Chapt 4 Fine structure in the Atomic spectra: electron spin

4.1. Magnetic moment by the electron obital motion

- **Classical expresssion**
- **Quantum expression**
- **Quantization of the angular moentum**

4. 1. 1. Classical expresssion

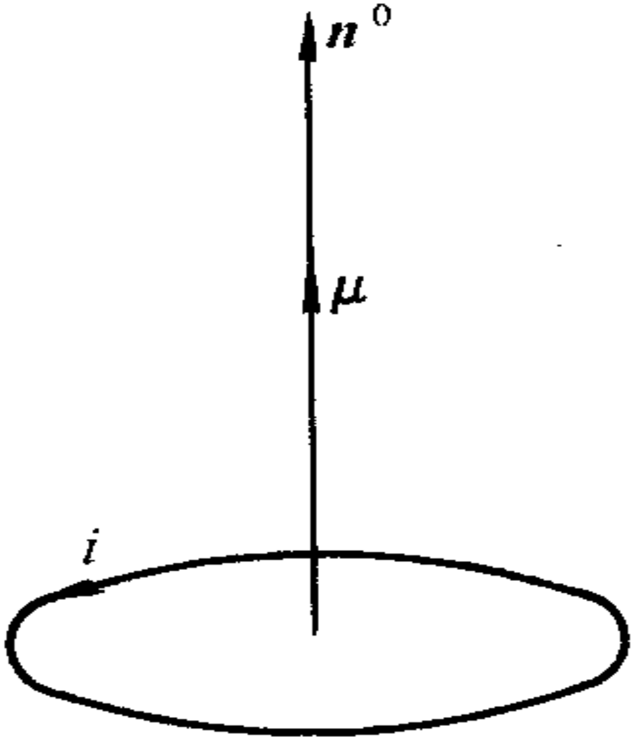
- **Magnetic moment for a small electric current**

$$\vec{\mu} = iS\vec{n}^{0}$$

current

Area

Unit vector normal the plane



MM by the electrons classical moving with v

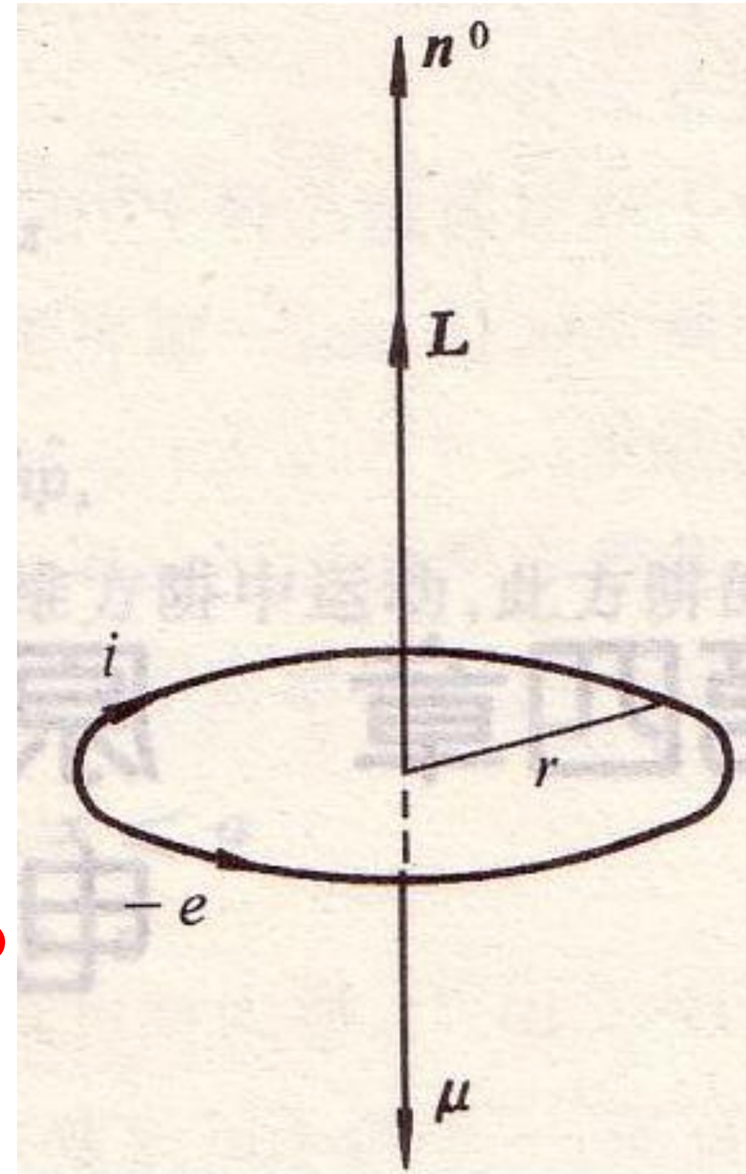
$$i = -\frac{e}{T} = -e\frac{v}{2\pi r}, \qquad S = \pi r^2$$

$$\vec{\mu} = iS\vec{n}^0 = -\frac{ev}{2\pi r}\pi r^2 \vec{n}^0$$

$$= -\frac{e}{2m_e} m_e v r \vec{n}^0 = -\frac{e}{2m_e}\vec{L}$$

$$\boxed{\vec{\mu} = -\gamma \vec{L}}$$

gyromagnetic ratio
旋磁比, γ



- The toque is giving by

$$\boxed{\vec{\tau} = \vec{\mu} \times \vec{B}} \qquad \vec{\tau} = \frac{d\vec{L}}{dt} \longleftarrow \boxed{\textbf{AM thorem}}$$

$$\frac{d\vec{L}}{dt} = \vec{\mu} \times \vec{B} \qquad \vec{\mu} = -\gamma \vec{L}$$

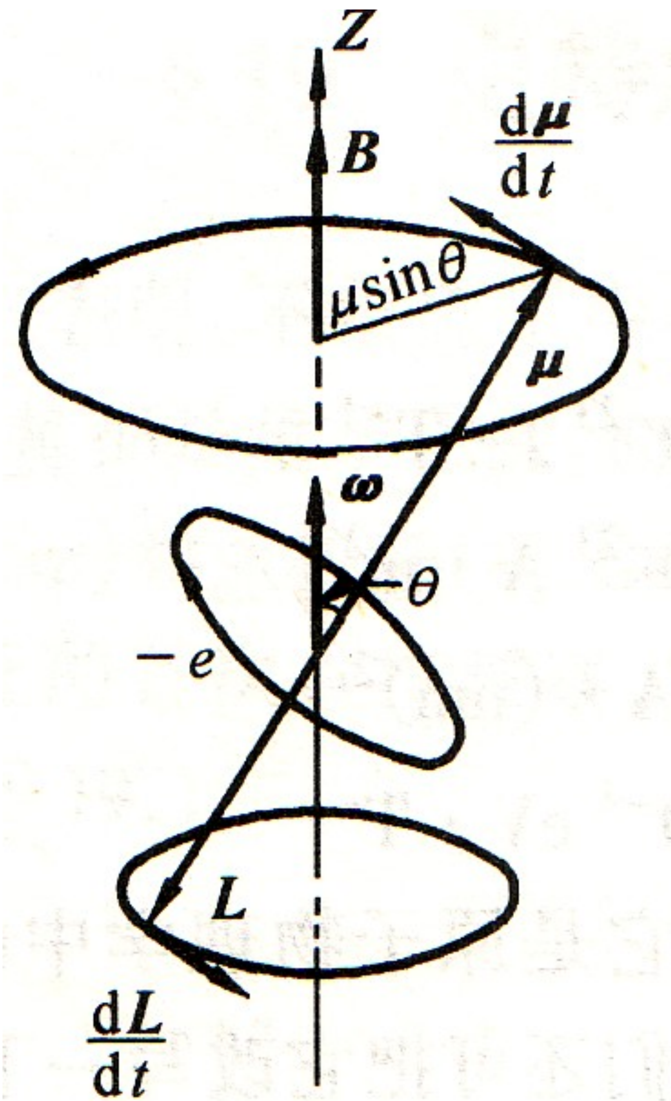
$$\frac{d\vec{\mu}}{dt} = -\gamma \vec{\mu} \times \vec{B} \qquad \vec{\omega} = \gamma \vec{B}$$

$$\boxed{\frac{d\vec{\mu}}{dt} = \vec{\omega} \times \vec{\mu}}$$

- # Larmor precession

$$\boxed{\frac{d\vec{\mu}}{dt} = \vec{\omega} \times \vec{\mu}}$$

the MM $\vec{\mu}$ precesses about B with angular velocity ω



Larmor AV $$\omega = \frac{e}{2m_e} B$$

Larmor freq. $$\nu = \omega / 2\pi = \frac{e}{4\pi m_e} B$$

4.1.2 Quantization conditions

- The MM induced by orbit motion

$$\boxed{\vec{\mu} = -\gamma \vec{L}} \quad \boxed{L = \sqrt{l(l+1)}\hbar, l = 0, 1, \ldots ;} \quad \gamma = \frac{e}{2m_e}$$

$$\mu_l = -\sqrt{l(l+1)}\frac{e\hbar}{2m_e} = -\sqrt{l(l+1)}\mu_B$$

$$\boxed{L_z = m_l\hbar, m_l = 0, \pm 1, \pm 2, \ldots \pm l}$$

$$\mu_{l,z} = -\frac{e}{2m_e}L_z = -\frac{e}{2m_e}\cdot m_l\hbar = -m_l\mu_B$$

Bohr magneton $\quad \mu_B = \dfrac{e\hbar}{2m_e}$

4.1.3. Quantization of L and is z component

- **Quantization of L**
- **Quantization of Lz**

$$L = \sqrt{l(l+1)}\hbar, l = 0, 1, \cdots;$$

$$L_z = m_l \hbar, m_l = 0, \pm 1, \pm 2, \cdots \pm l$$

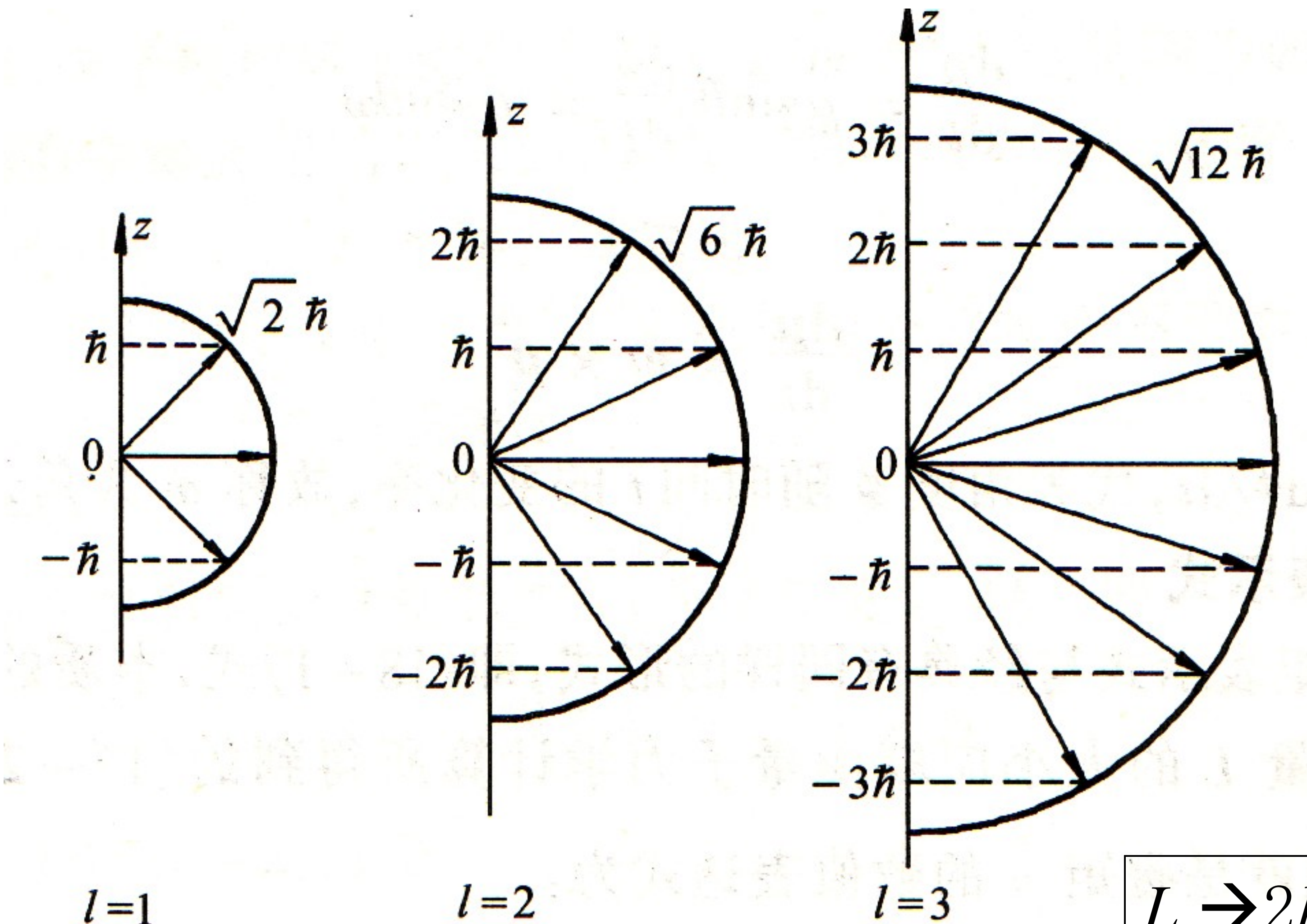
$\Longrightarrow$

- Quantization of MM
- Quantization of its z

$$\mu_l = -\sqrt{l(l+1)}\mu_B$$

$$\mu_{l,z} = -m_l \mu_B$$

L and its z components



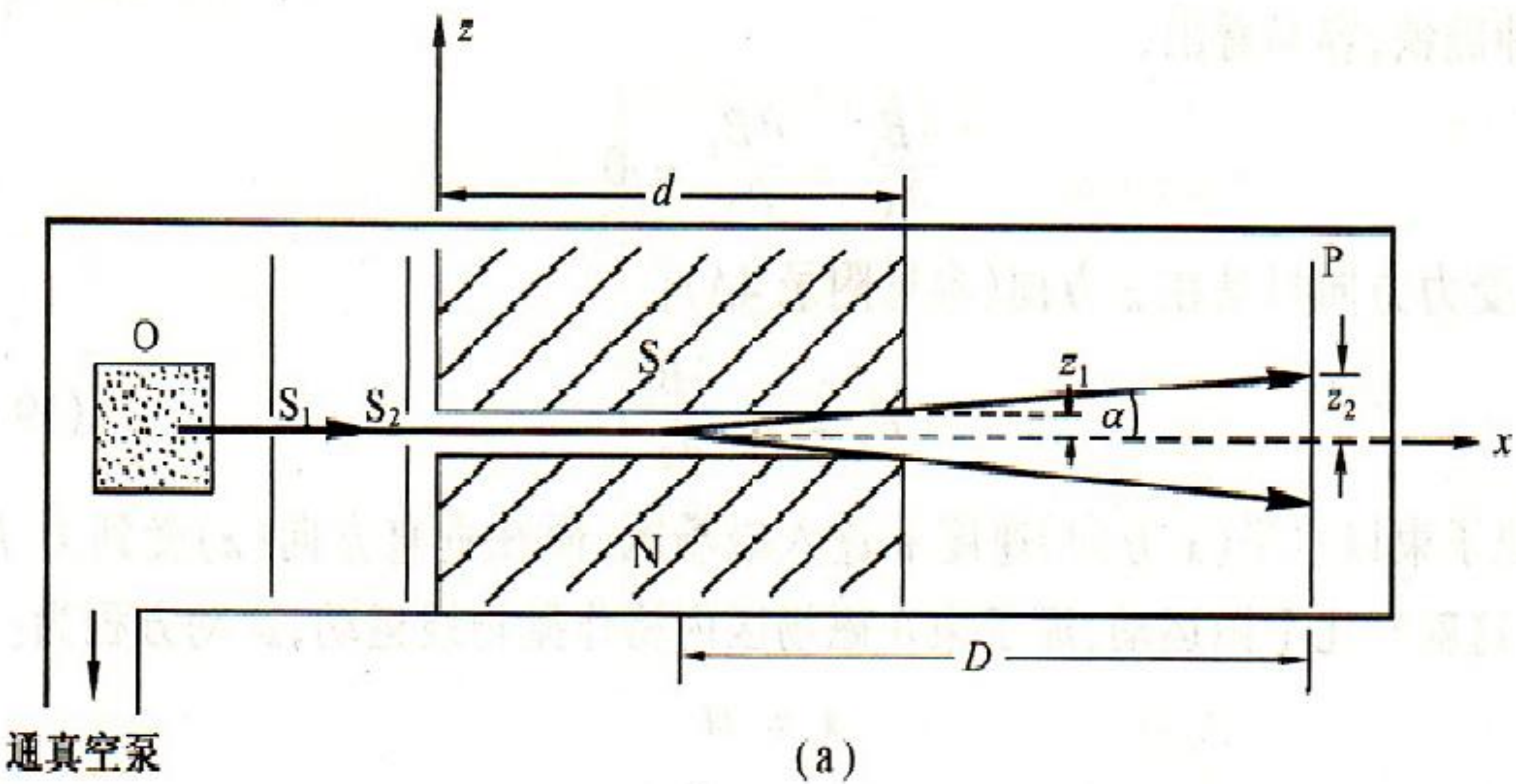
$\boxed{L \rightarrow 2l+1 \;\; m_l}$

4.2.Stern -Gerlach Experiment

- Set up
- principle
- analysis
- result

4.2.1. experiment setup

container **O**: heated atoms; slits **S_1, S_2**: atomic beam
Inhomogeneous magnetic field **SN**(B_z); **Photo**: record



(a)

4.2.2. experiment principle

- **container with H vapor at T**

$$E_k = \frac{1}{2}mv_x^2 = \frac{3}{2}KT$$

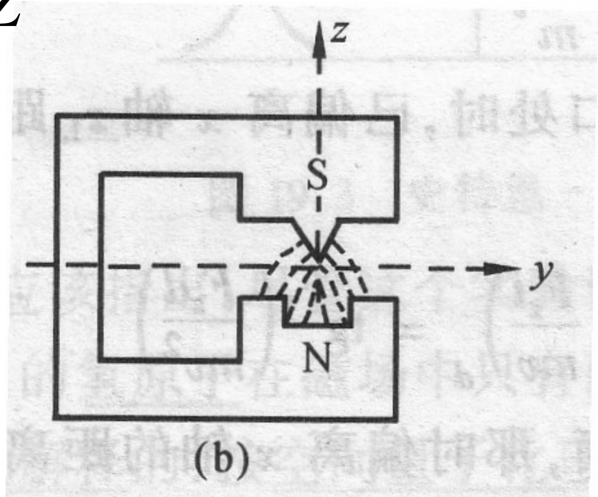
  - $T = 7\text{x}10^4\,K \rightarrow E_k = 9.0\text{eV} < 10.2\text{eV}$ **(1st excitation E)**

→ H atoms are in ground state

- **Magnetic field area(inhomo.** $\frac{\partial B}{\partial Z} \neq 0$ **)**
  - *force excert on* μ:
  - atoms motion

$$F_z = \mu_z \frac{\partial B}{\partial Z}$$

$$x = v_x t; \quad z = \frac{1}{2}\frac{F_z}{m}t^2$$



- **H atom's position** z_2

$$\boxed{a = \frac{F_z}{m}} \qquad \boxed{v_z = at_1}$$

$$z_2 = \frac{1}{2}at_1^2 + v_z t_2$$

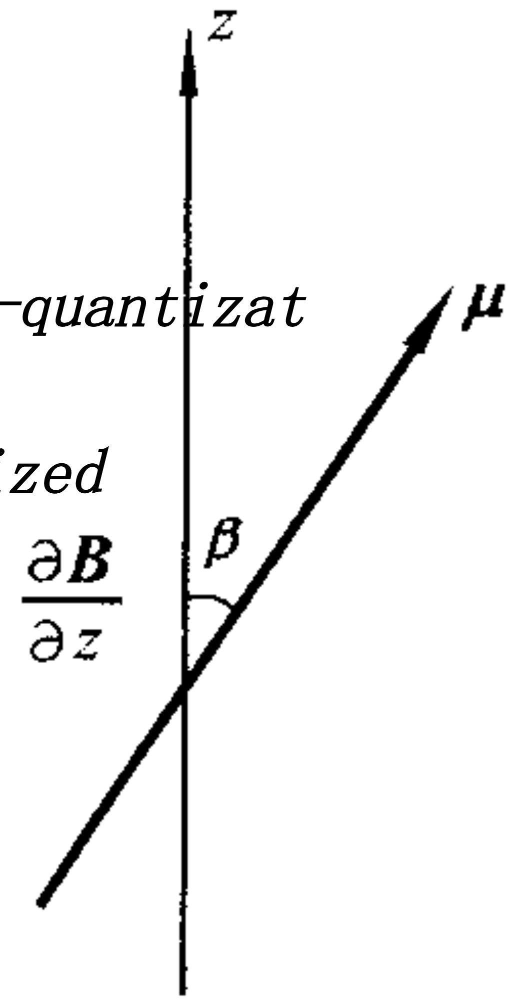
$$= \frac{1}{2}\frac{F_Z}{m}\left(\frac{d}{v_x}\right)^2 + \frac{F_Z}{m}\cdot\frac{d}{v_x}\cdot\frac{D-(1/2)d}{v_x}$$

$$= \frac{F_Z}{m}\cdot\frac{d}{v^2{}_x}\left(\frac{d}{2}+D-\frac{d}{2}\right) = \frac{F_Z}{m}\cdot\frac{dD}{v^2{}_x} = \mu_z\frac{\partial B}{\partial Z}\frac{dD}{3kT}$$

4.2.3. experiment analysis

$$z_2 = \mu_z \frac{\partial B}{\partial Z} \frac{dD}{3kT} \qquad \mu_z = \mu \cos\beta$$

fixing $\boldsymbol{\mu}$, $\boldsymbol{\mu}_z$ *non-quantizatio* → z_2 *non-quantizat*

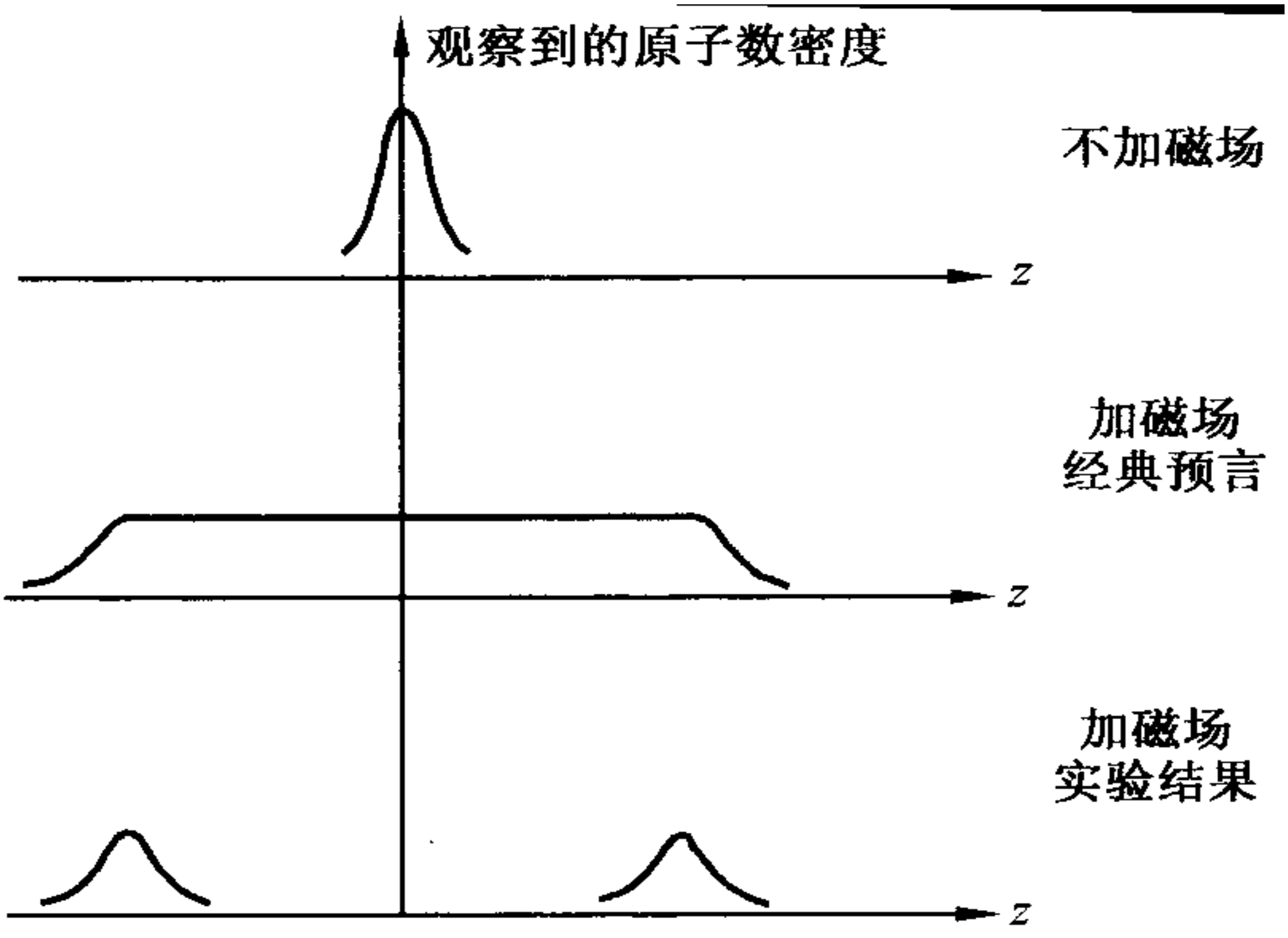


$\boldsymbol{\mu}$ *fixing* , $\boldsymbol{\mu}_z$ *Quantized* → z_2 *quantized*

$$\mu = -\sqrt{l(l+1)}\mu_B, \quad l = 0, 1, 2, \ldots$$

$$\mu_z = -m_l \mu_B, \quad m_l = 0, \pm 1, \ldots \pm l$$

4.2.4.Experiment results



- z_2 ***Quantized*** → μ_z ***Quantized***
  (proved spatial quantization)
- **ground state H atom**
  - $l = 0$ → → $z_2 = 0$

$$\mu = 0, \quad \mu_z = 0$$

$$\boxed{\begin{array}{ll} \mu = -\sqrt{l(l+1)}\mu_B, & l = 0, 1, 2, \ldots \\ \mu_z = -m_l \mu_B, & m_l = 0, \pm 1, \ldots \pm l \end{array}}$$

not agree with experiment, description of atom was incomplete

4.3. Hypothesis of elctron spin

- Hypothesis of e spin
- Lande ***g-factor***
- ***Expression of g-factor***
- Interpretation of Stern-Gerlach Exp

4.3.1. Hypothesis of e Spin

- spin hypothesis ： **(Uhlenbeck &Goudsmit basing on SG experiment data made a bold suggestion:**

(1) Electron is not a point charge, it rotates like a
this new intrinsic motion is "spin", with SAM and SMM

(2) electron spin angular moment S:

$$\boxed{\left|\vec{S}\right| = S = \sqrt{s(s+1)}\hbar}$$

***s*=1/2** spin QN

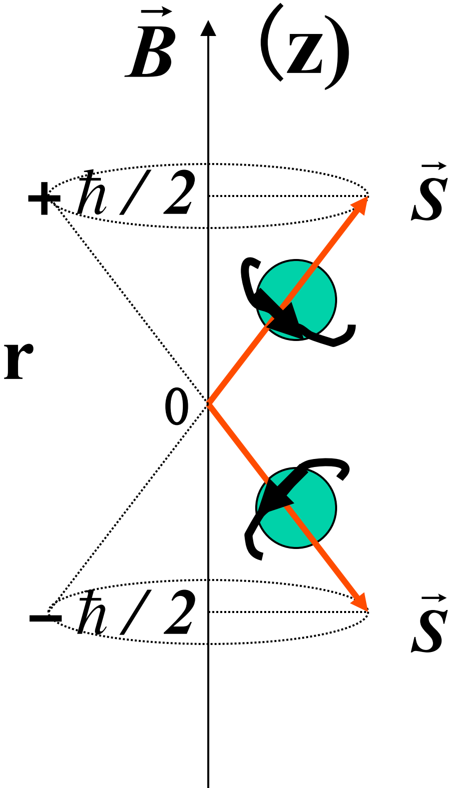
Spatial quantization of spin

(3) electron's SAM satifies spatial quantization WRT B (*z direction*) :

$$\boxed{S_z = m_s \hbar}$$

$m_s = \pm 1/2,$

magnetic quantum number



4. 3. 2. Lande *g* factor

- **orbital AM** → orbital MM

$$\mu_l = -\sqrt{l(l+1)}\mu_B, \quad l = 0, 1, 2, \ldots$$

$$\mu_{l,z} = -m_l \mu_B, \quad m_l = 0, \pm 1, \ldots \pm l$$

- Spin AM → Spin MM

$$\mu_s = -\sqrt{s(s+1)}\mu_B = -\frac{1}{2}\sqrt{3}\mu_B$$

$$\mu_{s,z} = -m_s \mu_B = \mp\frac{1}{2}\mu_B$$

contradict with Exp

- SAM→ SMM
  - ansatz

$$\mu_s = -2\sqrt{s(s+1)}\mu_B = -\sqrt{3}\mu_B, \quad \mu_{s,z} = -2m_s\mu_B = \mathrm{m}\mu_B$$

  - agree with data

- Lande g-Factor
  - ***AM j* → MM $\boldsymbol{\mu_j}$**

$$\boxed{\begin{aligned} \mu_j &= -\sqrt{j(j+1)}\,g_j\mu_B \\ \mu_{j,z} &= -m_j g_j \mu_B \end{aligned}}$$

- Lande g-factor

$$j = l : g_j = 1 \rightarrow \mu_l = -\sqrt{l(l+1)}\mu_B, \;\; \mu_{l,z} = -m_l \mu_B$$

$$j = s = \frac{1}{2} : g_s = 2$$

$$\rightarrow \mu_s = -2\sqrt{s(s+1)}\mu_B = -\sqrt{3}\mu_B, \;\; \mu_{s,z} = -2 m_s \mu_B = \mathrm{m}\mu_B$$

4.3.3 Expression of g-factor for a single electron

Orbital AM,Spin AM →total AM

$$\vec{J} = \vec{L} + \vec{S}$$

- Vector adding rules and quantization

$$\boxed{L = \sqrt{l(l+1)}\hbar} \qquad \boxed{S = \sqrt{s(s+1)}\hbar} \qquad \boxed{J = \sqrt{j(j+1)}\hbar}$$

$$\boxed{l = 0, 1, \cdots, n-1;} \qquad \boxed{s = 1/2} \longrightarrow \boxed{j = l \pm s = l \pm 1/2}$$

$$\boxed{L_z = m_l \hbar} \qquad \boxed{S_z = m_s \hbar} \qquad \boxed{J_z = m_j \hbar}$$

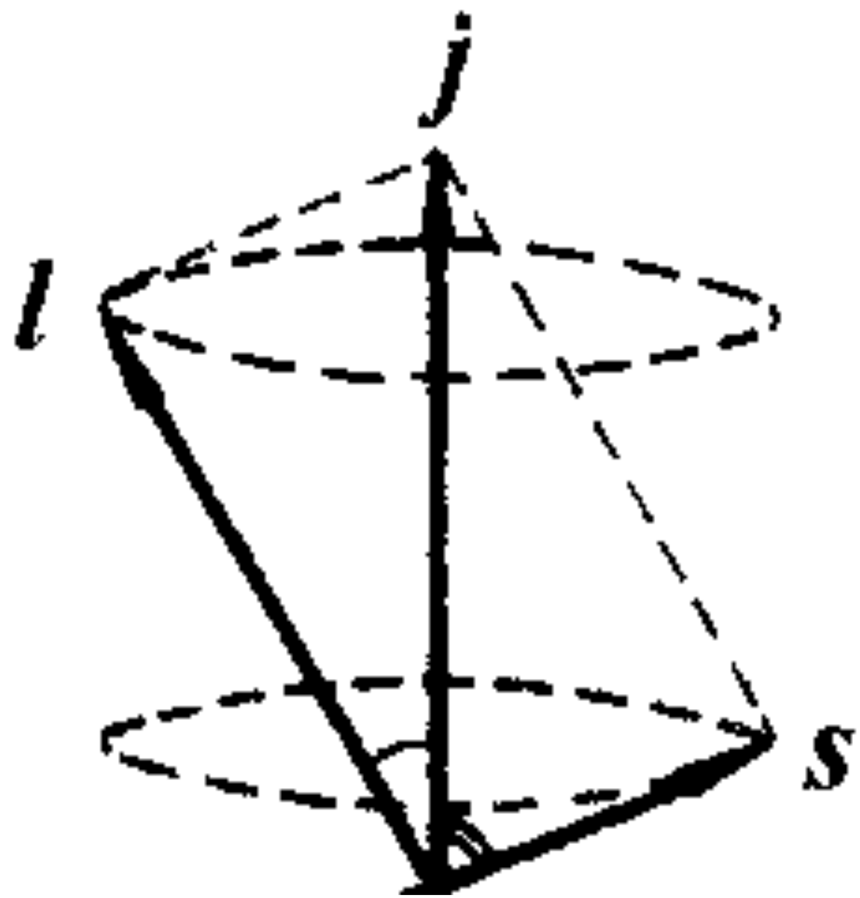
$$\boxed{m_l = 0, \pm 1, \pm 2, \cdots \pm l} \qquad \boxed{m_s = \pm 1/2} \longrightarrow \boxed{m_j = m_l + m_s}$$

$$\boxed{m_j = -j, -(j-1), \cdots (j-1), j}$$

- **adding rules of AM**

L and S are precessin

about J



- State of electron, state of atom

1e atoms : SOA= SOE

electron state: (n, l, m_l, m_s) , (n, l, j, m_j)

For a fixing n, the number of states

$$\sum_{l=0}^{n-1} 2(2l+1) = 2n^2$$

$$\sum_{l=0}^{n-1} \sum_{j=l-1/2}^{j+1/2} (2j+1)$$

$$= \sum_{l=0}^{n-1} 2(2l+1)$$

$$= 2n^2$$

- State of Atom (SOA)
  - With spin, the SOA of 1e atom

$$\boxed{n^{(2s+1)}L_j}$$

$$n=1: \quad 1^2S_{1/2}$$

$$n=2: \quad 2^2S_{1/2}, \quad 2^2P_{1/2}, \quad 2^2P_{3/2}$$

$$n=3: \quad 3^2S_{1/2}, \quad 3^2P_{1/2}, \quad 3^2P_{3/2}, \quad 3^2D_{3/2}, \quad 3^2D_{5/2}$$

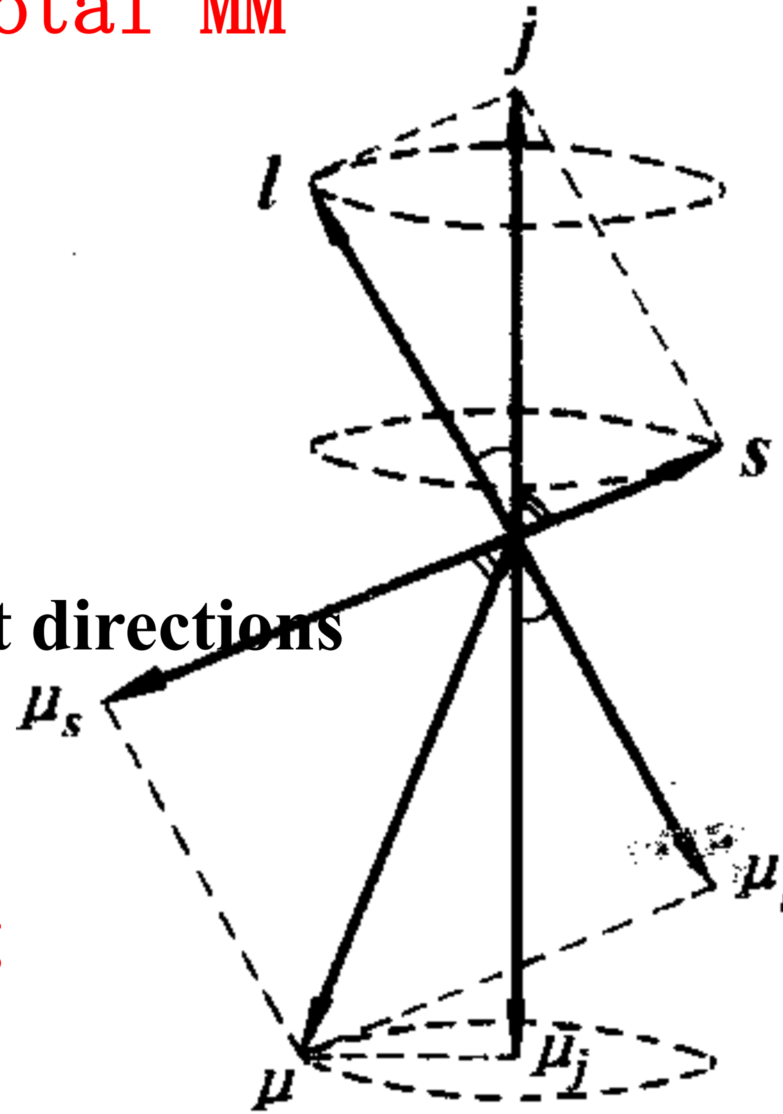
- **Orbital MM, Spin MM→**total MM

$$\vec{\mu} = \vec{\mu}_l + \vec{\mu}_s$$

$$\mu_l = -\sqrt{l(l+1)}\,g_l\mu_B, \quad g_l = 1$$

$$\mu_s = -\sqrt{s(s+1)}\,g_s\mu_B, \quad g_s = 2$$

→ $\vec{\mu}$ $\vec{J}$ **different directions**



$\vec{L}, \vec{S}$ ab $\vec{J}$ Precessing

→ $\vec{\mu}_l, \vec{\mu}_s, \vec{\mu}$ ab $\vec{J}$ **precessing**

$\vec{\mu}$ **no definite direction**

- **decompose total MM into two directions**

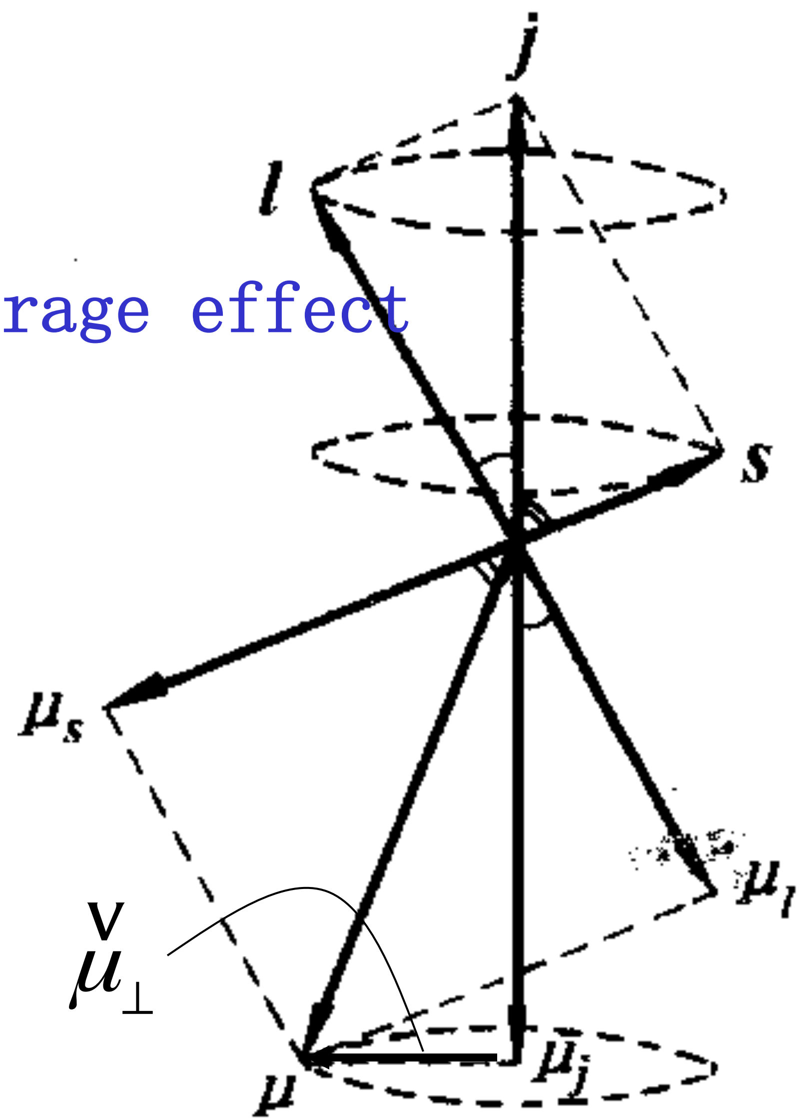
$$\vec{\mu} = \vec{\mu}_j + \vec{\mu}_\perp$$

$\vec{\mu}_\perp$ abt $\vec{J}$ **precessing** , no average effect

$\vec{\mu}_j$ al $\vec{J}$ anti-direction

total MM of electron

$$\mu_j = \mu_l \cos(\vec{L}, \vec{J}) + \mu_s \cos(\vec{S}, \vec{J})$$



$$\mu_j = \mu_l \cos(\vec{L}, \vec{J}) + \mu_s \cos(\vec{S}, \vec{J})$$

$$\boxed{\begin{aligned} \hat{l} &= \sqrt{l(l+1)} \\ \hat{s} &= \sqrt{s(s+1)} \end{aligned}}$$

$$= -\left\{ g_l \hat{l} \cos(\vec{L}, \vec{J}) + g_s \hat{s} \cos(\vec{S}, \vec{J}) \right\} \mu_B$$

$$\boxed{\begin{aligned} \mu_l &= -g_l \hat{l} \mu_B \\ \mu_s &= -g_s \hat{s} \mu_B \end{aligned}}$$

$$\boxed{S^2 = L^2 + J^2 - 2LJ \cos(\vec{L}, \vec{J})}$$

$$\hat{j} = \sqrt{j(j+1)}$$

$$\cos(\vec{L}, \vec{J}) = \frac{\hat{j}^2 + \hat{l}^2 - \hat{s}^2}{2\hat{l}\hat{j}} \qquad \cos(\vec{S}, \vec{J}) = \frac{\hat{j}^2 + \hat{s}^2 - \hat{l}^2}{2\hat{s}\hat{j}}$$

g-factor for a single electron

$$\rightarrow \quad \mu_J = -\left\{ g_l \frac{\hat{j}^2 + \hat{l}^2 - \hat{s}^2}{2\hat{j}^2} + g_s \frac{\hat{j}^2 + \hat{s}^2 - \hat{l}^2}{2\hat{j}^2} \right\} \hat{j} \mu_B$$

$$\boxed{\mu_j = -\hat{j} g_j \mu_B, \quad \mu_{j,z} = -m_j g_j \mu_B}$$

$\boxed{g \text{ factor}}$

$$g_j = g_l \frac{\hat{j}^2 + \hat{l}^2 - \hat{s}^2}{2\hat{j}^2} + g_s \frac{\hat{j}^2 + \hat{s}^2 - \hat{l}^2}{2\hat{j}^2}$$

$$= \frac{g_l + g_s}{2} + \left(\frac{g_l - g_s}{2} \right) \left(\frac{\hat{l}^2 - \hat{s}^2}{\hat{j}^2} \right) = \frac{3}{2} + \frac{1}{2} \left(\frac{\hat{s}^2 - \hat{l}^2}{\hat{j}^2} \right)$$

Two assumptions were used

* ***L-S coupling*** **: into *J*, *S* , *L precess about J* .**

only work for weak external B; For strong B,

S and L precess about B

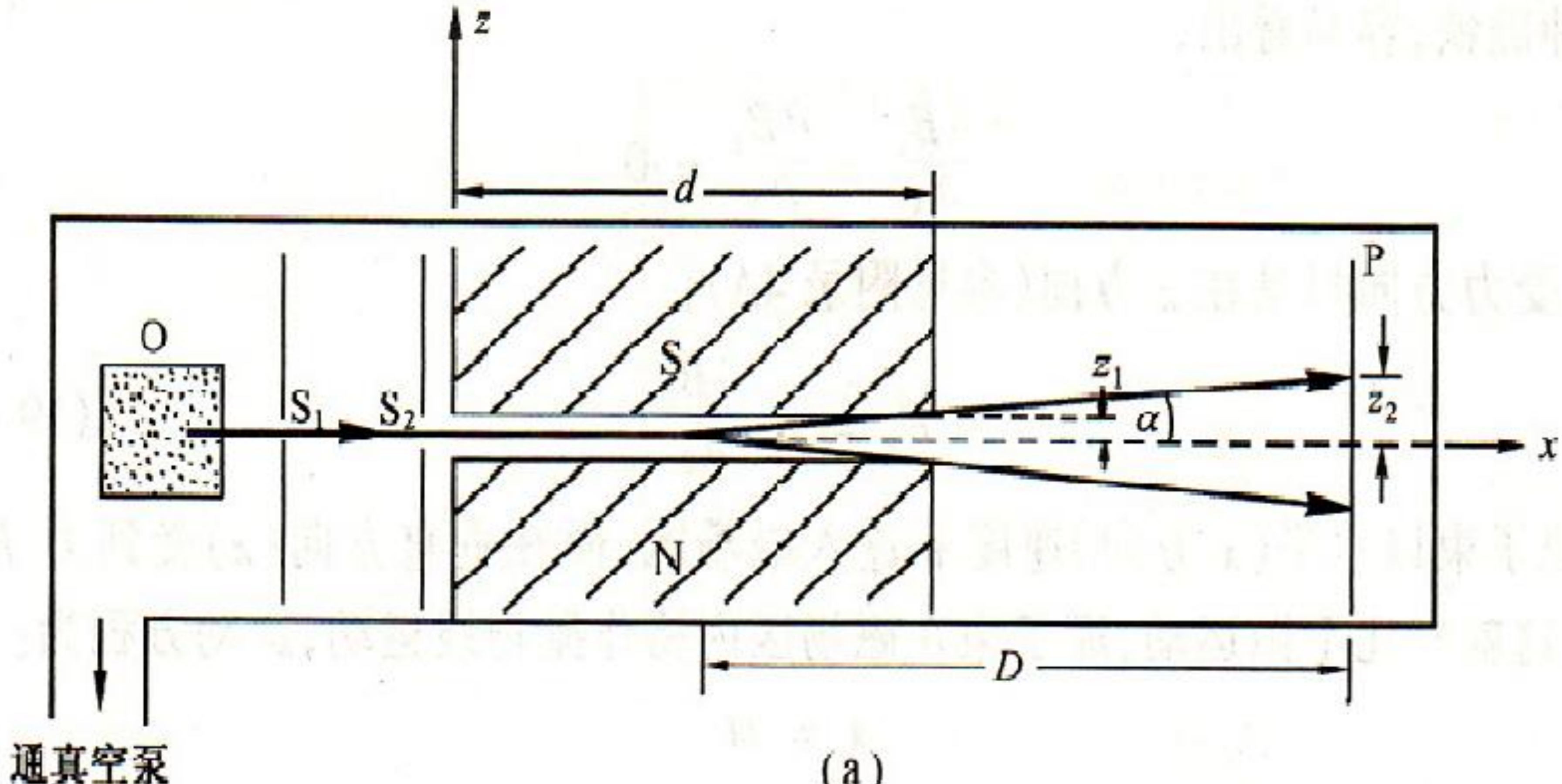
* **Only considered single electron .**

For atom with more electrons :

$$g_J = \frac{3}{2} + \frac{1}{2}\left(\frac{\hat{S}^2 - \hat{L}^2}{\hat{J}^2}\right)$$

$\hat{S}, \hat{L}, \hat{J}$: total spin, orbital AM and total AM of composed by the s, l, j of all electrons

4.3.4. Interpretation of the Stern-Gerlach Experiment



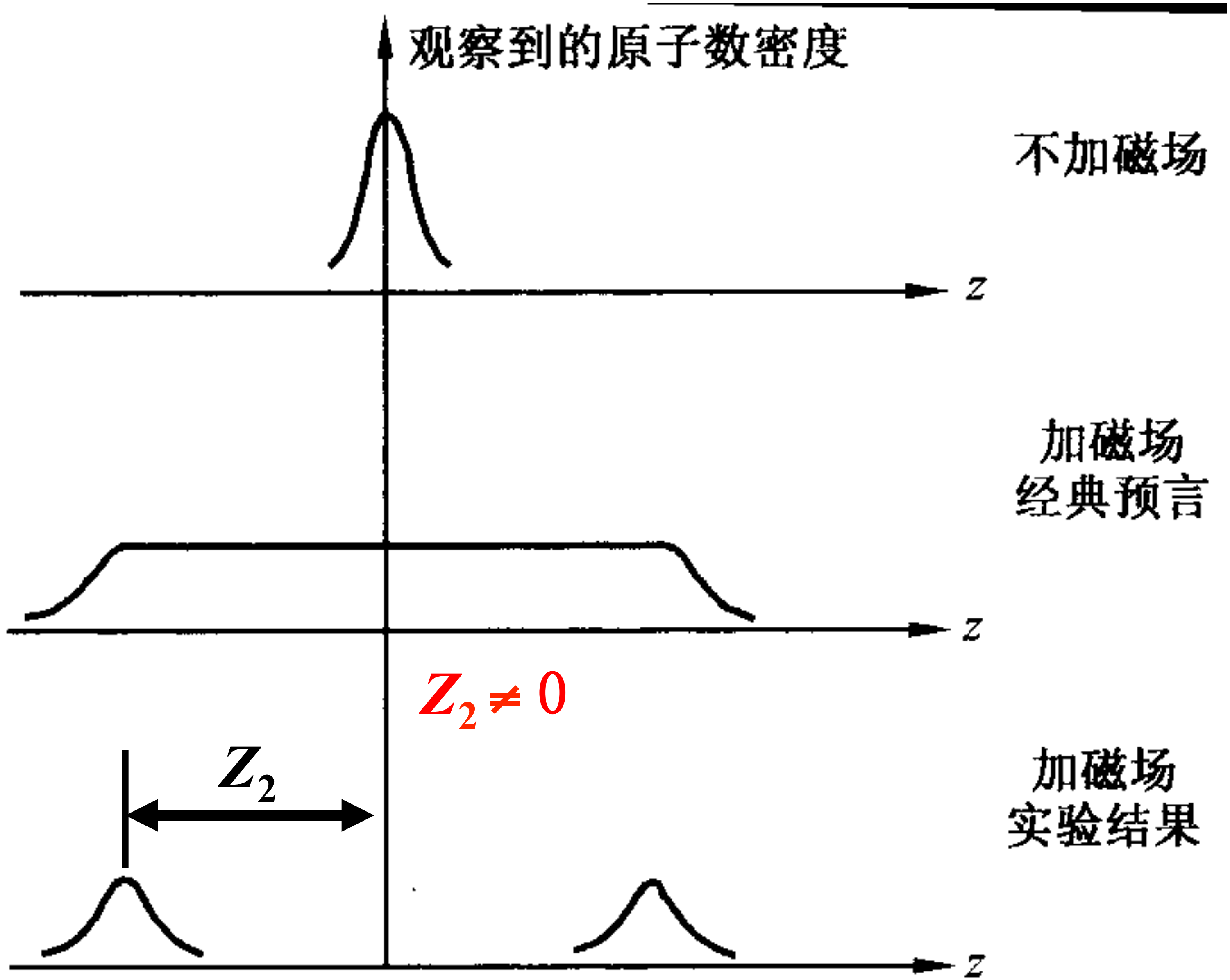
(a)

$$z_2 = \mu_z \frac{\partial B}{\partial Z} \frac{dD}{3kT}$$

$$\boxed{\begin{aligned} &\mu = -\sqrt{l(l+1)}\,\mu_B, \quad l = 0, 1, 2, \ldots \\ &\mu_z = -m_l \mu_B, \quad m_l = 0, \pm 1, \ldots \pm l \end{aligned}}$$

$$l = 0 \rightarrow \mu = 0, \; \mu_z = 0 \rightarrow z_2 = 0$$

for ground state Hydrogen without spin


观察到的原子数密度
不加磁场
z
加磁场
经典预言
z
$Z_2 \neq 0$
Z_2
加磁场
实验结果
z

For ground state Hydrogen with spin

$$1^2S_{\frac{1}{2}} : l = 0, j = 1/2, s = 1/2$$

$$\rightarrow \quad m_j = \pm 1/2; \quad g_j = \frac{3}{2} + \frac{1}{2}\left(\frac{\hat{s}^2 - \hat{l}^2}{\hat{j}^2}\right) = 2$$

$$z_2 = \mu_{j,z} \frac{\partial B}{\partial Z} \frac{dD}{3kT}; \quad \mu_{j,z} = -m_j g_j \mu_B$$

$$\rightarrow \quad z_2 = \pm \mu_B \frac{\partial B}{\partial Z} \frac{dD}{3kT}$$

exper. : $\frac{\partial B}{\partial z} = 10T/m, d = 1m, D = 2m, T = 400K$

theory: $k = 8.617\times10^{-5} e/K, \mu_B = 0.5788\times10^{-4} eV/K$

→ $z_2 = \pm 1.12cm$ agrees well with experiment

Stern-Gerlach experiment proved :

- Spatial Quantization
- Electron spin
- Spin MM $g_s = 2$

4.4. Doublet lines of Alkali Metals

- Fine structure : qualitative consieration
- Spin-orbit interaction:quantative consideration

4.4.1. Fine structure： qualitative consieration

- Four mian series of lines in atomic spectra of alkali metals
  - principle ： $nP \rightarrow 2S$
  - sharp ： $nS \rightarrow 2P$（第二辅线系）
  - diffuse ： $nD \rightarrow 2P$（第一辅线系）
  - fundamental ： $nF \rightarrow 3D$（柏格蔓线系）

fixing: Final S

Initial S

$$\boxed{\tilde{\nu} = T(n,l) - T(n',l')}$$

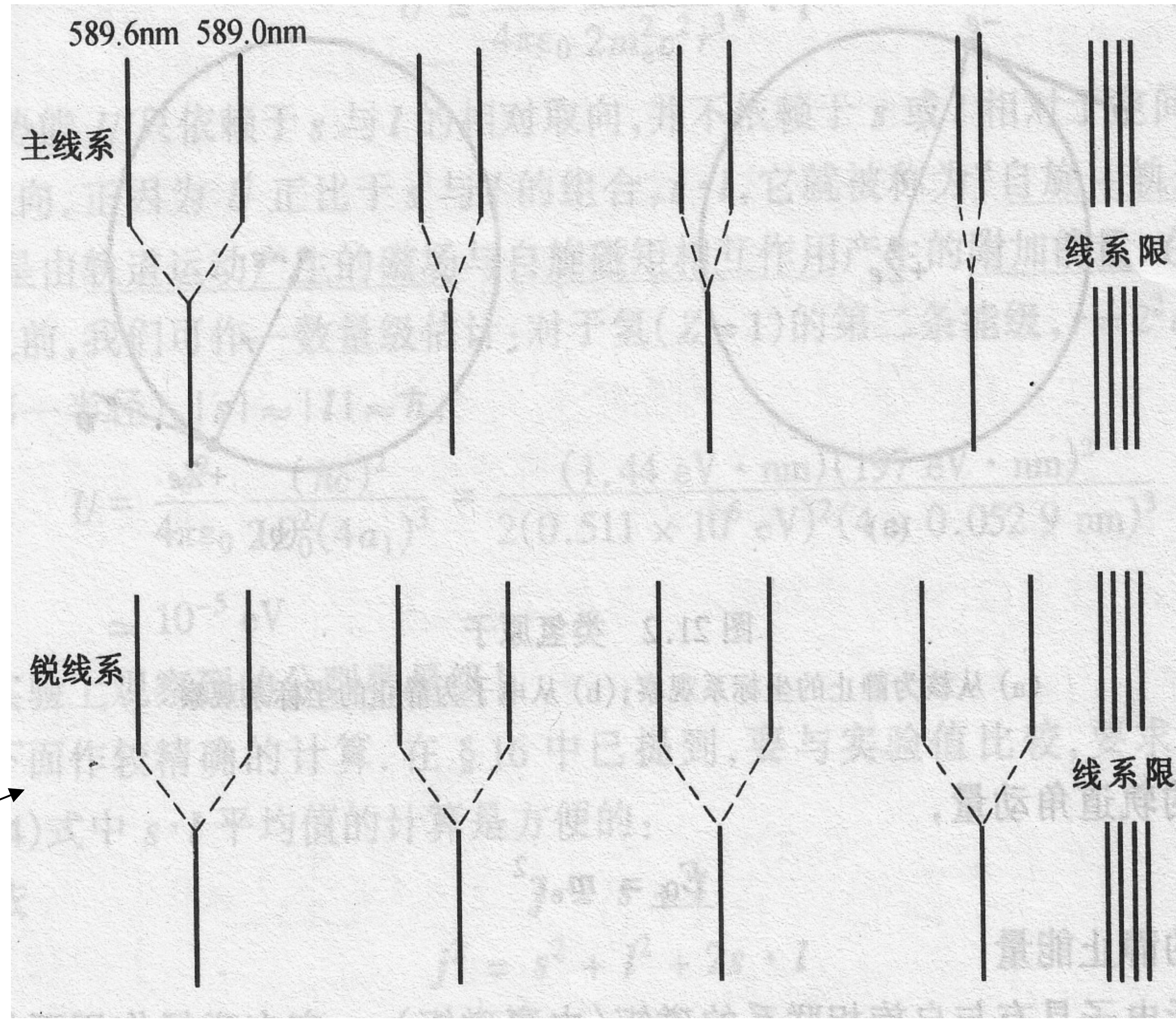
$$\boxed{E_{nl} = -T(n,l)hc}$$

- Doublets spectral of alkali metal

principle

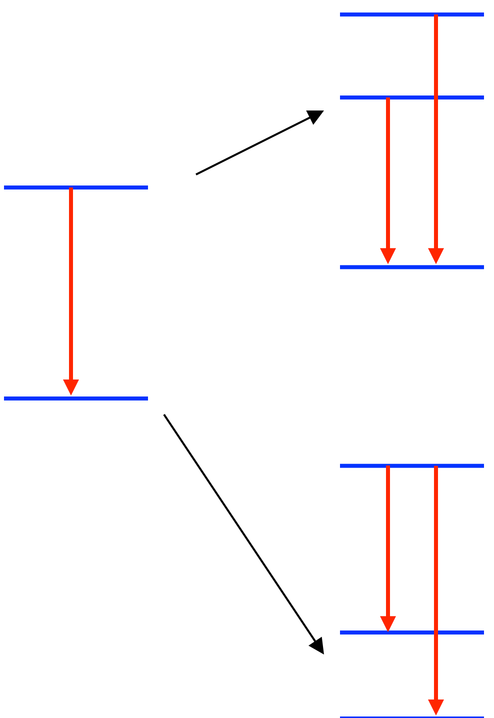
not single line, but doublet , triplet lines

sharp



understanding the doublet lines

one line splits into two lines : → Intial state or final state splitting,



Intial state splitting

principle series splitting

$$\boldsymbol{nP \rightarrow 2S} \Rightarrow n^2P_{1/2}, n^2P_{3/2} \rightarrow 2^2S_{1/2}$$

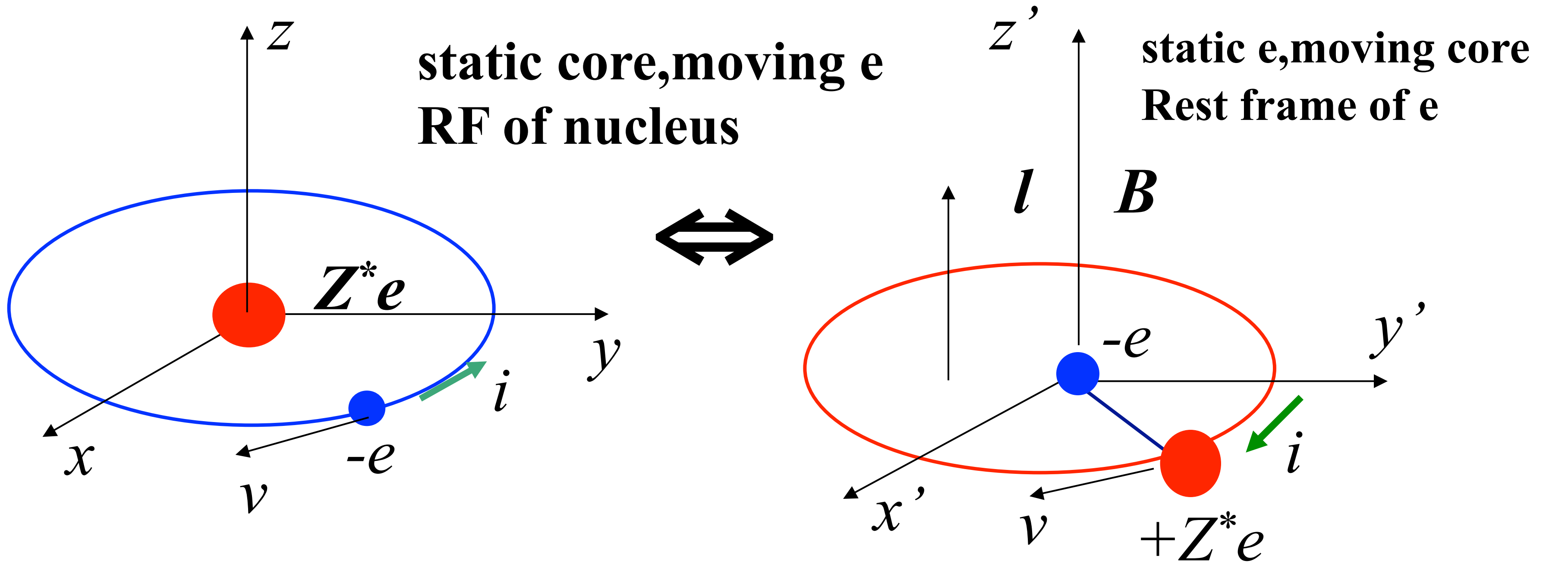
Final state splitting

sharp series splitting

$$\boldsymbol{nS \rightarrow 2P} \Rightarrow n^2S_{1/2} \rightarrow 2^2P_{1/2}, 2^2P_{3/2}$$

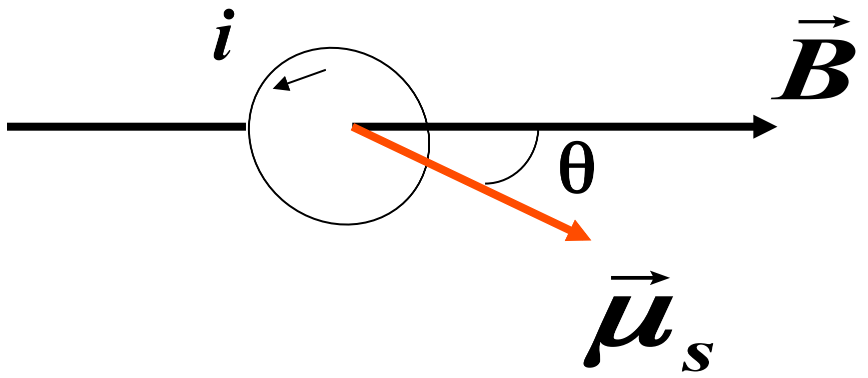
4.4.2.spin-robit interaction: quantitative

- SL interaction induces fine structure



For static electron, moving core circling around the electron with *v* , electron in the magnetic field B by the current of core with spin and spin magnetic moment (SMM) μ_s .

- SL interaction induces fine structure



– **Th spinMM μ_s produces magnetic energy**

$$U = -\vec{\mu}_s \cdot \vec{B}$$

The magnetic induction B produced by i of core

$$\vec{B} = -\frac{\mu_0}{4\pi}\frac{Z^* e\,\vec{v}\times\vec{r}}{r^3} = \frac{\mu_0}{4\pi}\frac{Z^* e}{m_e r^3}\vec{l}$$

$$= \frac{Z^* e}{4\pi\varepsilon_0 m_e c^2 r^3}\vec{l}$$

$$= \frac{Z^* e}{4\pi\varepsilon_0 E_0 r^3}\vec{l}$$

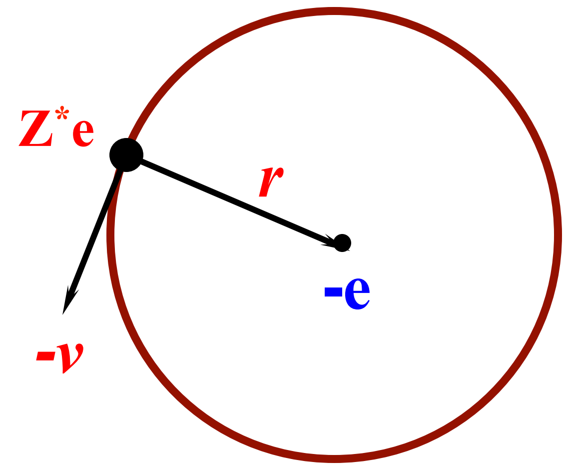
$$\boxed{\vec{l} = m_e \vec{r}\times\vec{v}}$$

Electron orbital L

$$\boxed{\frac{1}{c^2} = \mu_0\varepsilon_0}$$

$$\boxed{E_0 = m_e c^2}$$

Static energy



– **Spin MM of the valence electrons**

$$\vec{\mu}_s = -g_s \cdot \frac{\mu_B}{\hbar} \vec{s}$$

– $\boldsymbol{\mu_s}$ **'s magnetic energy in *B***

$$\vec{B} = \frac{Z^* e}{4\pi\varepsilon_0 E_0 r^3} \vec{l}$$

$$U = -\vec{\mu}_s \cdot \vec{B} = \frac{1}{4\pi\varepsilon_0} \frac{Z^* g_s \mu_B e}{E_0 \hbar r^3} \vec{s} \cdot \vec{l}$$

With relativity

$$\rightarrow U = \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \frac{Z^* g_s \mu_B e}{E_0 \hbar r^3} \vec{s} \cdot \vec{l}$$

- **The Magnetic E of SMM μ_s in B**

$$\boxed{U = \frac{1}{4\pi\varepsilon_0}\frac{Z^* e^2}{2m_e^2 c^2}\frac{1}{r^3}\vec{s}\cdot\vec{l}}$$

$$\boxed{g_s = 2}$$

$$\boxed{\mu_B = \frac{e\hbar}{2m_e}}$$

$$\boxed{E_0 = m_e c^2}$$

$U : \vec{s}\cdot\vec{l} \longrightarrow$ **S-L coupling**

SMM **B**

The magnitude of the Magnetic E

$$Z^* = 1,\ r = r_2 = 2^2 a_1,\ |\vec{s}| \approx |\vec{l}| = \hbar$$

$$U = \frac{1}{4\pi\varepsilon_0}\frac{Z^* e^2}{2m_e^2c^2}\frac{1}{r^3}\vec{s}\cdot\vec{l} = \frac{e^2}{4\pi\varepsilon_0}\frac{(\hbar c)^2}{2(m_ec^2)^2}\frac{1}{(4a_1)^3}$$

$$= 10^{-5}\,e\text{V}$$

The same order As experiment

$$e^2/4\pi\varepsilon_0 = 1.44\text{fm}\cdot\text{MeV} = 1.44\text{nm}\cdot\text{eV}$$

$$\hbar c = 197\text{fm}\cdot\text{MeV} = 197\text{nm}\cdot\text{eV}$$

$$m_ec^2 = 0.511\text{MeV} = 511\text{keV}$$

$$a_1 \approx 0.053\text{nm}$$

Spin-orbit coupling energy of Hydrogen

$$\vec{j} = \vec{l} + \vec{s} \longrightarrow \vec{j}^{\,2} = \vec{l}^{\,2} + \vec{s}^{\,2} + 2\vec{s}\cdot\vec{l}$$

$$\vec{s}\cdot\vec{l} = \frac{1}{2}(\vec{j}^{\,2} - \vec{s}^{\,2} - \vec{l}^{\,2}) = \frac{1}{2}[j(j+1) - s(s+1) - l(l+1)]\hbar^2$$

$$j = l \pm \frac{1}{2} \qquad = \begin{cases} \dfrac{1}{2} l\hbar^2, & j = l + \dfrac{1}{2}; \\ -\dfrac{1}{2}(l+1)\hbar^2, & j = l - \dfrac{1}{2}. \end{cases}$$

$$< \frac{1}{r^3} > = \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \psi_{nlm}^{*}\left(\frac{1}{r^3}\right)\psi_{nlm} r^2 \sin\theta \mathrm{d}r \mathrm{d}\theta \mathrm{d}\varphi$$

$$= \frac{Z^{*3}}{n^3 l(l+1/2)(l+1)a_1^3}$$

$$\boxed{\alpha = \frac{e^2}{4\pi\varepsilon_0 \mathrm{h} c}}$$

$$U = \frac{1}{4\pi\varepsilon_0}\frac{Z^{*}e^2}{2m_e^{\,2}c^2}\frac{1}{r^3}\vec{s}\cdot\vec{l}$$

$$\boxed{a_1 = \frac{\mathrm{h}}{\alpha m_{\mathrm{e}} c}}$$

$$= \frac{(\alpha Z^{*})^4 m_{\mathrm{e}} c^2}{2n^3}\left[\frac{j(j+1) - l(l+1) - s(s+1)}{l(2l+1)(l+1)}\right]$$

$$U = \frac{(\alpha Z^*)^4 m_e c^2}{2n^3}\left[\frac{j(j+1)-l(l+1)-s(s+1)}{l(2l+1)(l+1)}\right]$$

$$= \begin{cases} \dfrac{(\alpha Z^*)^4 m_e c^2}{2n^3(2l+1)(l+1)}, & j = l + \frac{1}{2}, l \neq 0 \\ -\dfrac{(\alpha Z^*)^4 m_e c^2}{2n^3 l(2l+1)}, & j = l - \frac{1}{2}, l \neq 0 \end{cases}$$

Energy difference is

$$\Delta U = \frac{Z^{*4}\alpha^4 E_0}{2n^3 l(l+1)}$$

SL coupling E→fine structure

$$E_n = -\frac{m_0 Z^{*2} e^4}{(4\pi\varepsilon_0)^2 2n^2 \mathrm{h}^2} = \frac{1}{2}\alpha^2 E_0 \frac{Z^{*2}}{n^2}, \qquad \alpha = \frac{e^2}{4\pi\varepsilon_0 \mathrm{h} c} = \frac{1}{137}$$

Coulomb interaction → gross energy level

- **2*P* splitting of Hydrogen (j=1/2,3/2)**

$$\boxed{Z^* = 1, n = 2, l = 1}$$

$$\Delta U = \frac{Z^{*4}\alpha^4 E_0}{2n^3 l(l+1)} = \frac{1\times\alpha^4 E_0}{2\times 2^3\times 1\times(1+1)}$$

$$= \frac{0.511\times 10^6\text{eV}}{2\times 2^3\times 1\times(2)\times(137)^4} = 4.53\times 10^{-5}\text{eV}$$

Agrees with experiment

- **Splitting rules of two levels**

$$\Delta U = \frac{Z^{*4}\alpha^4 E_0}{2n^3 l(l+1)}$$

$\Rightarrow$

- Decrease with increasing ***n***
- **Decrease with increasing *l***
- Increase with increasing Z^*

$\downarrow$

Agrees with experiments

•**2p spliiting of H** $\Delta U = 4.53\times10^{-5}\,\text{eV}$

Observable w hight-resolution spectrometer

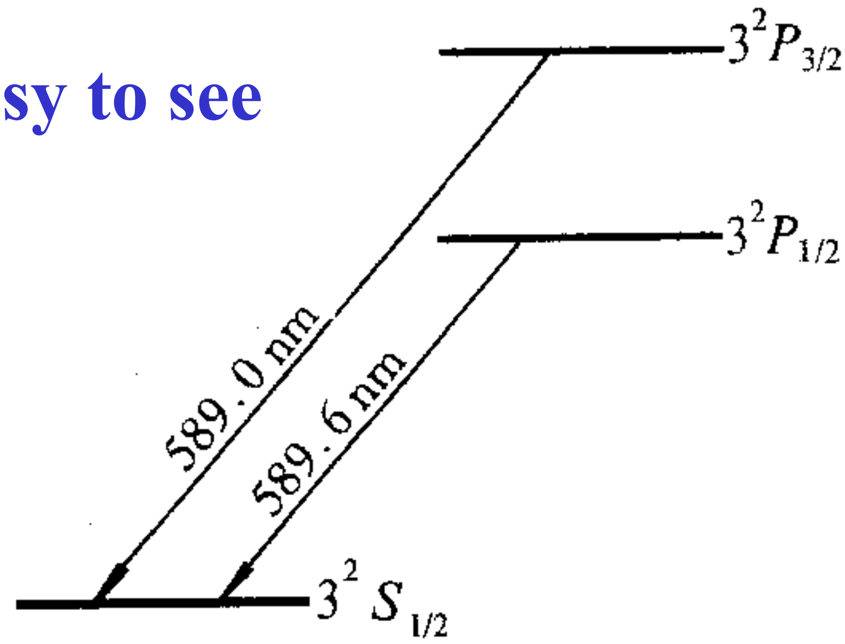
•**Famous yellow doublets in sodium Na**

$\Delta U = 2.1\times10^{-3}\,\text{eV}$ **easy to see**

$$\Delta U = \frac{Z^{*4}\alpha^4 E_0}{2n^3 l(l+1)}$$

$$l = 1, n = 3$$

$$\rightarrow Z^* = 3.5$$



4.5. Zeaman Effect

- The Normal Zeaman effect
- The polarization characterof the Zeaman spectra
- The anomalous Zeaman effect
- Grotrian Diagram

4. 5. 1. Normal Zeaman Effect

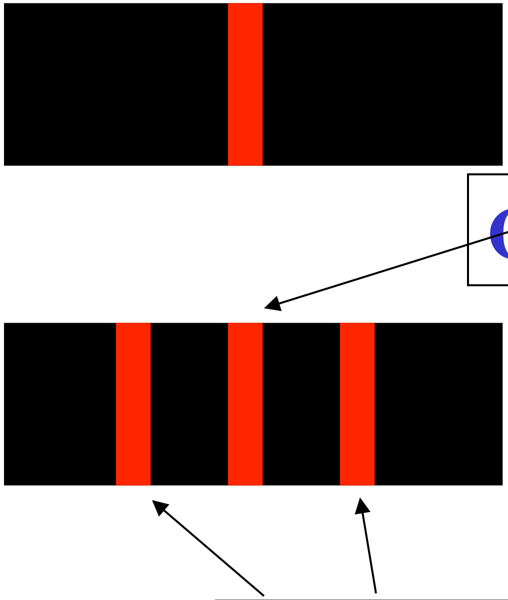
– **The spectral line emitted from a spin 0 atom is splitted into three equal-distance lines under B**

镉Cadmium

$^{1}D_{2} \rightarrow {}^{1}P_{1}$

wo $\boldsymbol{B}$

$\perp \vec{B}$



Why?

- **Atom had a MM** $\vec{\mu}$
- Under ***B, there is a magnetic potential energy***

$$U = -\vec{\mu} \cdot \vec{B} = -\mu_z B$$

$$= mg\mu_B B \qquad \boxed{\mu_z = -mg\mu_B}$$

- **Without B, the optical transition between two atomic levels** E_2 , E_1

$$h\nu = E_2 - E_1$$

$$h\nu = E_2 - E_1$$

Without *B*

$$E_2 + m_2 g_2 \mu_B B \qquad E_1 + m_1 g_1 \mu_B B$$

Under *B*

– **With B ,the transition energy will be**

$$h\nu' = h\nu + (m_2 g_2 - m_1 g_1)\mu_B B$$
$$= h\nu + (m_2 - m_1)\mu_B B$$

For total Spin zero

→ $g_2 = g_1 = 1$

$$h\nu' = h\nu + (m_2 - m_1)\mu_B B$$

$$= h\nu + \begin{bmatrix} \mu_B B \\ 0 \\ -\mu_B B \end{bmatrix}$$

Selection rule

$\Delta m = 0, \pm 1$

Under B, one spectral line is splitted into 3 with equal distance

$\mu_B B$

Explain the normal zeaman effect successfully!

Eg : Cadmium S=0 (1)

w/o B

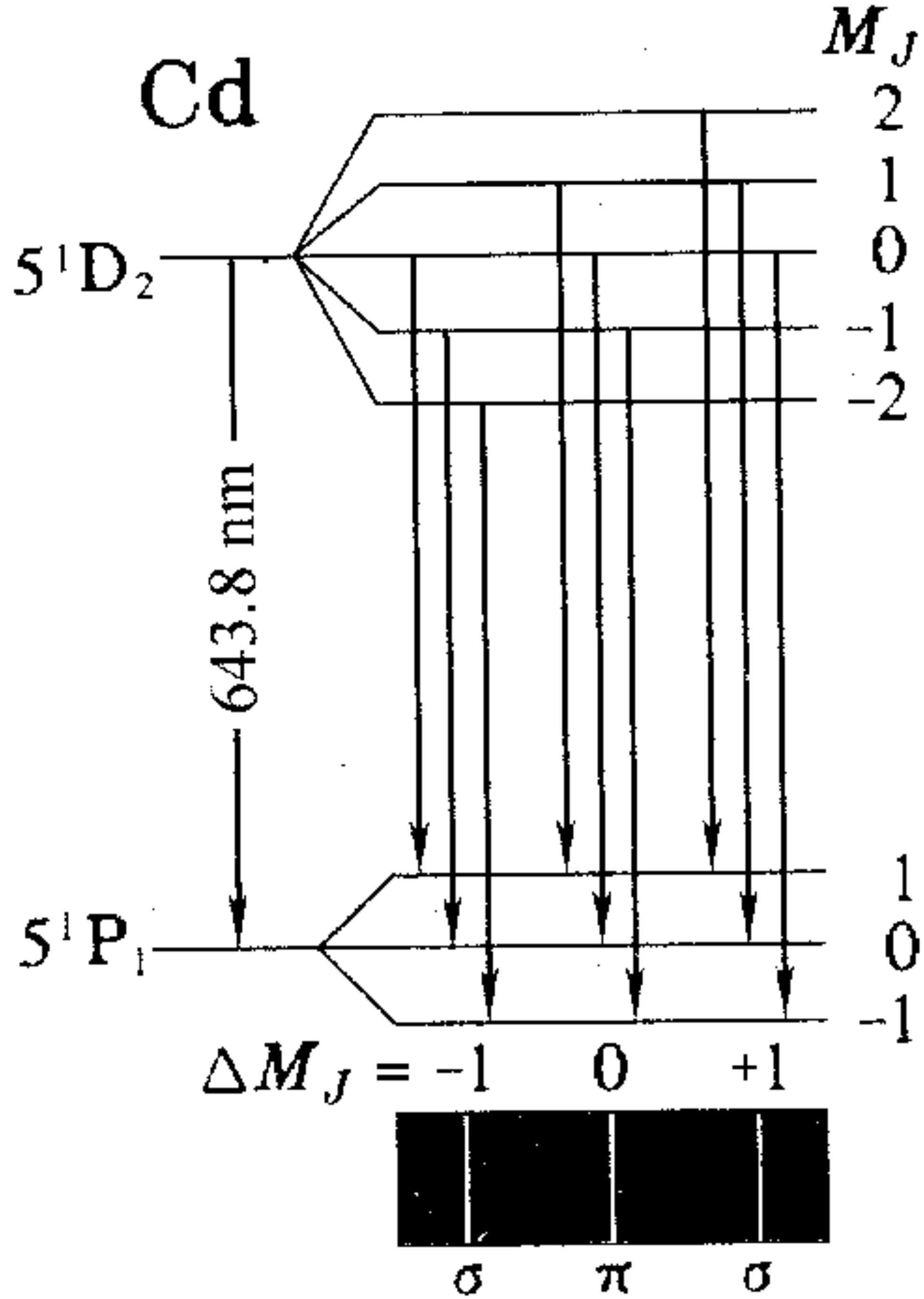
w/ B $\quad {}^1D_2 \longrightarrow {}^1P_1$

$\downarrow$ **Split 5** $\qquad \downarrow$ **Split 3**

9 transitions

3 energy gaps

3 spectral lines



For Cadmium , 9 transitions, 3 energy gaps

$$h\nu' = h\nu + \begin{bmatrix} \mu_B B \\ 0 \\ -\mu_B B \end{bmatrix} \qquad \nu' = \nu + \begin{bmatrix} \dfrac{eB}{4\pi m_e} \\ 0 \\ -\dfrac{eB}{4\pi m_e} \end{bmatrix}$$

Lorentz unit

Lorentz unit ←→**Lamor freq.**

$$\nu = \frac{\omega}{2\pi} = \frac{eB}{2m_e}\frac{1}{2\pi} = \frac{eB}{4\pi m_e}$$

$$\boxed{\frac{d\vec{\mu}}{dt} = \vec{\omega} \times \vec{\mu}}$$

Lamor precess velocity

$$\frac{d\nu}{dB} = \frac{e}{4\pi m_e} = 14\text{GHz/T}$$

Each T of B induces 14GHz splitting

Zeeman effect & charge-mass ratio

- Normal Zeeman effect with equal E gap

$$\Delta E = \mu_B B$$

measuring $\Delta E, B \rightarrow \mu_B$

$$\mu_B = \frac{e\hbar}{2m_e}$$

giving $\hbar \rightarrow \dfrac{e}{m_e}$

$\boxed{\textbf{agree with other method}}$

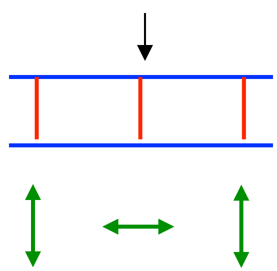
The polarization character of Zeeman spectrum

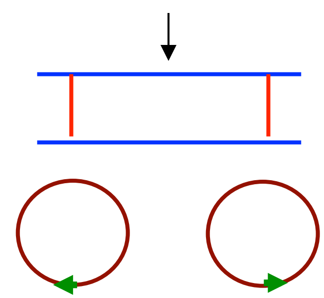
- Observation of the PL character

镉Cadmium $\perp \vec{B}$ Linear PL // $\boldsymbol{B}$, **Circular PL**

$^1D_2 \rightarrow {}^1P_1$

splitting





$\boldsymbol{\sigma}$ $\boldsymbol{\pi}$ $\boldsymbol{\sigma}$ $\qquad$ $\boldsymbol{\sigma^-}$ $\boldsymbol{\sigma^+}$

$\Delta m =$ **-1 0 +1** $\qquad$ $\Delta m =$ **-1 +1**

Π: Ev // B

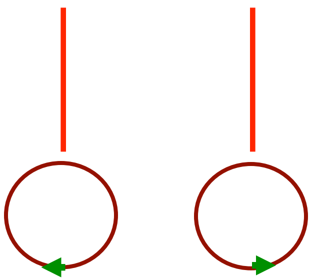
Σ Ev $\perp \vec{B}$

σ^- right-hand

σ^+ left-hand

// B observing, Circular PL

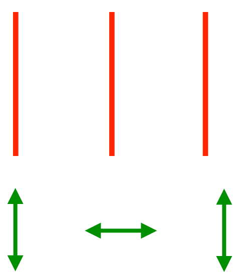
σ^- σ^+



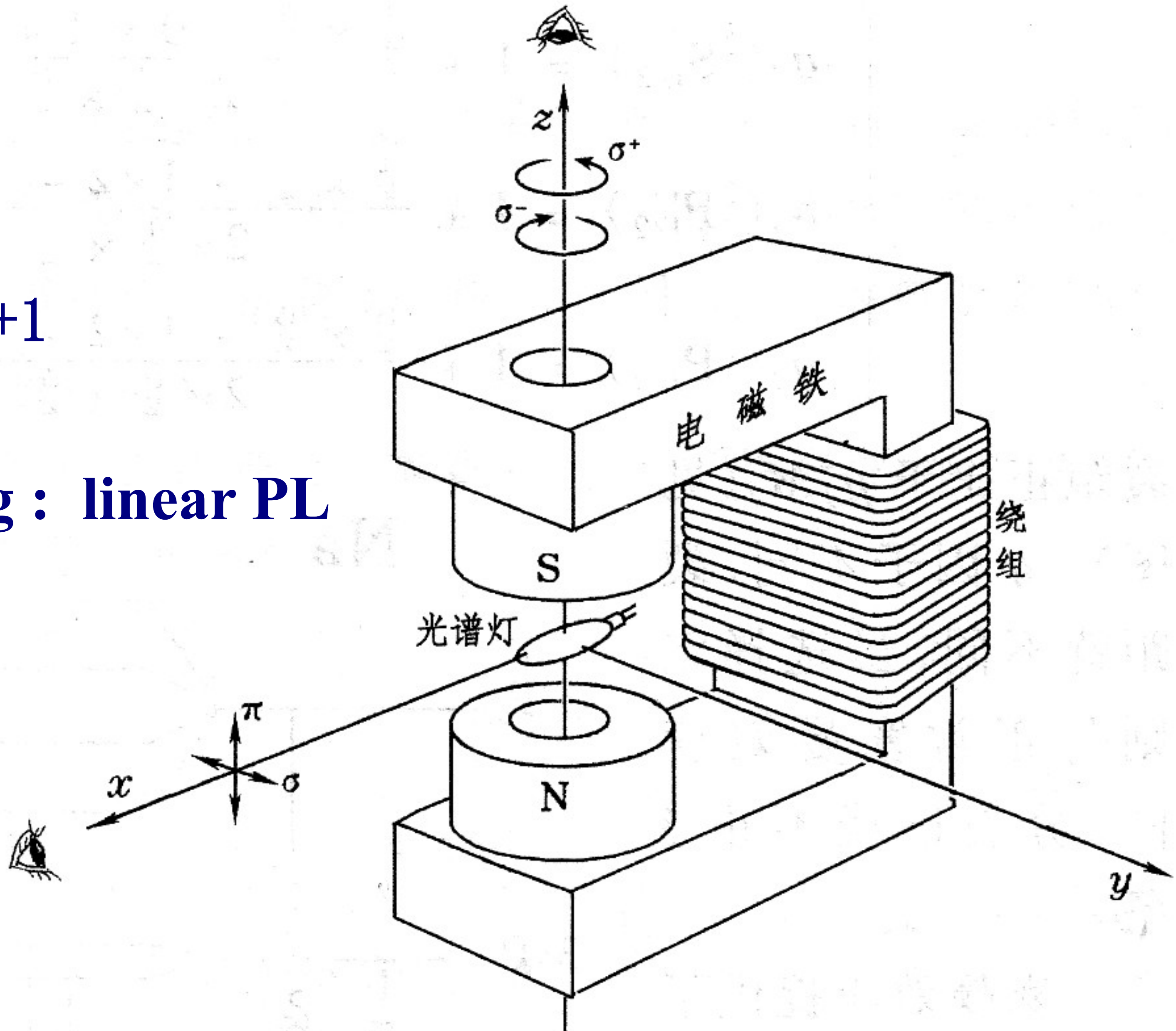
Δm -1 $+1$

$\perp \vec{B}$ observing : linear PL

σ π σ



Δm -1 0 +1



Theorectic explaination of PL

- For circular PL

  EM waves along z, its E vector lies in the *xy plan*, can be resolved into :

$$E_x = A\cos\omega t, \qquad E_y = B\cos(\omega t - \alpha)$$

$\alpha = 0 \rightarrow$ linear PL

$\alpha = \pi/2, A = B \rightarrow$ Circular PL

- Right-hand σ^-

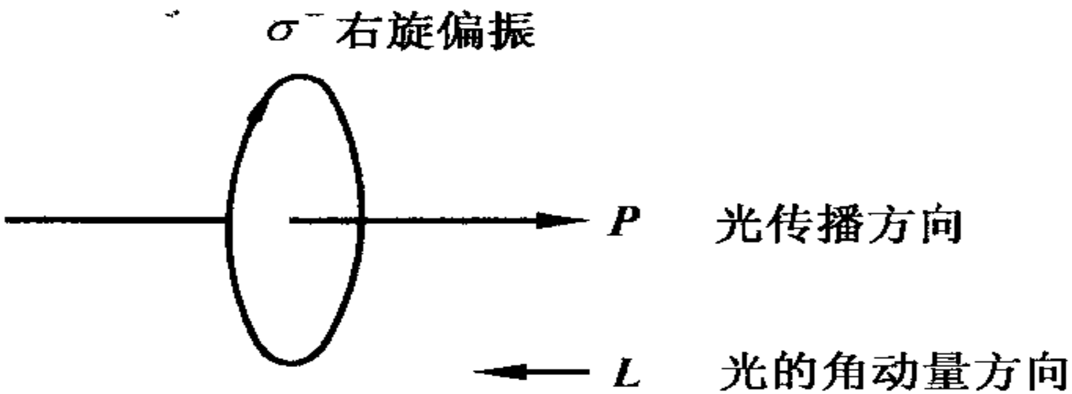
  looking at light as it travels to us along *z* ,if the end of Ev goes around clockwise, we call it Right-hand

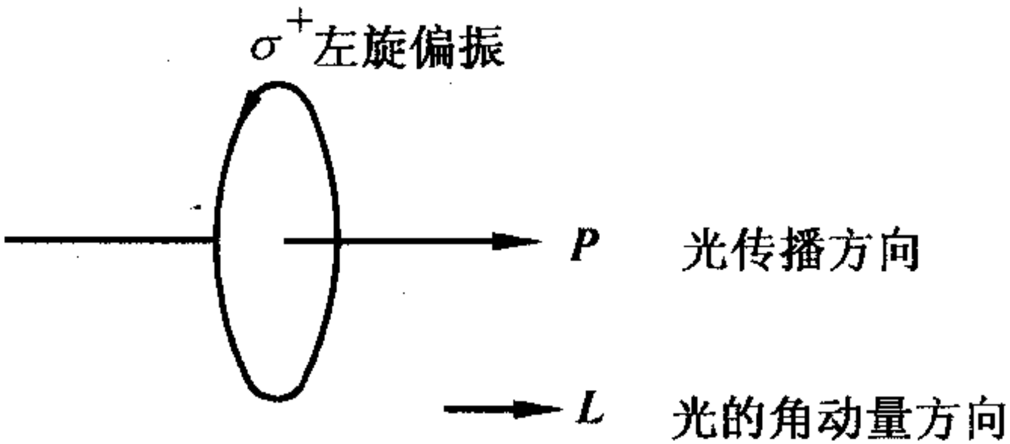
- Left-hand σ^+

- **looking at light as it travels to us along *z* ,if the end of Ev goes around counter clockwise, we call it left-hand**

Definitions of the PL and the direction of angular momentum

– **Angular M direction depends on the rotation direction Ev in the right-hand screw sense**





AM conservation explains the PL

a photon has AM $j=1$

- The AM of the system (atom+photon) conserv.

$\Delta m = m_1 - m_2 = +1$ **transition**

m **loses 1 unite**

AM conservation

→photon : $m = 1$

photon $j=1$

→ Photon AM along z

RH screw relation

→**observ along** z, LH **σ**+

Transerve wave

→Ev lies in xy-plane; **observe along *x*, LPL along y**

AM conservation explains the PL

a photon has AM $j=1$

- The AM of the system (atom+photon) conserv.

$$\Delta m = m_1 - m_2 = -1$$

AM conservation

***m* increases 1 unite**

→photon : $m = -1$

photon $j=1$

→ Photon AM along $-z$

RH screw relation

→**observ along *z*,** RH

Transerve wave

→Ev lies in xy-plane; **observe along *x*, LPL along y**

$\Delta m = m_1 - m_2 = 0$ **transition**

AM conservation

***m* unchanged**

→photon ： $m = 0$

Photon j=1

→j ⊥ $\vec{B}$ ， **lies in *xy***

RH Screw

→Ev lies in ***yz plane***

transverse

along *z*， see nothing

→**along *x*， see linear PL in z**

4-5-3 Anomalous Zeeman Effect

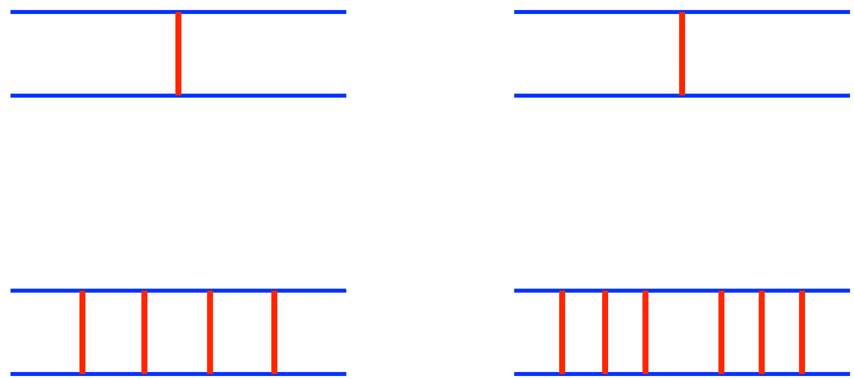
- Observation **The spectral line is splitted into more than three lines under B**

Na Sodium

$2^2P_{1/2} \rightarrow 2^2S_{1/2}$ $\quad$ $2^2P_{3/2} \rightarrow 2^2S_{1/2}$

Wo/ B

$\perp \vec{B}$



Why?

- **Atom had a MM** $\vec{\mu}$
- Under ***B, there is a magnetic potential energy***

$$U = -\vec{\mu}\cdot\vec{B} = -\mu_z B$$

$$= mg\mu_B B \qquad \boxed{\mu_z = -mg\mu_B}$$

- **Without B, the optical transition between two atomic levels E_2 , E_1**

$$h\nu = E_2 - E_1$$

$$h\nu = E_2 - E_1$$

Without *B*

$$E_2 + m_2 g_2 \mu_B B \qquad E_1 + m_1 g_1 \mu_B B$$

Under *B*

– **With B ,the transition energy will be**

$$h\nu' = h\nu + (m_2 g_2 - m_1 g_1)\mu_B B$$

$$g_J = \frac{3}{2} + \frac{1}{2}\left(\frac{\hat{S}^2 - \hat{L}^2}{\hat{J}^2}\right)$$

Theoretical explaination

- 钠sodium

$$2^2P_{1/2} \rightarrow 2^2S_{1/2} \qquad 2^2P_{3/2} \rightarrow 2^2S_{1/2}$$

	m_J	g_J	$m_J g_J$
$^2P_{3/2}$	$\pm 3/2, \pm 1/2$	$4/3$	$\pm 2, \pm 2/3$
$^2P_{1/2}$	$\pm 1/2$	$2/3$	$\pm 1/3$
$^2S_{1/2}$	$\pm 1/2$	2	± 1

$$2^2P_{1/2} \rightarrow 2^2S_{1/2}$$

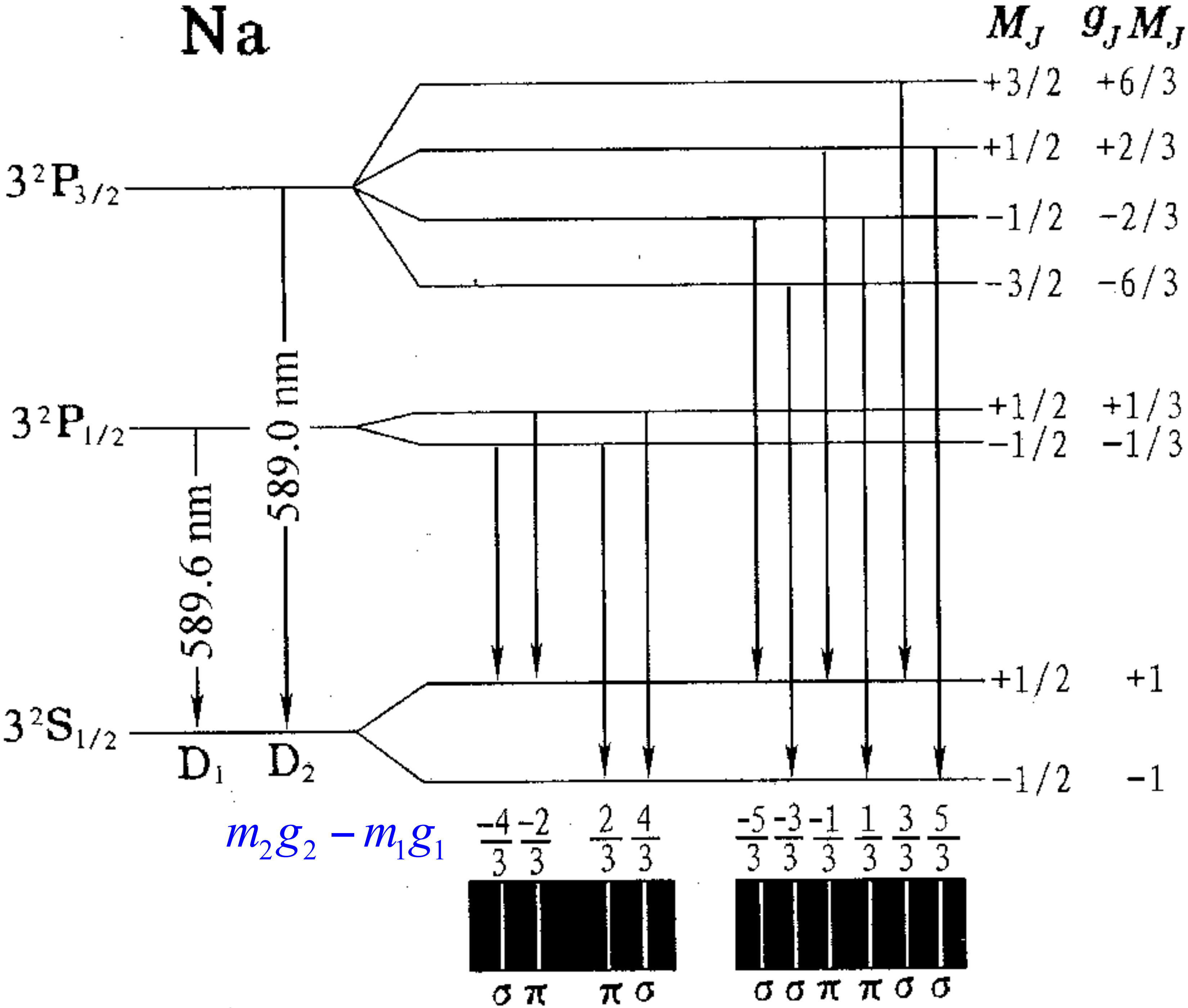
$$m_2 g_2 - m_1 g_1 = -\frac{4}{3}, -\frac{2}{3}, \frac{2}{3}, \frac{4}{3}$$

$$2^2P_{1/2} \rightarrow 2^2S_{1/2}$$

$$m_2 g_2 - m_1 g_1 = -\frac{5}{3}, -\frac{3}{3}, -\frac{1}{3}, \frac{1}{3}, \frac{3}{3}, \frac{5}{3}$$

Selection rule

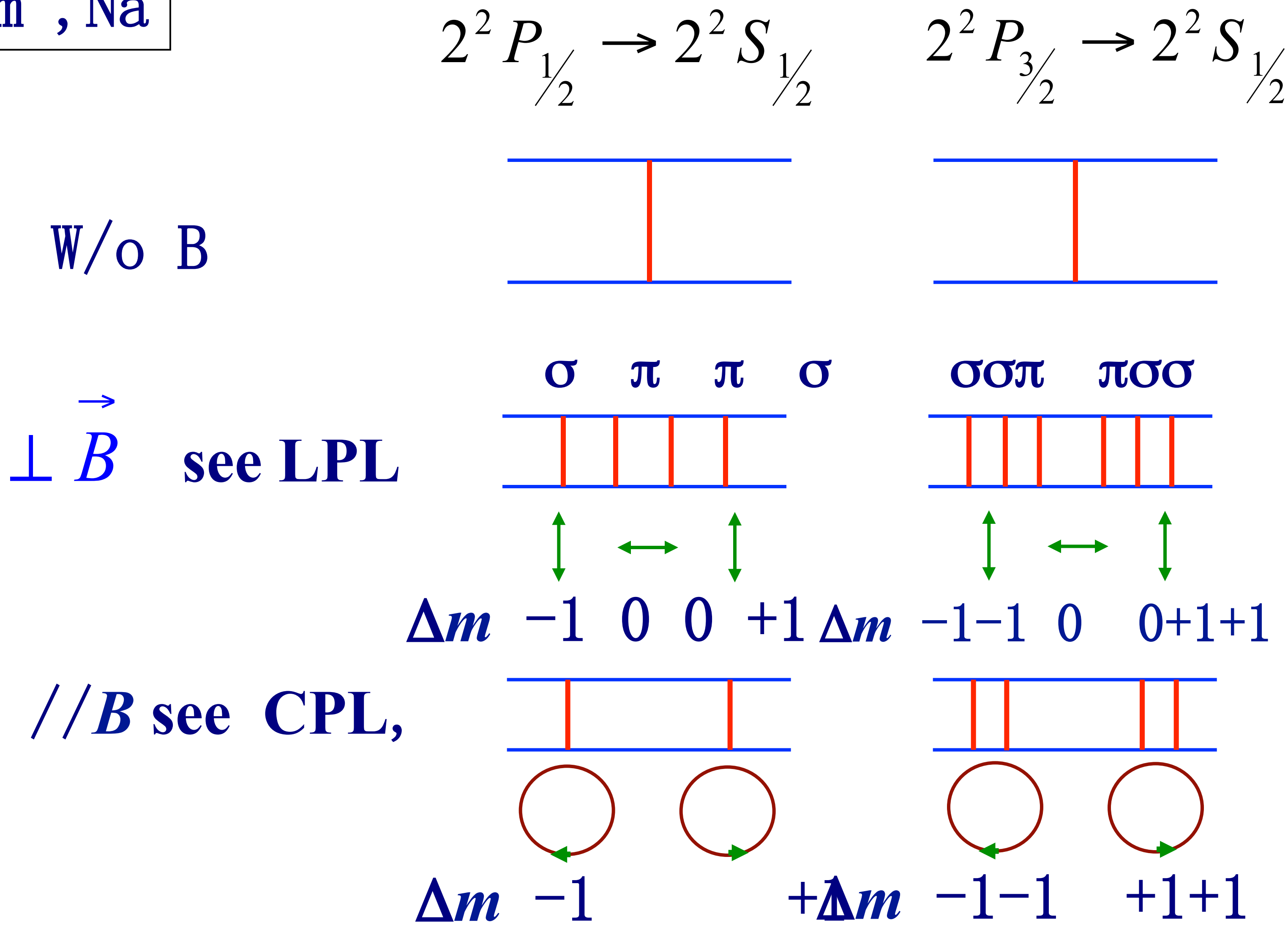
$$\boxed{\Delta m = 0, \pm 1}$$



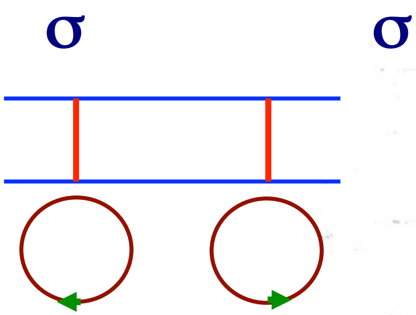
Na
M_J $g_J M_J$
$3^2P_{3/2}$
$+3/2$ $+6/3$
$+1/2$ $+2/3$
$-1/2$ $-2/3$
$-3/2$ $-6/3$
589.0 nm
$3^2P_{1/2}$
$+1/2$ $+1/3$
$-1/2$ $-1/3$
589.6 nm
$3^2S_{1/2}$
$+1/2$ $+1$
$-1/2$ -1
D_1 D_2
$m_2g_2 - m_1g_1$
$\frac{-4}{3}$ $\frac{-2}{3}$ $\frac{2}{3}$ $\frac{4}{3}$
$\frac{-5}{3}$ $\frac{-3}{3}$ $\frac{-1}{3}$ $\frac{1}{3}$ $\frac{3}{3}$ $\frac{5}{3}$
σ π π σ
σ σ π π σ σ

• Observing Anomalous Zeeman Effect

Sodium , Na

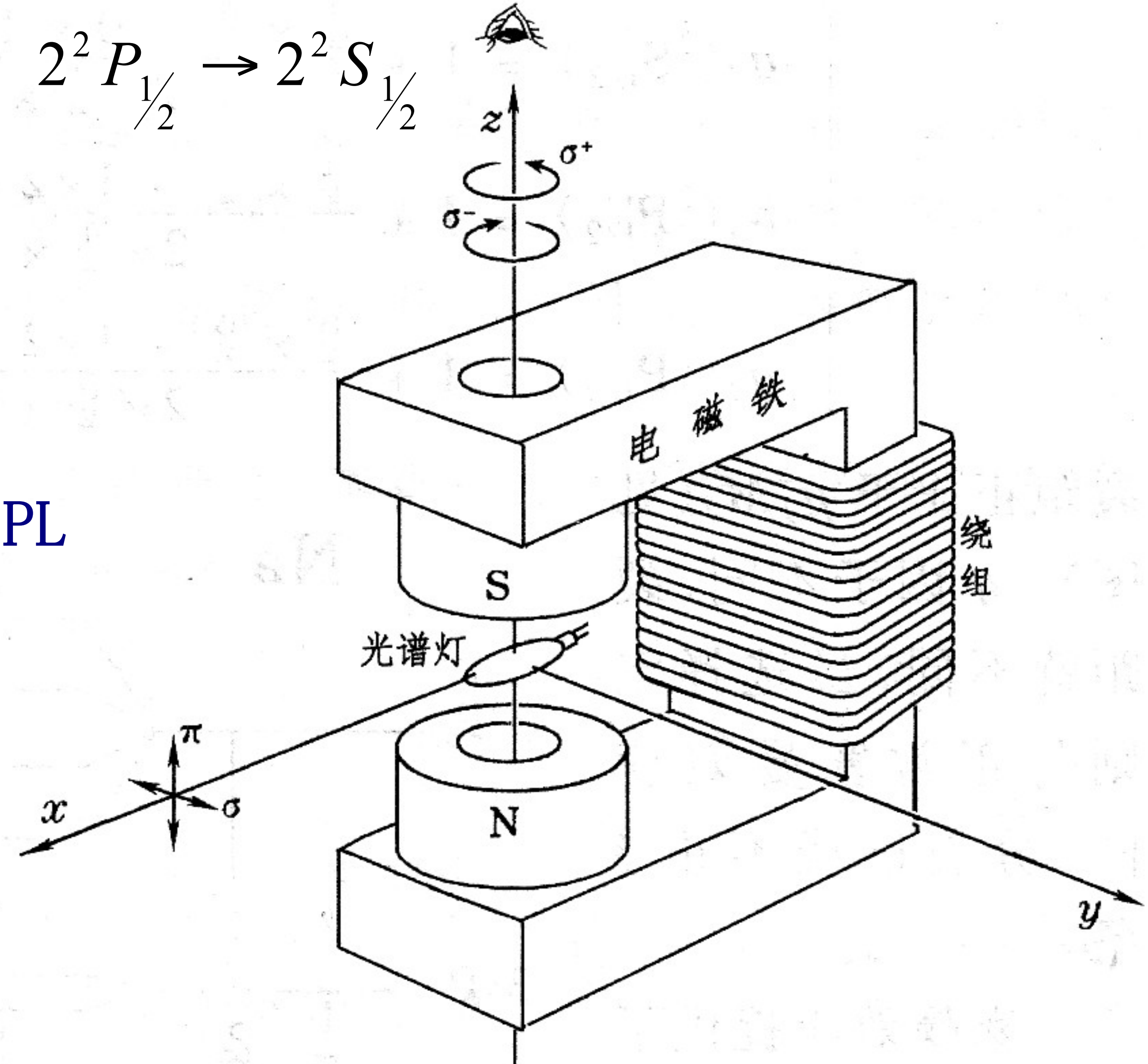


// B see circular PL

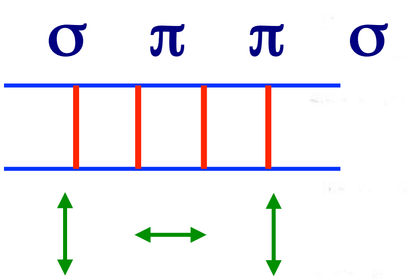


Δm −1 +1

$$2^2P_{1/2} \rightarrow 2^2S_{1/2}$$



$\perp \vec{B}$ see Linear PL

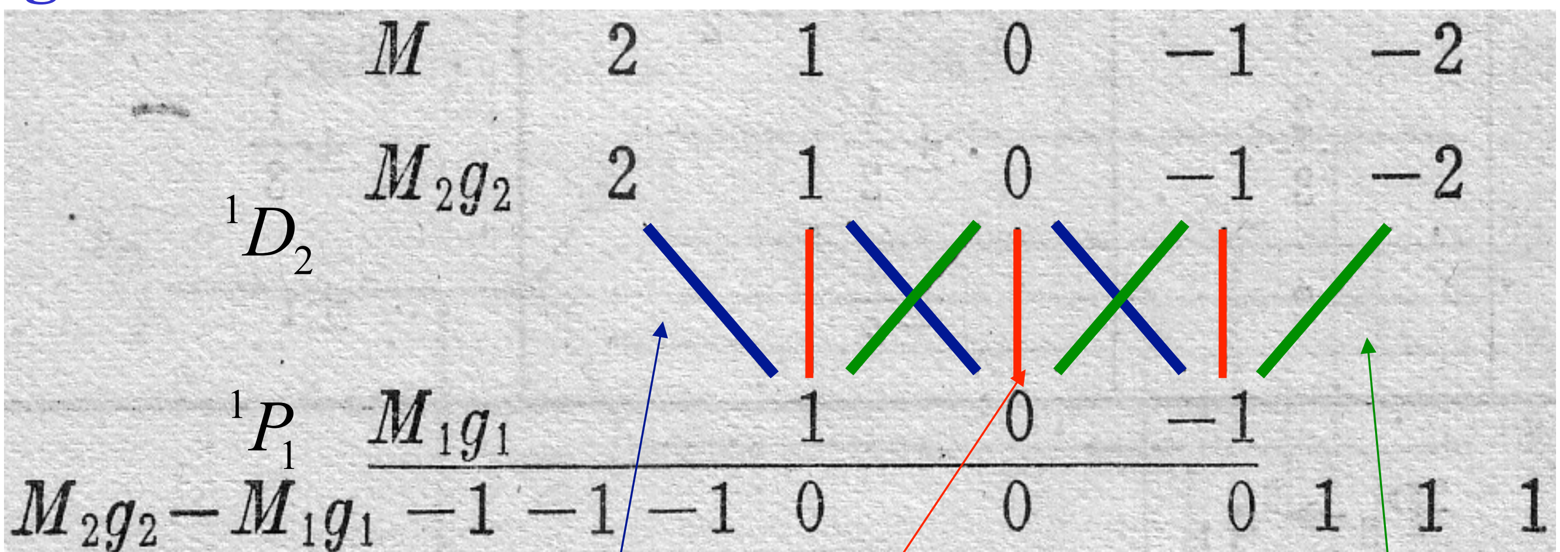


Δm −1 0 0 +1

4.5.4. Grotrian Diagram

- **Simplified method to compute Zeeman E level splitting**
- E.g. Cadmium 镉

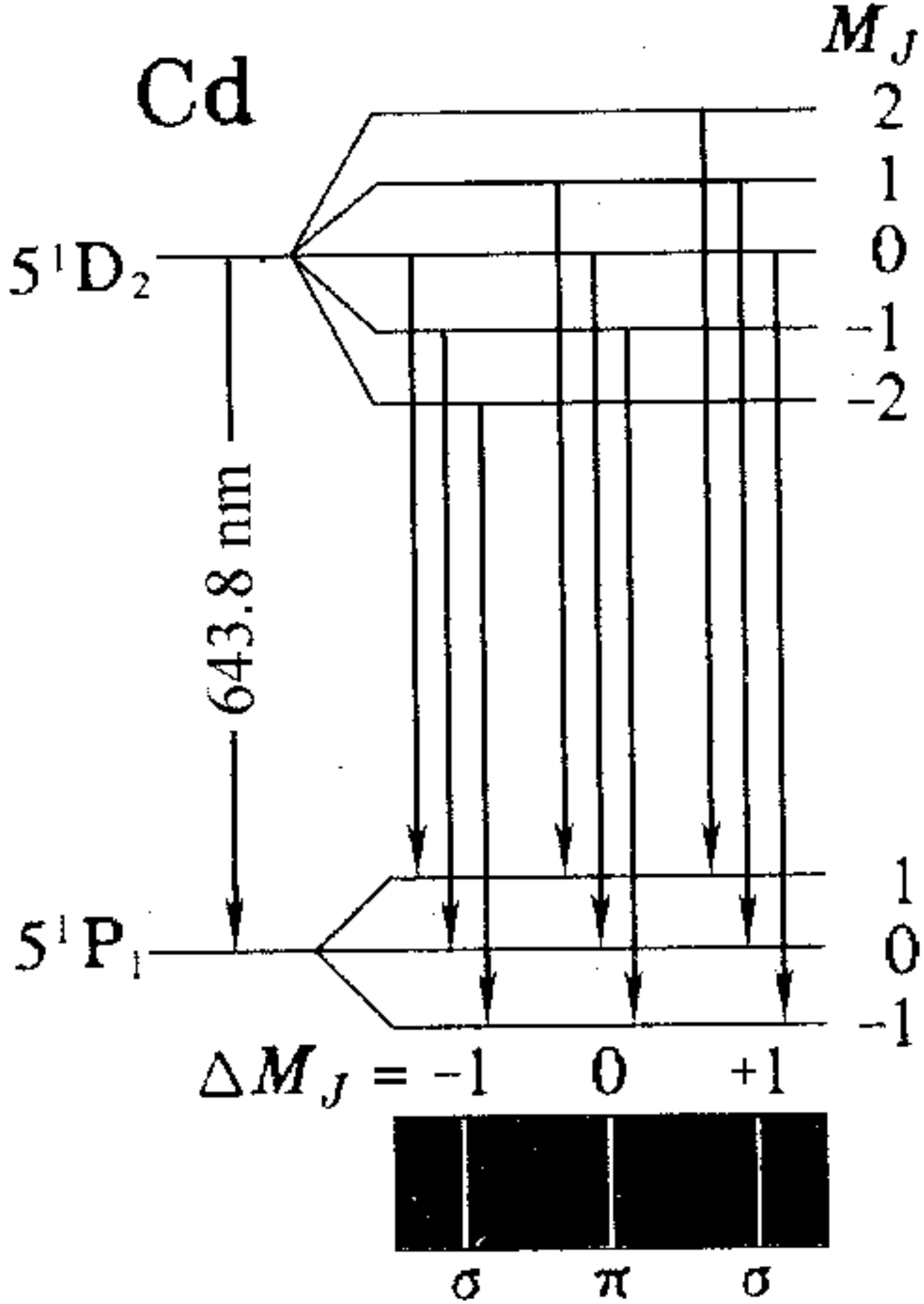
$$^1D_2 \rightarrow {}^1P_1$$



$\Delta M = 0$

$\Delta M = +1$ $\Delta M = -1$

9 transitions
3 lines of energy



9 transitions
3 lines of EL

Eg: Sodium $2^2P_{3/2} \rightarrow 2^2S_{1/2}$

– data table

M	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$
M_2g_2	$\frac{6}{3}$	$\frac{2}{3}$	$-\frac{2}{3}$	$-\frac{6}{3}$
M_1g_1		1	-1	

$$M_2g_2 - M_1g_1 \quad -\frac{5}{3} \quad -\frac{3}{3} \quad -\frac{1}{3} \quad +\frac{1}{3} \quad +\frac{3}{3} \quad +\frac{5}{3}$$

$\Delta M = +1$ $\quad$ $\Delta M = 0$ $\quad$ $\Delta M = -1$

6 transitions
6 lines of EL

- **E.g：Sodium** $2^2P_{1/2} \rightarrow 2^2S_{1/2}$
  - Data table

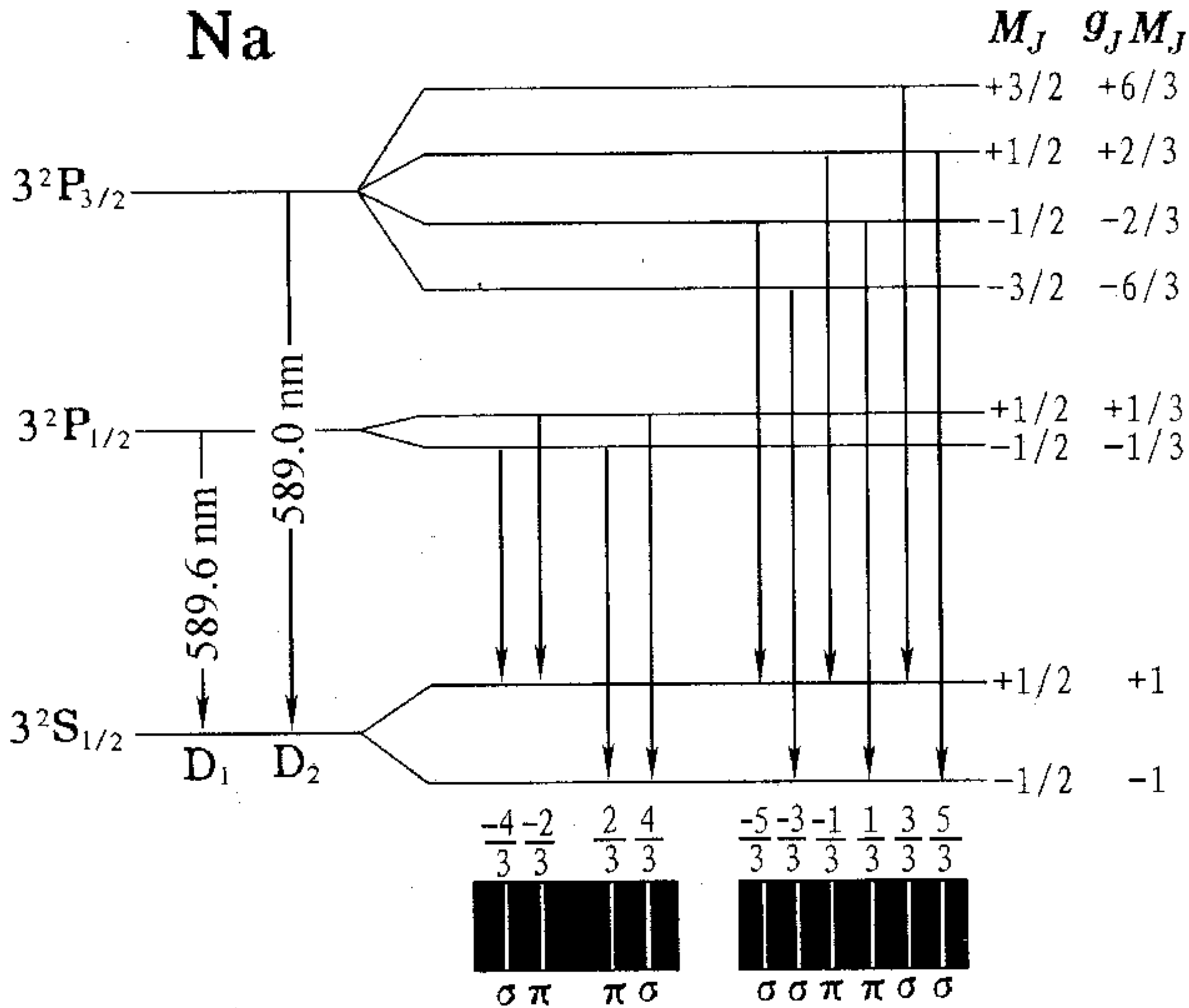
M	$\frac{1}{2}$		$-\frac{1}{2}$	
M_2g_2	$\frac{1}{3}$		$-\frac{1}{3}$	
M_1g_1	1		-1	
$M_2g_2 - M_1g_1$	$-\frac{4}{3}$	$-\frac{2}{3}$	$+\frac{2}{3}$	$+\frac{4}{3}$

$\Delta M = 0$

$\Delta M = -1$

$\Delta M = +1$

4 transitions
4 lines of EL



Na
M_J $g_J M_J$
$3^2P_{3/2}$
$3^2P_{1/2}$
$3^2S_{1/2}$
589.0 nm
589.6 nm
D_1 D_2
+3/2 +6/3
+1/2 +2/3
−1/2 −2/3
−3/2 −6/3
+1/2 +1/3
−1/2 −1/3
+1/2 +1
−1/2 −1
$-\frac{4}{3}$ $-\frac{2}{3}$ $\frac{2}{3}$ $\frac{4}{3}$
$-\frac{5}{3}$ $-\frac{3}{3}$ $-\frac{1}{3}$ $\frac{1}{3}$ $\frac{3}{3}$ $\frac{5}{3}$
σ π π σ
σ σ π π σ σ

4.6. Summary of Hydrogen Energy Spectra

- **Bohr E spectral (1913):**
  - **Consider the static electric interaction between eN ;**

$$T_n = -\frac{E}{hc} = \frac{R}{n^2}$$

Explained Balmer series

- **Sommerfeld**（1916）
  - **Elliptic orbits and relativistic effect**

$$T_{n,k} = \frac{R}{n^2} + \frac{R\alpha^2}{n^4}\left(\frac{n}{k} - \frac{3}{4}\right)$$

$$k = 1, 2, \ldots, n$$

Agress with precise measurement

- **Heisenberg(1926):** **with quantum mechanics**

$$T_{n,l} = \frac{R}{n^2} + \frac{R\alpha^2}{n^4}\left(\frac{n}{l + \frac{1}{2}} - \frac{3}{4}\right) = \frac{R}{n^2} + \Delta T_r$$

disagree with data

- **Dirac (1928)**
  - **RQM with spin of electron**

$$T_{n,j} = \frac{R}{n^2} + \frac{R\alpha^2}{n^4}\left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4}\right) = \frac{R}{n^2} + \Delta T_r + \Delta T_{l,s}$$

Agree with experiments. Coincides with Sommerfeld (*k* ↔ *j*+1/2), but physically total different

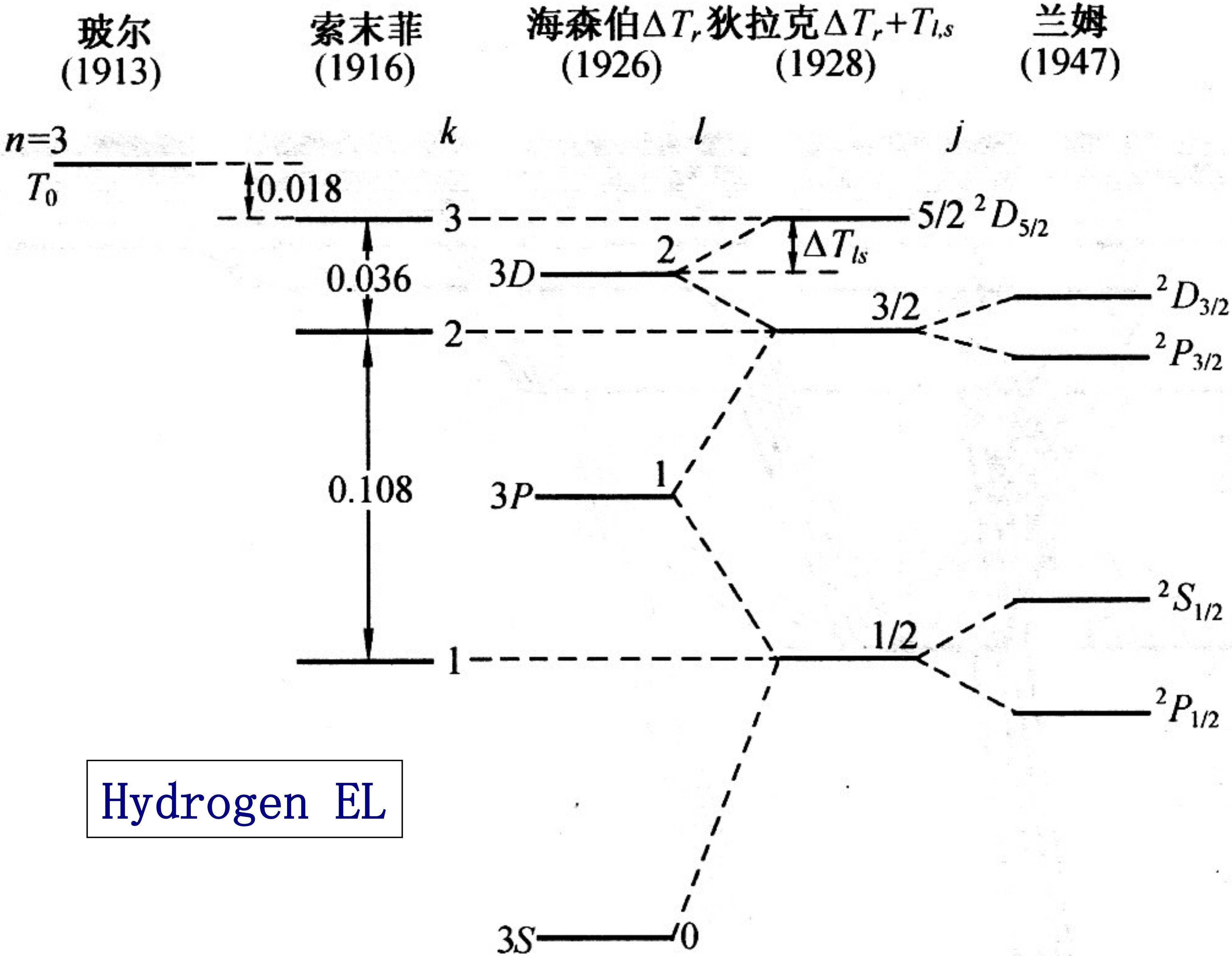
- $T_n \sim j, n$, ***with fixing j, n*** **,energy levels are degenerate wrt** l

$$3\,{}^2P_{1/2}\ \mathbf{w}\ \ 3\,{}^2S_{1/2} \qquad 3\,{}^2D_{3/2}\ \mathbf{w}\ \ 3\,{}^2P_{3/2} \qquad 2\,{}^2P_{1/2}\ \mathbf{w}\ \ 2\,{}^2S_{1/2}$$

- **Lamb shift(1974)**
  - precise measurement detected

$2\,{}^2P_{1/2} \qquad 2\,{}^2S_{1/2}$ **Energy splitting**

$\boxed{\textbf{Need QED}}$


玻尔
(1913)
索末菲
(1916)
海森伯ΔT_r
(1926)
狄拉克$\Delta T_r+T_{l,s}$
(1928)
兰姆
(1947)
$n=3$
T_0
k
l
j
0.018
0.036
0.108
3
2
1
$3D$
$3P$
$3S$
2
1
0
ΔT_{ls}
5/2
3/2
1/2
$^2D_{5/2}$
$^2D_{3/2}$
$^2P_{3/2}$
$^2S_{1/2}$
$^2P_{1/2}$

Hydrogen EL

- $H_\alpha(n=3 \rightarrow n=2)$ **fine structure spectra**