Correspondence Principle

- In the region of very large quantum numbers (n in this case) quantum calculation and classical calculation must yield the same results.
- let us compare the frequency of a transition between level $n_i = n$ and
- level $n_f = n - 1$ for large n with the classical frequency, which is the frequency of revolution of the electron.

$$f = \frac{c}{\lambda} = \frac{Z^2 m k^2 e^4}{4\pi\hbar^3}\left[\frac{1}{(n-1)^2} - \frac{1}{n^2}\right] = \frac{Z^2 m k^2 e^4}{4\pi\hbar^3}\frac{2n-1}{n^2(n-1)^2}$$

- For large n we can neglect the ones subtracted from n and 2n to obtain

$$f = \frac{Z^2 m k^2 e^4}{4\pi\hbar^3}\frac{2}{n^3} = \frac{Z^2 m k^2 e^4}{2\pi\hbar^3 n^3}$$

- The classical frequency of revolution of the electron is

$$f_{\text{rev}} = \frac{v}{2\pi r} \qquad v = n\hbar/mr \qquad r = n^2\hbar^2/mkZe^2$$

$$f_{\text{rev}} = \frac{(n\hbar/mr)}{2\pi r} = \frac{n\hbar}{2\pi m r^2} = \frac{n\hbar}{2\pi m(n^2\hbar^2/mkZe^2)^2}$$

$$f_{\text{rev}} = \frac{m^2 k^2 Z^2 e^4 n\hbar}{2\pi m n^4 \hbar^4} = \frac{m k^2 Z^2 e^4}{2\pi\hbar^3 n^3}$$

Successes and Failures of the Bohr Model

Reduced Mass Correction

The electron and hydrogen nucleus actually is a two-body problem. From classical mechanics this two-body problem can be reduced to an equivalent one-body problem in which the motion of a particle of mass m_e moves in a central force field around the center of mass. We replace the electron mass m_e by its reduced mass μ_e where

$$\mu_e = \frac{m_e M}{m_e + M} = \frac{m_e}{1 + \frac{m_e}{M}}$$

and M is the mass of the nucleus

- The Bohr model may be applied to any single-electron atom (hydrogen like) even if the nuclear charge is greater than 1 proton charge (e+). The only change needed is in the calculation of the Coulomb force, where e^2 is replaced by Ze^2 to account for the nuclear charge of + Ze.
- Limitations of Bohr model

1. It could be successfully applied only to single-electron atoms (H, He^+, Li^{++}, and so on).
2. It was not able to account for the intensities or the fine structure of the spectral lines.
3. Bohr's model could not explain the binding of atoms into molecules.

Characteristic X-Ray Spectra and Atomic Number

- **<u>Characteristic x-ray wavelength</u>**
- Bohr's model suggests that an electron shell based on the radius r_n can be associated with each of the principal quantum numbers n.
- Electrons with lower values of n are more tightly bound to the nucleus than those with higher values.
- The radii of the electron orbits increase in proportion to n^2. A specific energy is associated with each value of n.
- We may assume that when we add electrons to a fully ionized many-electron atom, the inner shells (low values of n) are filled before the outer shells.
- Historically, the shells were given letter names: the n = 1 shell was called the K shell, n =2 was the L shell, and so on.

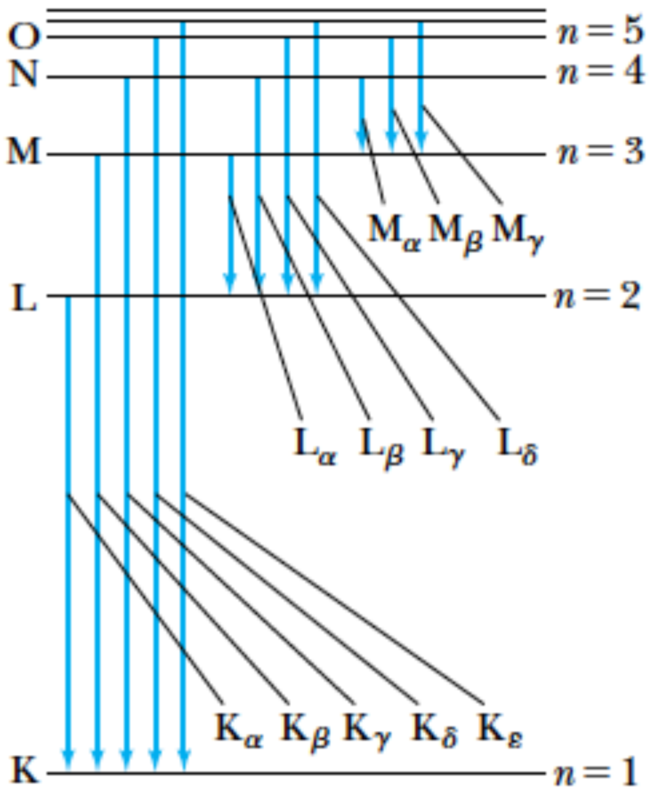
- Moseley measured the wavelengths of the characteristic x-ray line spectra for about 40 different target elements.
- He noted that the x-ray line spectra varied in a regular way from element to element, unlike the irregular variations of optical spectra.
- He surmised that this regular variation occurred because characteristic x-ray spectra were due to transitions involving the innermost electrons of the atoms.
- According to the Bohr theory, the energy of an electron in the first Bohr orbit is proportional to the square of the nuclear charge

- Moseley reasoned that the energy, and therefore the frequency, of a characteristic x-ray photon should vary as the square of the atomic number of the target element in the x-ray tube.
- Accordingly, he plotted the square root of the frequency of a particular characteristic line in the x-ray spectrum of various target elements versus the atomic number Z of the element

$$f^{1/2} = A_n(Z - b)$$

where A_n and b are constants for each characteristic x-ray line

The photon produced when the electron falls from the L shell into the K shell is called a K_α x ray; when it falls from the M shell into the K shell, the photon is called a K_β x ray



- The radius of the n = 1 orbit in the hydrogen atom is a_0 =5 0.053 nm. (a) Compute the radius of the n = 6 orbit.

$$r_n = \frac{n^2 a_0}{Z} \qquad r_6 = \frac{6^2(0.053nm)}{1} = 1.91nm$$

- On the average, a hydrogen atom will exist in an excited state for about 10^{-8} s before making a transition to a lower energy state. About how many revolutions does an electron in the n = 4 state make in 10^{-8} s?