Chap 4

# Structure of the atom

- Thomson model
- Rutherford scattering experiment
- Atomic spectra
- Bohr model of the hydrogen atom
- Characteristic X-ray spectra
- Atomic excitation

1900, evidences that the atom was not a fundamental unit:

- 1) There are many kinds of atoms, each belonging to a distinct chemical element.
- Certain elements combine with some elements but not with others.
   This indicates an internal atomic structure.
- 3) The emission of cathode rays from atoms indicates that there are electrons inside the atom. Furthermore, Lorentz's theoretical explanation of the Zeeman effect (chap 8) using classical mechanics enables us to determine the q/m ratio of the negative changes inside (1896). (Tomonaga, p.78 QM)
- 4) The discoveries of radioactivity etc.

Q: An atom has both positive and negative (electron) charges. What is its distribution of charges?

## Models of atom before Rutherford

- Lorentz's oscillator model (1878): electrons bound to atoms by elastic force
- Thomson's model (1904): positive charges spread uniformly throughout a sphere (liquid-like) with the newly discovered "negative" electrons embedded (could be thousands of them in Thomson's mind).



- In Thomson's view, the electrons arranged themselves in concentric shells. When the atom was heated, electrons could vibrate about their equilibrium positions, thus producing EM radiation.
- Nagaoka's planetary model (1904) 長岡半太郎

J.J.湯木生:原子世界的啟蒙者 QuBear 你的h從哪裡冒出來的?量子突破! QuBear Alpha particles scattered from a Thomson atom (for a derivation, see <u>wiki</u>)

• Deflection due to 79 electrons in a gold atom

 $\overline{\theta_1} \simeq 0.004 \text{ degrees}$ 

• Deflection due to the sphere with positive charges

 $\overline{\theta_2} \simeq 0.007$  degrees

$$ar{ heta} = \sqrt{ar{ heta}_1^2 + ar{ heta}_2^2} pprox 0.008 ext{ degrees}$$

If the alpha particle suffers from *N* scatterings in a gold film, then the total angle of deflection

$$\Theta\simeq \sqrt{N}\theta$$

Assuming 10,000 collisions, the average deflection would be 0.8°.

# Before Rutherford's experiment

- 1896, Becquerel tried to observe the X-rays out of the uranium compound exposed to the sun. He thought that the positive result is form X-ray. But later found out that the sunlight plays no role. This leads to the discovery of radioactivity.
- 1898, Rutherford realized that there are 2 kinds of radiation from the uranium. He called them alpha and beta. In a few years people realized that beta ray is cathode ray (electrons).
- 1900, Villard found the third, gamma ray (~X-ray).
- 1904, Rutherford becomes convinced that alpha particles are helium ions He<sup>2+</sup> by measuring the q/m ratio (not an easy measurement).
   He later collected enough alpha particles to observe its spectrum (1907).

Note: Rutherford got a Nobel prize on chemistry at 1908 for these studies.

Segre, From X-rays to quarks.

# Use $\alpha$ -particle scattering to probe atom structure



- A α-particle is 7000 times heavier than an electron. So the deflection would mainly be due to positive charges in the atom.
- The deflection could give some clue to the distribution of the positive charges inside.

Experimental result (by Geiger and Marsden) :

- Most of the  $\alpha$ -particles passed through the foil with few collisions
- Around 0.14% of the incident  $\alpha$ -particles scattered by more than 1°
- Around 1 in 10000  $\alpha$ -particles deflected by more than 90°

"I may tell you in confidence that I did not believe that they would be, since we knew the alpha-particle was a very fast, massive particle with a great deal of energy .... Then I remember two or three days later Geiger coming to me in great excitement and saying 'We have been able to get some of the alphaparticles coming backward' ... It was quite the most incredible event that ever happened to me in my life." -- Rutherford



This implies that the mass of positive charge > the mass of  $\alpha$ -particle.

Estimate the 3 ize of the positive core (Weinberg, p.75)

For simplicity, consider head-on collision. The  $\alpha$ -particle momentarily stops when

$$\frac{1}{4\pi\varepsilon_0}\frac{Z_1Z_2e^2}{r_0} = \frac{m_\alpha v_\alpha^2}{2} (=K)$$

$$r_0 = \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0} \frac{1}{K} \simeq 1.44 \frac{Z_1 Z_2}{K(\text{in MeV})} \text{ fm}$$

5.5 MeV  $\alpha\text{-particle}$  decayed from radon 222 to polonium 218  $v_{\alpha}\simeq 1.6\times 10^7 \text{ m/sec}$ 

 $r_0 \simeq 0.5 \times Z_2$  fm

Much smaller than the size of an atom



Rutherford proposed that an atom has a heavy, positively charged core (nucleus) surrounded by negative electrons.

- An atom is mostly empty space. We now know that if the nucleus has the size of an apple, then the atom has a radius of roughly 1 km.
- How positive charges could stick together without exploding apart was of course a puzzle at that time.



Rutherford's assumption (to simplify the analysis):

- 1. The scatterer is so massive that it does not recoil significantly.
- 2. The target is so thin that only a single scattering occurs.
- 3. The bombarding particle and target scatterer are so small that they may be treated as point masses.
- 4. Only the Coulomb force is effective.



## Rutherford scattering formula

The number of particles scattered into the ring at scattering angle  $\theta$ , divided by the solid angle d $\Omega$  of the ring :

$$M(\theta) = N_i nt \frac{r_0^2}{16 \sin^4 \frac{\theta}{2}} \qquad r_0 = \frac{1}{4\pi\varepsilon_0} \frac{Z_1 Z_2 e^2}{K}$$

 $N_{\rm i}$ : total number of incident particles

*nt*: number of target atoms per unit area (number density × thickness)

Note: the  $N(\theta)$  in textbook =  $M(\theta)/r^2$ 

- The scattering is inversely proportional to the square of electron kinetic energy K (confirmed)
- The scattering is inversely proportional to the fourth power of  $sin(\theta/2)$  (see fig).
- The scattering is proportional to the square of the atomic numbers (Z<sub>1</sub>,Z<sub>2</sub>). This helps determining Z<sub>2</sub> (~ A/2).



# optional

Impact parameter *b* and scattering angle  $\theta$  (Tomonaga, p.85)



Conservation of angular momentum

$$mv_0b = mv_m \overline{OA} \longrightarrow \frac{v_m}{v_0} = \frac{b}{\overline{OA}}$$

Conservation of energy

$$\frac{1}{2}mv_0^2 = \frac{1}{2}mv_m^2 + \frac{1}{4\pi\varepsilon_0}\frac{2Ze^2}{\overline{OA}} \longrightarrow 1 = \left(\frac{v_m}{v_0}\right)^2 + \frac{r_0}{\overline{OA}} \longrightarrow \frac{1}{2}mv_0^2 = \frac{1}{4\pi\varepsilon_0}\frac{Z_1Z_2e^2}{r_0}$$

 $\implies b^2 = \overline{OA}(\overline{OA} - r_0) \quad (1)$ 

# optional



$$\overline{A} = \overline{OB} + \overline{AB}$$
$$= O\overline{B}(1 + \cos\psi)$$
$$= b\cot\frac{\psi}{2} \qquad (2)$$

Combine (1) with (2)

or 
$$\tan\frac{\theta}{2} = \frac{r_0}{2b}$$

• Scattering cross section for particles scattered by an angle  $\theta$  or more

$$\sigma(\theta) = \pi b^2$$
$$= \pi \left(\frac{r_0}{2}\right)^2 \cot^2 \frac{\theta}{2} \qquad r_0 = \frac{1}{4\pi\varepsilon_0} \frac{Z_1 Z_2 e^2}{mv_0^2/2}$$

Differential cross section

Particles pass through the ring within radii [*b*, *b*+d*b*] would scatter between  $[\theta, \theta + d\theta]$ 



 $r d\theta$ 

 $r\sin\theta$ 

The discussion so far is for 1 on 1 (1 incident particle, 1 target)

Suppose there are *Ni* incident particles in a beam with cross section *A* 



• The fraction f of incident particles scattered by an angle of  $\theta$  or greater

$$f = \frac{\sigma}{A} = \frac{\pi b^2}{A} = \frac{\pi}{A} \left(\frac{r_0}{2}\right)^2 \cot^2 \frac{\theta}{2}$$

• The fraction *df* of incident particles scattered between  $[\theta, \theta + d\theta]$ :

$$df = \frac{N_i / A (2\pi b db)}{N_i} = \frac{\mathrm{d}\sigma}{A}$$

#### Ni on many



• Particle density in foil

$$n = \frac{\rho\left(\frac{g}{cm^{3}}\right) N_{A}\left(\frac{molecules}{mol}\right)}{M_{g}\left(\frac{g}{mol}\right)}$$
Gram-atomic wright

• The number of target atoms per unit area

$$nt = rac{
ho N_{
m A} t}{M_g} rac{
m atoms}{
m cm^2}$$

Number of target atoms in area A:  $N_t = ntA$ 

• The fraction of incident particles scattered by an angle of  $\theta$  or greater

$$f = \frac{N_t \pi b^2}{A} = nt\pi b^2 = nt\pi \left(\frac{r_0}{2}\right)^2 \cot^2 \frac{\theta}{2}$$

Finally, • The number of  $\alpha$ -particles scattered into the ring at angle  $\theta$ , divided by d $\Omega$  of the ring :

$$M(\theta) = \frac{N_i |df|}{d\Omega} = N_i nt \left(\frac{r_0}{4}\right)^2 \frac{1}{\sin^4 \frac{\theta}{2}}$$

Note: This analysis is based on classical mechanics. We are lucky that it coincides with the result from quantum mechanics. **.2:** Find the fraction of 7.7-MeV  $\alpha$  particles that is deflected at an angle of 90° or more from a gold foil of  $10^{-6}$  m thickness.

**Solution** The density of gold is  $19.3 \text{ g/cm}^3$ , and the atomic weight is 197 u. Equation (4.8) determines *n*.

$$n = \frac{\rho\left(\frac{g}{cm^{3}}\right) N_{A}\left(\frac{molecules}{mol}\right)}{M_{g}\left(\frac{g}{mol}\right)}$$

$$= 5.90 \times 10^{22} \frac{atoms}{cm^{3}} = 5.90 \times 10^{28} \frac{atoms}{m^{3}} \qquad f = \pi nt \left(\frac{Z_{1}Z_{2}e^{2}}{8\pi\epsilon_{0}K}\right)^{2} \cot^{2}\frac{\theta}{2}$$
We insert this value of *n* into Equation (4.12) and find
$$f = \pi \left(5.90 \times 10^{28} \frac{atoms}{m^{3}}\right) (10^{-6} \text{ m})$$

$$\times \left[\frac{(79)(2)(1.6 \times 10^{-19} \text{ C})^{2}(9 \times 10^{9} \text{ N} \cdot \text{m}^{2}/\text{C}^{2})}{2(7.7 \text{ MeV})(1.60 \times 10^{-13} \text{ J}/\text{MeV})}\right]^{2}$$

$$\times (\cot 45^{\circ})^{2}$$

$$= 4 \times 10^{-5}$$

$$r_{0} = \frac{Z_{1}Z_{2}e^{2}}{4\pi\epsilon_{0}K} \simeq 1.44 \frac{Z_{1}Z_{2}}{K(\text{in MeV})} \text{ fm}$$

One  $\alpha$  particle in 25,000 is deflected by 90° or greater.

## Ex 4.2:

## optional

Stability of the planetary model:

This is a serious problem known by Rutherford and others

 According to classical electrodynamics, the radiating power from an accelerating electron is

$$P=rac{2}{3}rac{q^2}{4\piarepsilon_0 c}igg(rac{\dot{v}}{c}igg)^2$$

• Power loss in one revolution

$$P \simeq \frac{q^2}{4\pi\varepsilon_0 a_0} \frac{a_0}{c} \left(\frac{v^2}{ca_0}\right)^2$$

Assume  

$$v \simeq 0.01c$$
  $\simeq 13.6 \ eV \times \left(\frac{v}{c}\right)^3 \frac{v}{a_0}$   
 $\simeq 13.6 \times (10^{-2})^3 \times \frac{3 \cdot 10^6}{0.5 \cdot 10^{-10}}$   
 $\simeq 10^{12} \ eV/s$ 

Larmor formula (1897)



The atom would collapse in about 10<sup>-11</sup> sec

• 1911, young Bohr went from Denmark to learn from Thomson/Rutherford at England, so he is well aware of the new atom model.

"My starting point was not at all the idea that an atom is a small-scale planetary system and as such governed by the laws of astronomy ... My starting point was rather the stability of matter, a pure miracle when considered from the standpoint of classical physics." — Bohr (Quote from Physics and beyond, by Heisenberg)

- There is also the size problem: In Rutherford model, it's hard to explain why atoms of same material have the same size.
- Furthermore, among a few others, Bohr also attempted to put *h* in atoms.

1913, Bohr: "As soon as I saw Balmer's formula the whole thing was immediately clear to me."

#### Spectra of hydrogen atom



• Among different substances, the spectrum of hydrogen atom has the simplest pattern. Balmer (1885) noticed that 4 lines  $(H_{\alpha}, H_{\beta}, H_{\gamma}, H_{\delta})$  in the visible part have wavelengths (656.23, 486.1, 434.0, 410.2) µm.

$$\frac{9}{5}a, \quad \frac{15}{12}a, \quad \frac{25}{21}a, \quad \frac{36}{32}a, \quad a = 3645.6 \text{ A}$$

$$\Rightarrow \quad \lambda = \frac{n^2}{n^2 - 2^2}a, \quad n = 3,4,5,6$$

Balmer predicted a new line for *n*=7

<u>物理學史上最神秘的數學公式</u> QuBear



Bohr's model of the hydrogen atom (1913)

#### **Assumptions:**

- A. "Stationary states" or orbits must exist in atoms, i.e., orbiting electrons do not radiate energy in these orbits. These orbits or stationary states are of a fixed definite energy *E* (i.e., energy levels).
- B. The emission or absorption of electromagnetic radiation can occur only in conjunction with a transition between two stationary states. The frequency, *f*, of this radiation is proportional to the *difference* in energy of the two stationary states:

 $E = E_1 - E_2 = hf$ , where *h* is Planck's constant

C. Classical laws of physics do not apply to transitions between stationary states. (In fact, quantum mechanics cannot really explain it either)

"A Research Programme Progressing on Inconsistent Foundations." -- Lakatos

Energy levels and spectrum



How do we determine the energy  $E_n$  of the stationary states

• First, Bohr noticed that [h]=[E][T]=[L]

Earlier, Nicholson (1912) "*if, therefore, the constant h of Planck has, as Sommerfeld has suggested, an atomic significance, it may mean that the angular momentum of an atom can only rise or fall by discrete amounts when electrons leave or return.*" This paper is cited by Bohr (wiki)

Suppose  $L = mvr = n\hbar$  *n* is an integer

$$\hbar = \frac{h}{2\pi}$$
, but suppose we still don't know this here

How do we determine the energy  $E_n$  of the stationary states

$$L = mvr = n\hbar$$

$$\frac{mv^{2}}{r} = \frac{e^{2}}{4\pi\epsilon_{0}r^{2}}$$

$$r_{n} = \frac{4\pi\epsilon_{0}n^{2}\hbar^{2}}{me^{2}} \equiv n^{2}a_{0}$$
Radii of orbits
$$a_{0} = \frac{4\pi\epsilon_{0}\hbar^{2}}{me^{2}} \equiv 0.53 \times 10^{-10} \text{ m}$$

$$r_{n} = -\frac{e^{2}}{8\pi\epsilon_{0}r_{n}} = -\frac{e^{2}}{8\pi\epsilon_{0}a_{0}n^{2}} \equiv -\frac{E_{0}}{n^{2}}$$

The energy of the lowest stable state (ground state)

$$E_0 = \frac{e^2}{8\pi\epsilon_0 a_0} = 13.6 \text{ eV}$$



One way to pin down  $\hbar$ :

The correspondence principle (Bohr 1913)

It is a useful guidance *before* the discovery of quantum mechanics

The numerical results of quantum theory should coincide with those of the classical theory when n>>1.

• frequency of the radiation emitted  $f_{\text{classical}}$ 

= orbital frequency  $f_{orb}$  of the electron around the nucleus.

$$mvr = n\hbar \qquad f_{\text{classical}} = \frac{\omega}{2\pi} = \frac{1}{2\pi} \left(\frac{e^2}{4\pi\varepsilon_0 mr^3}\right)^{1/2} = \frac{1}{2\pi} \frac{me^4}{(4\pi\varepsilon_0)^2} \frac{1}{n^3\hbar^3}$$

• For 
$$n >> 1$$
,  
 $f_{\text{Bohr}} = \frac{E_0}{h} \left[ \frac{1}{n^2} - \frac{1}{(n+1)^2} \right] = \frac{E_0}{h} \left[ \frac{2n+1}{n^2(n+1)^2} \right] \approx \frac{2nE_0}{h}$ 
 $f_{\text{Bohr}} = f_{\text{classical}}$ 

 $\implies \qquad \hbar = \frac{h}{2\pi}$ 

Wiki: This symbol is first introduced in Dirac's book (1930)

The 4<sup>th</sup> coming of *h* (the 3<sup>rd</sup> is Einstein's model of specific heat, 1907)



# optional

The electron's velocity in the Bohr model:

$$\nu_n = \frac{n\hbar}{mr_n} = \frac{1}{n} \frac{e^2}{4\pi\varepsilon_0 \hbar}$$

• On the ground state,

 $v_1 = 2.2 \times 10^6$  m/s ~ 1% of the speed of light

• The ratio of  $v_1$  to *c* is the fine structure constant.

$$\frac{v_1}{c} = \alpha \qquad \qquad \alpha \equiv \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137}$$

• This important constant appears elsewhere. For example, in the ratios between various length scales

• classical electron radius 
$$r_{\rm e} = \frac{1}{4\pi\varepsilon_0} \frac{e^2}{m_{\rm e}c^2} \sim 2.8 \, {\rm fm}$$
  
• Compton wavelength  $\lambda = \frac{\hbar}{m_e c} \sim 0.38 \, {\rm pm}$   $\lambda = \frac{h}{m_e c}$   
• Bohr radius  $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{e^2m_{\rm e}} \sim 0.053 \, {\rm nm}$   
 $\Rightarrow r_{\rm e} = \alpha \lambda_{\rm e} = \alpha^2 a_0$ 

## From the Bohr model, we have

- Obtained the radii (size of atom), velocities, and energies of electron states
- Explained the Rydberg series, and got the Rydberg const.
- ...

#### On the other hand,

- **1.** It could be successfully applied <u>only to single-electron atoms</u> (H, He<sup>+</sup>, Li<sup>++</sup>, and so on).
- 2. It was not able to account for the intensities or the <u>fine structure of the</u> <u>spectral lines</u>.
- 3. Bohr's model could not explain the binding of atoms into molecules.

#### Also, we still don't know

- 1. Why there are stationary states?
- 2. Why there are quantum jumps?



This explanation offered an important support of Bohr's theory.

- Thomson model
- Rutherford scattering experiment
- Atomic spectra
- Bohr model of the hydrogen atom
- Characteristic X-ray spectra
- Atomic excitation

# ~ anode Characteristic X-rays from the anti-cathode materials



**Braking radiation** 



Properties of the characteristic X-rays (Ref: Chap 14 of Tomonaga QM I)

#### Moseley experiment

(1913, when he was a graduate student)

- 1. For elements lighter than Na, there is no sharp line.
- 2. For heavier elements, the pattern of sharp lines are similar, but wavelengths get shorter with increasing
  - Z. (Note that it's monotonic, not periodic).
- 3. The characteristics remain the same, unrelate to what compound the element is in.
- 4. The sharp lines appear only in the emission spectra, not in absorption spectra.



"A striking feature of x-ray line spectra is that the frequencies and wavelengths of the lines vary smoothly from element to element. There are none of the abrupt changes from one element to the next which occur in atomic spectra in the optical frequency range."

Eisberg and Resnick

- To understand these properties, Kossel considered the following scenario: The cathode ray knocks out an electron from the inner core of the atom in anti-cathode. Then an electron from outer orbit jumps down to fill the vacancy and emits X-ray.
- Under the approximation of spherical symmetry, the electric field felt by the innermost electrons in any atom arises entirely from the nucleus, not from electrons outside. Hence the energy of the EM wave emitted when an electron falls from a higher state to the n = 1 state of any atom is given by Bohr's formula :  $E_1 = -13.6 Z^2 eV$ For Z > 10 this is an X-ray energy. ( $Z_{Na}=11$ ) (Weinberg, p.83)

莫色勒對物理學和化學做出的最重大的貢獻就是打破先前物理學理論的成見,發現了原子序這一概念。(wiki)

• Atomic number Z = Number of protons in a nucleus

"Moseley could solve the problem that had baffled chemists for many decades and establish the true atomic number of possible rare earths. When the famous French chemist Urbain brought him rare earth samples on which he had labored for years, Moseley could analyze them in a few hours and reveal their content to the amazed chemist." (Segre, From X-rays to quarks)

• Mosley (1887-1915) dies at the age of 27

"In view of what he [Moseley] might still have accomplished ... his death might well have been the most costly single death of the War to mankind generally." Asimov's Biographical Encyclopedia of Science and Technology Determination of the nucleus charge (= number of electrons = atomic number)

 With Bohr's formula, Moseley found a relationship between the frequencies of the characteristic X-ray and Z: This holds for the K<sub>α</sub> X-ray



# Ex 4.10:

Moseley found experimentally that the equation describing the frequency of the  $L_{\alpha}$  spectral line was

$$f_{\rm L_{\alpha}} = \frac{5}{36} cR(Z - 7.4)^2 \tag{4.44}$$

How can the Bohr model explain this result? What is the general form for the L-series wavelengths  $\lambda_L$ ?

**Solution** We replace Z by  $Z_{\text{eff}}$  in Equation (4.38) and find

$$f_{\mathrm{L}_{\alpha}} = \frac{c}{\lambda_{\mathrm{L}_{\alpha}}} = cRZ_{\mathrm{eff}}^{2} \left(\frac{1}{2^{2}} - \frac{1}{3^{2}}\right)$$
(4.45)  
$$f_{\mathrm{L}_{\alpha}} = \frac{5cRZ_{\mathrm{eff}}^{2}}{36}$$

According to Moseley's data the effective charge  $Z_{eff}$  must be Z - 7.4. This result is within the spirit of the Bohr model, which applied primarily to hydrogen-like atoms.

We rewrite Equation (4.45) to determine  $\lambda_L$  for the entire series:

$$\frac{1}{\lambda_{\rm L}} = R Z_{\rm eff}^2 \left( \frac{1}{2^2} - \frac{1}{n^2} \right) = R (Z - 7.4)^2 \left( \frac{1}{4} - \frac{1}{n^2} \right) \quad (4.46)$$

Next, experimental verification of

- Energy level: Frank-Hertz experiment
- Quantization of angular momentum: Stern-Gerlach experiment (ch 7)

Frank-Hertz experiment (1914), bombarding atoms with electrons



Note: They were unaware of Bohr's model when they did this experiment. This experiment confirmed quantum energy levels Frank-Hertz experiment



- Hg has an excitation energy of 4.88 eV in the first excited state.
- No energy can be transferred to Hg below 4.88 eV because not enough energy to excite an electron to the next energy level .
- Above 4.88 eV, the current drops because scattered electrons no longer reach the collector until the accelerating voltage reaches 9.8 eV and so on.

**Ex 4.11:** Would it be experimentally possible to observe radiation emitted from the first excited state of Hg after it was produced by an electron collision?

**Solution** If the collision of the bombarding electron with the mercury atom is elastic, mercury will be left in its ground state. If the collision is inelastic, however, the mercury atom will end up in its excited state at 4.9 eV (see Figure 4.22). The mercury atom will not exist long in its first excited state and should decay quickly ( $\sim 10^{-8}$  s) back to the ground state. Franck and Hertz considered this possibility and looked for x rays. They observed no radiation emitted when the electron's kinetic energy was below about 5 V, but as soon as the current dropped as the voltage went past 5 V, indicating excitation of Hg, an emission line of wavelength 254 nm (ultraviolet) was observed. Franck and Hertz set E = 4.88 eV $= hf = (hc)/\lambda$  and showed that the value of h determined from  $\lambda = 254$  nm was in good agreement with values of Planck's constant determined by other means.