Part I. Fundamentals of Quantum Mechanics

The study of spectroscopy will bring us into a "Quantum World", so it is important for us to study a new language — the "Quantum Physics".

The main goal of Part I is to study this new language so that we can use "Quantum" languge to describe experiments, understand phenomena, and explore the nature principles behind them.

Part I consists of three chapters:

Chapter 1. Concepts of Quantum and Experimental Facts

Chapter 2. Wave - Particle Duality

Chapter 3. Quantum Mechanics Postulates, Principles, and Mathematic Formalism

We start from several key experiments to introduce the concepts of quantum, and then discuss the "famous" wave-particle duality, and systematically review quantum mechanics postulates, principles, and how to use QM to calculate physical quantities.

The knowledge gained in Part I will be immediately applied in Part II to study atomic structure and atomic spectra.

Chapter 1. Concepts of Quantum and Experimental Facts

* Electromagnetic radiation was well known as EM waves by the end of 19th century. This was mainly due to demonstration experiments like Young's double-slit interference experiments, and other diffraction and interference experiments.

* However, several "simple" experimental phenomena, like blackbody radiation, photoelectric effect, proved the inefficiency of classical physics, including the wave theory of EM radiation. The explanations of these phenomena led to the revolution of physics — the beginning of Quantum Physics !!!

* In this class, we choose 4 famous "revolusionary" experiments to reveal the necessaty and characteristics of EM radiation the quanta of. Some of the phenomena are also related to remote sensing applications.

$\boxed{\text{Blackbody radiation, Photoelectric effect, Compton effect, H-spectra}}$

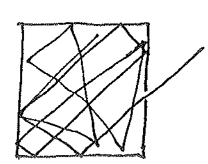
§1.1. Blackbody Radiation and Planck's Radiation Law

Blackbody radiation is one kind of "Thermal Radiation".

* Thermal Radiation is the EM radiation emitted by any objects at any temperature above absolute zero, which only depends on the temperature of the objects.

* Blackbody is an object that absorbs all EM radiation that falls onto it. Absolute blackbody is idealized object, nonexist.

But blackbody can be simulated by a cavity with a very small hole. "Blackbody" is not really black, as they still radiate energy, depending on T.



Three main properties of (blackbody) thermal radiation

(1) Thermal radiation occurs at a wide range of frequency, even at a single temperature.

— The energy density vs. frequency is governed by the Planck's Radiation Law. [ρ_ν is energy density in unit frequency range]

$$\rho(\nu) = \rho_\nu = \frac{8\pi h \nu^3}{c^3} \cdot \frac{1}{e^{h\nu/k_B T} - 1} \quad (1)$$

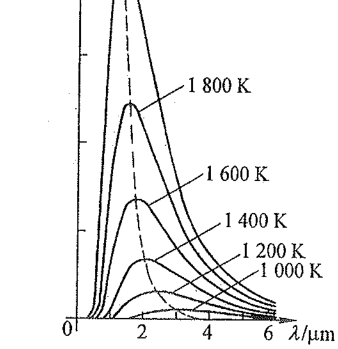
(2) The peak frequency of the thermal radiation increases as the temperature increases. When expressed in wavelength, the product of wavelength and temperature is a constant, and govern by the Wien's Displacement Law:

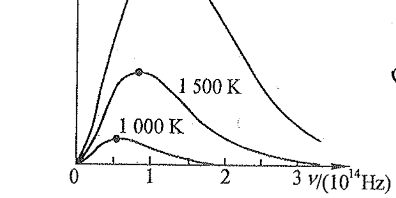
$$\lambda_{max} T = \frac{hc}{4.9651\, k_B} = 2.898 \times 10^{-3}\ m \cdot K. \quad (2)$$

(3) The total radiation energy density of all frequency, goes up very fast as the temperature rises. The relation of total radiation (integrating through all frequencies) vs. temperature is govern by the Stefan-Boltzmann Law: (3)

$$\rho = \int_0^{\nu} \rho_\nu \, d\nu = \frac{4}{c} \sigma T^4, \qquad \sigma = \frac{2\pi^5 k_B^4}{15 h^3 c^2} = 5.67 \times 10^{-8}\ W/(m^2 \cdot K^4) \quad (4)$$

σ is stefan-Boltzmann constant.





⟸ Observed Blackbody Radiation

How to explain the observed blackbody radiation?

Historically, there were three attemps

① Wien's Equation: assuming radiation ν is related to velocity v.

$$\Rightarrow \rho_T(\nu) = \frac{\alpha \nu^3}{c^2} e^{-\beta\nu/T} \quad \text{or} \quad \rho_T(\lambda) = \frac{\alpha c^2}{\lambda^5} e^{-\beta c/\lambda T}$$

where α, β are constants.

Wien's equation agrees with the experimental data in short wavelength, but has a systematic discrepancy in long λ.

② Rayleigh-Jeans Equation: starting from equipartition of energy (能量按自由度均分)

$$\rho_T(\nu) = g(\nu)\,\bar{\varepsilon}(\nu, T) \quad (6)$$

$g(\nu)$ is EM wave mode per unit volume, per unit freq. interval.
$\bar{\varepsilon}(\nu, T)$ is mean energy of oscillator with freq ν and temp T.

In thermal equilibrium, EM wave mode number is given by

$$g(\nu) = \frac{8\pi\nu^2}{c^3} \quad (7)$$

i.e., the independent freedom number. (State density in unit freq. interval)

In thermal equilibrium, the probability of energy ε is proportional to $e^{-\varepsilon/k_BT}$ (Boltzmann distribution Law)

$$\boxed{P(\varepsilon) \propto e^{-\varepsilon/k_BT}} \quad (8)$$

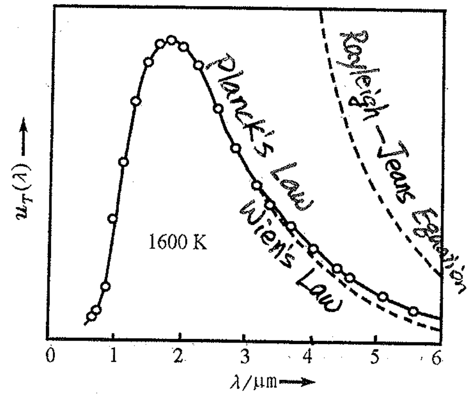
From classical physics, the linear oscillator's energy ε varies from 0 to ∞ continuously. Thus, mean energy

$$\bar{\varepsilon} = \frac{\int_0^\infty \varepsilon e^{-\varepsilon/k_BT} d\varepsilon}{\int_0^\infty e^{-\varepsilon/k_BT} d\varepsilon} = k_BT \quad (9)$$

Therefore, $\rho_T(\nu) = g(\nu)\,\bar{\varepsilon}(\nu, T) = \frac{8\pi\nu^2}{c^3} k_BT$ (10)

Rayleigh-Jeans' equation agrees with data in long wavelength, but completely disagrees with data in short wavelength. Espeically, when $\lambda \to 0$, $\rho_T(\nu) \to \infty$: "UV catastrophe"!!!

③ Planck's Law: to solve problems, Planck made an unusual assumption: oscillator's energy has to be multiple of a basic unit, i.e., $\varepsilon = \varepsilon_0, 2\varepsilon_0, 3\varepsilon_0, \cdots$



Various blackbody radiation Equations compared to experimental data

Thus, $$\bar{\varepsilon}(\cancel{\nu}, T) = \frac{\sum_{n=0}^{\infty} n\varepsilon_0 e^{-n\varepsilon_0/k_BT}}{\sum_{n=0}^{\infty} e^{-n\varepsilon_0/k_BT}} \qquad (11)$$

In other words, the integration of continuous energy is replaced by the sum of discrete energy.

Above $$\bar{\varepsilon} = -\left[\frac{\partial}{\partial\beta}\ln\left(\sum_{n=0}^{\infty} e^{-n\varepsilon_0\beta}\right)\right]\Bigg|_{\beta=\frac{1}{k_BT}}$$

$$\because \sum_{n=0}^{\infty} e^{-n\varepsilon_0\beta} = \frac{1}{1-e^{-\varepsilon_0\beta}}$$

$$\therefore \bar{\varepsilon} = \frac{\varepsilon_0}{\exp(\varepsilon_0/k_BT)-1} \qquad (12)$$

$$\therefore \rho_T(\nu) = g(\nu)\,\bar{\varepsilon}(\nu, T) = \frac{8\pi\nu^2}{c^3}\cdot\frac{\varepsilon_0}{\exp(\varepsilon_0/k_BT)-1} \qquad (13)$$

Let $\boxed{\varepsilon_0 = h\nu}$, then we obtain

$$\rho_T(\nu) = \frac{8\pi h\nu^3}{c^3}\,\frac{1}{\exp(h\nu/k_BT)-1}. \qquad (14)$$

$\varepsilon_0 = h\nu$ (15) — quantum of energy of a linear oscillator!!! △ △ △

From Planck's Law ⟹ Wien's Law and Stefan–Boltzmann Law.

Wien's Displacement Law: to find the λ corresponding to ρ_ν peak:

$$\frac{\partial\rho_\lambda}{\partial\lambda} = 0 \Longrightarrow \lambda_m T = \frac{hc}{4.9651\,k_B} \qquad (16)$$

Stefan–Boltzmann Law: integration of ρ_ν through entire freq. $(0\to\infty)$

$$\rho = \int_0^\infty \rho_\nu\,d\nu = \frac{4}{c}\sigma T^4. \qquad (17)$$

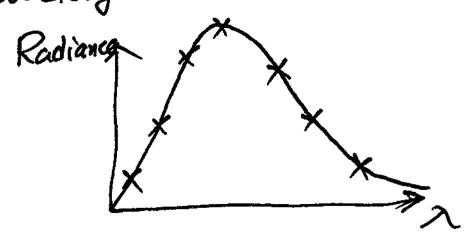
Application of (Blackbody) Thermal Radiation:

(1) Infrared viewer for detecting objects:

Any object emits thermal radiation, and the peak wavelength depends on the object's temperature. For example, the Sun has surface temperature $\sim 6000K \Rightarrow$ the peak wavelength ~ 502 nm. For normal objects on Earth, they have much lower temperature $\sim 300K$. So their thermal radiation is in much longer IR wavelength. This is how IR viewer can detect objects.

(2) Surface Temperature Mapping

Sea surface temperature mapping: radiometer measures the IR radiance from sea surface (top 1 mm) at several wavelength channels.



① From fitting blackbody radiation $\Rightarrow$ Brightness temp.

② However, sea is not perfect blackbody, so its emissivity is lower than blackbody (because its absorption is lower than blackbody):

$$\text{Emissivity} = \frac{\text{radiance by sea @ certain } T}{\text{radiance by blackbody @ the same } T}$$

③ $$\text{Total radiance} = \sigma_1 T_{real}^4 * \text{Emissivity}(\lambda, T) = \sigma_2 T_{Brightness}^4$$

$$\Rightarrow T_{real} = \left(\frac{\sigma_2}{\sigma_1} \cdot \frac{1}{\text{Emissivity}}\right)^{1/4} * T_{Brightness}$$

$\therefore$ Radiometer utilizes the thermal radiation to map sea surface temp, which is important to ocean study.

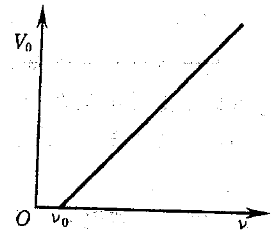
* Blackbody radiation is only dependent on temperature, but independent of materials. So in principle radiometer only cares about the radiance, but does not care about the materials and structures.

(3) 2.7 K Radiation in the Universe: (Cosmic Background Radiation)

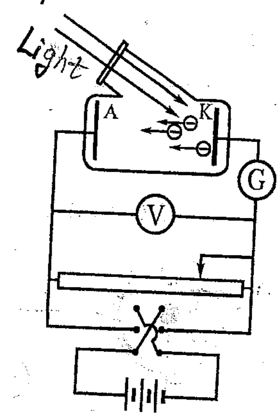
Thermal radiation is in the background of spectrum of our universe. It was found the radiation corresponds to 2.7 K ($\lambda_{max} \approx 1$ mm), distributing homogeneously in the universe. $\rightarrow$ due to the expansion of the universe.

§1.2. Photoelectric Effect and Quantized Energy

* Photoelectric effect is the phenomenon of the emission of electrons from the surface of a metal which is illuminated by ultraviolet light.



Cut-off frequency



Experimental Setup for photoelectric effect

* observed properties:

① Electrons are only emitted if the freq. of the U.V. light exceeds a certain threshold value ν_0, which is a specific property of the metal.
If the frequency falls below the threshold freq. ν_0, the current drops to zero, no matter what the intensity of the incident light is.

② When $\nu > \nu_0$, and use very weak light, there are still electrons come out but with very few numbers. In this limit, it appears as if all the energy in the light wave falling on the surface would have to be concentrated on a single electron in order to give it the observed kinectic energy. This seems to be contradictary to classical electrodynamics, for the energy in a light wave is usually assumed to be distributed uniformly across the wavefront.

* Einstein's quantum explanation of photoelectric effect.

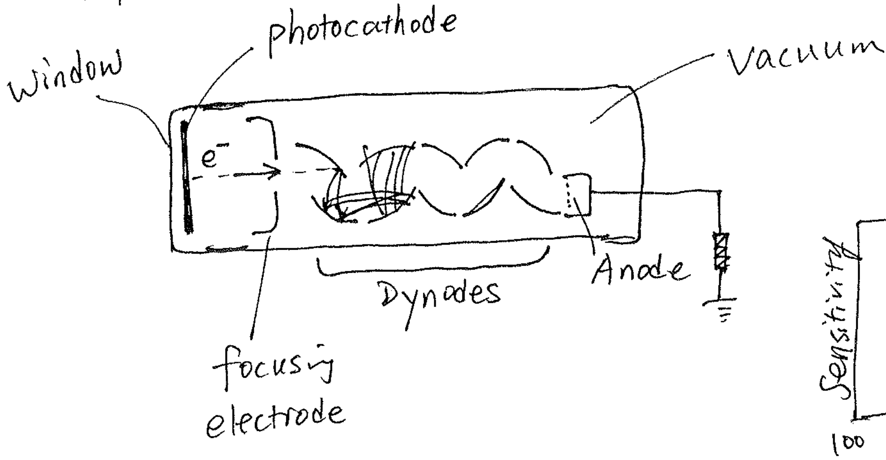
Einstein made a bold hypothesis that ① the energy in the radiation field actully existed as discrete quanta, called "photons", each having an energy of $h\nu$, and that ② in interactions between radiation and matter, this energy is essentially localized at one electron. An electron at the surface of metal gains an energy $h\nu$ by absorbing a photon, then overcomes the work function, and emerges from the metal surface with the maximum kinetic energy: $\frac{1}{2} m V_{max}^2 = h\nu - \phi$, (18)

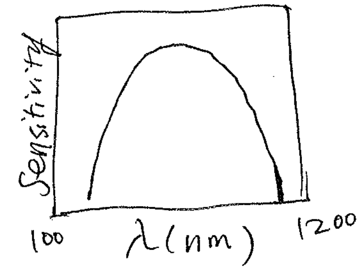
Where ϕ is the work function of the surface.

* Application of photoelectric effect.

Have you seen or used photoelectric effect?

of course, you have — the PMT – Photomultiplier Tube!





⇒ Photocathode: material with photoelectric effect. which prefers shorter wavelength: $\lambda < \lambda_0$

⇒ Window: material ~~has~~ can absorb short UV light, So window prefers longer wavelength: $\lambda > \lambda_0'$

Therefore, the PMT response falls in a certain wavelength range. $\boxed{\lambda_0' < \lambda < \lambda_0}$

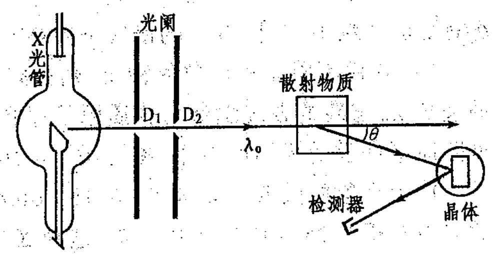
Most photocathodes are made of a compound semiconductor mostly consisting of alkali metals with a low work function.

Most photocathodes have high sensitivity down to the UV region. However, because UV radiation tends to be absorbed by the window material, the short wavelength limit is determined by the UV transmittance of the window material.

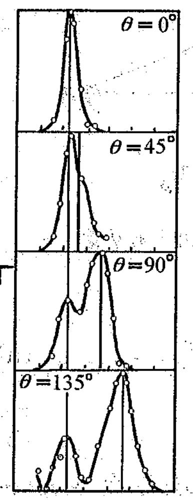
§1.3. Compton Effect and Quantized Momentum

* Compton effect, also known as Compton Scattering, is the phenomenon of X-ray or γ-ray (photons) scattered by electrons. If the incident radiation has a wavelength of λ_0, then besides the original wavelength λ_0, radiation with wavelength λ longer than λ_0 ($\lambda > \lambda_0$) also occurs in the scatter radiation at different scattering angle.

(1) 设入射线的波长为 λ_0，沿不同方向的散射线中，除原波长外都出现了波长 $\lambda > \lambda_0$ 的谱线。

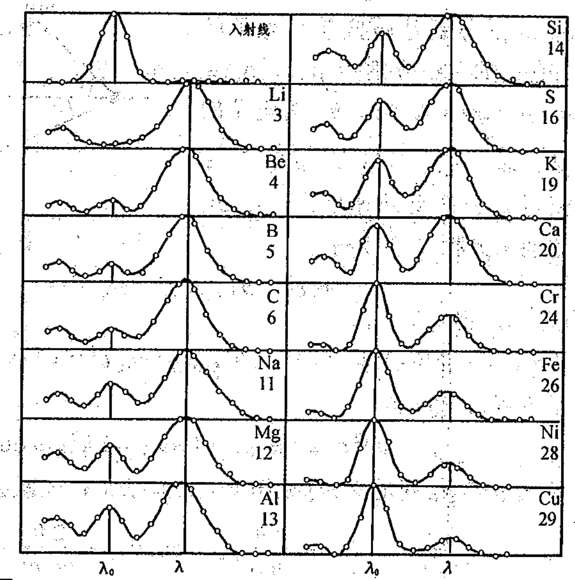


Experimental Setup for Compton effect



λ_0 = 0.0712605nm(钼谱线)
散射物质 —— 石墨

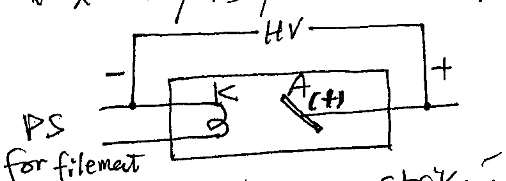
Compton Scattering vs. angle



λ_0 = 0.056267nm(银谱线)，元素符号下的数字为原子序数

Compton Scattering vs. Atomic Z

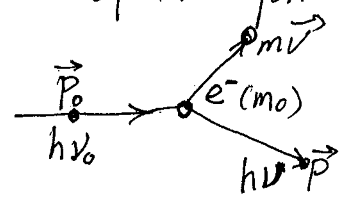
* X-ray is produced by



accelerated electrons striking anode under 100KV.

X-ray is the photons produced by inner electron transition.

* Compton effect can only be explained by the elastic collision between (X-ray) photons and electrons. Electrons within atoms can be regarded as free and at rest (due to high energy of X-ray and γ-ray photons). During the collision process, total energy and total momentum of the "photon + electron" system are conservative:



$$\begin{cases} h\nu_0 + m_0 c^2 = h\nu + mc^2 & (19) \\ \vec{P_0} + 0 = \vec{p} + m\vec{v} & (20) \end{cases}$$

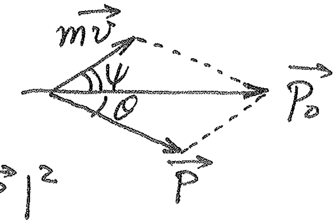
m_0 - electron mass at rest

(Consider relativity theory) $m = \dfrac{m_0}{\sqrt{1-(v/c)^2}}$ (21)

Photons have momentum $P_0 = \dfrac{h}{\lambda_0} = \dfrac{h\nu_0}{c}$ (22)

$$P = |\vec{P}| = h\nu/c$$

From momentum vector relation, we have



$$m\vec{v} = \vec{P_0} - \vec{P} \Rightarrow |m\vec{v}|^2 = |\vec{P_0} - \vec{P}|^2$$

$$\therefore (mv)^2 = |\vec{P_0}|^2 + |\vec{P}|^2 - 2\vec{P_0}\cdot\vec{P}$$

$$= \left(\frac{h\nu_0}{c}\right)^2 + \left(\frac{h\nu}{c}\right)^2 - 2\left(\frac{h\nu_0}{c}\right)\left(\frac{h\nu}{c}\right)\cos\theta$$

$$\Rightarrow m^2 v^2 c^2 = (h\nu_0)^2 + (h\nu)^2 - 2h^2\nu_0\nu\cos\theta$$

From energy conservation equation,

$$[mc^2]^2 = [h(\nu_0 - \nu) + m_0 c^2]^2$$

$$\Rightarrow m^2c^4 = h^2\nu_0^2 + h^2\nu^2 - 2h^2\nu_0\nu + m_0^2c^4 + 2m_0c^2h(\nu_0 - \nu)$$

Take the difference between above two equations:

$$m^2c^4\left(1 - \frac{v^2}{c^2}\right) = m_0^2c^4 - 2h^2\nu_0\nu(1 - \cos\theta) + 2m_0c^2h(\nu_0 - \nu)$$

Recall relativity relationship: $m\left(1 - \dfrac{v^2}{c^2}\right) = m_0$

$$\therefore m^2c^4\left(1 - \frac{v^2}{c^2}\right) = m_0^2c^4$$

$$\therefore \cancel{m_0^2c^4} = \cancel{m_0^2c^4} - 2h^2\nu_0\nu(1 - \cos\theta) + 2m_0c^2h(\nu_0 - \nu)$$

$$\Rightarrow \cancel{2}m_0c^2\cancel{h}(\nu_0 - \nu) - \cancel{2}h^{\cancel{2}}\nu_0\nu(1 - \cos\theta) = 0$$

Divide by m_0c and $\nu_0\nu$, we obtain

$$\frac{c}{\nu} - \frac{c}{\nu_0} = \frac{h}{m_0c}(1 - \cos\theta) \qquad (23)$$

$$\therefore \boxed{\Delta\lambda = \lambda - \lambda_0 = \frac{h}{m_0c}(1 - \cos\theta)} \qquad (24)$$

$$\Delta\lambda = \lambda - \lambda_0 = \frac{h}{m_0 c}(1-\cos\theta).$$

Several features can be derived from this equation:

① $\Delta\lambda$ is independent of incidenct wavelength λ_0.

② When $\theta = 90°$, $\Delta\lambda = \frac{h}{m_0 c} = \frac{6.626\times10^{-34}}{9.1\times10^{-31}\times3\times10^{8}} = 0.0242621$ Å agreeing with data

③ When $\theta = 0°$, $\Delta\lambda = 0$, no wavelength shift.

④ Spread of wavelength change: this is because electrons are not at rest before scattering.

⑤ Component of λ_0 in the scattering radiation: this is due to the collision between photon and the atom which has much larger mass than electron, i.e., if m_0 is replaced by atom mass (instead of electron mass), the shift $\Delta\lambda$ is neglegible. Photons only change direction, but almost no change in energy. $\Rightarrow$ λ_0 line.

⑥ When Z increases, intensity of λ component decreases and intensity of λ_0 increases:

λ_0 comes from the contribution of inner electrons, while λ comes from outer electron scattering.

When Z increases, more inner electrons $\Rightarrow$ λ_0 component $\uparrow$

less outer " $\Rightarrow$ λ " $\downarrow$

⑦ Comparison of photoelectric effect with Compton effect:

Photoelectric effect: low photon energy (< 0.5 MeV)

photon is completely absorbed, and an electron is ejected from the atom (ionization)

A major Attenuation of X-ray by matter

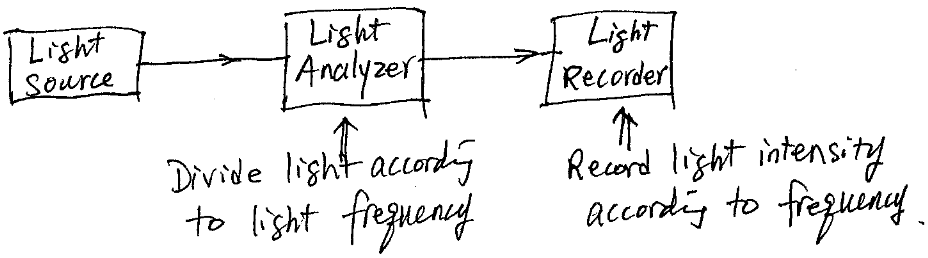
Compton effect: medium high photon energy (0.5–3.5 MeV)

photon is not absorbed, but transfer part of energy to electron (and eject electron from atom) while another photon with reduced energy scattered.

§1.4. Hydrogen Spectra and Discrete Energy Levels

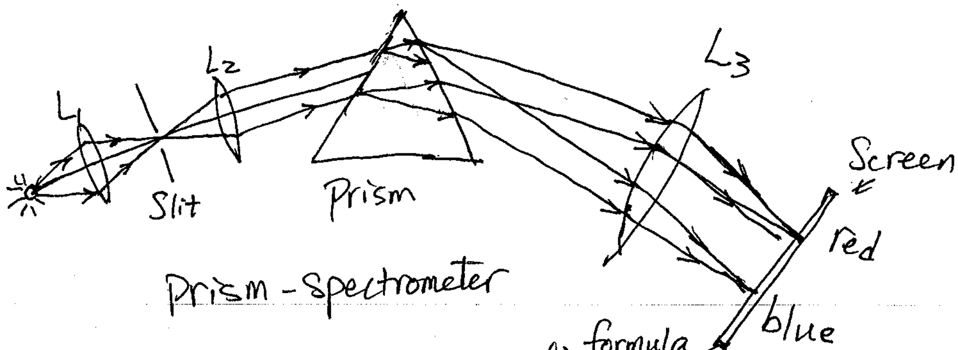
* Spectrum is the intensity distribution of the frequency of radiation. It is the most important approach to study matter internal structure.

* Spectrometer in principle consists of three major parts:



Example:

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



Prism-Spectrometer

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

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

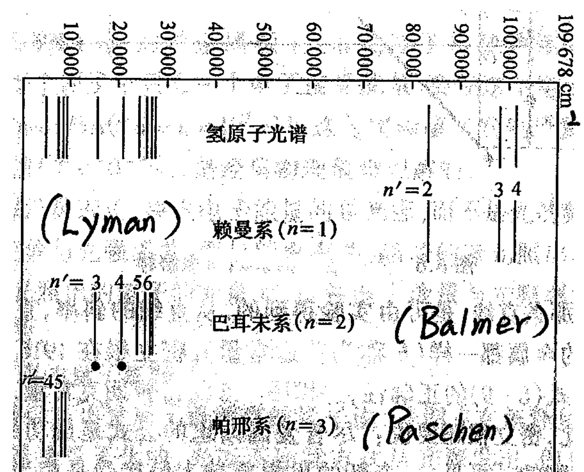
1889, J.R. Rydberg proposed a more general equation:

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

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

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

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



From Rydberg equation,

$n=1$, $n'=2,3,4,5,\cdots$, T. Lyman **series** (UV), found in 1914.

$n=2$, $n'=3,4,5,6,\cdots$, J. Balmer **series** (Visible), 1885.

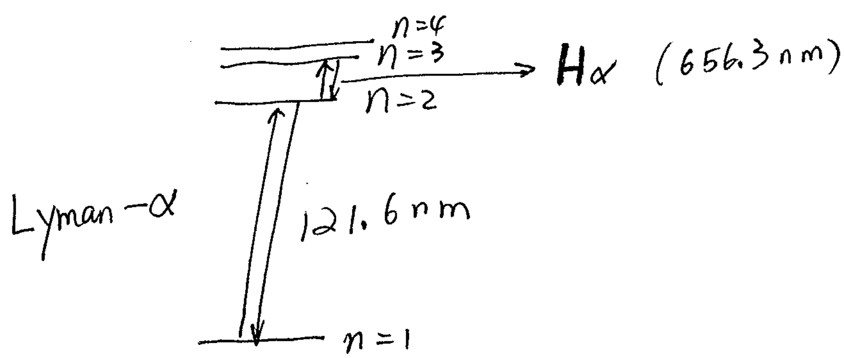
The most famous line is $\lambda = 656.3\,nm$ from $n'=3 \Rightarrow n=2$. observed by A. J. Ångström in 1853.

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

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

$n=5$, $n'=6,7,8,9,\cdots$, 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)



Examples:

① Lyman-α line dissociates water vapor (H_2O) in the upper atmosphere → influence PMC brightness

② Fraunhofer Lines:

Sun (blackbody radiation) → Continuous spectral density

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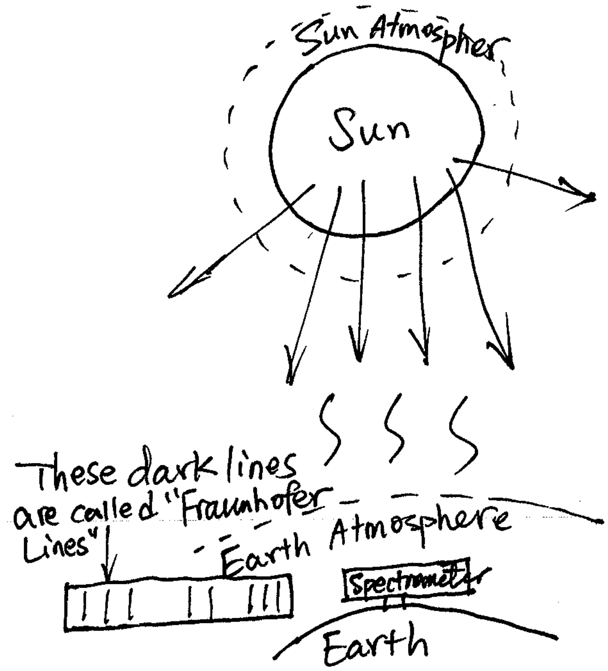
Sun Atmosphere and Earth Atmosphere (atomic and molecular absorption)

⇓

Dark lines at these resonance wavelengths in the solar radiation.



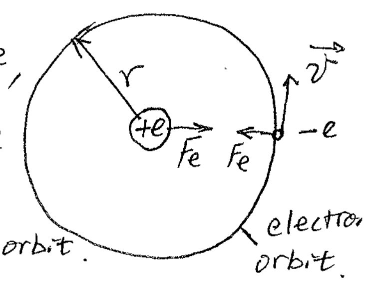
§1.5. Bohr's Theory (Model)

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 $E_1, E_2, \ldots, E_i, \cdots$.

Electron orbits the H-nucleus in circle,
(me, e) (mp, +e)



it needs central force $F = m_e \frac{v^2}{r}$ v – velocity, r – radius of electron orbit.

It is provided by Coulomb force between electron and nucleus:

$$F = m_e \frac{v^2}{r} = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} \Rightarrow m_e v^2 = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

$$\Downarrow$$

$$v = \sqrt{\frac{e^2}{4\pi\varepsilon_0 m_e r}} \qquad (26)$$

Total energy of electron is given by

$$E_{total} = E_{kinetic} + E_{potential}$$
$$= \frac{1}{2} m_e v^2 - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$
$$= -\frac{1}{2}\cdot\frac{e^2}{4\pi\varepsilon_0 r} \qquad (27)$$

The frequency of electron orbital motion is given by

$$f = \frac{1}{T} = \frac{1}{2\pi r / v} = \frac{v}{2\pi r}$$
$$= \frac{e}{2\pi}\sqrt{\frac{1}{4\pi\varepsilon_0 m_e r^3}} \qquad (28)$$

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

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

Compare Bohr's frequency condition with Rydberg equation:

$$\left.\begin{array}{l} \frac{1}{\lambda} = R_H \left[\frac{1}{n^2} - \frac{1}{(n')^2}\right] = \frac{\nu}{c} \\ E_{n'} - E_n = h\nu \end{array}\right\} \Rightarrow$$

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

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

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

Recall classical $E = -\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 r}$,

$$-\frac{R_H hc}{n^2} = -\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 r}$$

$$\Rightarrow r_n = \frac{1}{4\pi\varepsilon_0}\cdot\frac{e^2}{2R_H hc}n^2, \quad (31)$$

n is integer (positive), orbits are discret.

Postulate 3 Correspondence Principle.

"When extending laws in atomic field (micro world) to 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 $n'-n=1$, we get

$$\nu \approx R_H c\frac{2n\times 1}{n^4} = \frac{2R_H c}{n^3} = \frac{e}{2\pi}\sqrt{\frac{1}{4\pi\varepsilon_0 m_e r^3}}$$

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

$$r = \sqrt[3]{\frac{1}{4\pi\varepsilon_0}\frac{e^2}{16\pi^2 R_H^2 c^2 m_e}}\cdot n^2 \quad (32)$$

According to correspondence principle,

$$r = r_n \Rightarrow \frac{1}{4\pi\varepsilon_0} \cdot \frac{e^2}{2R_H hc} n^2 = \sqrt[3]{\frac{1}{4\pi\varepsilon_0} \cdot \frac{e^2}{16\pi^2 R_H^2 c^2 m_e}} \cdot n^2$$

therefore, we obtain Rydberg Constant:

$$\boxed{R_H = \frac{2\pi^2 e^4 m_e}{(4\pi\varepsilon_0)^2 \cdot ch^3}} \quad (33)$$

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:

$$r_n = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2} \cdot n^2, \quad (34) \quad \text{here, } \hbar \equiv \frac{h}{2\pi}.$$

Substitute R_H in E_n equation, we obtain the electron energy

$$E_n = -\frac{m_e e^4}{(4\pi\varepsilon_0)^2 \cdot 2\hbar^2 n^2}. \quad (35)$$

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

$$L = m_e v r = m_e \cdot \sqrt{\frac{e^2}{4\pi\varepsilon_0 m_e r}} \cdot r = \sqrt{\frac{m_e e^2 r}{4\pi\varepsilon_0}}$$

Replace r by r_n, $\Rightarrow L = \sqrt{\frac{m_e e^2}{4\pi\varepsilon_0} \cdot \frac{4\pi\varepsilon_0 \hbar^2 n^2}{m_e e^2}} = n\hbar,$

$$\therefore L = n\hbar, \quad (36) \quad n = 1, 2, 3, \cdots$$

This is the quantazed 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

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} \simeq \frac{1}{137} = \frac{1}{137.035999\,11(46)} \quad (37)$$

Bohr radius : $r_1 \equiv a_1 = \dfrac{4\pi \varepsilon_0 \hbar^2}{m_e e^2} \approx 0.053\,nm$ (38)

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

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

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

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 $\mu = \dfrac{m_e M}{m_e + M}$ (i.e., $\dfrac{1}{m_e} + \dfrac{1}{M} = \dfrac{1}{\mu}$)

Replace m_e with μ in R_H equation :

$$R_H = \frac{2\pi^2 e^4 \mu}{(4\pi\varepsilon_0)^2 \cdot c h^3} = \frac{2\pi^2 e^4}{(4\pi\varepsilon_0)^2 \cdot c h^3} \cdot \frac{m_e M}{m_e + M}$$

$$= R_\infty \cdot \frac{1}{1 + \frac{m_e}{M}}$$

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