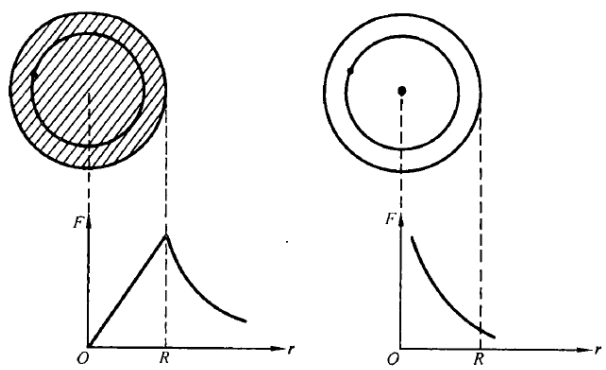
Lecture 1: Old Quantum Theory

September 3, 2019

1 Early Atom Models

1. Thompson Model



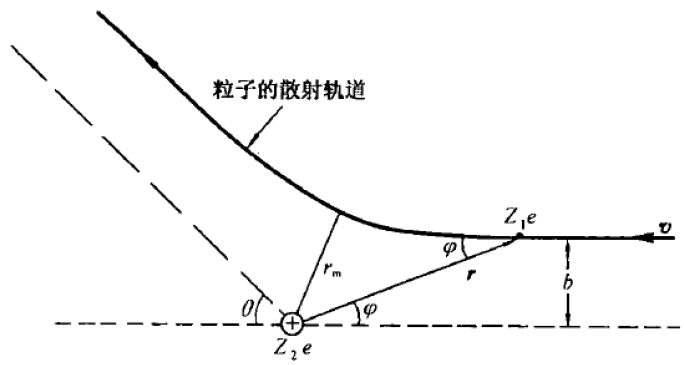
$$\theta \sim \frac{\Delta p}{p} \sim \frac{F\Delta t}{p} \sim \frac{\left(ZZ_1e^2/4\pi\varepsilon_0R^2\right)\cdot(2R/v)}{mv} \sim \frac{ZZ_1}{RE}\left(\frac{e^2}{4\pi\varepsilon_0}\right)$$

$$e'^2 = \frac{e^2}{4\pi\varepsilon_0} = 1.44\text{fm Mev}$$

- For $R \sim 1.0\text{Å} = 10^5\text{fm}$, α particle $Z = 2$, $\theta \sim \frac{Z}{E} \times 10^{-5}$(very small)
- The effect of electrons can be neglected (because the mass of electron is very small)

2. Rutherford Model

   (a) Coulomb scattering formula



Coulomb Scattering Formula: $b = \dfrac{a}{2}\cot\left(\dfrac{\theta}{2}\right)$ with $a = \dfrac{ZZ_1e'^2}{E}$ scattering factor

$$m\frac{d\mathbf{v}}{dt} = \frac{ZZ_1e'^2}{r^2}\hat{\mathbf{r}}$$
$$mr^2\frac{d\phi}{dt} = L = mvb$$

The trajectory is then

$$d\mathbf{v} = \frac{ZZ_1e'^2}{mvb}\hat{\mathbf{r}}d\phi$$

Integrate both sides

$$\int_i^f d\mathbf{v} = \mathbf{v}_f - \mathbf{v}_i = 2v\sin\left(\frac{\theta}{2}\right)$$

$$\int_i^f \hat{\mathbf{r}}d\phi = \int_0^{\pi-\theta}\left(\mathbf{i}\cos\phi + \mathbf{j}\sin\phi\right)d\phi = \mathbf{i}\sin\theta + \mathbf{j}\left(1+\cos\theta\right) = 2\cos\left(\frac{\theta}{2}\right)\left[\mathbf{i}\sin\frac{\theta}{2} + \mathbf{j}\cos\frac{\theta}{2}\right]$$

Note the direction of $\mathbf{v}_f - \mathbf{v}_i$ is $(\pi-\theta)/2$, i.e, $\mathbf{i}\sin\frac{\theta}{2} + \mathbf{j}\cos\frac{\theta}{2}$, the same with $\int_i^f \hat{\mathbf{r}}d\phi$. Thus we have

$$2v\sin\frac{\theta}{2} = 2\cos\frac{\theta}{2}\cdot\frac{ZZ_1e'^2}{mvb}$$
$$b = \frac{ZZ_1e'^2}{mv^2}\cot\left(\frac{\theta}{2}\right) = \frac{a}{2}\cot\left(\frac{\theta}{2}\right)$$

with Coulomb scattering factor

$$a = \frac{ZZ_1e'^2}{E}.$$

Clearly, $\theta \to 0$ for $b \to \infty$, and $\theta = \pi$ for $b = 0$.

(b) Rutherform Scattering Formula

i. Question: Given N incident particles, how many scattering in the solid angle $d\Omega = 2\pi \sin\theta d\theta$ per unit area, per target particle?

ii. This gives the differential cross section (DCS)

$$\sigma_c(\theta) = \frac{1}{Nnd}\frac{dN'}{d\Omega}$$

where n is the number density and d the sample depth (ndA gives the number of target particles with A the area)

iii. Particles in $b \to b + db$, scattering between angle $\theta \to \theta + d\theta$. Assume the target particles scatter the incident particle independently.

$$\frac{dN'}{N} = \frac{2\pi b|db|}{A} \cdot (ndA) = 2\pi \left(\frac{a^2 \cot(\theta/2)}{8\sin^2(\theta/2)} d\theta\right) \cdot nd$$

Thus

$$\sigma_c(\theta) = \frac{1}{Nnd}\frac{dN'}{d\Omega} = 2\pi \left(\frac{a^2 \cot(\theta/2)}{8\sin^2(\theta/2)} d\theta\right) \frac{1}{2\pi \sin\theta d\theta} = \frac{a^2}{16\sin^4(\theta/2)}$$

iv. Written explicitly

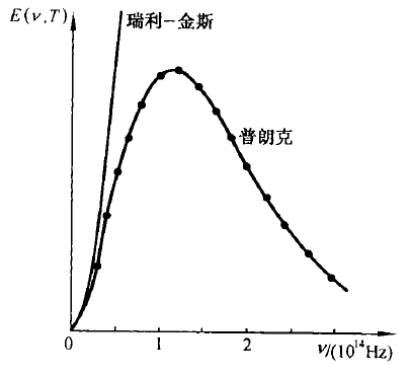
$$\sigma_c(\theta) = \left(\frac{ZZ_1 e'^2}{4E}\right)^2 \cdot \frac{1}{\sin^4(\theta/2)}$$

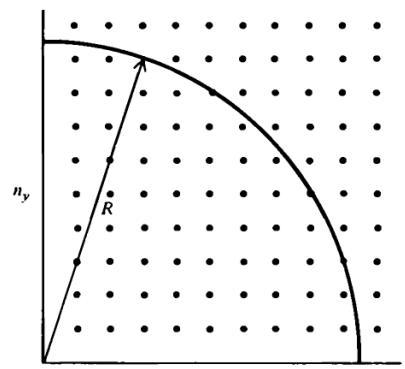
v. This DCS can be verified experimentally. It has the dimension of area (Note $e'^2 = 1.44$ fm Mev). If this formula holds, then $dN' \sin^4(\theta/2)$, $dN' \cdot E^2$, and dN'/Z^2 should be constants given other paramaters fixed. These were verified in 1913.

(c) Rutherford Planet model fails for the following reasons. A charged particle like the electron circulating in orbit would be expected to radiate light, with the same frequency as the orbital motion. The frequencies of these orbital motions could be anything. Worse, as the electron lost energy to radiation it would spiral down into the atomic nucleus. Atoms cannot remain stable.

2 Planck Quantum Concept

1. Rayleigh-Jeans formula





(a) Question: The energy density $E(\nu, T)$ in the frequency range $\nu \to \nu + d\nu$ at temperature T?

(b) According to classical physics, the radiation field is the sum of Fourier normal modes proportional to $\exp(i\mathbf{q} \cdot \mathbf{r})$ with

$$\mathbf{q} = 2\pi\mathbf{n}/L$$

where $\mathbf{n} = (n_1, n_2, n_3)$ and L is the length of a cubic box. $n_{1,2,3}$ are intergers.

(c) # of modes within $d\mathbf{q} = dq_x dq_y dq_z$ is $d\mathbf{n} = (L/2\pi)^3 d\mathbf{q}$. # of modes with $q \to q + dq$ is then $\frac{V}{8\pi^3} 4\pi q^2 dq = \frac{V}{2\pi^2} q^2 dq$. Since $q = 2\pi/\lambda$, $\nu = c/\lambda$, thus $q = 2\pi\nu/c$.

(d) The number of normal modes in the range $\nu \to \nu + d\nu$ is then

$$N(\nu)\, d\nu = 2 \times \frac{V}{2\pi^2} q^2 dq = 2 \times \frac{V}{2\pi^2} \left(\frac{2\pi\nu}{c}\right)^2 \frac{2\pi}{c} d\nu = \frac{8\pi\nu^2 V}{c^3} d\nu$$

where the first factor 2 stands for two polorization directions.

(e) At temperture T, according to classical statistical mechanics, the average energy of the normal modes (viewed as harmonic oscillators) is given by

$$\overline{E} = \frac{\int_0^\infty \exp(-\beta E)\, E dE}{\int_0^\infty \exp(-\beta E)\, dE} = \beta^{-1} = k_B T$$

(f) The energy density is then

$$E(\nu, T)\, d\nu = \frac{N(v)\, d\nu \cdot \overline{E}}{L^3} = \frac{8\pi\nu^2}{c^3} \cdot k_B T d\nu$$

which is Rayleigh-Jeans (RJ) formula

(g) The R-J formula fails in two aspects: Deviates badly for large ν, called *ultraviolet catastrophe*. Also the integration $\int E(\nu, T)\, d\nu$ diverges if it holds for any ν.

2. Planck Formula

   (a) 1900, proceedings of German Physical Society, Planck noted the data can be fitted very well by (a guess work)

   $$E(\nu, T)\, d\nu = \frac{8\pi v^2}{c^3} \cdot \frac{h\nu}{\exp(h\nu/k_B T) - 1} d\nu$$

   with fitting constants

   $$k_B \simeq 1.4 \times 10^{-23}\text{J/K and } h \simeq 6.6 \times 10^{-34}\text{J·s} = 6.63 \times 10^{-27}\text{erg s}$$

   (b) Planck's quantization assumption: the radiation was the same as if it were in equilibrium with a large number of charged oscillators with different frequencies, the energy of any oscillator of frequency ν being an integer multiple of $h\nu$. Later, Lorenz gave a derivation in 1910, simply assuming discrete energy:

   $$\overline{E} = \frac{\sum_0^\infty \exp(-\beta n h\nu) \cdot (nh\nu)}{\sum_0^\infty \exp(-\beta n h\nu)} = -\frac{\partial}{\partial \beta} \ln\left(\sum_0^\infty \exp(-\beta n h\nu)\right)$$
   $$= -\frac{\partial}{\partial \beta} \ln\left(\frac{1}{1 - \exp(-\beta h\nu)}\right) = \frac{h\nu \exp(-\beta h\nu)}{1 - \exp(-\beta h\nu)} = \frac{h\nu}{\exp(\beta h\nu) - 1}$$

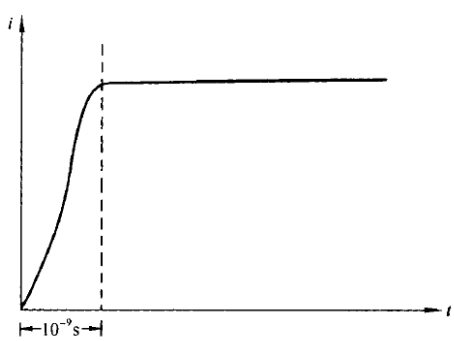
   (c) Hence

   $$E(\nu, T)\, d\nu = \frac{8\pi \nu^2}{c^3} \cdot \overline{E} d\nu = \frac{8\pi v^2}{c^3} \cdot \frac{h\nu}{\exp(h\nu/k_B T) - 1} d\nu$$
   $$\int_0^\infty E(\nu, T)\, dv = \alpha_B T^4 \text{ with } \alpha_B = \frac{8\pi^5 k_B^4}{15 h^3 c^3}$$

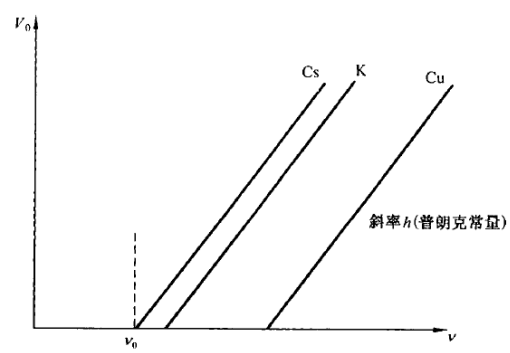
   (d) Application of Planck's work: Calculate $N_A = R/k_B$, the size of atom, the electron charge ...

3 Einstein Photon Assumption

1. Photo-Electronic Effect



光强 I 和频率 ν 一定时，光电流 i 与产生光电子的时间 t 的关系



对特定金属表面，遏止电压 V_0 与频率 ν 的关系

Some basic facts:

(a) About 10^{-9}s, electronic current becomes saturated immediately

(b) Threshold frequency, below which no photo-electron comes out

Classically, the energy of lights are proportional to the intensity, which cannot understand the above facts. Einstein assumes *light quanta*:

$$E = h\nu$$

and the kinetic energy of photo-electron is given by

$$K = h\nu - W$$

2. Compton Scattering (1922-23)

   Accordingly, the momentum of the photon is given by

$$p = E/c = h/\lambda \left(m^2c^4 = E^2 - p^2c^2 = 0\right)$$

   For X-ray scattering by electron, assuming the light scattering backwards with frequency ν', then the electron forwards with momentum $h\nu/c + h\nu'/c$, and energy conservation gives

$$h\nu + m_ec^2 = h\nu' + \sqrt{m_e^2c^4 + \left(\frac{h\nu + h\nu'}{c}\right)^2 c^2}$$

   Thus

$$2h\left(\nu - \nu'\right)m_ec^2 = 4h^2\nu\nu' \to \nu' = \frac{m_ec^2\nu}{2h\nu + m_ec^2}$$

   Written in the wave-length

$$\lambda' = c/\nu' = \lambda + \frac{2h}{m_ec} = \lambda + 2 \times \left(2.425 \times 10^{-10}\right)\text{ cm}$$

   $h/m_ec = 2.425 \times 10^{-10}$cm is known as Comptom wavelength of electron. If scattering at an angle θ, the factor 2 before h/m_ec is replaced by $1 - \cos\theta$. Later after verification of this relation, chemist Lewis gave the name *photon*.

4 Bohr Model

1. Bohr was a visitor to Rutherford's group in 1913. He proposed in the first place that the energies of atoms are quantized, in the sense that atoms exist in only a discrete set of states.

   - Discrete stable orbital:

$$m\frac{v^2}{r} = \frac{Ze'^2}{r^2}$$

- Angular momentum quantization: ($\hbar$ is a new parameter)

$$mvr = n\hbar\,(n = 1, 2, 3\dots) \to r = \frac{n\hbar}{mv}$$

- Substitute into the first Eq., we get

$$v_n = \frac{Ze'^2}{n\hbar}$$
$$r_n = \frac{n\hbar}{mv_n} = \frac{n^2\hbar^2}{mZe'^2} = n^2\frac{a_1}{Z} \text{ with } a_1 = \frac{\hbar^2}{me'^2}$$

- Energy

$$E_n = \frac{1}{2}mv_n^2 - \frac{Ze'^2}{r_n} = -\frac{1}{2}\frac{Z^2}{n^2}\frac{m_e e'^4}{\hbar^2}$$

- Transition frequency

$$\nu = \frac{E_m - E_n}{h} = \left(\frac{1}{n^2} - \frac{1}{m^2}\right)\frac{Z^2 m_e e'^4}{2\hbar^2 h}$$

For transition $n \to n+1$ and $n \to \infty$,

$$\nu \simeq \frac{2}{n^3}\cdot\frac{Z^2 m_e e'^2}{2\hbar^2 h} = \frac{Z^2 m_e e'^4}{n^3\hbar^2 h}$$

- Correspondence principle: If an electron in an atom is moving on an orbit with period T, classically the electromagnetic radiation will repeat itself every orbital period. If the coupling to the electromagnetic field is weak, so that the orbit doesn't decay very much in one cycle, the radiation will be emitted in a pattern which repeats every period, so that the Fourier transform will have frequencies which are only multiples of 1/T. This is the classical radiation law: the frequencies emitted are integer multiples of 1/T. For $n \to \infty$, ν should be the frequency of the orbital

$$f = \frac{v_n}{2\pi r_n} = \frac{Ze'^2/n\hbar}{2\pi n^2\hbar^2/m_e Ze'^2} = \frac{Z^2 m_e e'^4}{n^3\hbar^2\,(2\pi\hbar)}$$

Letting $f = \nu$, we thus obtain as expected

$$\hbar = h/2\pi$$

- Results

$$v_n = \frac{Ze'^2}{n\hbar} = \frac{Z}{n}\left(\frac{e'^2}{\hbar c}\right)c = \frac{Z}{n}\alpha c \text{ with } \alpha = \frac{e'^2}{\hbar c} \simeq \frac{1}{137}$$
$$r_n = \frac{n^2\hbar^2}{mZe'^2} = \frac{n^2}{Z}a_1 \text{ with } a_1 = \frac{\hbar^2}{me'^2} = 0.529\times 10^{-8}\text{cm}$$
$$E_n = -\frac{1}{2}\frac{Z^2}{n^2}\frac{m_e e'^4}{\hbar^2} = -\frac{1}{2}\frac{Z^2}{n^2}\times 27.2\text{ eV}$$

2. Atomic spectrum of Hydrogen

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} = \left(\frac{1}{n^2} - \frac{1}{m^2}\right)\frac{Z^2 m_e e'^4}{2\hbar^2 hc} = \left(\frac{1}{n^2} - \frac{1}{m^2}\right) R_H$$

$$R_H = \frac{1}{hc}\frac{Z^2 m_e e'^4}{2\hbar^2} = \frac{-E_1}{hc}$$

For Hydrogen, $E_1 = -13.6$ eV,

$$R_H = \frac{13.6 \times 1.6 \times 10^{-19}(\mathrm{J})}{6.63 \times 10^{-34}(\mathrm{J\ s}) \times 3 \times 10^{10}(\mathrm{cm/s})} \simeq 109677.58\ \mathrm{cm}^{-1}$$

Actually, for hydrogen atom, m_e should be replaced by reduced mass

$$\mu_H = \frac{m_e m_H}{m_e + m_H} \simeq \frac{1837}{1838}$$

If we consider Deuterium, then the reduced mass is

$$\mu_D = \frac{m_e m_D}{m_e + m_D} \simeq \frac{3674}{3675}$$

Thus we have slight isotrope effect for Hydrogen spectrum. This is the evidence of the existence of Deuterium. For instance, for transition $n = 2 \to n' = 3$ (the H_α line), λ for H is 656.279 nm, we can obtain that for D is 656.10 nm ($\mu_D > \mu_H$, thus $\tilde{\nu}_D > \tilde{\nu}_H$ and $\lambda_D < \lambda_H$).

3. Failures of Bohr model: How do the transitions take place? Fails for other simple atoms even like He.