, r = 52.92 pm the Bohr radius

- Total E of our e-:

P.E. for an e- and a proton separated by distance r is $-\frac{e^2}{8\pi\varepsilon_0 r}$

$$E = K.E. + P.E. = \tfrac{1}{2}mv^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

recall $\frac{m_e v^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2}$ or $\tfrac{1}{2}m_e v^2 = \frac{e^2}{8\pi\varepsilon_0 r}$

$$\therefore E = -\frac{e^2}{8\pi\varepsilon_0 r}$$

substituting $r = \frac{4\pi\varepsilon_0 n^2\hbar^2}{m_e e^2}$ yields $E_n = -\frac{e^2}{8\pi\varepsilon_0} \bullet \frac{\pi m_e e^2}{\varepsilon_0 h^2 n^2} = -\frac{m_e e^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2}$ *where* $n = 1, 2, 3, \ldots$

- Relationship btwn E_n and Rydberg

-- $\Delta E_n = E_f - E_i = h\nu = -\frac{m_e e^4}{8\varepsilon_0^2 h^2}\frac{1}{n_f^2} + \frac{m_e e^4}{8\varepsilon_0^2 h^2}\frac{1}{n_i^2} = \frac{m_e e^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$

-- This expression looks suspiciously like the Rydberg expression

$$h\nu = hc\tilde{\nu} \text{ or } \tilde{\nu} = \frac{m_e e^4}{8\varepsilon_0^2 ch^2}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \therefore \frac{m_e e^4}{8\varepsilon_0^2 ch^2} \sim R_H$$

- Limitations of this lovely description

-- does not work for a system containing more than one e-
-- fails when a magnetic field is applied to the system

* More Uncertainty - Heisenberg
- Heisenberg uncertainty principle: the exact momentum and the position of e- cannot be know simultaneously or $\Delta x \Delta p \geq h$
  -- if we wish to know the location of an e- within a certain distance Δx we need a light source whose resolution is on the order of Δx or $\Delta x \approx \lambda$
  -- unfortunately as soon as we shine this light on our e- we change its momentum, Δp
  -- using the de Broglie relationship we obtain the Heisenberg uncertainty principle
  -- we will be revisiting this later
- Consequences of this uncertainty
  -- we do not know what the velocity is if we know the e- is in the atom
  -- Bohr assumed that the e- was a particle with known velocity and position
  -- in order to complete the picture we need a true wavelike description of e-'s