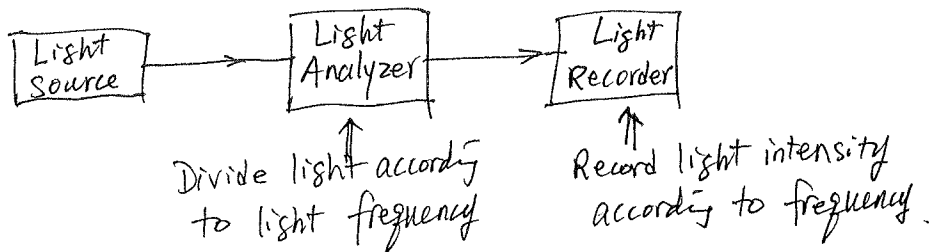


§ 1.4. Hydrogen Spectra

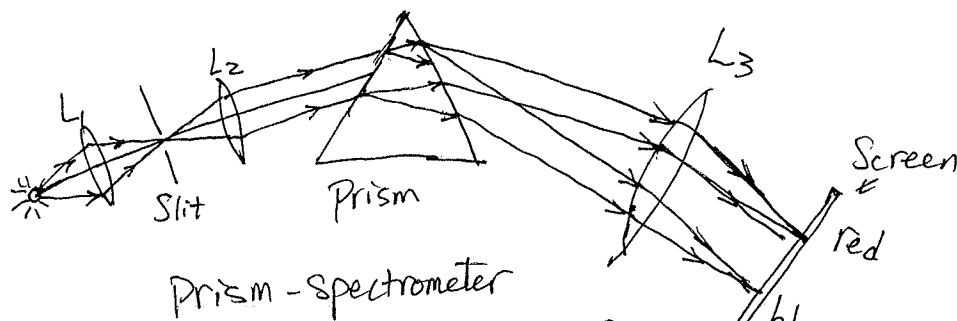
* Spectrum is the intensity distribution of the frequency of radiation. It is the most important approach to study matter internal structure.

* Spectrometer in principle consists of three major parts:



Example:

(See textbook Chapter 4 for the operation principle of Spectrometer)



1885, J. Balmer proposed an empirical formula for H-spectra

$$\tilde{\nu} \equiv \frac{1}{\lambda} = \frac{4}{B} \left(\frac{1}{2^2} - \frac{1}{n^2} \right), \quad n=3, 4, 5, \dots, \text{ where } B=364.56 \text{ nm}$$

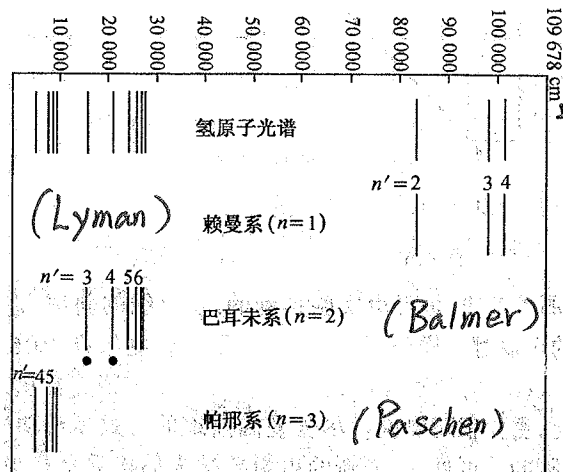
1889, J.R. Rydberg proposed a more general equation:

$$\tilde{\nu} \equiv \frac{1}{\lambda} = R_H \left[\frac{1}{n^2} - \frac{1}{(n')^2} \right], \quad = T(n) - T'(n') \quad (25)$$

Where $R_H = \frac{4}{B} = 109677.58 \text{ cm}^{-1}$

$n=1, 2, 3, \dots, \quad n'=n+1, n+2, n+3, \dots$

H-spectra consists of many sharp lines of definite frequency, in contrast to the continuous spectra emitted by blackbody sources.



From Rydberg equation,

$n=1, n'=2, 3, 4, 5, \dots$, T. Lyman Series ^(UV) ↓, found in 1914.

$n=2, n'=3, 4, 5, 6, \dots$, J. Balmer Series ^(Visible) ↓, 1885.

The most famous line is $\lambda = 656.3 \text{ nm}$ from $n'=3 \Rightarrow n=2$.

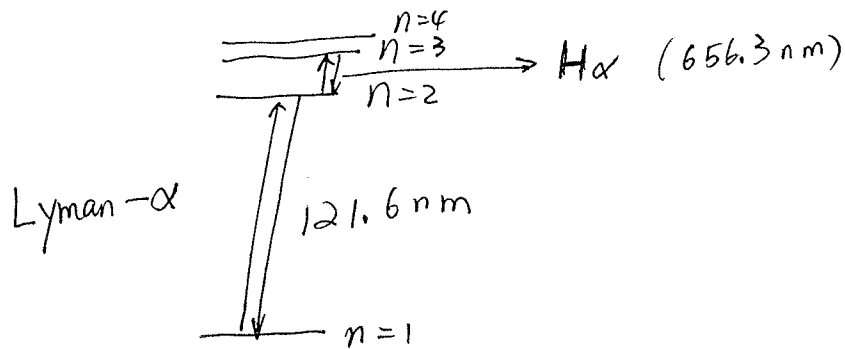
observed by A.J. Ångström in 1853.

$n=3, n'=4, 5, 6, 7, \dots$; F. Paschen series in IR, found in 1908.

$n=4, n'=5, 6, 7, 8, \dots$; F. Brackett series in IR, found in 1922.

$n=5, n'=6, 7, 8, 9, \dots$, H.A. Pfund series in IR, found in 1924.

($n=4, n' \geq 7$; $n=5, n' \geq 7$, $n=6, n' \geq 7$, observed by C.S. Humphreys)



Lyman- α line dissociates water vapor (H_2O)
in the upper atmosphere \rightarrow influence PMC brightness

* Refraction index of air: 1.000 292

§1.5. Bohr's Theory (Model)

In order to develop a quantitative theory of the H-atom, Bohr put forward three basic postulates.

Postulate 1 classical orbit plus stationary state condition:

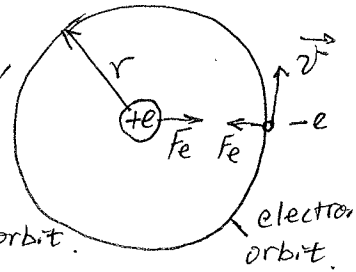
A bound atomic or molecular system can exist only in certain discrete energy levels denoted by the values $E_1, E_2, \dots, E_i, \dots$.

Electron orbits the H-nucleus in circle,
(m_e, e) ($m_p, +e$)

it needs central force $F = m_e \frac{v^2}{r}$

v - velocity

r - radius



It is provided by Coulomb force between electron and nucleus of electron orbit.

$$F = m_e \frac{v^2}{r} = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} \Rightarrow m_e v^2 = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

Total energy of electron is given by

$$E_{\text{total}} = E_{\text{kinetic}} + E_{\text{potential}}$$

$$= \frac{1}{2} m_e v^2 - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$$

$$= -\frac{1}{2} \cdot \frac{e^2}{4\pi\epsilon_0 r} \quad (27)$$

$$v = \sqrt{\frac{e^2}{4\pi\epsilon_0 m_e r}}$$

(26)

The frequency of electron orbital motion is given by

$$f = \frac{1}{T} = \frac{1}{2\pi r/v} = \frac{v}{2\pi r}$$

$$= \frac{e}{2\pi} \sqrt{\frac{1}{4\pi\epsilon_0 m_e r^3}} \quad (28)$$

Postulate 2 Frequency condition:

In stationary state, the electron won't emit EM radiation. But when electron transits from one stationary state to another, it will emit or absorb a photon with energy $h\nu$ given by

$$h\nu = E_{n'} - E_n \quad (29)$$

Compare Bohr's frequency condition with Rydberg equation:

$$\frac{1}{\lambda} = R_H \left[\frac{1}{n^2} - \frac{1}{(n')^2} \right] = \frac{\nu}{c} \quad \Rightarrow$$

$$E_{n'} - E_n = h\nu$$

$$E_{n'} - E_n = h\nu = R_H h c \left[\frac{1}{n^2} - \frac{1}{(n')^2} \right]$$

$$\Rightarrow E_n = - \frac{R_H h c}{n^2} \quad (30)$$

This indicates the meaning of Rydberg formula - representing the energy released when electron transits from n' stationary state to n stationary state.

Recall classical $E = - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0 r}$

$$- \frac{R_H h c}{n^2} = - \frac{1}{2} \frac{e^2}{4\pi\epsilon_0 r}$$

$$\Rightarrow r_n = \frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{2R_H h c} n^2 \quad (31) \quad n \text{ is integer (positive), orbits are discrete.}$$

Postulate 3 Correspondence Principle.

"When extending laws in atomic field to (micro world) classical field (macro world), the atomic laws should give the same results as classical laws."

Rydberg equation can be written as

$$\nu = \frac{c}{\lambda} = R_H c \left[\frac{1}{n^2} - \frac{1}{(n')^2} \right] = R_H c \frac{(n'+n)(n'-n)}{n^2 (n')^2}$$

When n is very large, considering transition between $n' - n = 1$,

$$\text{We get } \nu \approx R_H c \frac{2n \times 1}{n^4} = \frac{2 R_H c}{n^3} = \frac{e}{2\pi} \sqrt{\frac{1}{4\pi\epsilon_0 m e r^3}}$$

According to correspondence principle, this ν should be equal to classical orbital motion frequency. Therefore,

$$r = \sqrt[3]{\frac{1}{4\pi\epsilon_0} \frac{e^2}{16\pi^2 R_H^2 c^2 m e}} \cdot n^2 \quad (32)$$

According to correspondence principle,

$$r = r_n \Rightarrow \frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{2R_H hc} n^2 = \sqrt[3]{\frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{16\pi^2 R_H^2 c^2 m_e} \cdot n^2}$$

therefore, we obtain Rydberg Constant:

$$R_H = \frac{2\pi^2 e^4 m_e}{(4\pi\epsilon_0)^2 \cdot ch^3} \quad (33)$$

From fundamental constants, we can calculate

$$R_H = 109737.315 \text{ cm}^{-1}$$

Substitute R_H into r_n equation, we obtain electron orbital

radius: $r_n = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \cdot n^2$, here, $\hbar \equiv \frac{h}{2\pi}$. (34)

Substitute R_H in E_n equation, we obtain the electron energy

$$E_n = -\frac{m_e e^4}{(4\pi\epsilon_0)^2 \cdot 2\hbar^2 n^2} \quad (35)$$

According to classical theory, the angular momentum of electron (orbital motion) is given by

$$L = m_e v r = m_e \cdot \sqrt{\frac{e^2}{4\pi\epsilon_0 m_e r}} \cdot r = \sqrt{\frac{m_e e^2 r}{4\pi\epsilon_0}}$$

Replace r by r_n , $\Rightarrow L = \sqrt{\frac{m_e e^2}{4\pi\epsilon_0} \cdot \frac{4\pi\epsilon_0 \hbar^2 n^2}{m_e e^2}} = n\hbar$, (36)

$$\therefore L = n\hbar, \quad n=1, 2, 3, \dots$$

This is the quantized angular momentum.

Although these equations are derived for large n , according to Bohr's correspondence principle, they should also be right for small n , due to the fact that energy is still conservative.

Here, we introduce a fine structure constant α

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137} = \frac{1}{137.03599911(46)} \quad (37)$$

$$\text{Bohr radius: } r_1 \equiv a_1 = \frac{4\pi \epsilon_0 \hbar^2}{m_e e^2} \approx 0.053 \text{ nm} \quad (38)$$

$$\text{Electron energy: } E_n = -\frac{1}{2} m_e (\alpha c)^2 \frac{1}{n^2} \quad (39)$$

$$\text{Rydberg constant: } R_\infty = 109\,737.315 \text{ cm}^{-1}$$

$$\text{Measured } R_H = 109\,677.58 \text{ cm}^{-1}$$

The difference is caused by the fact that the nucleus does not have infinite mass. The electron mass should be replaced

by the reduced mass $\mu = \frac{m_e M}{m_e + M}$ (i.e., $\frac{1}{m_e} + \frac{1}{M} = \frac{1}{\mu}$)

Replace m_e with μ in R_H equation:

$$\begin{aligned} R_H &= \frac{2\pi^2 e^4 \mu}{(4\pi\epsilon_0)^2 \cdot c h^3} = \frac{2\pi^2 e^4}{(4\pi\epsilon_0)^2 \cdot c h^3} \cdot \frac{m_e M}{m_e + M} \\ &= R_\infty \cdot \frac{1}{1 + \frac{m_e}{M}} \end{aligned}$$

$$\therefore R_H = R_\infty \frac{1}{1 + \frac{m_e}{M}} \quad (40)$$

Chapter 2. Wave - Particle Duality

In a brief summary of Section 2.1.1. Concept of Quantum,

(1) Blackbody Thermal Radiation \Rightarrow linear oscillator's energy is discrete: $E = n h \nu$, $n = 0, 1, 2, \dots$

($h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$) (Planck Quanta ~~Assumption~~ ^{Hypothesis})

(2) Photoelectric Effect \Rightarrow particle property of light: photon

Photon energy $E = h \nu$. (Einstein Photon ~~Assumption~~ ^{Hypothesis})

(3) Compton Effect \Rightarrow Photon has momentum

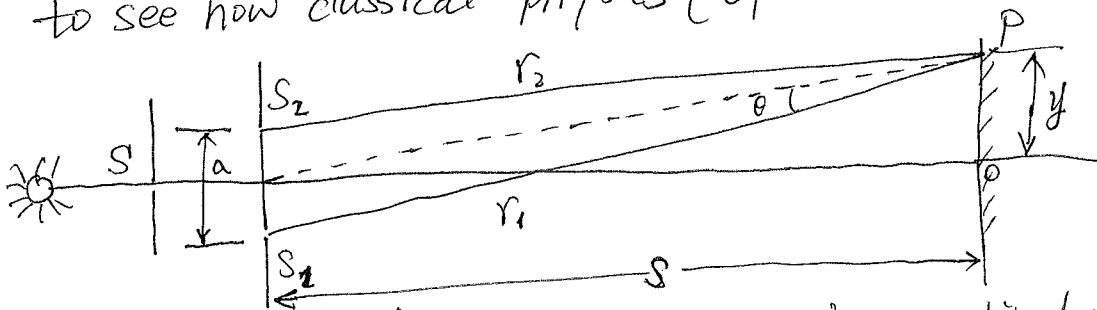
$$\vec{p} = \hbar \vec{k}, \quad |\vec{p}| = p = \frac{h}{\lambda}$$

(4) Hydrogen Spectra \Rightarrow Bound Atom has discrete energy levels
Transition occurs only when $h \nu = E_{n'} - E_n$.

§2.1. Wave Behavior of Light.

Wave behavior of light has been proven for many years through interferent, diffraction, etc. experiments, and through the unification of Maxwell Equation of EM waves.

Let's use Young's double-slit experiment as an example, to see how classical physics (Optics and EM) explain it.



Two waves interfere at point P. Wave amplitudes are superposed at P, so the wave amplitude at P is given by

$$\tilde{U}(x', y') = \tilde{U}_1(x', y') + \tilde{U}_2(x', y'), \quad I(x', y') = \tilde{U}^*(x', y') \tilde{U}(x', y')$$

When $r_2 - r_1 = m \lambda$, constructive interference \Rightarrow intensity maximum

$r_2 - r_1 = (m + \frac{1}{2}) \lambda$, destructive " \Rightarrow " minimum

I19

Thus, the fringe interval (distance between two bright fringes) is given

$$\Delta y = \frac{s}{a} \lambda$$

For normal light, $a \sim 0.1-1 \text{ mm}$, $s \sim 1-10 \text{ m}$, $\lambda \sim 1-10 \text{ cm}$

Wave Amplitude Superposition \Rightarrow Interference

§2.2. Single Photon Experiment:

If we decrease the light source intensity, until photons go through the experiment setup one-by-one. What's going to happen? Will we still see the interference fringes? And how?

— We can use film as a screen to record the experiment.

① If expose the film for a long time to capture a large number of photons, the fringes do not disappear. Therefore, the pure particle interpretation that the fringes are due to interaction between different photons, must be rejected.

② If only expose the film to a very short period, so that only a few photons are received, observation shows that each photon produces a localized impact on the film, but not a very weak interference pattern. Therefore, the purely wave interpretation must be rejected.

③ When more and more photons strike the photographic film, the distribution of photon impacts begins to have a continuous aspect. The density (i.e., the probability) of the impacts at each point of the film corresponds to the interference fringes. max on a bright fringe and zero on a dark fringe.

— Please look at the real experimental image of Single-photon interference.

Single Photon Double-Slit Interference Experiment

