4.5: Successes and Failures of the Bohr Model

- The electron and hydrogen nucleus actually revolved about their mutual center of mass.

- The electron mass is replaced by its reduced mass.

\[ \mu_e = \frac{m_e M}{m_e + M} = \frac{m_e}{1 + \frac{m_e}{M}} \]

In the case of hydrogen atom, M is the proton mass, and the correction for the hydrogen atom is \( \mu_e = 0.999456m_e \).

- The Rydberg constant for infinite nuclear mass should replaced by \( R \).

\[ R = \frac{\mu_e}{m_e} R_{\infty} = \frac{1}{1 + \frac{m_e}{M}} \quad R_{\infty} = \frac{\mu_e e^4}{\hbar^2 c^2 m_e} \]

The Rydberg constant for hydrogen is \( R_{\infty} = 1.096776 \times 10^7 \text{ m}^{-1} \).

Limitations of the Bohr Model

The Bohr model was a great step of the new quantum theory, but it had its limitations.

1) Works only to single-electron atoms (H, He\(^+\), Li\(^{++}\),..)
2) Could not account for the intensities or the fine structure of the spectral lines*
3) Could not explain the binding of atoms into molecules

In Ch.7, we will discuss the full QM theory of the hydrogen atom, which accounts for all of these phenomena.

As the level of precision increased in optical spectrographs, it was observed that each of the lines, originally believed to be single, actually could be resolved into two or more lines, known as fine structure.
4.6: Characteristic X-Ray Spectra and Atomic Number

- Shells were given letter names:
  - K shell for \( n = 1 \)
  - L shell for \( n = 2 \)

- The atom is most stable in its ground state.
  - An electron from higher shells will fill the inner-shell vacancy at lower energy.

- When it occurs in a heavy atom, the radiation emitted is an x-ray.

- It has the energy \( E_{\text{x-ray}} = E_u - E_L \).

- By 1913 when Bohr’s model was published, little progress had been made in understanding the structure of many-electron atoms.

We can now understand the characteristic x-ray wavelength by adopting Bohr’s electron shell hypothesis. His model suggests that an electron shell based on the radius \( r_n \) can be associated with each of the principle quantum \# \( n \).

\[
 r_n = \frac{4\pi\varepsilon_0 n^2 \hbar^2}{m_e^2} = n^2 a_0
\]

4.7: Atomic Excitation by Electrons

- In 1914, Franck and Hertz studied the phenomenon of ionization.

Another way of studying atomic structure is by using electron scattering rather than photon or optical methods.

F&H were able to confirm the quantized structure of the atom & determined a value of Planck’s constant \( h \) in good agreement with other methods.
Atomic Excitation by Electrons

- Ground state has $E_0$, to be zero.
- First excited state has $E_1$.
- The energy difference $E_1 - 0 = E_1$ is the excitation energy.
- Hg has an excitation energy of 4.88 eV in the first excited state.
- As long as the accelerating electron’s KE is below 4.88 eV, no energy can be transferred to Hg because not enough energy is available to excite an electron to the next energy level.

Above 4.88 eV, the current drops because scattered electrons no longer reach the collector until the accelerating voltage reaches 9.8 eV and so on.

(when the accelerating voltage reaches 9.8 eV, the electrons have enough energy to excite 2 Hg atoms in successive inelastic collision, losing 4.88 eV in each (9.8 eV))

5.1: X-Ray Scattering

- By 1912, it became clear that x rays were a form of EM radiation and must have wave properties. Max von Laue made the suggestion that x ray should scatter from the atom of crystals and suggested that interference effects should be observed.
- Crystals act as three-dimensional gratings, scattering the waves and producing observable interference effects.

Bragg’s Law

- William Lawrence Bragg interpreted the x-ray scattering as the reflection of the incident x-ray beam from a unique set of planes of atoms within the crystal.
- There are two conditions for constructive interference of the scattered x rays:
  1) The angle of incidence must equal the angle of reflection of the outgoing wave.
  2) The difference in path lengths must be an integral number of wavelengths.

Bragg’s Law:

\[ n \lambda = 2d \sin \theta \]

(n = integer)

The crystal structure of NaCl (rock salt) showing two of the possible sets of lattice planes (Bragg planes).

Schematic diagram illustrating x-ray scattering from Bragg lattice planes. The path difference of the two waves illustrated is $2d \sin \theta$. Notice that the actual scattering angle from the incident wave is $2\theta$. 

We can explain the experimental results of F&H within the context of Bohr’s quantized atomic energy level.
Bragg’s Law

- The interference is constructive when the phase shift is a multiple of $2\pi$; this condition can be expressed by Bragg's law,

$$n\lambda = 2d\sin \theta,$$

- $n$ is an integer determined by the order given, $\lambda$ is the wavelength of the X-rays, $d$ is the spacing between the planes in the atomic lattice, and $\theta$ is the angle between the incident ray and the scattering planes.

- Bragg’s Law is the result of experiments into the diffraction of X-rays off crystal surfaces at certain angles. Bragg’s law confirmed the existence of real particles at the atomic scale, as well as providing a powerful new tool for studying crystals in the form of X-ray diffraction.

5.2 De Broglie Hypothesis

The E&M waves can be described using the language of quantum particles (photons). Q: Can particles behave as waves?

De Broglie (1923) suggested that a plane mono-energetic wave is associated with a freely moving particle:

$$\Psi(x) = \Psi_0 e^{i(kx - \omega t)}$$

This is a solution of the wave equation in 1-dimension:

$$\frac{\partial^2 \psi}{\partial t^2} = v^2 \frac{\partial^2 \psi}{\partial x^2}$$

$$v = \frac{\omega}{k}$$

We’ll apply the same logic which helped us to establish the relationship between $p$ and $\lambda$ for photons:

For photon, $E = pc$ and $E = hf$

$$hf = pc \Rightarrow h = pc/f = p\lambda \Rightarrow \lambda = h/p$$

De Broglie wavelength

$p$ - the object’s $m/m$

$$\lambda = \frac{2\pi}{k} = \frac{h}{p}$$

- depends on the momentum rather than energy (e.g., for an object at rest, $\lambda = \infty$)

Compare with Compton wavelength of the particle

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