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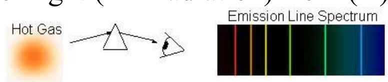
Origins of Quantum Theory

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



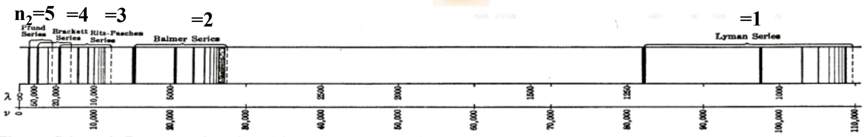


Fig. 8. Schematic Representation of the H-atom Spectrum. The intensity is indicated roughly by the thickness of the lines. The dotted lines correspond to the series limits, at which a continuous spectrum sometimes joins the series. (See section 2 of this chapter.)

G. Herzberg, *Atomic Spectra and Atomic Structure*

- Able to fit to following series expression

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

R=Rydberg Constant (~109,7=677.581cm^{-1})
n_2=1, 2, 3, … $n_1=n_2+1$, n_2+2, ….

λ=wavelength, ν=frequency, c=speed light

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

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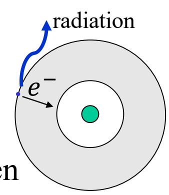
Bohr Model of Atom

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



Bohr Orbitals

- **Bohr's 2nd postulate** leads to assumption that **angular momentum is quantized**

$$L = m_e v_e r = m_e \omega r^2 = n\frac{h}{2\pi} = n\hbar$$

h ← Planck's Constant (introduced by him 1900) (photon explanation Einstein 1905)

n ← quantum number

- Combine with electrostatic attraction force balanced by centrifugal force

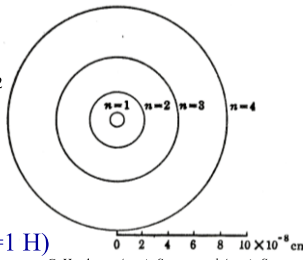
$$\frac{Ze^2}{r^2} = m_e\frac{v_e^2}{r} \Rightarrow Ze^2 m_e r = m_e^2 v_e^2 r^2 = L^2 = n^2\hbar^2$$

- Solve for r

Spherical Electron Orbitals

$$r = \frac{n^2\hbar^2}{m_e Ze^2} = \frac{n^2}{Z}r_o \qquad n = 1,2,\ldots$$

r_o ← 1st Bohr radius H atom; Z ← nuclear charge (=1 H)



G. Herzberg, *Atomic Spectra and Atomic Structure*

Bohr Energy Levels

- Electron in orbit has kinetic (KE) and potential (PE) energy
- Let $PE \rightarrow 0$ as $r \rightarrow \infty$ (zero PE definition) $PE = \frac{-Ze^2}{r}$

$$KE = \frac{m_e v_e^2}{2}$$

Energy of electron in nth orbit

$$\varepsilon_n = \frac{m_e v_e^2}{2} - \frac{Ze^2}{r} = \frac{Ze^2}{2r} - \frac{Ze^2}{r}$$

$$\varepsilon_n = -Ze^2/2r$$

$\frac{m_e v_e^2}{r} = \frac{Ze^2}{r^2}$ already showed

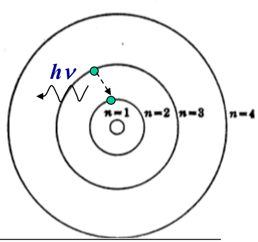
- Bohr then used Planck/Einstein theories

$$\Delta\varepsilon_{ji} = h\nu = \frac{-Ze^2}{2}\left(\frac{1}{r_j} - \frac{1}{r_i}\right)$$

already showed $r = \frac{n^2\hbar^2}{m_e Ze^2}$

$$\frac{\nu}{c} = \frac{2e^4 m_e \pi^2}{h^3 c} Z^2 \left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

$\frac{2e^4 m_e \pi^2}{h^3 c}$ ***=R, Rydberg Constant***



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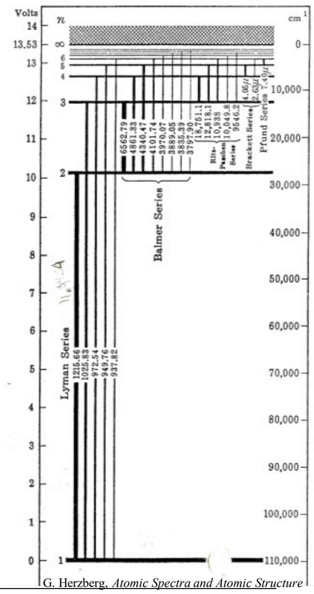
Bohr's H Energy Levels

$$\varepsilon_n = -Ze^2/2r$$

$$\frac{1}{\lambda} = \frac{\nu}{c} = \frac{2\pi^2 e^4 m_e}{h^3 c}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

Good agreement with Balmer series (H) data n_2=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)



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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

$$m_e \rightarrow \mu = \frac{m_1 m_2}{m_1 + m_2} \qquad \mu_{H\,atom} = \frac{m_e m_{nucl}}{m_e + m_{nucl}} \cong 0.99945 m_e$$

   - changes R but does not explain splitting $R = \frac{2\pi^2 \mu e^4}{h^3 c}$

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 $p_i \equiv \dfrac{\partial KE}{\partial \dot{q}_i}$ ← *d/dt* of general coordinate (e.g., velocity in *i* direction)
- **Sommerfeld Action Integral** (over 1 period of motion) $\oint p_i dq_i = n_i h$
  - each gen'l. mom. ordinate quantized
  - e.g., 1-d: $KE = m\mathrm{v}_x^2/2$; $\mathrm{v}_x = dx/dt \Rightarrow \dfrac{\partial KE}{\partial \mathrm{v}_x} = m\mathrm{v}_x = p_x$

- 2-d (r, θ)
  - azimuthal coord.

$$\oint p_\theta dq_\theta = n_\theta h$$

$$\oint (m_e \mathrm{v}_\theta)(r d\theta) = n_\theta h$$

L=ang. mom. $\int_0^{2\pi} L d\theta = n_\theta h$

L=constant for isolated sys. $L\int_0^{2\pi} d\theta = n_\theta h$

same as Bohr assumption $\Rightarrow L = n_\theta \hbar$ (1)

$n_\theta \equiv k = 1, 2, 3, \ldots$ azimuthal quantum number

≠0 else electron inside nucleus

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Elliptical Orbits: Sommerfeld

- 2-d (r, θ)
  - radial coord. $\oint p_r dr = n_r h$ (2)
    - for circular orbit, p_r=0

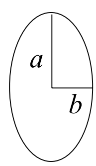
radial quantum number $n_r = 0, 1, 2, \ldots$

n_r=0 is circular orbit

- Combine azimuthal and radial

$$p = \sum p_i$$

  - gen'l. solution of (1) and (2) is elliptical orbit



$$\frac{a}{b} = \frac{n}{k}$$

$$k = \frac{L}{2\pi}$$

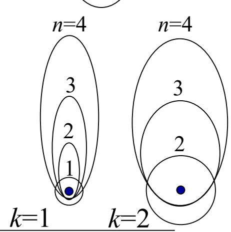
$$a = \frac{\hbar^2}{\mu e^2}\frac{n^2}{Z}$$

$$b = \frac{\hbar^2}{\mu e^2}\frac{nk}{Z}$$

principal quantum number $n = k + n_r$

$k = 1, 2, 3, \ldots, n$

smallest n for given k is $n=k \Rightarrow$ circular orbit



- So 2 quantum #'s, **but** $\varepsilon = \varepsilon(n)$: no splitting

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Special Relativity

- Einstein showed mass depends on velocity

$$m_e = \frac{m_{e,rest}}{\sqrt{1-\left(v_e/c\right)^2}}$$

  - electrons moving quickly, so important
- Include in energy of orbiting electron
  - result

$$\varepsilon_{n,k} = -\frac{2\pi^2 \mu e^4}{h^2}\frac{Z^2}{n^2}\left[1+\frac{\alpha^2 Z^2}{n}\left(\frac{1}{k}-\frac{3}{4n}\right)\right]$$

$$\alpha = \frac{e^2}{\hbar c} \sim 0.0073$$ Fine Structure Constant

  - now orbits with same n but different k have different energy ⇒ **line splitting**

Bohr Model-9

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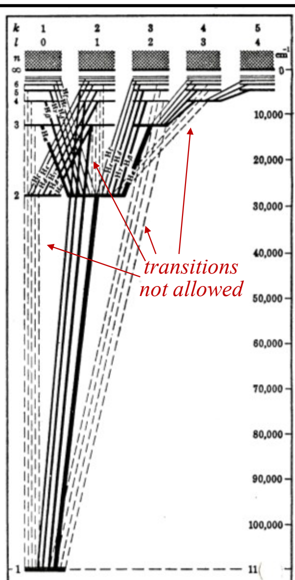
Bohr-Sommerfeld Orbits

- Energy depends primarily on principal quantum number (n)
  - small effect for different k
  - multiple transitions (lines) with same Δn but different k – which occur at different λ
    - e.g., 3 Balmer lines (n_i=2)
- Less lines found then possible ⇒ **selection rules** (Δk=±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**



$l=k-1$

G. Herzberg, *Atomic Spectra and Atomic Structure*

Bohr Model-10