Chapter 1 – The Dawn of Quantum Theory

* By the Late 1800’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
  and here are a few of them:
  -- 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
  *What is it?*
  -- Objects when heated will turn from red to white to blue which is an increase in energy/frequency
  -- the exact frequency emitted is dependent upon the composition of the body
  -- an ideal body absorbs/emits all frequencies and hence is also called a blackbody and the radiation that is emitted blackbody radiation

*Classical Physics Breakdown*
-- 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, v
-- Rayleigh-Jeans Law: used classical physics to generate the relationship between
spectral density, \( \rho(\nu, T) \), and \( \nu \\
d\rho(\nu,T) = \rho_\nu(T)d\nu = \frac{8\pi k_B T}{c^3} \nu^2 d\nu \to \rho_\nu(T) \propto \nu^2 \\

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

\[
k_B = \frac{R}{N_A} = \frac{8.314 \text{J}/\text{mol K}}{6.022 \times 10^{23} \text{particles/mol}} = 1.380 \times 10^{-23} \frac{J}{K} \quad \text{(Boltzmann constant)}
\]

\( T = \) absolute temperature (K) \( c = 2.998 \times 10^8 \text{m/s} \) (speed of light)

--- Experimentally we should see the graphs below: Similar to Figure 1.1 from the text

http://www.topmarksed.com/blog/2015/06/05/a-comprehensive-guide-to-black-body-radiation-in-the-hsc/ 

--- As T is increased you can see the color change 

--- Unfortunately, we actually see a break down with Rayleigh-Jeans Law called the UV-Vis catastrophe where as energy increased/wavelength reduced the RJL goes to infinity rather than back to zero

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

--- the dashed line is \( \nu^2 \) and is consistent with the Rayleigh-Jeans Law at low T 

--- this relationship does not work at high temperatures – called the UV catastrophe --- classical physics failure!

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

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

--- PLOT TWIST: Planck was one of the first to recognize variables may not have a continuum of values but instead be quantized

--- Blackbody radiation according to Planck

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

----- This expression can reproduce the RJLaw at low frequencies or for $h\nu \ll k_B T$

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

\[ e^{h\nu/k_BT} - 1 = 1 + \frac{h\nu}{k_B T} + \left( \frac{h\nu}{k_B T} \right)^2 \frac{1}{2!} + \ldots - 1 \]

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

\[ \rho_\nu(T) d\nu = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{h\nu/k_BT} - 1} d\nu = \frac{8\pi k_BT}{c^3} \frac{\nu^3 k_BT}{f^2} d\nu = \boxed{\frac{8\pi k_BT}{c^3} \nu^3} \longleftrightarrow \text{RJLaw} \]

- Photoelectric Effect

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


-- Classical physics states

that light is an electric field, $\overrightarrow{E}$, oscillating $\perp$ to its direction of propagation and the intensity of the radiation $\propto \overrightarrow{E}^2$

--- 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, \( \nu_0 \), 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 \( \nu \)

-- 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, \( E = h\nu \)

\[
E = h\nu \rightarrow K.E. = \frac{1}{2} m\nu^2 = h\nu - \Phi
\]

--- \( \Phi \) 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 \( \frac{1}{2} m\nu^2 \) must be \( \geq 0 \), 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

--- 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 \( n = 3, 4, 5, \ldots \)

--- From this pattern he derived the relationship:
\[ \nu = 8.2202 \times 10^{14} \left( 1 - \frac{4}{n^2} \right) \text{Hz} \] and \[ \tilde{\nu} = 109680 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{cm}^{-1} \quad n = 3, 4, 5, \ldots \]

--- 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

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

* Angular Momentum – Spinning Right Round

Figure 1.9 from text

- If we rotate a single particle around a fixed point with radius \( r \) we can write the kinetic energy \( T \) as:

\[ T = \frac{1}{2} m v^2 = \frac{1}{2} m r^2 \omega^2 = \frac{1}{2} I \omega^2 \text{ where } I \text{ is the moment of inertia} \]

- When we write the K.E. in terms of momentum: \( \text{linear}: T = \frac{p^2}{2m} \quad \text{angular}: T = \frac{l^2}{2I} \)

* 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

-- A tale of two forces

--- Coulomb’s law: force of attraction btwn an e- and a proton (the nucleus of hydrogen)

\[ f = \frac{e^2}{4\pi\varepsilon_0 r^2} \text{ where } -e \text{ is the charge of an e-, } e \text{ the charge of a proton, } r \text{ is the radius} \]

and \( \varepsilon_0 \) is the permittivity \( \approx 8.854 \times 10^{-12} \text{ C}^2/\text{J} \cdot \text{m} \)

--- Centrifugal force: \( f = \frac{m_e v^2}{r} \) where \( m_e \) is the mass of an e-

--- these two must be equal in order to ensure the e- doesn’t speed toward nucleus

---- Solving for \( r \) we will reproduce the Bohr radius of hydrogen:
Bohr’s orbit - forcing angular momentum to be quantized:

\[ \frac{m_e v^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2} \]

\[ \text{Bohr's Assumptions:} \\
\text{-- there are stable atomic states in which atoms do not radiate} \\
\text{--- these states are given by } E_n \text{ with } n = 1, 2, 3, ... \text{ where } n = 1 \text{ is the} \]
\text{lowest energy state or ground state and is the most negative} \\
\text{-- angular momentum is quantized or these stationary orbits require an integer} \\
\text{number of de Broglie wavelengths} \\
\text{- Total E of our e-:} \\
P.E. for an e- and a proton separated by distance } r \text{ is } \frac{e^2}{4\pi\varepsilon_0 r}

\[ E = K.E. + P.E. = T + V = \frac{\gamma}{2} m v^2 - \frac{e^2}{4\pi\varepsilon_0 r} \]

\[ \text{recall } \frac{m_e v^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2} \Rightarrow \gamma m_e v^2 = \frac{e^2}{8\pi\varepsilon_0 r} \]

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

\[ \text{substituting } r = \frac{\varepsilon_0 n^2 h^2}{\pi m_e e^2} \text{ yields } E_n = -\frac{e^2}{8\pi\varepsilon_0} \frac{\pi m_e e^2}{\varepsilon_0 h^2 n^2} = -\frac{m_e e^4}{8\varepsilon_0^2 h^2} \frac{1}{n^2} \text{ where } n = 1, 2, 3, ... \]

\[ \text{- Relationship btwn } E_n \text{ and Rydberg} \]

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

\[ \text{-- This expression looks suspiciously like the Rydberg expression} \]

\[ h\nu = \frac{m_e e^4}{8\varepsilon_0^2 c h^2} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = \frac{m_e e^4}{8\varepsilon_0^2 c h^2} - R_H \]

\[ \text{- Meet Reduced Mass} \]

Figure 1.11 from text
-- at the center of mass \( m_1 r_1 = m_2 r_2 \)

-- as we have said previously: \( T = \frac{1}{2} I \omega \)

-- where our moment of inertia can be written in terms of reduced mass:

\[
\text{reduced mass } \mu = \frac{m_1 m_2}{m_1 + m_2} \quad & I = \mu \nu^2
\]

-- looking back at our H-atom the reduced mass turns out to be \( m_e \)

-- Overall, the Bohr model works great for any H-like system (He\(^+\) or Li\(^{2+}\))

- 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

* 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 a particle then why can’t a particle act as a wave
  - Einstein proved that wavelength, \( \lambda \), and momentum, \( p \), are inversely proportional:

\[
\lambda = \frac{h}{p}
\]

- de Broglie claimed matter would also follow this relationship
  -- for matter \( p = mv \) where \( m = \text{mass} \) and \( v = \text{velocity} \)
  -- 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?

\[
\lambda_{\text{boy}} = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{75 \text{ kg} \times 10 \text{ miles/hour}} = \frac{6.626 \times 10^{-34} \text{ kg} \cdot \text{m}^2}{75 \times 10 \text{ miles/hour} \times \frac{1.6093 \text{ km}}{\text{miles}} \times \frac{3600 \text{ s}}{\text{hour}} \times \frac{1000 \text{ m}}{\text{km}}} = 1.98 \times 10^{-36} \text{ m}
\]

Too small to be detectable

\[
\lambda_e = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{9.109 \times 10^{-31} \text{ kg} \times 10 \text{ miles/hour}} = \frac{6.626 \times 10^{-34} \text{ kg} \cdot \text{m}^2}{9.109 \times 10^{-31} \text{ kg} \times 10 \text{ miles/hour} \times \frac{1.6093 \text{ km}}{\text{miles}} \times \frac{3600 \text{ s}}{\text{hour}} \times \frac{1000 \text{ m}}{\text{km}}} = 1.63 \times 10^{-7} \text{ m}
\]

On the order of UV

* de Broglie Applied to Bohr’s H-atom Model
  - Figure 1.12 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

\[ 2\pi r = n\lambda \quad \text{where} \quad n = 1, 2, 3, \ldots \quad \text{since} \quad \lambda = \frac{h}{p}, \quad \text{then} \quad 2\pi r = n\frac{h}{p} = \frac{nh}{m_v} \]

\[ v = \frac{nh}{2\pi m_v r} = \frac{nh}{m_v r} \quad \text{where} \quad h = \frac{\hbar}{2\pi} \]

* de Broglie In Real Life
- X-ray Diffraction
  -- occurs when X-rays are fired at a crystalline substance and is due to the interatomic spacing being on the order of the X-rays
  -- this phenomenon is another example of wave-particle duality
- Electron Microscopes
  -- Uses applied voltage through an electromagnetic field and are able to generate a much sharper images than their forefathers

* Two-Slit Experiments
- a light wave is initially allowed to pass through one slit and either hit or pass through two slits as shown in the figure to the left

https://practicallawandjustice.liberty.me/the-double-slit-experiment-a-rational-explanation/
- what results in a pattern of bands in which the light spaces are where the wave have acted in a constructive way and the dark is where they have acted destructively as shown on the right
- Below is a video of what happens when we allow only one particle at time to pass in our experiment:
  https://www.youtube.com/watch?v=TT_uCLwKhQ
* 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 \( \Delta x \) we need a light source whose resolution is on the order of \( \Delta x \) or \( \Delta x \approx \lambda \)
  -- unfortunately as soon as we shine this light on our e- we change its momentum, \( \Delta p \)
  -- 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