#### Chpt3. Quantum states of atoms: Bohr model

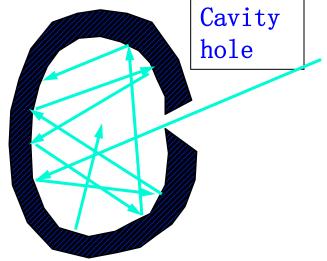
- 3-1 Background
- 3-2 Bohr Model
- 3-3 Experimental evidence I: Spectra
- 3-4 Experimental evidence II:Frank-Herz Exp
- 3-5 Extension of Bohr model
- 3-6 Summary

#### 3-1 Background

- Evidence of The quantum hypothsis I: Black body radiation (Max Plank 1900)
  Evidence of The quantum hypothsis II Photoelectric effect (Einstein 1905)
- Spectrum of light (Niels Bohr, 1913)

#### 3.1.1 Evidence I: Black body radiation

- What is blackbody:
  - A body absorbs all light incident upon it without reflecting any light back.
  - The hole in the cavity , Sun, High T furnance
  - Not necessarily be black, no reflecting but radiation
- Thermal radiation
  - Any objects with nonzero T, radiates out EM wave
- Equilibrium thermal radiation
  - Radiation E = Absoption Energy



#### • Radiant intensity $R(\lambda,T)$

- -The energy emitted per unit time unit area at T around wave length  $\lambda$  per unit WL
- Total radiant intensity  $R(T) = \int_0^\infty R(\lambda, T) d\lambda$
- $R(\lambda,T)$  versus  $R(\nu,T)$

$$R(T) = \int_0^\infty R(\lambda, T) d\lambda = \int_0^\infty R(\nu, T) d\nu \to R(\lambda, T) d\lambda = R(\nu, T) d\nu$$

$$R(\lambda,T) = R(\nu,T) \frac{d\nu}{d\lambda} \rightarrow R(\lambda,T) = \frac{c}{\lambda^2} R(\nu,T)$$

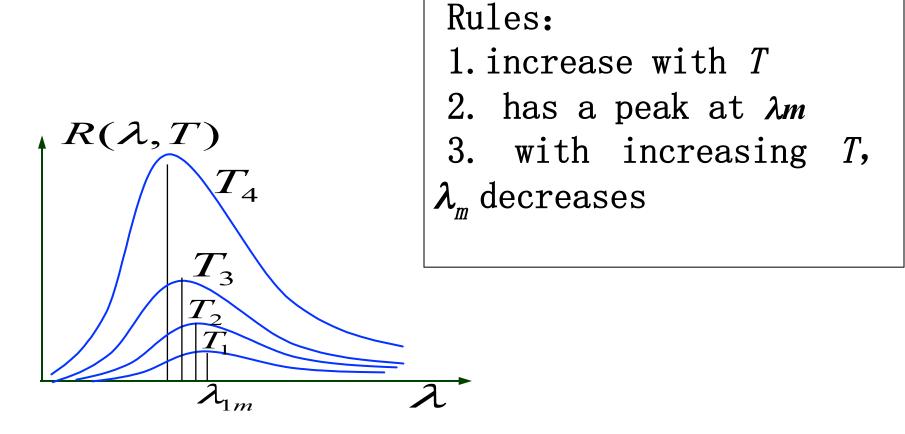
Energy density of radiation field E(v,T)
 The energy density around v per unit frequency

$$R(\nu,T) = \frac{c}{4}E(\nu,T)$$

Kirchhoff theorem

- In Eql., E(v,T) v curve only depens on T, independent of the cavity's structure

#### Radiant intensity curves



# Theorems of BBR

-Wien theorem

$$\lambda_m T = b$$

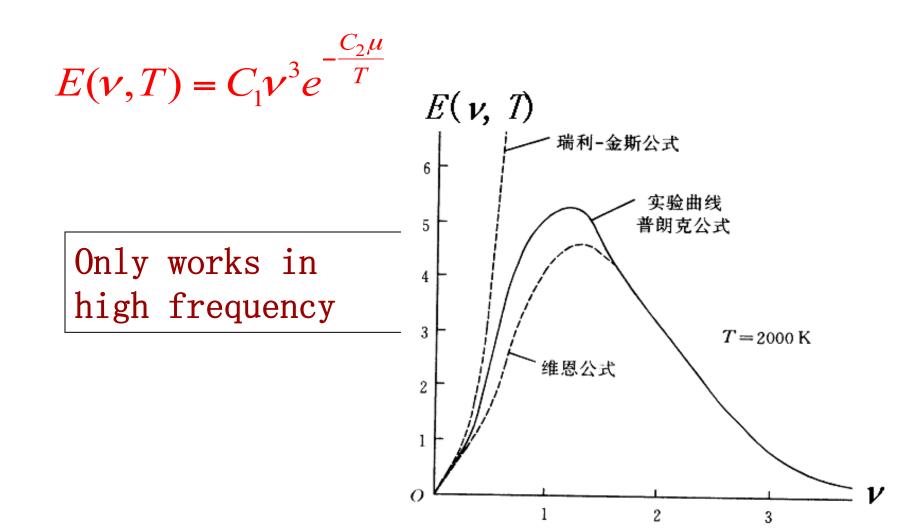
- Stefan-Bolzmann theorem-

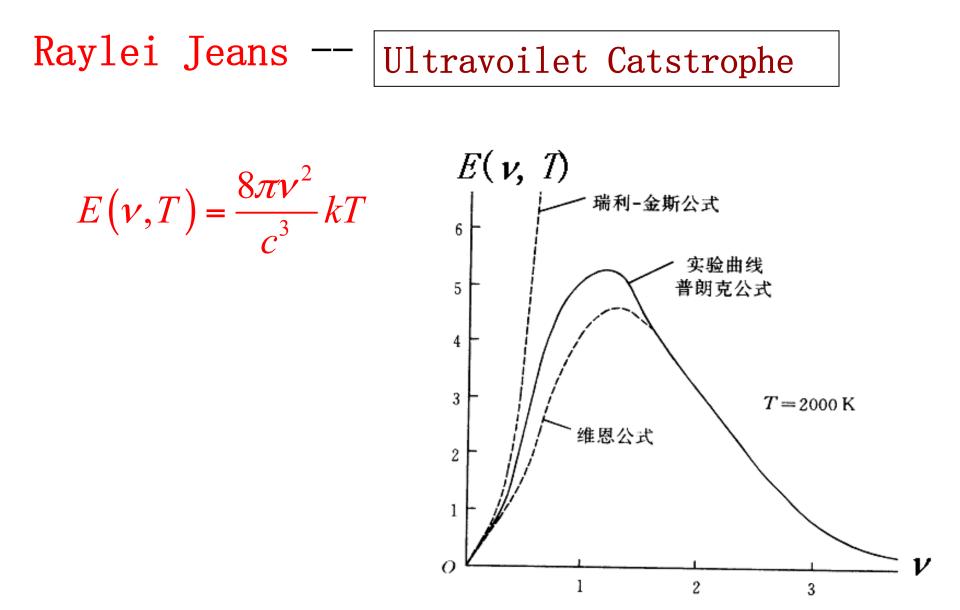
$$R(T) = \sigma T^4$$

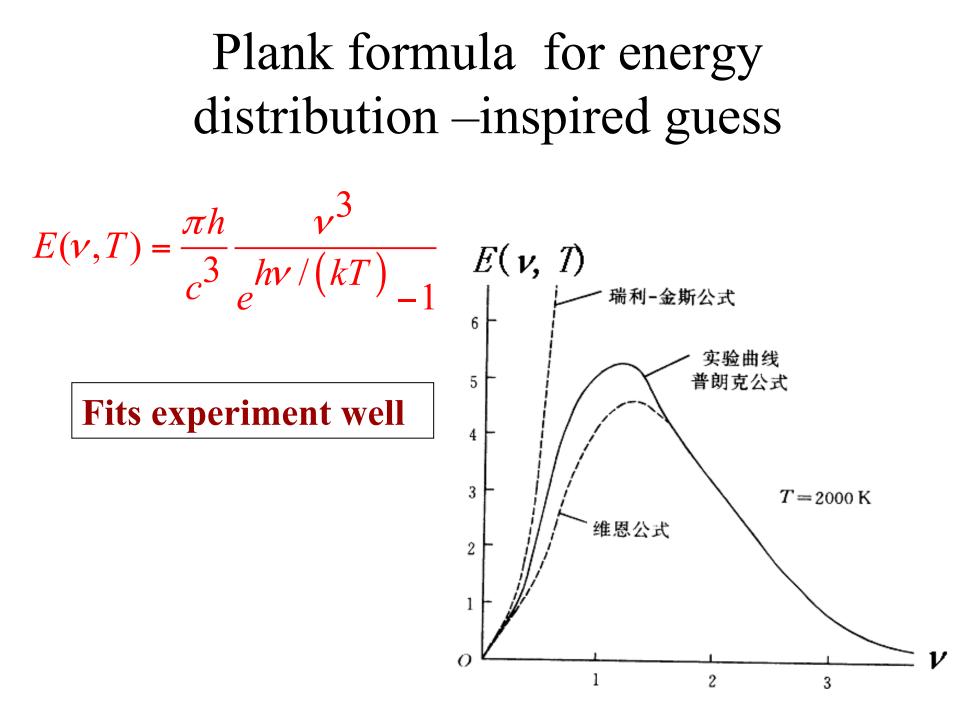
 $\sigma = 5.67051 \times 10^{-8}$  W/m<sup>2</sup>·K<sup>4</sup> (Stefan constant)

# Classic physics runs into trouble

• Wien formula







#### Plank's quantum hypothesis

- The energy exchange of the EM radiation can only be in the form of quanta: E=n hv. N=1,2,3...hvis the energy quanta, h is the Plank's constant  $h = 6.6260755 \times 10^{-34} \text{ J} \cdot \text{s}$
- Integrate the PLK formula , 0 → ∞ one obtains
   Stefan-Boltzmann theorem
  - -Maximizing it gives Wien theorm

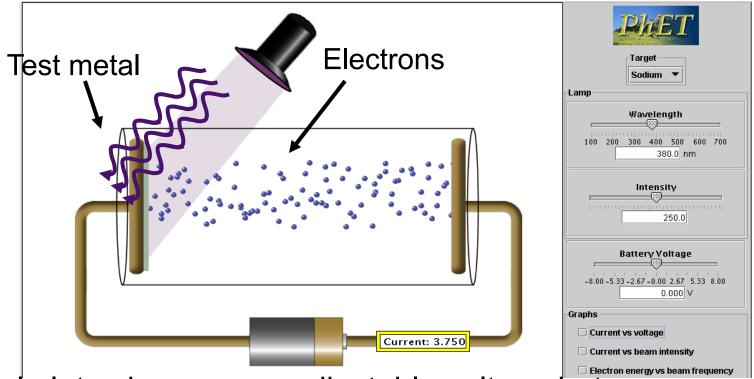
# Photoelectric Effect

(How Einstein really became famous!)

## 3.1.2 The Photoelectric Effect

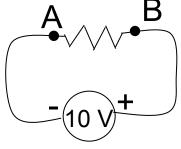
Photoelectric effect: experiment showing light is <u>also</u> a particle. Energy comes in particle-like chunks- basics of quantum physics. (energy of one chunk depends on frequency, wave-like beam of light has <u>MANY</u> chunks, energy of beam is sum)

#### Photoelectric effect experiment apparatus.



Two metal plates in vacuum, adjustable voltage between them, shine light on one plate. Measure current between plates.

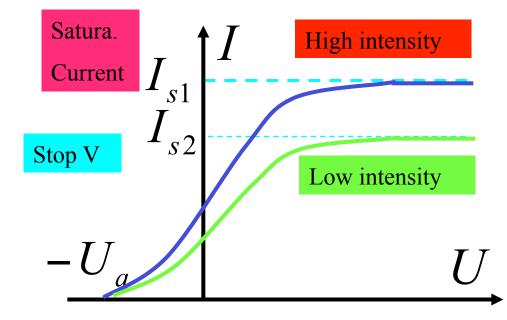
I. Understanding the apparatus and experiment.



Potential difference between A and B = +10 V Measure of energy an electron gains going from A to B. 14

#### Experimental results 1

#### PE current I is proportional to the light intensity emitted electron numbers proportinal to intensity



# Experimental results 2

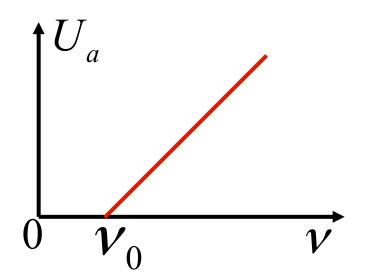
• With anti stopping voltage  $U_a$ , current vanishes The maximum kinetic energy

$$\frac{1}{2}mv_m^2 = eU_a$$

- Stoping V is linear in the freqency of incident light

$$\frac{1}{2}mv_m^2 = e(Kv - U_0)$$

Em is linear in \nu, Indep. of light intensity



#### Experimental result 3

$$\frac{1}{2}mv_m^2 = e(Kv - U_0), \quad \frac{1}{2}mv_m^2 > 0$$

$$\Rightarrow v \ge \frac{U_0}{K} \quad \text{Threshold frequency} \quad v_0 = \frac{U_0}{K}$$

 Current begins instantaneously(<1ns), regardless the light intensity

### Classical explaination of PEE

- Classical light wave theory tells
  - The electron kinetic energy depends on the intensity (amplitude) in contract with experiment result: dependent on frequency

 For strong enough light intensity, there should be PEE for any frequency:

this is a threshold frenquency 存在截止频率(红限)

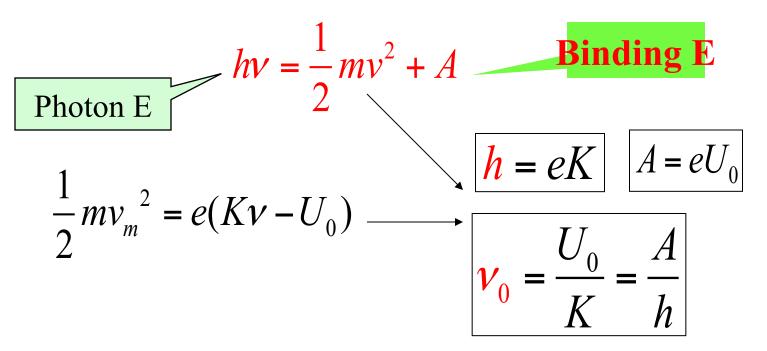
The energy gained continuously by e reached a certain value, it would be ejected from the metal Experiment: Current begins instantaneously(<1ns), regardless the light intensity</li>

- Einstein's light quantum theory
  - Photon

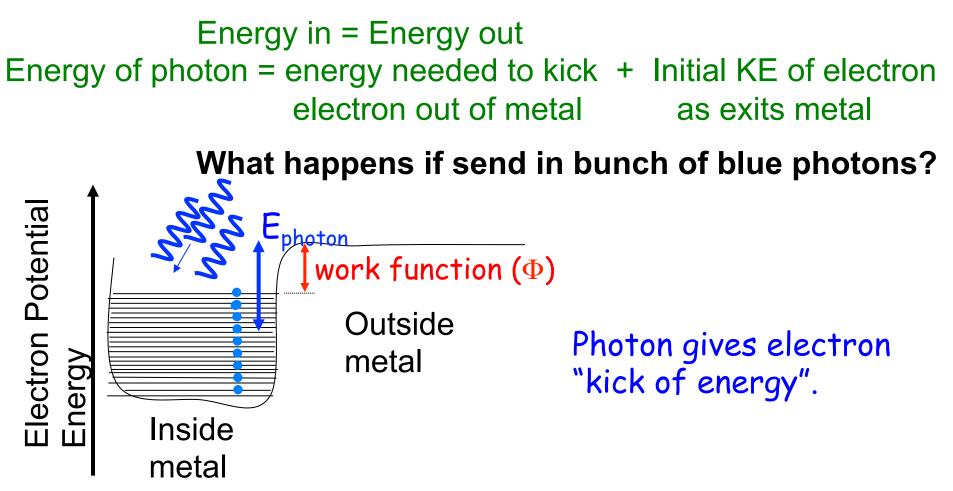
Light propogates as particle flow, Photon with frequency v has energy hv

#### Quantum explaination of PEE

- Einstein's photon theory
  - **PEE Equation** 
    - An electron absorbs a photon,



Apply Conservation of Energy.



#### **Electrons have equal chance of absorbing photon:**

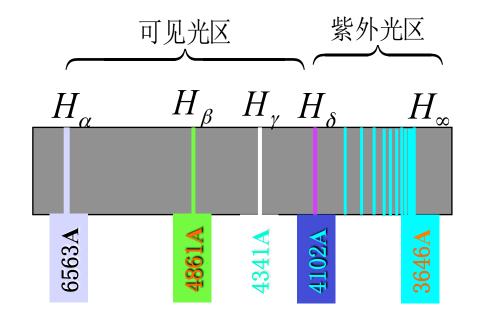
- $\rightarrow$  Max KE of electrons = photon energy  $\Phi$
- $\rightarrow$  Min KE = 0
- $\rightarrow$  Some electrons, not enough energy to pop-out, energy into heat

# Summary of PEE by QT

- High intensity→ more photons→ more electrons emitted→large current i
- Em is linear in  $\nu$ , Indep. of light intensity
- Only when  $v \ge A/h$ , PEE happens (threshold)
- Light's energy discontinuous absorbed at once

#### 3.1.3 SPECTRUM OF LIGHT

- The intensity distribution of EM radiation of atoms as wave length  $I(\lambda)$ - Measured by spectrometer  $\frac{1}{\sqrt{2}}$ 
  - -Different source has its  $\mathsf{own}^\lambda\operatorname{spectrum}$  . hydrogen atom



#### Rydberg formula

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n^2} - \frac{1}{n'^2}\right) = T(n) - T(n') \qquad n = 1, 2, L ;$$

$$R_{H} = 1.096776 \times 10^{7} \text{m}^{-1} \text{ Rydberg constant}$$
$$T(n') = \frac{R}{n'^{2}}, \quad T(n) = \frac{R}{n^{2}} \quad \text{Term values}$$

N gives the series; for a fix n, each n' gives a spectrum line

Wave number = the differnce of term values-

$$N = R_H (\frac{1}{n^2} - \frac{1}{n'^2})$$

● n=1, n'=2,3,... 赖曼系,紫外区
❷ n=2, n'=3,4,... 巴尔末系,可见光区

③ n=3, n'=4,5,... 帕邢系, 红外区
④ n=4, n'=5,6,... 布喇开系, 红外区
⑤ n=5, n'=6,7,... 普丰特系, 红外区
⑥ n=6, n'=7,8,... 哈菲莱系, 红外区

#### 3.2 Bohr model

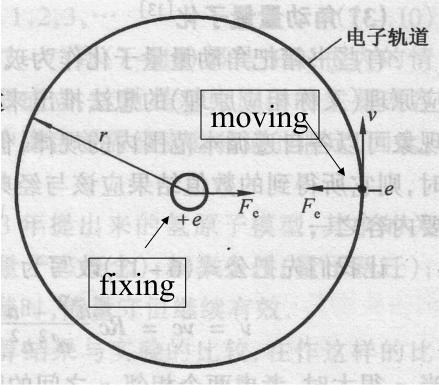
- Classic orbits with stationary state
- Frequency condition
- Angular momentum quantization
- Numerical computation method

# 3.2.1 Classic orbit with Stationary state Stationary state condition

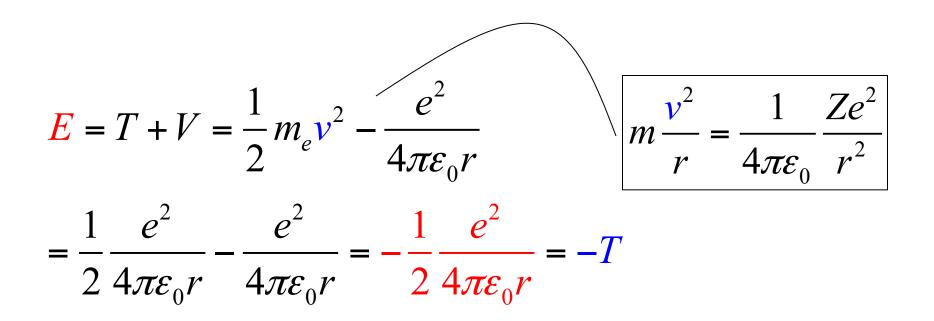
- Atoms can only in series stationary states with discrete energy ; electrons in certain discrete orbits, circling around without EMW radiation.

$$F = m_e \frac{v^2}{r}$$

$$m_e \frac{v^2}{r} = \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r^2}$$



## Stationary state condition

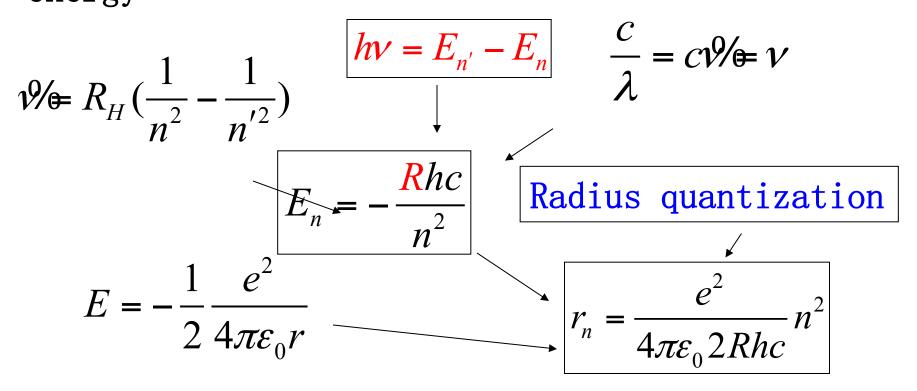


- Circling moving frequency

$$f = \frac{v}{2\pi r} = \frac{1}{2\pi r} \sqrt{\frac{e^2}{4\pi \varepsilon_0 m_e r}} = \frac{e}{2\pi} \sqrt{\frac{1}{4\pi \varepsilon_0 m_e r^3}}$$

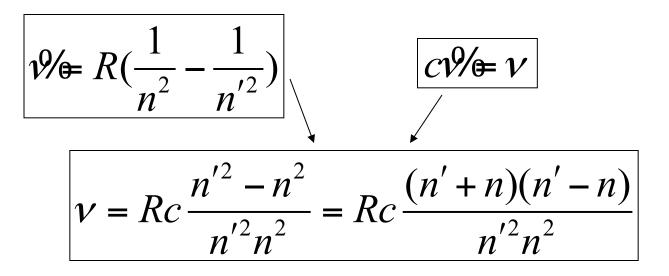
#### 3.2.2 Frequency condition

• The energy emitted when an electron jumps from a state  $E_{\rm n}$ , orbit to another orbit  $E_{\rm n}$ , with radiation or absorbtion of a photon energy

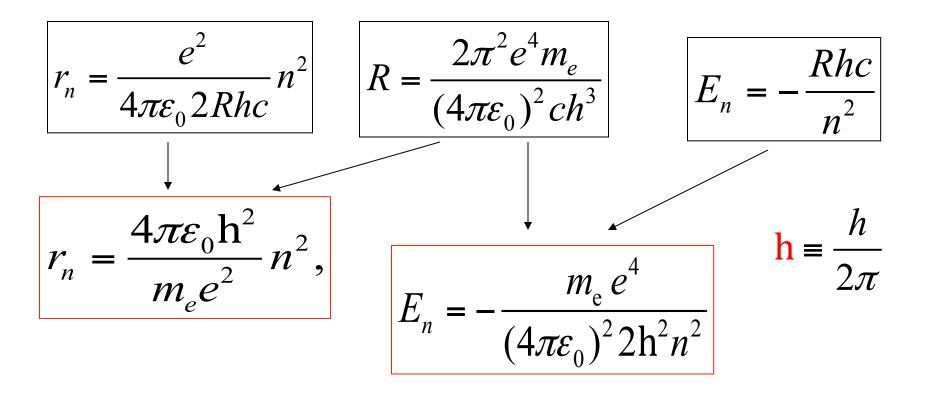


#### 3.2.3 Angular momentum quantization

- Correspondence principle
  - Phenomena in atomic field and in the macroscopic domain follow their own rules, but when extending the microscopic field to the classical field, numerical result should agree with that from classical rules
- $\rightarrow$  Angular momentum quantization condition



#### 3.2.3 AMQ



$$L = m_{e}vr = m_{e}\sqrt{\frac{e^{2}}{4\pi\varepsilon_{0}m_{e}r}} \cdot r = \sqrt{\frac{m_{e}e^{2}r}{4\pi\varepsilon_{0}}} \qquad r_{n} = \frac{4\pi\varepsilon_{0}h^{2}}{m_{e}e^{2}}n^{2},$$

$$L = nh, n = 1, 2, L \quad \leftarrow \text{AMQ condition} \qquad m\frac{v^{2}}{r} = \frac{1}{4\pi\varepsilon_{0}}\frac{Ze^{2}}{r^{2}}$$

- We expect it works for any *n*, not just for large n

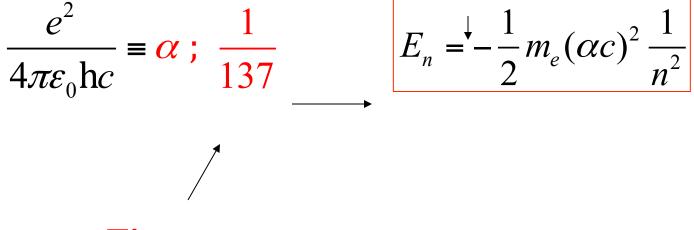
3.2.4 Numerical computation

- Composite constants  $hc = 197 \text{fm} \cdot \text{MeV} = 197 \text{nm} \cdot \text{eV}$   $e^2 / 4\pi\epsilon_0 = 1.44 \text{fm} \cdot \text{MeV} = 1.44 \text{nm} \cdot \text{eV}$  $m_e c^2 = 0.511 \text{MeV} = 511 \text{keV}$
- 1st born orbit radius of Hydrogen

$$r_{1} = a_{1} = \frac{4\pi\varepsilon_{0}h^{2}}{m_{e}e^{2}} = \frac{(hc)^{2}}{m_{e}c^{2}e^{2}/4\pi\varepsilon_{0}}$$
$$= \frac{(197)^{2}}{0.511 \times 10^{6} \times 1.44} \text{ nm ; } \frac{0.039 \times 10^{6}}{0.73 \times 10^{6}} \text{ nm ; } 0.053 \text{ nm}$$

• Energy of the electrons in H

$$E_n = -\frac{m_e e^4}{\left(4\pi\varepsilon_0\right)^2 \cdot 2h^2 n^2} = -\frac{m_e c^2}{2} \left(\frac{e^2}{4\pi\varepsilon_0 hc}\right)^2 \cdot \frac{1}{n^2}$$



**Fine structure constant** 

• Energy of the ground state of H

$$E_{1} = -\frac{1}{2}m_{e}(\alpha c)^{2} = -\frac{1}{2}m_{e}c^{2}\alpha^{2}$$
  
=  $-\frac{1}{2}(0.511 \times 10^{6}) \times (\frac{1}{137})^{2} \text{eV}; -13.6\text{eV}$   
 $E_{n} = -\frac{1}{2}m_{e}(\alpha c)^{2}\frac{1}{n^{2}}$ 

- Ionization energy
  - -Define the ground state energy in H is zero, move

$$E_{1} = -\frac{1}{2}m_{e}c^{2}\alpha^{2} + \frac{1}{2}m_{e}c^{2}\alpha^{2} = 0$$
$$E_{\infty} = 0 + \frac{1}{2}m_{e}(\alpha c)^{2} = 13.6\text{eV}$$

• 1st Bohr velocity

$$v_1 = \alpha c = \frac{c}{137} - \frac{1}{2} m_e c^2 \alpha^2 = -T = -\frac{1}{2} m_e v^2$$

• **Rydberg constant** Relativity effect nelegiable

$$\mathbf{R} = \frac{2\pi^2 e^4 m_e}{(4\pi\epsilon_0)^2 ch^3} = \frac{1}{2} m_e \left(\frac{e^2}{4\pi\epsilon_0 hc}\right)^2 (c)^2 \frac{1}{hc} = \frac{1}{2} m_e (\alpha c)^2 \frac{1}{hc}$$

• Wave number

Photon energy

$$E = hv$$

$$E = hv$$

$$\int \frac{1}{\lambda} = \frac{hv}{hc} \quad \lambda = \frac{hc}{E} = \frac{1.24}{E} \text{ nm} \cdot \text{keV} \quad \frac{hc}{L} = 1.24 \text{ nm} \cdot \text{keV}$$

3.3 Experimental evidence I :spectra

- Spectrum of Hydrogen
- Spectra of Hydrogenlike Ions
- Existance of Deuterium

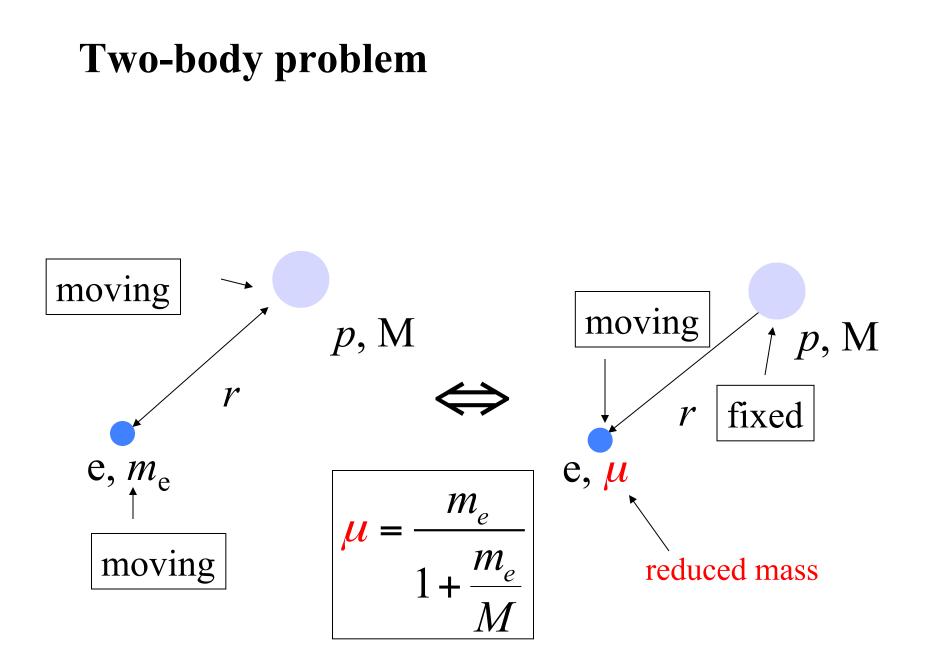
#### 3.3.1 Spectrum of Hydrogen

• Rydberg constant

theory 
$$R = \frac{1}{2} m_e (\alpha c)^2 \frac{1}{hc} = 109737.315 \text{ cm}^{-1}$$
  
Exp. value  $R_H = 109677.58 \text{ cm}^{-1}$ 

- Differenc exceeds  $5e^{-4}$ ; the experimental accuracy is about  $1e^{-4}$ :
- -Stationary nucleus was taken,
- Two-body

#### **Nucleus** –electron co-moving



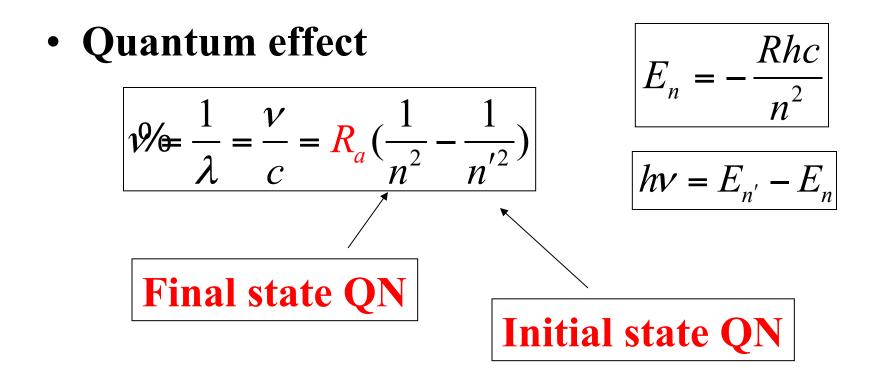
• Rydberg constant

$$R_{a} = \frac{1}{2} (\alpha c)^{2} \frac{1}{hc} \mu = \frac{1}{2} (\alpha c)^{2} \frac{1}{hc} m_{e} \frac{1}{1 + \frac{m_{e}}{M}} = R \frac{1}{1 + \frac{m_{e}}{M}}$$

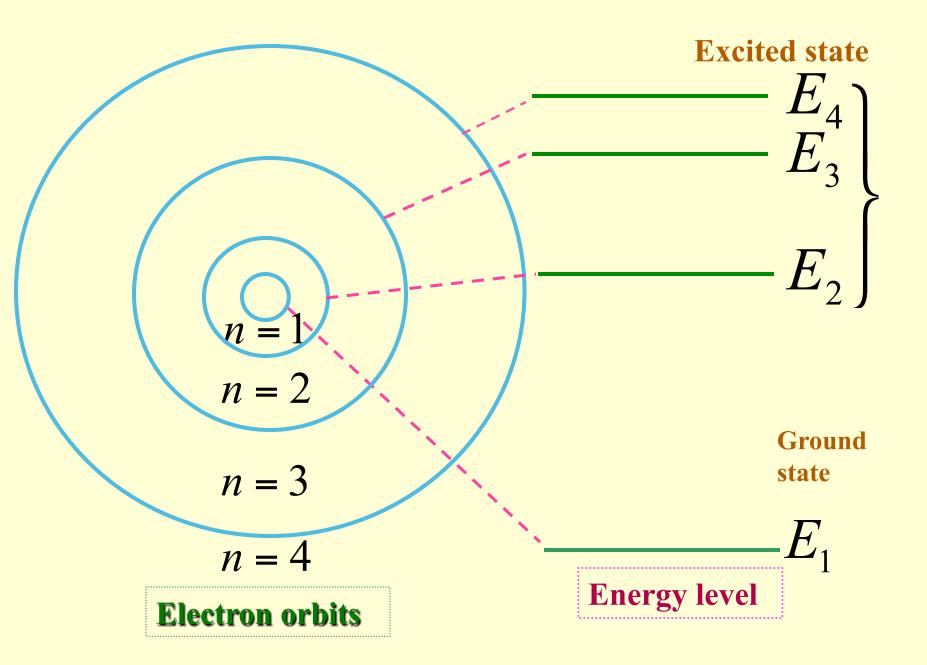
$$M \to \infty, \quad R_a = R_\infty = R$$

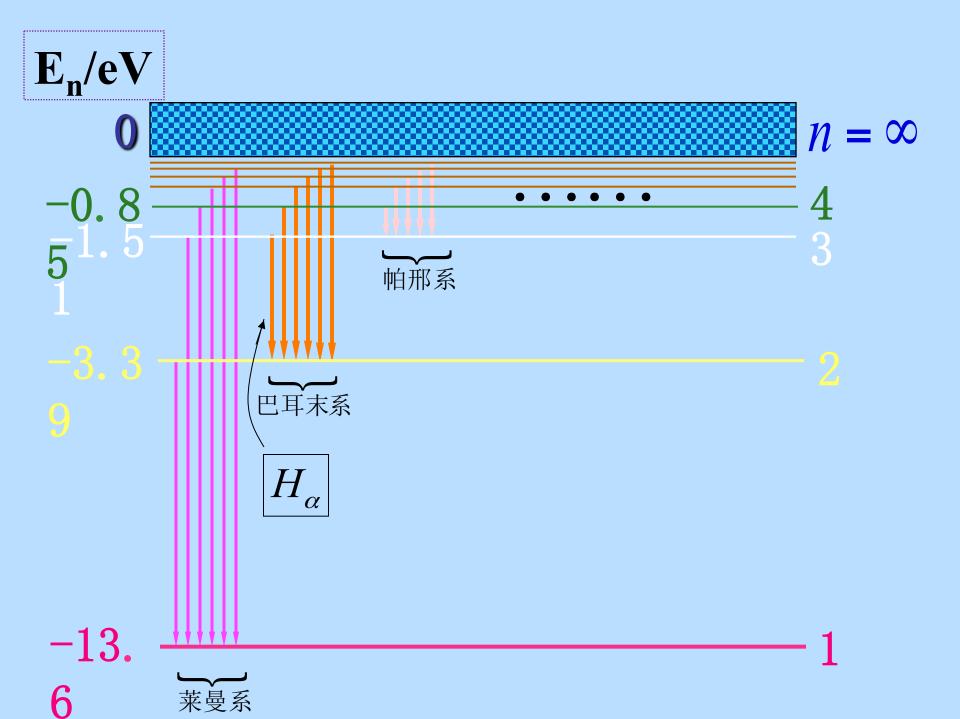
Exper. 
$$R_{H} = 109677.58 \text{ cm}^{-1}$$
  
theory  $R_{a} = \frac{1}{2} (\alpha c)^{2} \frac{1}{hc} \mu = R \frac{1}{1 + \frac{m_{e}}{M}}$  Agree

#### Spectra of Hydrogen



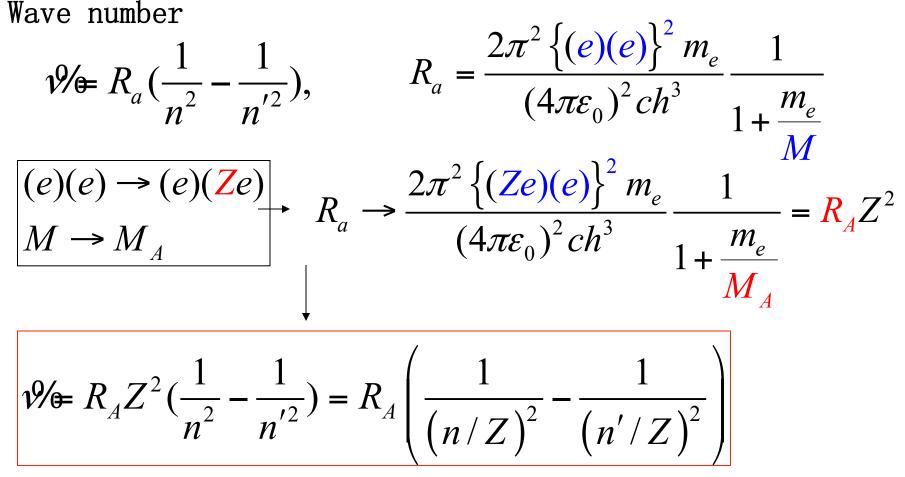
#### Orbits & spectra lines of hydrogen atom





#### 3.3.2 Spectra of Hydrogenlike Ions

- only 1 electron outside the nucleus with Ze positive charge ions
- Wave number



## He<sup>+</sup> : Z = 2, $M = M_{\text{He}^+}$ , n = 4, Pickering series founded

$$\mathscr{V} = R_{\mathrm{He}^{+}} \left( \frac{1}{(2)^{2}} - \frac{1}{(n'/2)^{2}} \right), \quad n' = 5, 6, 7, 8, 9, 10\mathrm{L}$$
$$\mathscr{V} = R_{\mathrm{H}} \left( \frac{1}{(2)^{2}} - \frac{1}{(n')^{2}} \right), \quad n' = 3, 4, 5, 6, \mathrm{L}$$
Balmer  
pickering.  
$$\overset{\mathrm{H}}{=} \frac{\mathrm{He}^{\mathrm{H}}}{\mathrm{He}^{\mathrm{H}}} + \frac{\mathrm{He}^{\mathrm{H}}}{\mathrm{He}^{\mathrm{H}}} + \frac{\mathrm{He}^{\mathrm{H}}}{\mathrm{He}^{\mathrm{H}}} + \frac{\mathrm{He}^{\mathrm{He}}}{\mathrm{He}^{\mathrm{H}}} + \frac{\mathrm{He}^{\mathrm{He}}}{\mathrm{He}^{\mathrm{H}}} + \frac{\mathrm{He}^{\mathrm{He}}}{\mathrm{He}^{\mathrm{He}}} + \frac{\mathrm{He}^{\mathrm{He}}}{+ \frac{\mathrm{He}^{\mathrm{He}}}} + \frac{\mathrm{He}^{\mathrm{H$$

3.3.4 The existence of DeuteriumDeutron -an isotope of H

$${}^{2}_{1}H(D) \quad M_{D} = 2M_{H}$$

$${}^{2}_{M} = R_{D} \left(\frac{1}{n^{2}} - \frac{1}{n'^{2}}\right) \qquad R_{D} = \frac{2\pi^{2}e^{4}m_{e}}{(4\pi\varepsilon_{0})^{2}ch^{3}} \frac{1}{1 + \frac{m_{e}}{2M_{H}}}$$
Exp.:  $H_{\alpha}(n^{2} = 3 \rightarrow n = 2)$ , 6562.79, 6561.00, 1.79  
 ${}^{2}_{M_{\alpha}} = R_{H} \left[\frac{1}{2^{2}} - \frac{1}{3^{2}}\right] = \frac{5}{36}R_{H}$ 
 $\lambda_{H} \qquad \lambda_{D} \qquad \lambda_{D} - \lambda_{H}$   
 $\lambda_{H} = \frac{36}{5R_{H}}, \quad \lambda_{D} = \frac{36}{5R_{D}} \qquad \Delta\lambda = \lambda_{H} - \lambda_{D} = \frac{36}{5}\frac{R_{D} - R_{H}}{R_{H}R_{D}} = 1.79$ 

Good agreement, proving the existence

3.4 Experimental evidence II :Frank-Hertz experiment

#### 3.4.1 Basic idea

Using e beam to excite atoms:

$$e + A = e' + A_{\bullet}^*$$

Excited state

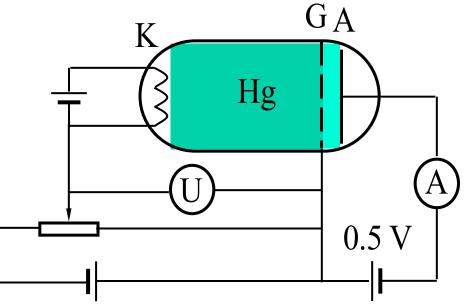
if *A* has discrete energy levels (quantized), if only the kinetic energy of *e* is higher than the lowest excitation energy of *A*, can transfer to *A*, excite it into  $A^*$ , causing sudden drop of the kinetic energy of e'.

# 3-4-2 Frank—Herz experiment (1914)

Glass container:gas ; cathode K: emitted e;

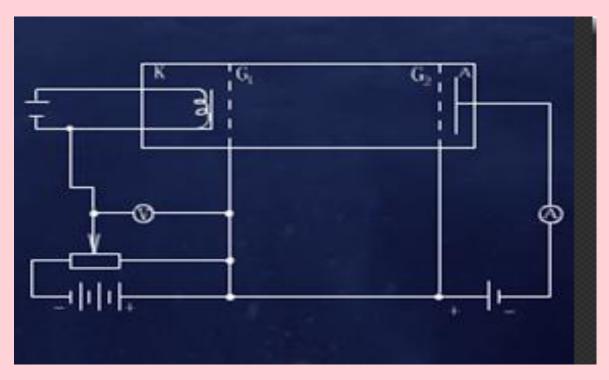
Between K & positive charged grid G: Btw G and receiver A: -0.5V negative voltage, Ammeter A

electrons pass through KG enter into GA.→large energy e reach A forming current; small Energy e can not reach A, no current



Electrons in the mercury atoms do not accept just any Energy

#### 3.4.3 Improved Frank—Herz experiment (1920)



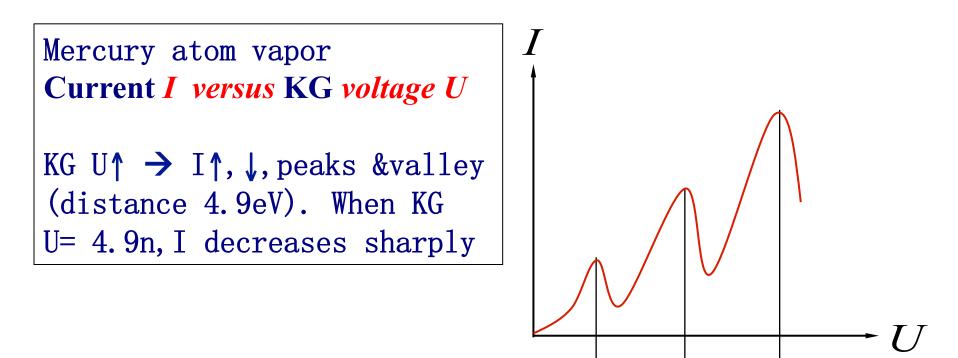
1.An electrode plate was added in front K

- 2 A grid G1 added near K, acceleration in kG1 without collisions
- 3. G1 and G2 at same electric potential : only collision

Separate acceleration from collision

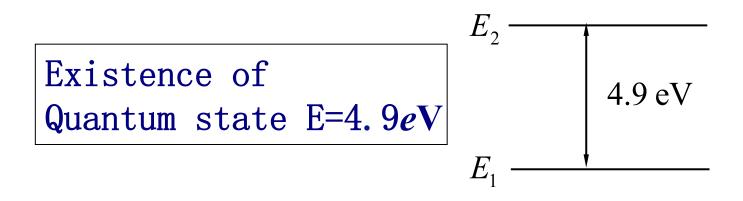


#### Frank-Herz experiment results



4.9 V

#### Experiment explaination



### When U < 4.9 eV: elastic , $U \uparrow \rightarrow \text{Ee} \uparrow \rightarrow$ $I \uparrow ;$

- U = 4.9 eV: inelastic, excited  $E_1$  to  $E_2$ ,  $\text{Ee} \downarrow \rightarrow I \downarrow$ 

- 4. 9eV < U < 2\*4. 9eV; Elastic,  $U^{\uparrow} \rightarrow Ee^{\uparrow} \rightarrow I^{\uparrow}$ 

- U = 2\*4.9 eV: inelastic, excited  $E_1$  to  $E_2$ ,  $\text{Ee} \downarrow \rightarrow I \downarrow$ 

- 3.5 Extension: Bohr-Sommerfeld model
  - Relativistic mass

$$m = \frac{m_0}{\sqrt{1 - \beta^2}}, \beta \equiv \frac{v}{c}$$

$$v = c \rightarrow \beta = 0 \rightarrow m \approx m_0$$

• Relativitic kinetic energy

$$E_{k} = (m - m_{0})c^{2} = m_{0}c^{2} \left(\frac{1}{\sqrt{1 - \beta^{2}}} - 1\right)$$
$$v = c \rightarrow \beta = 0 \rightarrow E_{k} \approx m_{0}c^{2} \left(1 + \frac{1}{2}\beta^{2} - 1\right) = \frac{1}{2}m_{0}v^{2}$$

#### Relativistic correction

• Modification of the circular orbits

$$E = E_k - \frac{Ze^2}{4\pi\varepsilon_0 r} \qquad r_n = \frac{4\pi\varepsilon_0 h^2}{m_e e^2} n^2, \qquad \frac{e^2}{4\pi\varepsilon_0 hc} = \alpha$$

$$\frac{Ze^2}{4\pi\varepsilon_0 r_n} = \frac{Z^2 e^2 m e^2}{(4\pi\varepsilon_0)^2 h^2 n^2} = \frac{Z^2}{n^2} \frac{e^4}{(4\pi\varepsilon_0)^2 h^2 c^2} mc^2 = \frac{Z^2}{n^2} \alpha^2 mc^2$$

$$E_n = -\frac{1}{2} m_e (\alpha c)^2 \left(\frac{Z}{n}\right)^2 = -T = -\frac{1}{2} m_e v^2 \qquad \beta = \frac{v_n}{c} = \frac{\alpha Z}{n^2}$$

$$E = E_k - \frac{Ze^2}{4\pi\varepsilon_0 r} = (m - m_0)c^2 - mc^2 \left(\frac{Z\alpha}{n}\right)^2$$
$$= -m_0c^2 + mc^2 \left(1 - \left(\frac{Z\alpha}{n}\right)^2\right) = -m_0c^2 + \frac{m_0c^2}{\sqrt{1 - \beta^2}}\left(1 - \beta^2\right)$$
$$= m_0c^2 \left(\sqrt{1 - \beta^2} - 1\right)$$
$$\beta = \frac{\alpha Z}{n^2}$$
$$m = \frac{m_0}{\sqrt{1 - \beta^2}}$$

$$E = m_0 c^2 \left( \sqrt{1 - \beta^2} - 1 \right)$$
  

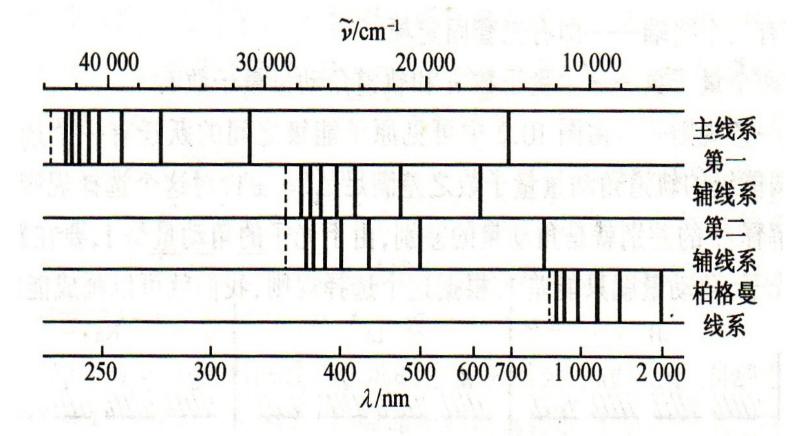
$$\approx m_0 c^2 \left( 1 - \frac{1}{2} \beta^2 + \frac{\frac{1}{2} \left( \frac{1}{2} - 1 \right)}{2!} \beta^4 - 1 \right) = -m_0 c^2 \left( \frac{1}{2} \beta^2 + \frac{1}{8} \beta^4 \right)$$
  

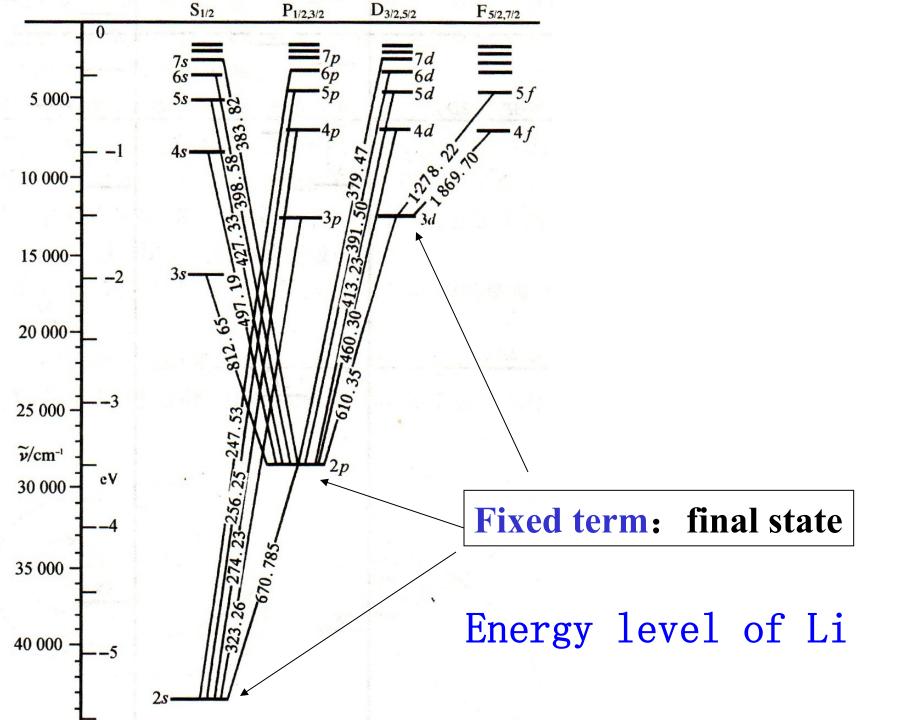
$$E \approx -\frac{m_0 c^2}{2} \left( \frac{Z\alpha}{n} \right)^2 - \frac{m_0 c^2}{8} \left( \frac{Z\alpha}{n} \right)^4$$
  
Bohr result  
Relativistic correction

#### Comparison with experiments

- Alkali atoms
  - The first column : Li, Na, K, Rb, Cs, Fr
  - Have one electron outside a closed electron shell.

**Spectral line series of Lithium** 

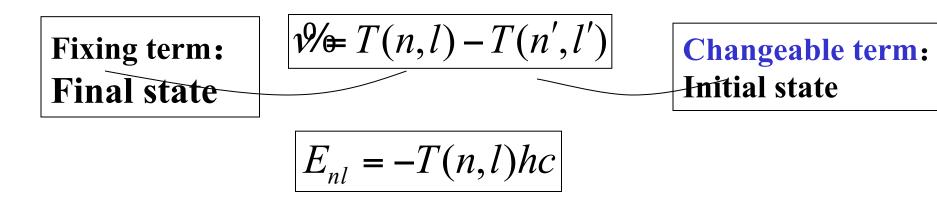




#### Understanding the spectrum

• Energy levels

- Combination principle :



- n stands for series; for a finxing n, each n'
 corresponds to a spectra line

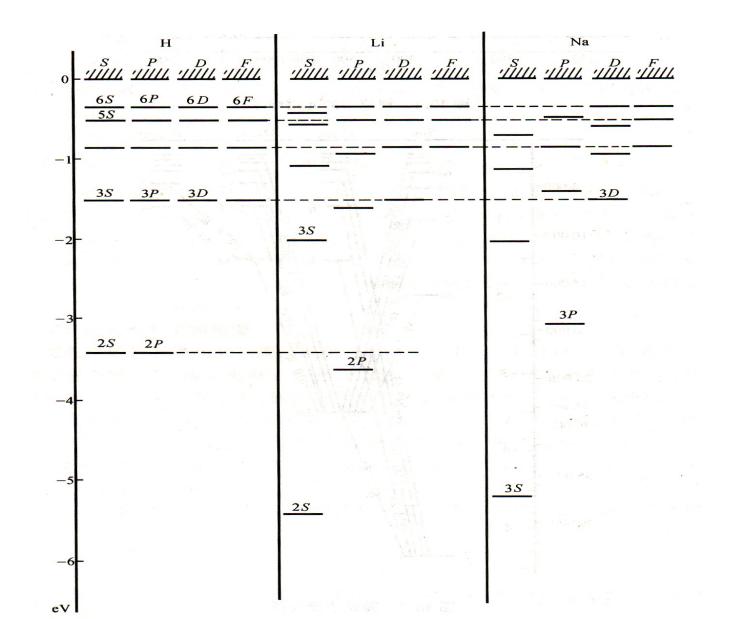
#### **Characters of the energy level**

- 4 sets spectral lines: 4 changeable terms
- 3 terminals : 3 fixed terms
- 2 quantum numbers : n, 1
- 1 rule: selection rule for the transition between 2 atomic energy levels

$$\Delta l = \pm 1$$

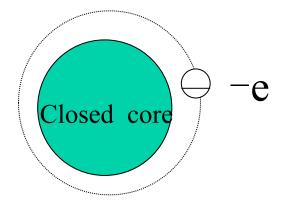
- Energy level classified by *l*:
- -principle:  $nP \rightarrow 2S$
- sharp:  $nS \rightarrow 2P$  (2nd subordinate)
- -diffuse:  $nD \rightarrow 2P$  (primary subordinate)
- -fundamental:  $nF \rightarrow 3D$  (Bergmann)

Comparison of the EL of Hydrogen, Lithium, and sodium



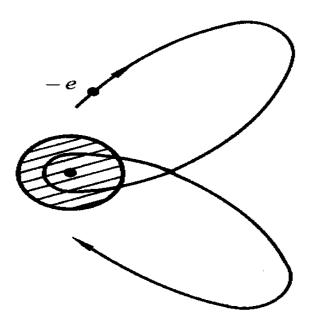
#### Splitting of the EL of H and Alkali atoms

- Alkali atom = valence e + closed core



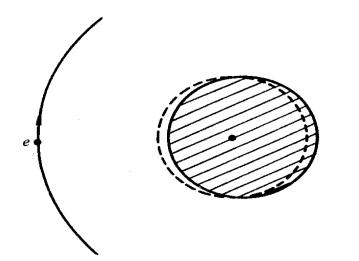
for fixing n, l larg→ e is far from the
 core, less impact on the core, similar to H.
n fixing, l small→ e is close to the
 core, more impact on the core (penetrating
 orbit, core polarization), different from H

- Penetrating orbit



*l* small, e penetrates throug the core and hence decrease its energy

#### polarization of the closed atomic core



/ small, e close to the core, produce slight relative displacement of the positive and negative charge centers, An electric dipole formed, attracting the electron and decreases its energy

Penetrating robit and polarization explain the splitting between the enery levels of H and Alkali atoms,

#### 3-6 Bohr model's S&D

Success: H spectra of light, Quantumstates(Frank-Herzexperiment) Transitions

Difficulties:

- (1) intensity of spectrum line, width, polarization(2) spectrum of multi-e atoms;
- (3) selection rules
- Need greater revolution!