Origins of Quantum Theory

- Measurements of emission of light (EM radiation) from (H) atoms found discrete lines

\[ \frac{1}{\lambda} = \frac{\nu}{c} = R \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \]

- e.g., \( n_2 = 1, 121.6 \text{ nm} \), \( 102.6 \text{ nm} \), … (Lyman Series, 1906)
- \( n_2 = 2, 656.5 \text{ nm} \), \( 486.3 \text{ nm} \), \( 434.2 \text{ nm} \), … (Balmer, 1885)

\( \lambda = \text{wavelength}, \ \nu = \text{frequency}, \ c = \text{speed light} \)

Bohr Model of Atom

- Bohr (1913) explanation for discrete lines
  1. atoms consist of heavy nucleus (positive charge) and lighter electron (negative charge)
  2. electrons orbit nucleus; only certain discrete orbits allowed that are stable → stationary quantum states
     - required to explain why there is no radiation (energy loss) by electron in orbit (classically, required for accelerating electron)
  3. EM radiation (energy) emitted/absorbed when orbit changes and frequency is \( \nu = \Delta E / h \)
Orbitals

- Bohr’s 2nd postulate leads to assumption that angular momentum is quantized
  \[ L = m_e v_e r = m_e \omega r^2 = n \frac{h}{2\pi} = n\hbar \]
  where \( n \) is a quantum number

- Combine with electrostatic attraction force balanced by centrifugal force
  \[ \frac{Ze^2}{r^2} = \frac{m_e v_e^2}{r} \Rightarrow Ze^2 m_e r = m_e v_e^2 r^2 = L^2 \]

Energy Levels

- Electron in orbit has kinetic (KE) and potential (PE) energy
  \[ E_n = \frac{m_e v_e^2}{2} - \frac{Ze^2}{r} = \frac{Ze^2}{2r} - \frac{Ze^2}{r} \]
  \[ E_n = -\frac{Ze^2}{2r} \]

- Bohr then used Planck/Einstein theories
  \[ \Delta E_{ji} = h\nu = -\frac{Ze^2}{2} \left( \frac{1}{r_j} - \frac{1}{r_i} \right) \]
  \[ \nu = \frac{2e^4 m_e \pi^2}{h^3 c} \left( \frac{1}{n_j^2} - \frac{1}{n_i^2} \right) \]
Bohr’s H Energy Levels

\[ E_n = -\frac{Z e^2}{2r} \]

\[ \frac{1}{\lambda} = \frac{\nu}{c} = \frac{2\pi^2 e^4 m_e}{\hbar^3 c} \left( \frac{1}{n^2} - \frac{1}{n_i^2} \right) \]

Good agreement with Balmer series (H) data \( n_i = 2, Z = 1 \)

**Problems**

- effective Rydberg constant different for non-Balmer series in data
- higher resolution spectra show “individual” lines actually multiple closely spaced lines, “line splitting” (e.g., each Balmer lines actually 3 lines)

\[ r = Z e^2 \frac{\mu}{\pi n^2} \]

Good agreement with Balmer series (H) data \( n_i = 2, Z = 1 \)

**Modifications to Bohr Atom**

1. Include motion of electron about atom center of mass (≠ center of nucleus)
   - use reduced mass (from classical mech.) of two-body system
     \[ m_e \rightarrow \mu = \frac{m_1 m_2}{m_1 + m_2}, \quad \mu_{\text{atom}} = \frac{m_e m_{\text{nucl}}}{m_e + m_{\text{nucl}}} \approx 0.99945 m_e \]
   - changes \( R \) but does not explain splitting
     \[ R = \frac{2\pi^2 \mu e^4}{\hbar^2 c} \]

2. Noncircular orbits
   - elliptical orbits can also satisfy balance of attraction/centrifugal forces
   - Sommerfeld’s generalized (mechanics) postulate

3. Special Relativity
   - from Einstein, effective \( m_e \) is function of velocity
Elliptical Orbits: Sommerfeld

- Use generalized momenta \( p_i = \frac{\partial KE}{\partial q_i} \)
- **Sommerfeld Action Integral** (over 1 period of motion) \( \oint p_i dq_i = n_i \hbar \)
  - each gen’l. mom. ordinate quantized
  - e.g., 1-d: \( KE = mv_x^2 \); \( v_x = dx/dt \) \( \Rightarrow \frac{\partial KE}{\partial v_x} = mv_x = p_x \)
- 2-d \((r, \theta)\)
  - azimuthal coord.
  - same as Bohr assumption
    \[
    \oint p_\theta dq_\theta = n_\theta \hbar \quad \Rightarrow \quad L = n_\theta \hbar \quad (1)
    \]
  - radial coord. \( \oint p_r dr = n_r \hbar \)
  - Combine azimuthal and radial
    \[ p = \sum p_i \]
  - gen’l. solution of (1) and (2) is elliptical orbit
- \( L = \text{ang. mom.} \), \( L = \text{constant for isolated sys.} \)
  \( L = n_\theta \hbar \)
  \( n_\theta \equiv k = 1, 2, 3, \ldots \) azimuthal quantum number
  \( \neq 0 \) else electron inside nucleus

Elliptical Orbits: Sommerfeld

- 2-d \((r, \theta)\)
  - radial coord. \( \oint p_r dr = n_r \hbar \quad (2) \)
    \( n_r = 0, 1, 2, \ldots \)
    \( n_r = 0 \) is circular orbit
  - for circular orbit, \( p_r = 0 \)
  - Combine azimuthal and radial
    \[ p = \sum p_i \]
  - gen’l. solution of (1) and (2) is elliptical orbit
- \( a/b = n/k \)
- \( a = \frac{\hbar^2 n^2}{\mu e^2 Z} \)
- \( b = \frac{\hbar^2 nk}{\mu e^2 Z} \)
- \( n = k + n_r \)
- \( k = 1, 2, 3, \ldots, n \)
  - smallest \( n \) for given \( k \) is \( n = k \Rightarrow \) circular orbit
- So 2 quantum #’s, but \( E = E(n) \): no splitting
Special Relativity

- Einstein showed mass depends on velocity
  \[ m_e = \frac{m_{e,\text{rest}}}{\sqrt{1 - \left(\frac{v_e}{c}\right)^2}} \]
  - electrons moving quickly, so important
- Include in energy of orbiting electron
  - result
  \[ E_{n,k} = -\frac{2\pi^2 \mu e^4 Z^2}{\hbar^2 n^2} \left[ 1 + \alpha^2 Z^2 \left( \frac{1}{k} - \frac{3}{4n} \right) \right] \]
  - now orbits with same \( n \) but different \( k \) have different energy
  \[ \Rightarrow \text{line splitting} \]

Bohr-Sommerfeld Orbits

- Energy depends primarily on principal quantum number (\( n \))
  - small effect for different \( k \)
  - multiple transitions (lines) with same \( \Delta n \) but different \( k \) at different \( \lambda \)
    - e.g., 3 Balmer lines (\( n=2 \))
- Less lines found then possible \( \Rightarrow \text{selection rules} \) (\( \Delta k=\pm 1 \))
- Theory successful at prediction spectra of H-like atoms (H, He\(^+\), Li\(^{++}\),…); helped build periodic table
  - requires some ad hoc assumptions
  - problems with multielectron atoms
  - impetus for quantum mechanics