

# 第四章 外场中的原子

4.1 塞曼效应

\*4.2 磁共振技术

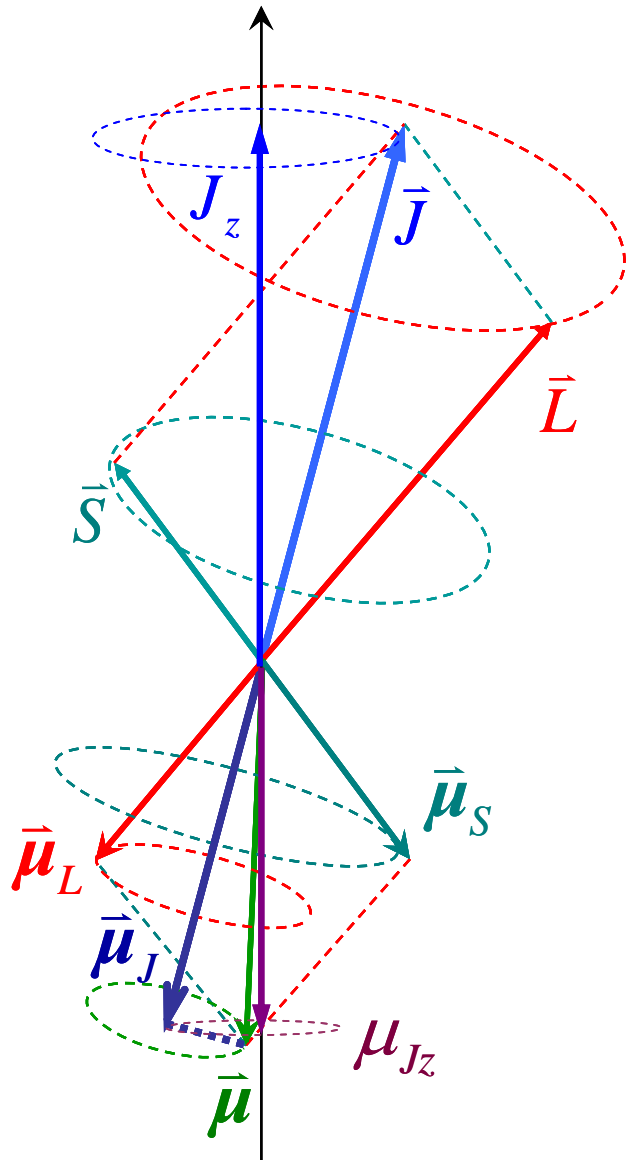
\*4.3 原子频标

4.4 斯塔克效应

## 4.1 塞曼效应

$$\hat{H} = \sum_{i=1}^N \left[ -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} + u_i(r_i) \right] \rightarrow \text{动能+中心势}$$
$$+ \left[ \frac{1}{2} \sum_i \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_i^N u_i(r_i) \right] \rightarrow \text{剩余静电势}$$
$$+ \sum_i \xi_i(r_i) \hat{L}_i \cdot \hat{S}_i \rightarrow \text{自旋-轨道相互作用}$$

## 4.1.1 原子磁矩



原子总磁矩：

$$\bar{\mu} = \bar{\mu}_L + \bar{\mu}_S = -\frac{\mu_B}{\hbar} (g_l \bar{L} + g_s \bar{S})$$

$$g_l=1, g_s=2$$

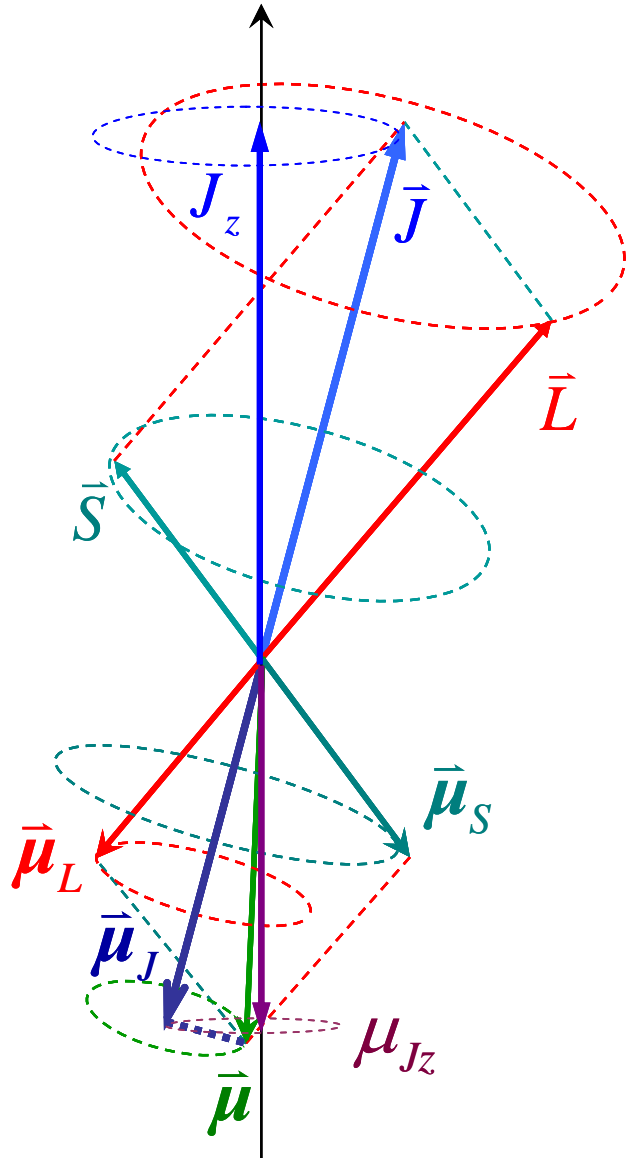
$$\bar{\mu} = -\frac{\mu_B}{\hbar} (\bar{L} + 2\bar{S}) = -\frac{\mu_B}{\hbar} (\bar{J} + \bar{S})$$

$$\frac{d\bar{J}}{dt} = 0, \quad \frac{d\bar{S}}{dt} = \xi(r) \bar{J} \times \bar{S}$$

$$\frac{d\bar{\mu}}{dt} \neq 0$$

原子总磁矩不是守恒量

# 4.1.1 原子磁矩



原子总磁矩:

$$\vec{\mu} = -\frac{\mu_B}{\hbar} (\vec{L} + 2\vec{S}) = -\frac{\mu_B}{\hbar} (\vec{J} + \vec{S})$$

$$\frac{d\vec{\mu}}{dt} \neq 0 \quad \text{原子总磁矩不是守恒量}$$

原子磁矩: 原子总磁矩在J上的分量

$$\bar{\mu}_J = \frac{\vec{\mu} \cdot \vec{J}}{J^2} \cdot \vec{J}$$

$$\frac{d\vec{S}}{dt} = \xi(r) \vec{J} \times \vec{S} \rightarrow \frac{d\vec{S}}{dt} \cdot \vec{J} = 0$$

$$\frac{d\bar{\mu}_J}{dt} = 0 \quad \text{原子磁矩是守恒量}$$

$$\vec{\mu} = -\frac{\mu_B}{\hbar} (\vec{L} + 2\vec{S}) = -\frac{\mu_B}{\hbar} (\vec{J} + \vec{S})$$

$$(\vec{\mu} \cdot \vec{J}) \cdot \vec{J} = -\frac{\mu_B}{\hbar} (\vec{J}^2 + \vec{S} \cdot \vec{J}) \cdot \vec{J}$$

$$\vec{L}^2 = (\vec{J} - \vec{S})^2 = \vec{J}^2 + \vec{S}^2 - 2\vec{J} \cdot \vec{S}$$

$$\vec{J} \cdot \vec{S} = \frac{1}{2} (\vec{J}^2 + \vec{S}^2 - \vec{L}^2)$$

$$\vec{\mu}_J = -\frac{\mu_B}{2\hbar} \left(1 + \frac{\vec{J}^2 + \vec{S}^2 - \vec{L}^2}{2\vec{J}^2}\right) \cdot \vec{J} = -g_J \frac{\mu_B}{\hbar} \vec{J}$$

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

朗德因子

$$\vec{\mu}_J = -g_J \frac{\mu_B}{\hbar} \vec{J}$$

$$\mu_J = -g_J \sqrt{J(J+1)} \mu_B$$

$$\mu_{Jz} = -m_J g_J \mu_B \quad m_J = -J, -J+1, \dots, J-1, J$$

上述推导是在假设外磁场远远小于原子内部磁场的情况下获得的，也即外磁场很弱，并不破坏自旋-轨道耦合的情况。因此朗德因子只适用于弱外磁场的情形。

*LS*耦合的最后一步也是自旋-轨道相互作用，所以上述公式对于*LS*耦合也适用。

## 4.1.2 塞曼效应



塞曼（P. Zeeman，1865-1943），荷兰人，1902年诺贝尔物理学奖获得者

"in recognition of the extraordinary service they rendered by their researches into the influence of magnetism upon radiation phenomena"

1896年，塞曼在研究磁场对光的影响实验时发现

One of the items in the Zeeman archive is a laboratory notebook that contains the first recorded observation of the Zeeman effect [8]. The entry is dated 2 September 1896 and is preceded by many pages of notes on totally unrelated experimental work. It opens with the words: 'Influence of magnetization on flame.' The notes that follow describe a very simple experiment: a piece of asbestos, soaked in a solution of kitchen salt, is put in a flame placed between the poles of a magnet. With the help of a grating, a spectrum is created. The yellow sodium D-lines appear as narrow and sharp lines. 'When the magnet is switched on', the description continues, 'the lines become wider until they are two to three times as wide'. This simple sentence describes the discovery

something new. A publication describing his experiments was presented by Kamerlingh Onnes at the monthly meeting of Saturday 31 October of the Section of Sciences of the Dutch Academy of Sciences. In it Zeeman concluded:

The experiments have made it increasingly probable that absorption and thus also emission lines of a gaseous substance are widened by magnetic forces. [4]

A. J. Kox, Euro. J. Phys. 18 (1997) 139-144

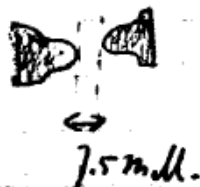
bale dicht maken.  
 lang vóór in bale plaatsen  
 ook dicht bij vibrator

~~schakel~~

~~Maandag~~ 2 Sept. woensdag 2 Sept.

Involves anisotropie op glas

Een stuk kristal  
 doort te vliegen met  
 kenpen <sup>analyse</sup>  
 wordt in <sup>analyse</sup> ~~aan~~  
~~de~~ getracht



Zee  
 P  
 P  
 P

Met Rowland's  
 tralie wordt  
 een spectrum  
 verkregen. Het

deelt bij de D lijne een lichte  
 van Fresnel bekeken.

De lijne zijn voor scherp te krijgen  
 Wordt de magnet aangezet  
 dan verbreedt zich

de lijnen en wel zoveel tot  
 ze 2 à 3 malen breiden worden.

De stroom was 30 Amp.

De verbreding schijnt

symmetrisch te zijn

Om dit te bevestigen werd

de stroom in de lengte van  
 Fresnel op't midden van de  
 streep gebracht. Bij het aanstellen  
 van de anisotropie schreef  
 dan de verbreding een vreesing  
 den gelijkt te zijn. En hield  
 brennende ik het een  
 de zijde van het rood  
 de verbreding grooter was.

Donnerdag 3 Sept

Hi opvoerd en Pub. Chlor aat  
 het caustic als rood driest, of  
 in asbest of in kool.

Het eerste schijnt het zwaar te  
 maar de rest meer kool.

Het tweede en het derde in  
 Druiven

Figure 3. Two pages from Zeeman's notebook with the first recorded observation of the Zeeman effect.





塞曼在1896-1897年几个月的时间里：

1. 发现了谱线在磁场中被展宽
2. 被展宽的谱线边界上的光有偏振，验证了洛伦兹的解释
3. 测量了原子中谐振子的荷质比，比氢离子大1000倍

●进一步的实验研究发现，展宽的谱线包含三条分裂的谱线，正如洛伦兹的理论预言。

●再进一步的实验研究发现，光谱线在外磁场中分裂会出现多于或少于三条的情形，而这无法由洛伦兹的理论予以解释。

光谱线在外磁场中分裂为三条的现象就称为正常塞曼效应，否则就称为反常塞曼效应。



## The Nobel Prize in Physics 1902

"in recognition of the extraordinary service they rendered by their researches into the influence of magnetism upon radiation phenomena"



**Hendrik Antoon Lorentz**

1/2 of the prize

the Netherlands

**Leiden University  
Leiden, the Netherlands**

**b. 1853**

**d. 1928**



**Pieter Zeeman**

1/2 of the prize

the Netherlands

**Amsterdam University  
Amsterdam, the Netherlands**

**b. 1865**

**d. 1943**

塞曼效应就是原子磁矩与外磁场发生相互作用，导致了原子能级和原子光谱线的分裂现象。

弱磁场中：
$$U = -\vec{\mu}_J \cdot \vec{B} = -\mu_{J_z} B$$

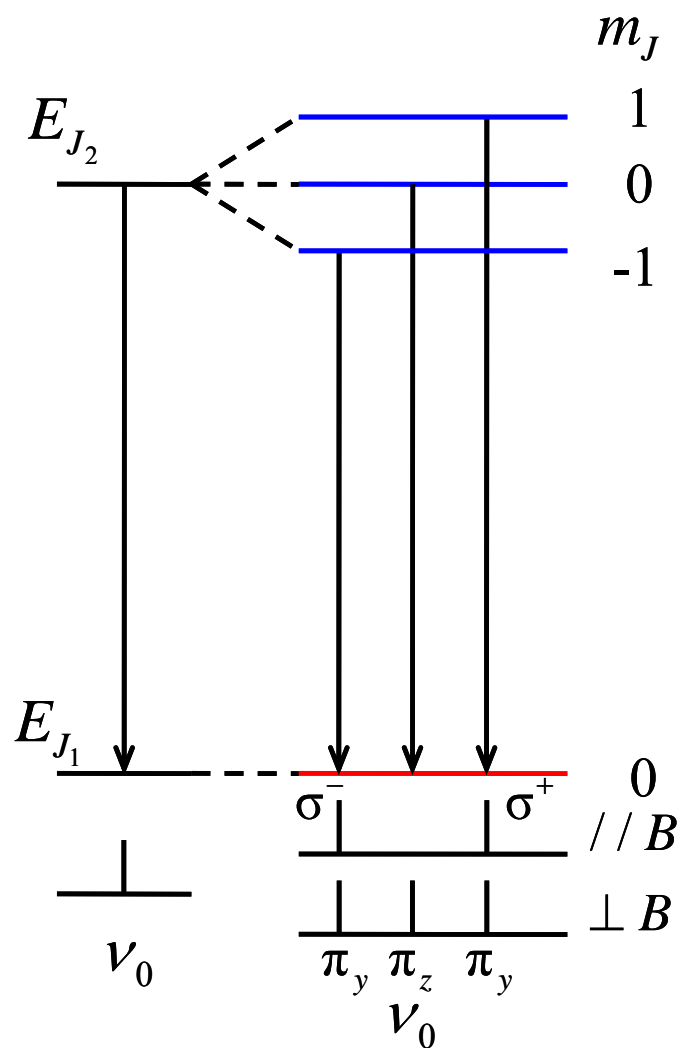
$$U = m_J g_J \mu_B B$$

$$E'_J = E_J + m_J g_J \mu_B B$$

无外磁场( $B \rightarrow 0$ )时，此 $2J+1$ 个态简并

有外磁场时，能级分裂为 $2J+1$ 条

$m_J$ ：磁量子数



$$\begin{aligned}
 h\nu &= E'_{J_2} - E'_{J_1} \\
 &= (E_{J_2} - E_{J_1}) + (m_{J_2}g_2 - m_{J_1}g_1)\mu_B B \\
 &= h\nu_0 + (m_{J_2}g_2 - m_{J_1}g_1)\mu_B B
 \end{aligned}$$

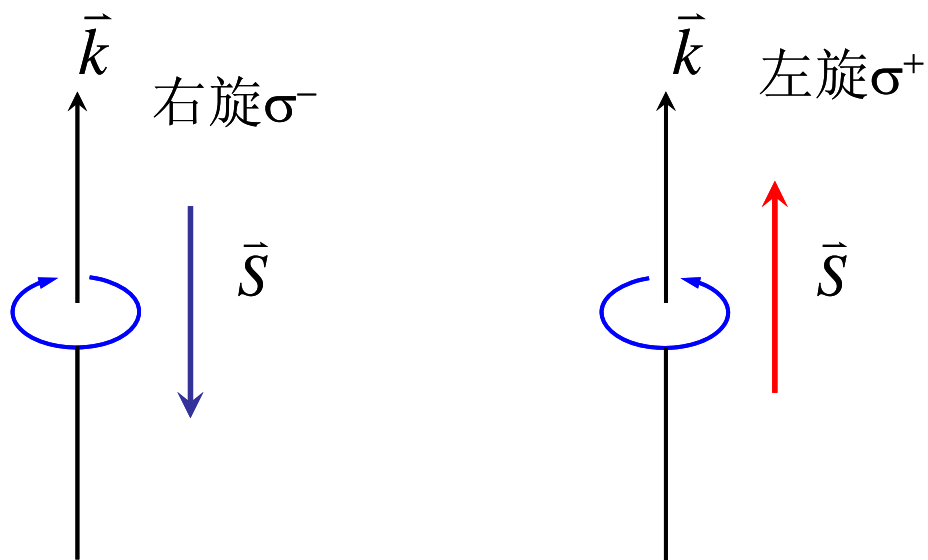
$$\frac{1}{\lambda} - \frac{1}{\lambda_0} = \frac{(m_{J_2}g_2 - m_{J_1}g_1)\mu_B B}{hc} = (m_{J_2}g_2 - m_{J_1}g_1)\mathcal{L}$$

$$\mathcal{L} = \frac{\mu_B B}{hc} = \frac{eB}{4\pi m_e c} \quad \text{洛伦兹单位}$$

$$B=1\text{T时}, \mathcal{L}=0.466 \text{ cm}^{-1}$$

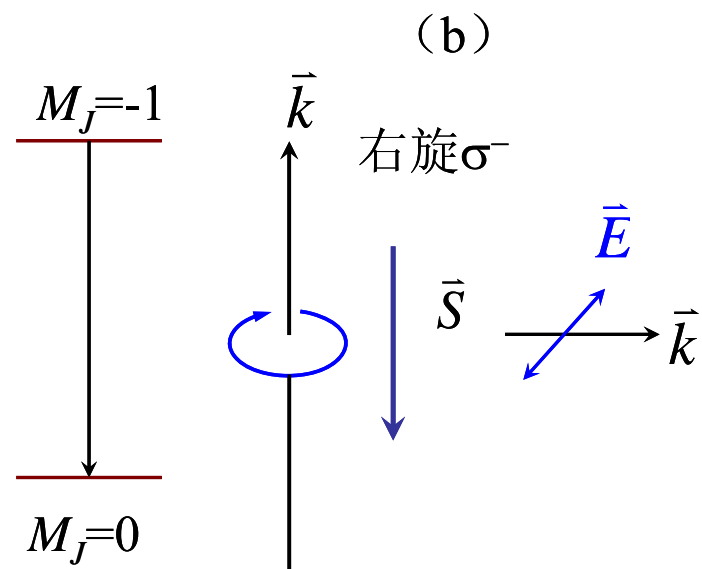
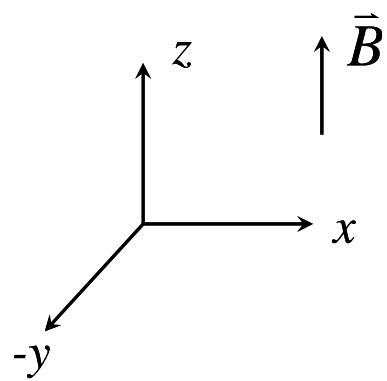
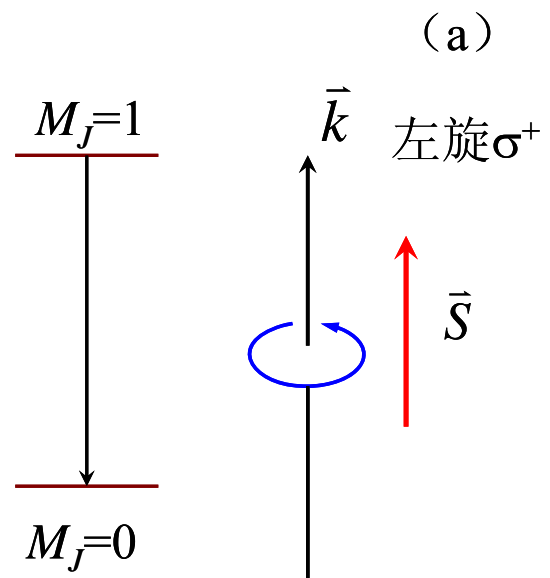
磁量子数选择定则:  $\Delta m = m_{J_2} - m_{J_1} = 0, \pm 1$  (当  $\Delta J = 0, 0 \not\leftrightarrow 0$ )

## 塞曼效应的发射光谱具有偏振特性



光子具有自旋，其自旋量子数  
 **$S=1$ ,  $S_z=\pm 1$**

光子的自旋本征态



## 塞曼效应的发射光谱具有偏振特性

### ● 沿着外磁场方向观察:

只能看到 $\Delta m = \pm 1$ 的**两条**谱线，均为**圆**偏振光

$\Delta m = +1$ ，左旋圆偏振光， $\sigma^+$

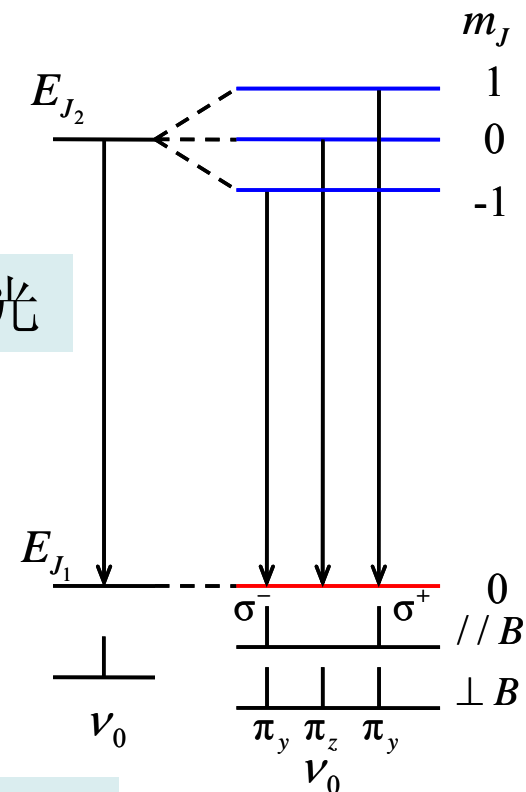
$\Delta m = -1$ ，右旋圆偏振光， $\sigma^-$

### ● 垂直外磁场方向观察:

能看到 $\Delta m = 0, \pm 1$ 的**三条**谱线，均为**线**偏振光

$\Delta m = 0$ ，偏振方向沿外磁场方向 $z$ ， $\pi_z$

$\Delta m = \pm 1$ ，垂直于观测方向 $x$ 与外磁场方向 $z$ ， $\pi_y$





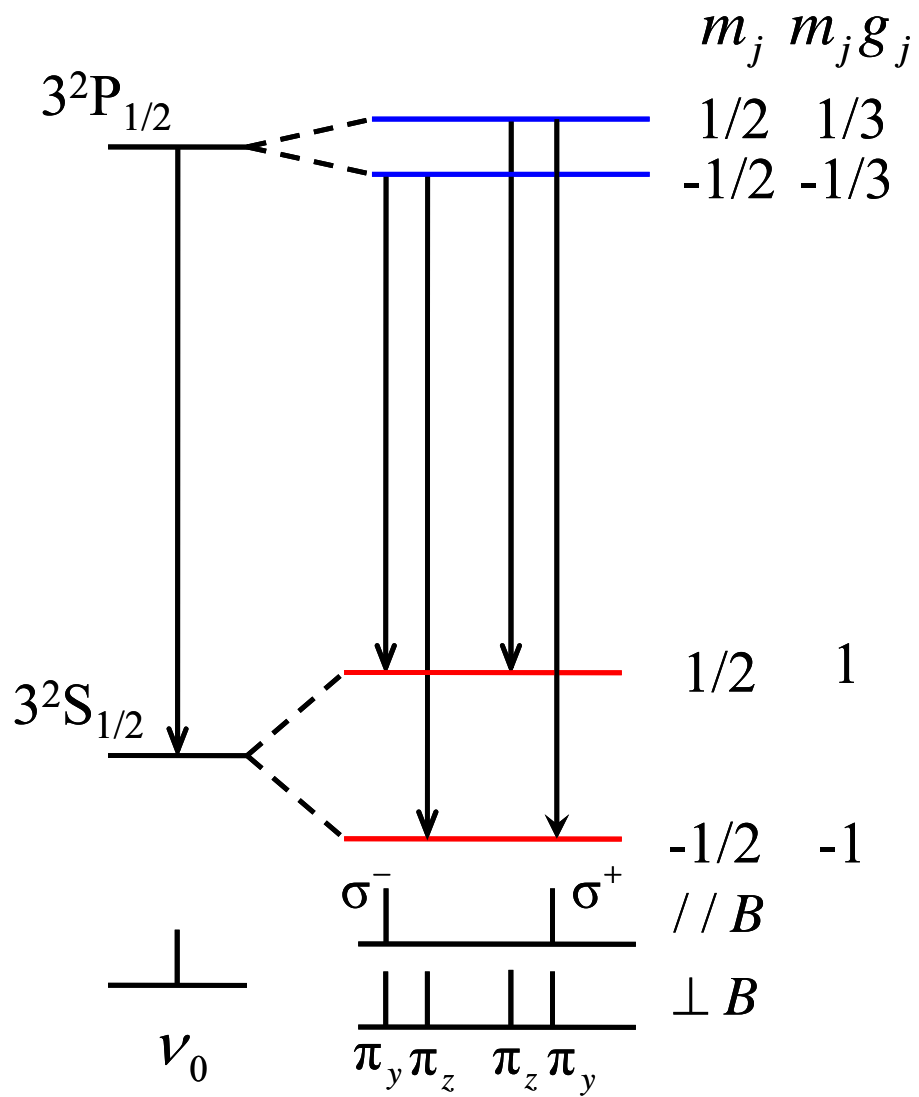
例4.1.1 试分析钠原子 $3^2P_{3/2,1/2} \rightarrow 3^2S_{1/2}$ 跃迁在弱外磁场中的分裂情况，并给出其发射光谱。

解： 朗德因子：

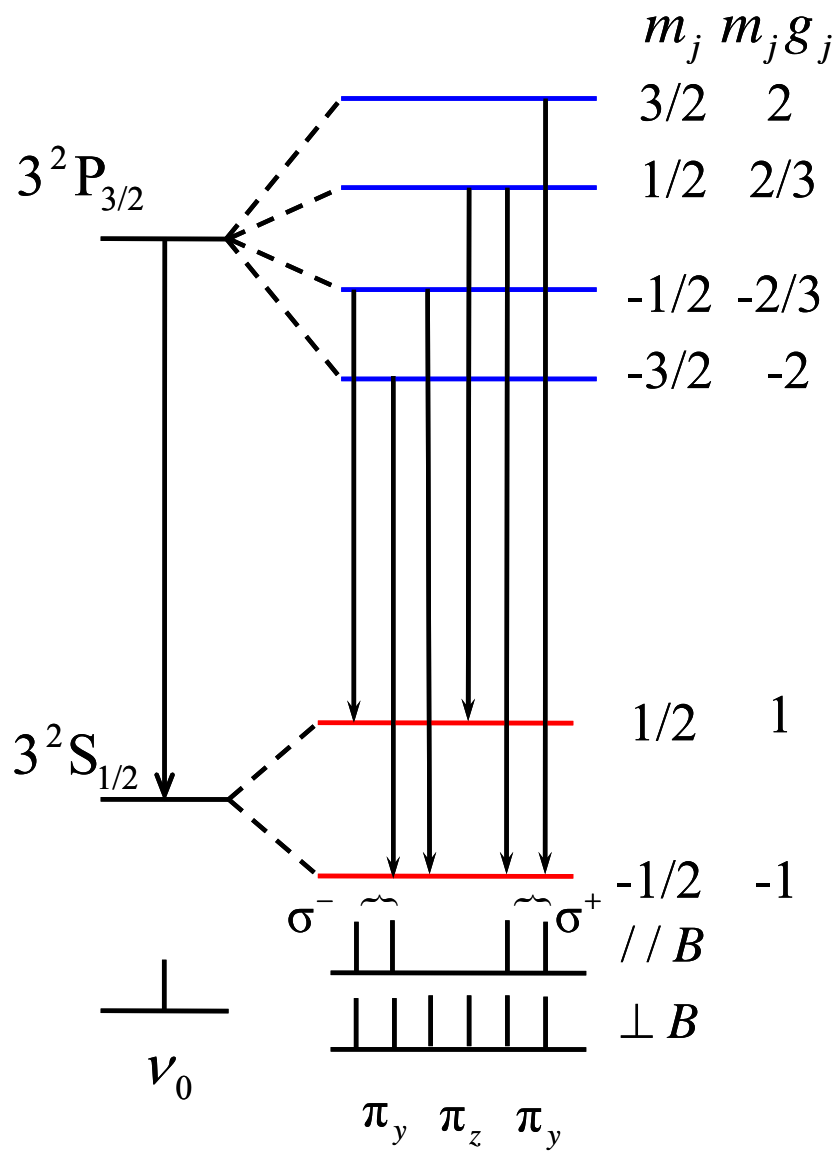
$$3^2S_{1/2}: g_{j_1} = 1 + \frac{\frac{1}{2} \times \frac{3}{2} + \frac{1}{2} \times \frac{3}{2} - 0}{2 \times \frac{1}{2} \times \frac{3}{2}} = 2$$

$$3^2P_{1/2}: g_{j_2} = 1 + \frac{\frac{1}{2} \times \frac{3}{2} + \frac{1}{2} \times \frac{3}{2} - 1 \times 2}{2 \times \frac{1}{2} \times \frac{3}{2}} = \frac{2}{3}$$

$$3^2P_{3/2}: g_{j_3} = 1 + \frac{\frac{3}{2} \times \frac{5}{2} + \frac{1}{2} \times \frac{3}{2} - 1 \times 2}{2 \times \frac{1}{2} \times \frac{3}{2}} = \frac{4}{3}$$

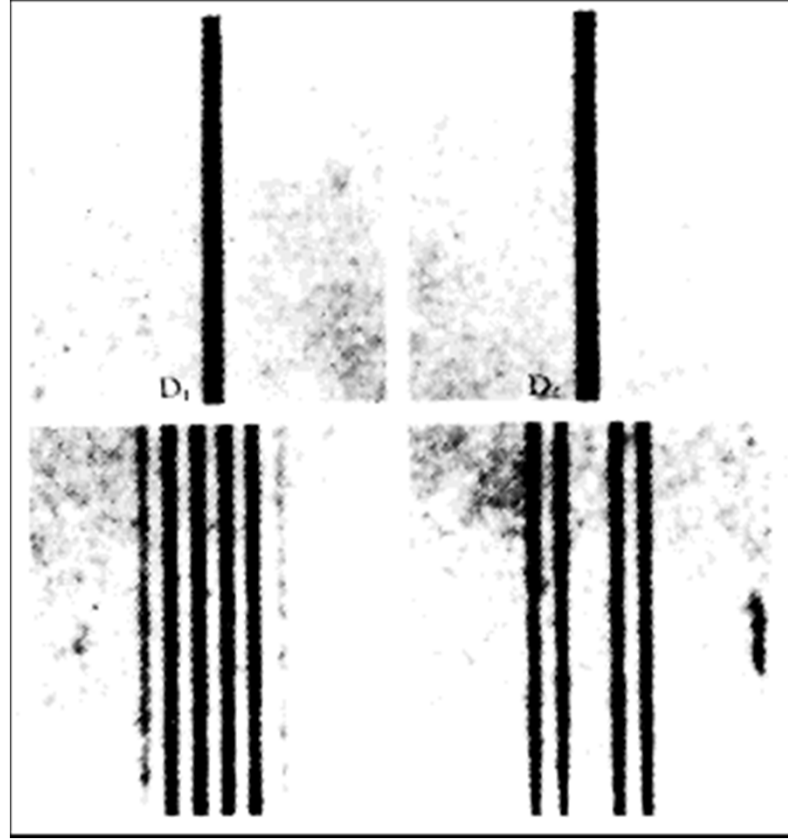


$$\frac{1}{\lambda} - \frac{1}{\lambda_0} = \left\{ \begin{array}{c} -\frac{4}{3} \\ -\frac{2}{3} \\ \frac{2}{3} \\ \frac{4}{3} \end{array} \right\} \mathcal{L}$$



$$\frac{1}{\lambda} - \frac{1}{\lambda_0} = \left\{ \begin{array}{c} -\frac{5}{3} \\ -1 \\ -\frac{1}{3} \\ \frac{1}{3} \\ 1 \\ \frac{5}{3} \end{array} \right\} \mathcal{L}$$

$$\frac{1}{\lambda} - \frac{1}{\lambda_0} = \left\{ \begin{array}{c} \frac{5}{3} \\ -1 \\ \frac{1}{3} \\ \frac{1}{3} \\ 1 \\ \frac{5}{3} \\ 3 \end{array} \right\} \mathcal{L}$$



$$\frac{1}{\lambda} - \frac{1}{\lambda_0} = \left\{ \begin{array}{c} \frac{4}{3} \\ -\frac{2}{3} \\ \frac{2}{3} \\ 3 \\ \frac{4}{3} \\ 3 \end{array} \right\} \mathcal{L}$$

思考题：如何判断外磁场是强还是弱呢？

### 3.4节，第118页

碱金属原子最外层电子感受到的内磁场

原子	Li	Na	K	Rb	Cs
能级分裂 ( $\text{cm}^{-1}$ )	0.34	17.2	57.7	237.6	554.1
$B_{\text{内}}$ (T)	0.728	38.8	121	509.0	1187

塞曼效应就是原子磁矩与外磁场发生相互作用，导致了原子能级和原子光谱线的分裂现象。

弱磁场中：
$$U = -\vec{\mu}_J \cdot \vec{B} = -\mu_{J_z} B$$

$$U = m_J g_J \mu_B B$$

$$E'_J = E_J + m_J g_J \mu_B B$$

无外磁场( $B \rightarrow 0$ )时，此 $2J+1$ 个态简并

有外磁场时，能级分裂为 $2J+1$ 条

$m_J$ ：磁量子数

例4.1.2 试分析氦原子 $2^1P_1 \rightarrow 1^1S_0$ 在弱外磁场中的分裂和跃迁情况。

解：

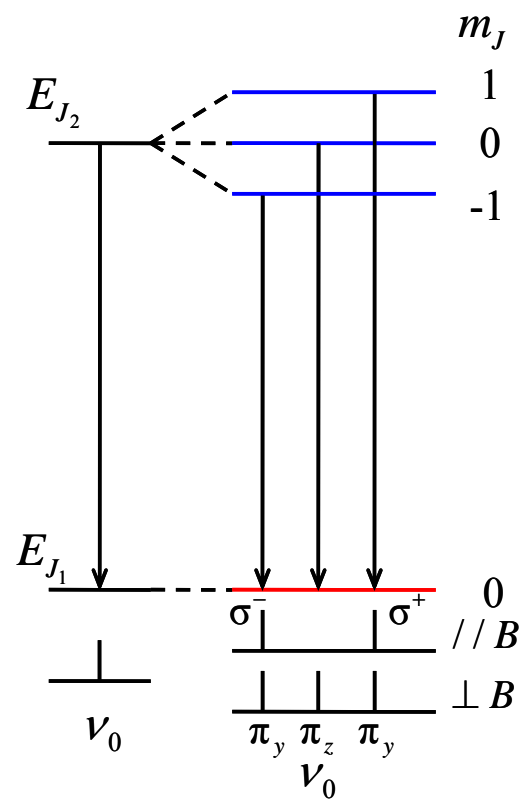
对于氦原子基态 $1^1S_0$ ，由于它的总角动量量子数 $J=0$ ，因此该能级在弱外磁场中不发生分裂与移动

而对于氦原子的 $2^1P_1$ ，可计算出它的朗德因子为：

$$g_J = 1 + \frac{1 \times 2 + 0 \times 1 - 1 \times 2}{2 \times 1 \times 2} = 1$$

$2^1P_1$ 的能级在外磁场中分裂为三条，其能级移动分别为：

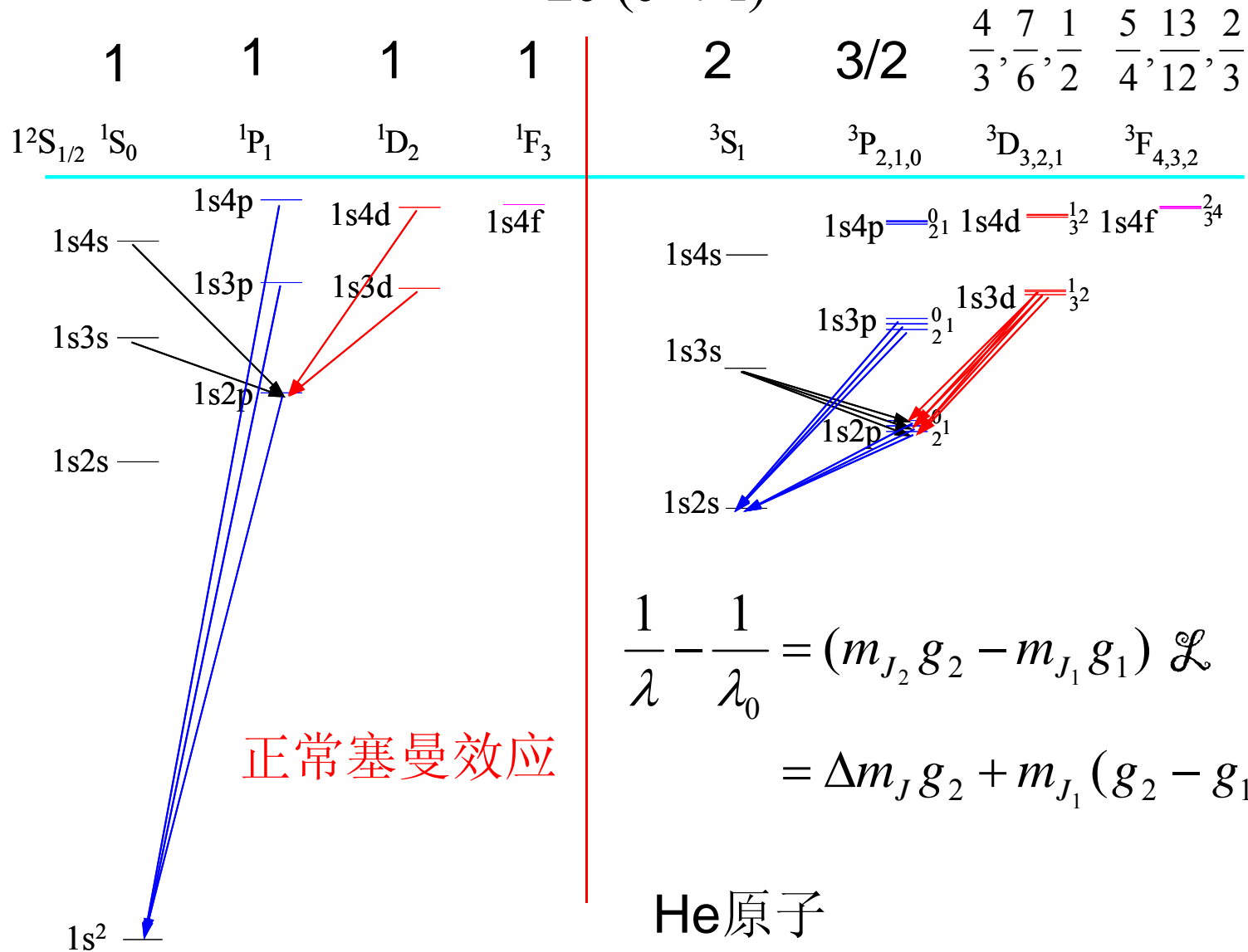
$$U = M_J g_J \mu_B B = \begin{cases} \mu_B B & (M_J = 1) \\ 0 & (M_J = 0) \\ -\mu_B B & (M_J = -1) \end{cases}$$



$$\frac{1}{\lambda} - \frac{1}{\lambda_0} = \left\{ \begin{array}{c} 1 \\ 0 \\ -1 \end{array} \right\} \mathcal{L}$$



$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$



$$S = 0$$

$$\bar{\mu} = \bar{\mu}_l = \bar{\mu}_J = -g_J \frac{\mu_B}{\hbar} \bar{J}$$

$$\bar{\mu}_l = -g_l \frac{\mu_B}{\hbar} \bar{L} = -g_l \frac{\mu_B}{\hbar} \bar{J}$$

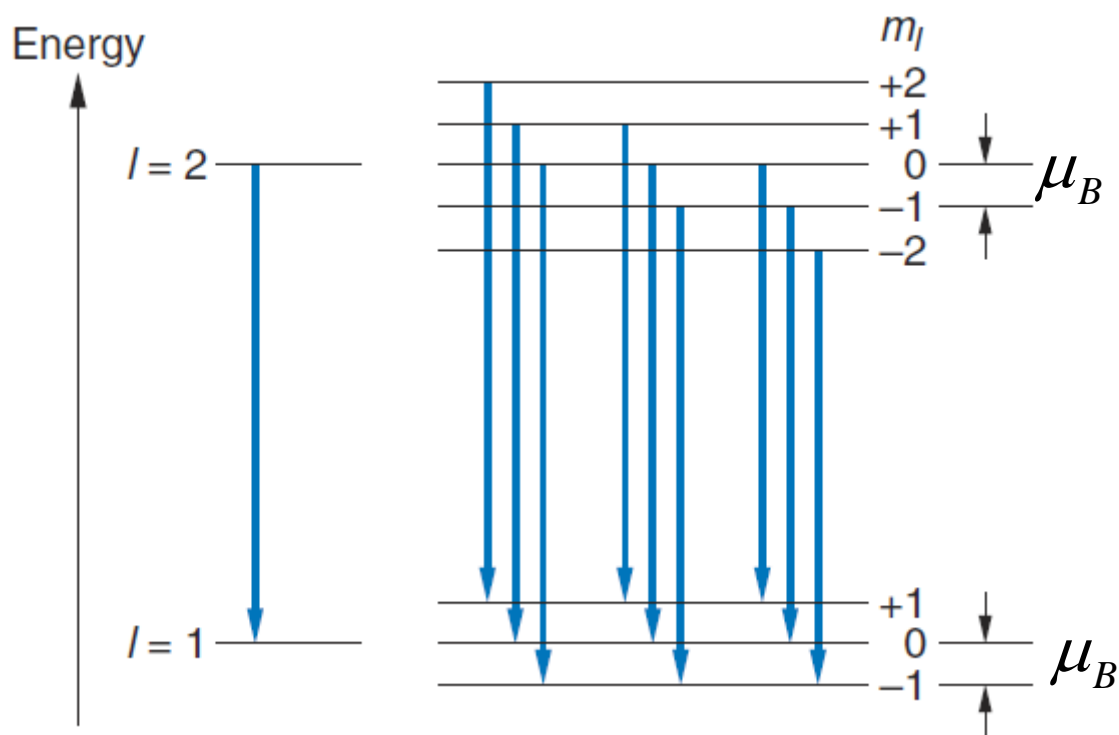
$$g_J = g_l = 1$$

$$\bar{\mu}_J = -\sqrt{L(L+1)}\mu_B$$

$$\mu_{J_z} = -m_l \mu_B$$

$$\Delta E = -\bar{\mu} \cdot \vec{B} = -\mu_{J_z} B = m_l \mu_B B$$

正常塞曼效应

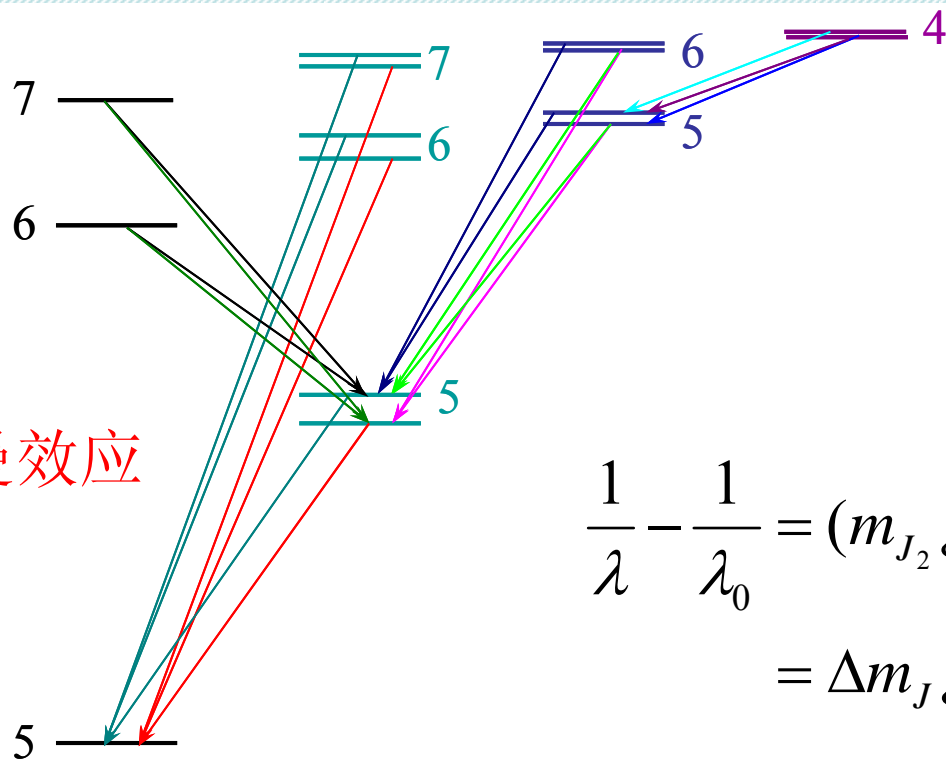


$S \neq 0$

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

$$2 \quad \frac{4}{3}, \frac{2}{3} \quad \frac{4}{5}, \frac{6}{5} \quad \frac{6}{7}, \frac{8}{7}$$

$ns^2S_{1/2}$      $np^2P_{1/2,3/2}$      $nd^2D_{3/2,5/2}$      $nf^2F_{5/2,7/2}$

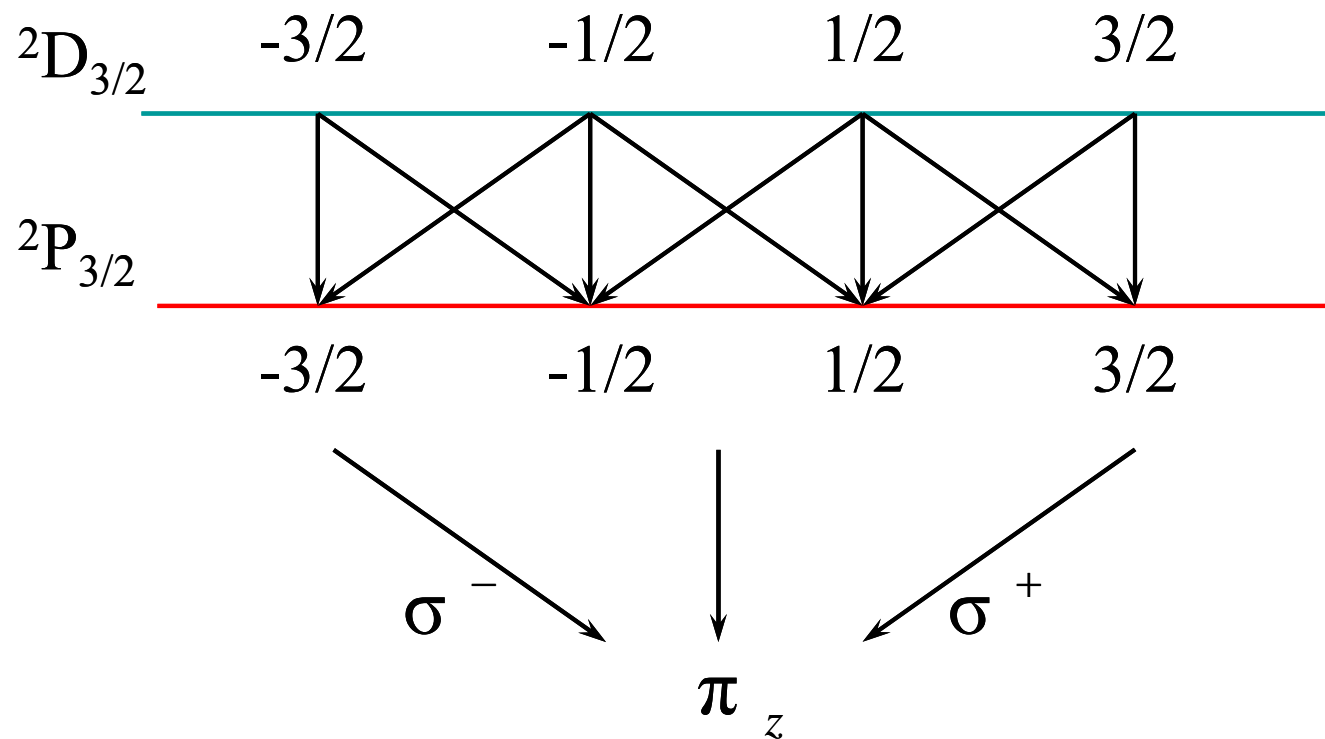


反常塞曼效应

$$\begin{aligned} \frac{1}{\lambda} - \frac{1}{\lambda_0} &= (m_{J_2} g_2 - m_{J_1} g_1) \mathcal{L} \\ &= \Delta m_J g_2 + m_{J_1} (g_2 - g_1) \mathcal{L} \end{aligned}$$

Ag原子

# 格罗春图



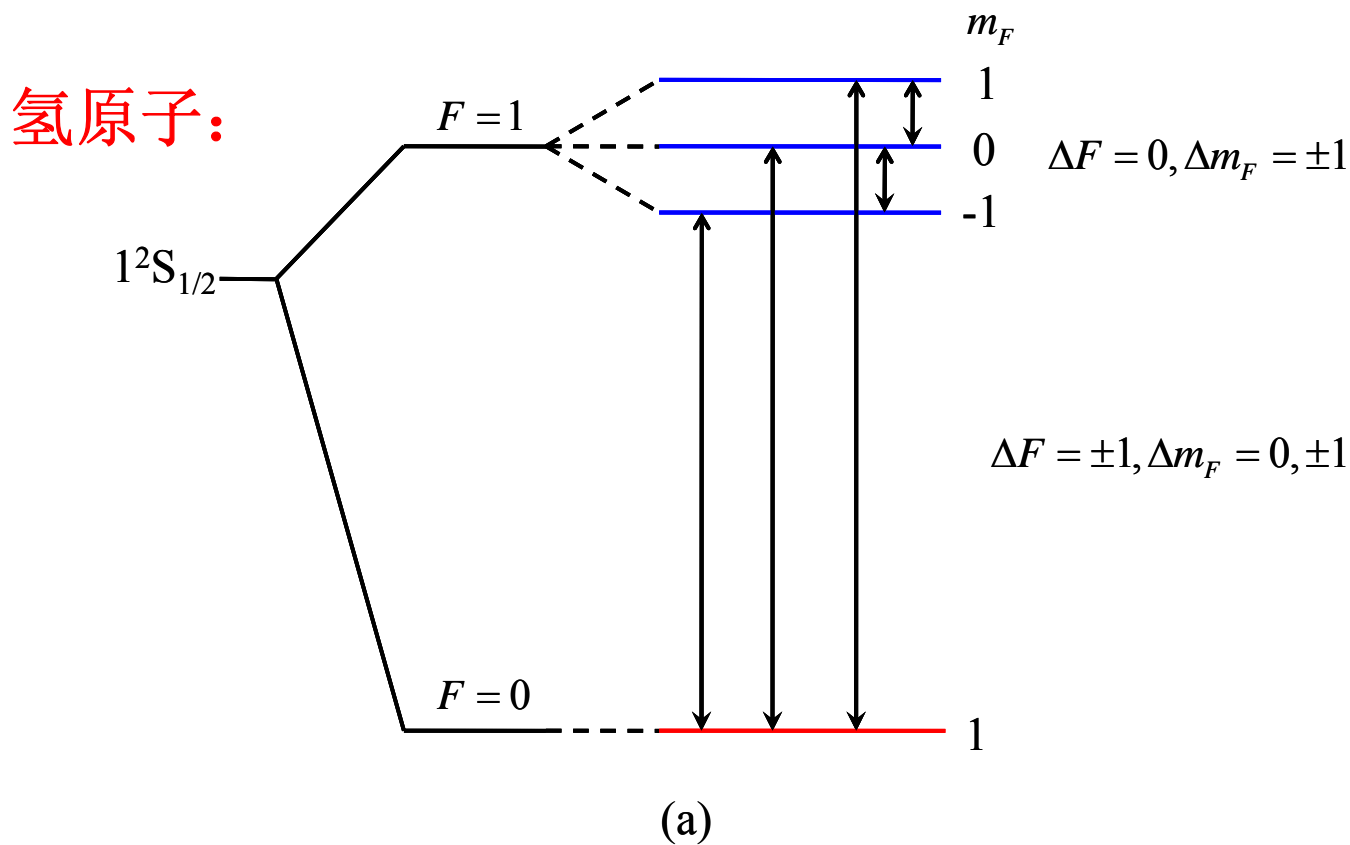
$$\begin{aligned} \frac{1}{\lambda} - \frac{1}{\lambda_0} &= (m_{J_2} g_2 - m_{J_1} g_1) \mathcal{L} \\ &= \Delta m_J g_2 + m_{J_1} (g_2 - g_1) \mathcal{L} \end{aligned}$$

## 小知识：超精细结构的塞曼分裂

外磁场的强度远小于原子核感受到的电子磁矩产生的磁场强度时

(对应于弱磁场情况)

$$U = m_F g_F \mu_B B$$



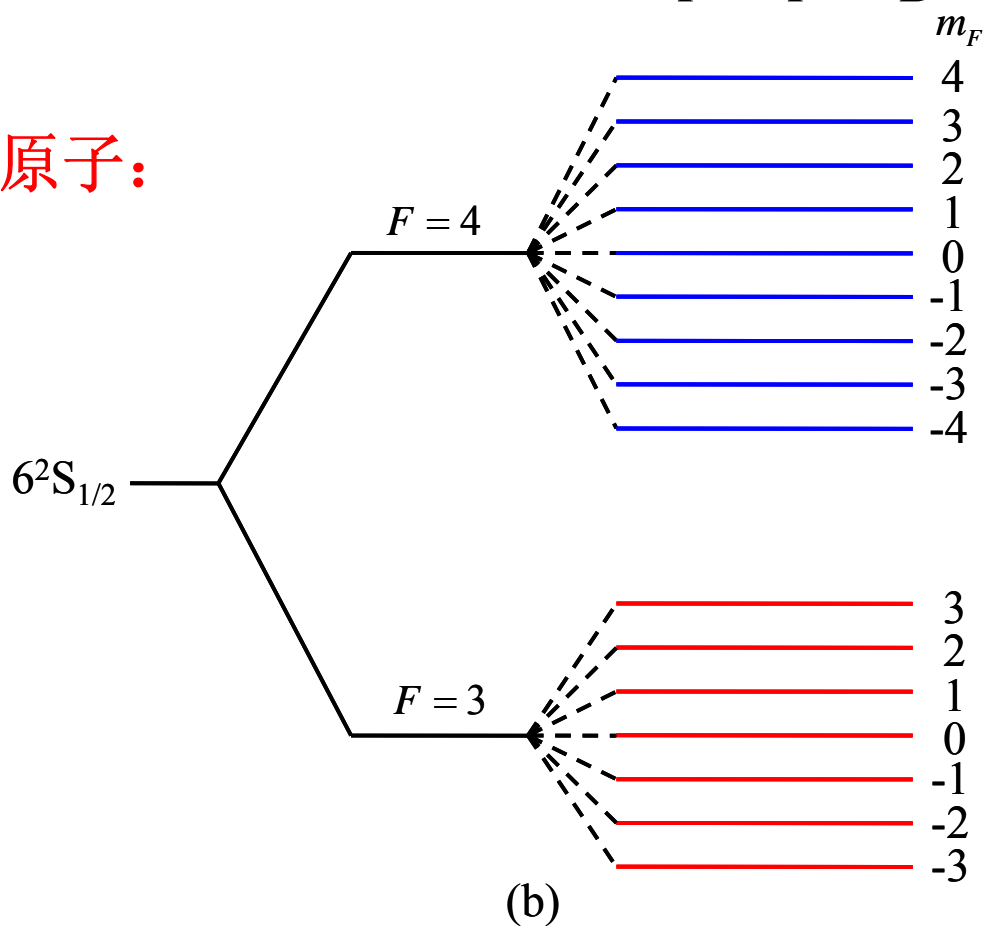
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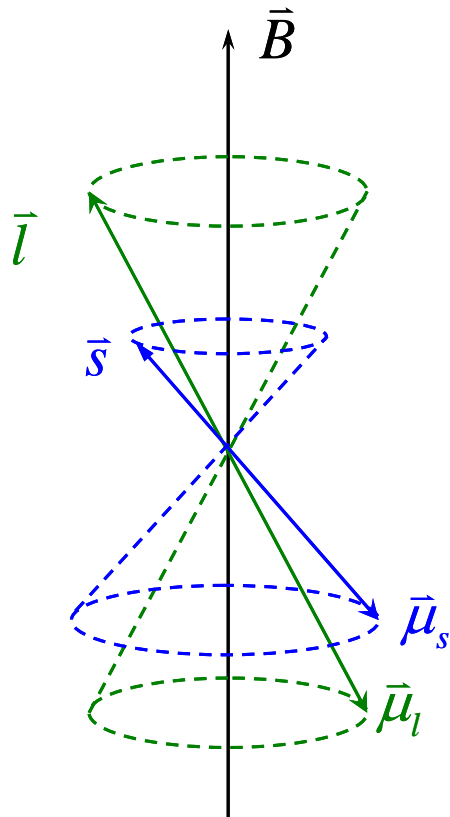
铯-133原子:



### 4.1.3 帕邢—巴克 (Paschan-Back)效应

原子光谱在强外磁场中的分裂现象被称为帕邢-巴克效应

在强外磁场条件下，电子的轨道磁矩和自旋磁矩与外磁场耦合要比两者之间的耦合强得多，这时可以认为外磁场已经破坏了自旋-轨道耦合。



$$\vec{\mu} = \vec{\mu}_l + \vec{\mu}_s = -\frac{\mu_B}{\hbar} (g_l \vec{l} + g_s \vec{s})$$

$$\mu_z = -\frac{\mu_B}{\hbar} (g_l L_z + g_s S_z) = -(m_l + 2m_s) \mu_B$$

$$U = -\vec{\mu} \cdot \vec{B} = (m_l + 2m_s) \mu_B B$$

### 4.1.3 帕邢—巴克 (Paschan-Back)效应

原子光谱在强外磁场中的分裂现象被称为帕邢-巴克效应

$$U = -\vec{\mu} \cdot \vec{B} = (m_l + 2m_s)\mu_B B$$

选择定则:

$$\begin{cases} \Delta m_s = 0 \\ \Delta m_l = 0, \pm 1 \end{cases}$$

光谱分裂:

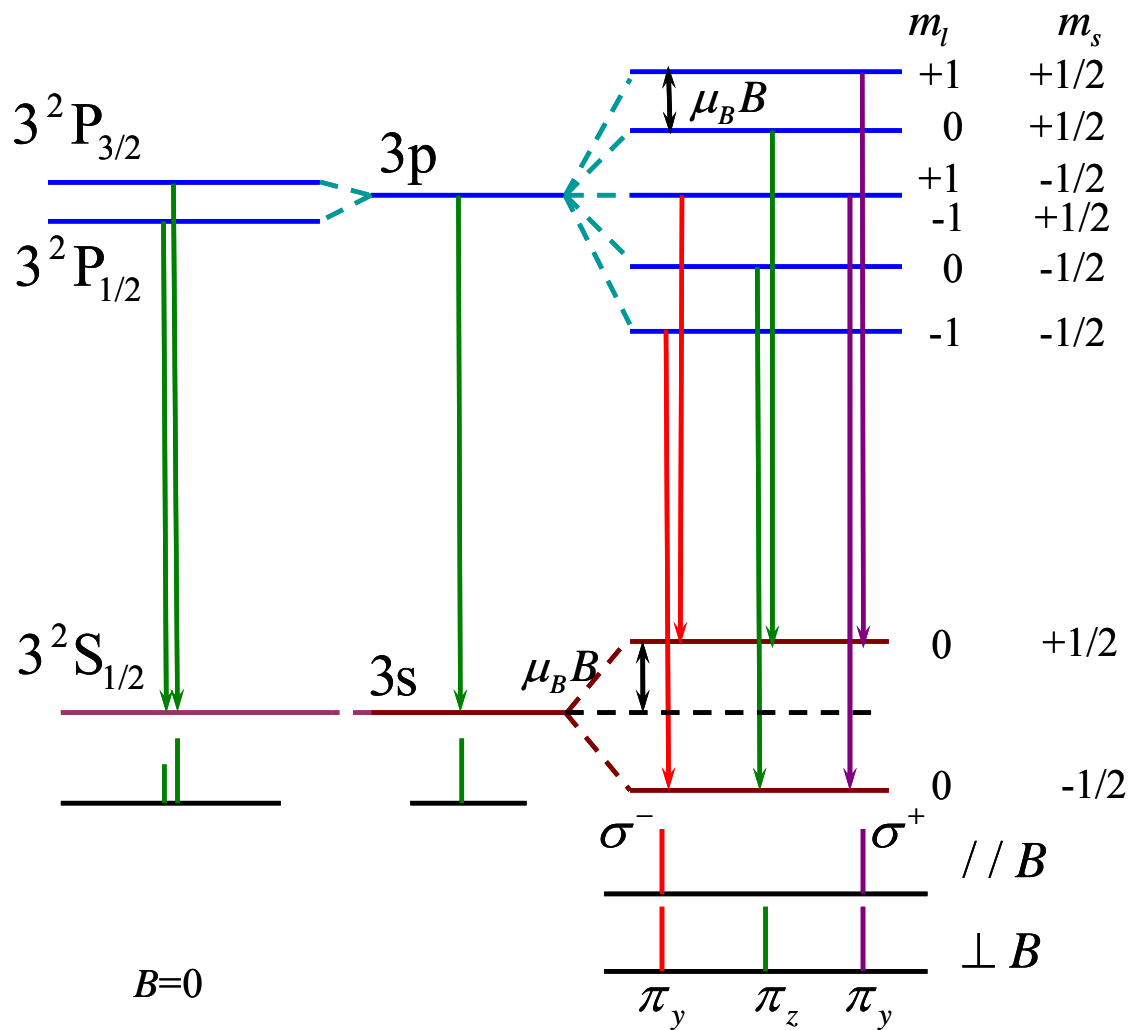
$$\begin{aligned} h\nu &= E_2' - E_1' \\ &= \left[ E_2 + (m_{l_2} + 2m_{s_2})\mu_B B \right] - \left[ E_1 + (m_{l_1} + 2m_{s_1})\mu_B B \right] \\ &= (E_2 - E_1) + (m_{l_2} - m_{l_1})\mu_B B \\ &= h\nu_0 + \Delta m_l \mu_B B \end{aligned}$$

三条谱线，表现为正常塞曼效应



### 例4.1.3 试分析强外磁场条件下钠原子 $3p \rightarrow 3s$ 跃迁的发射光谱。

解：



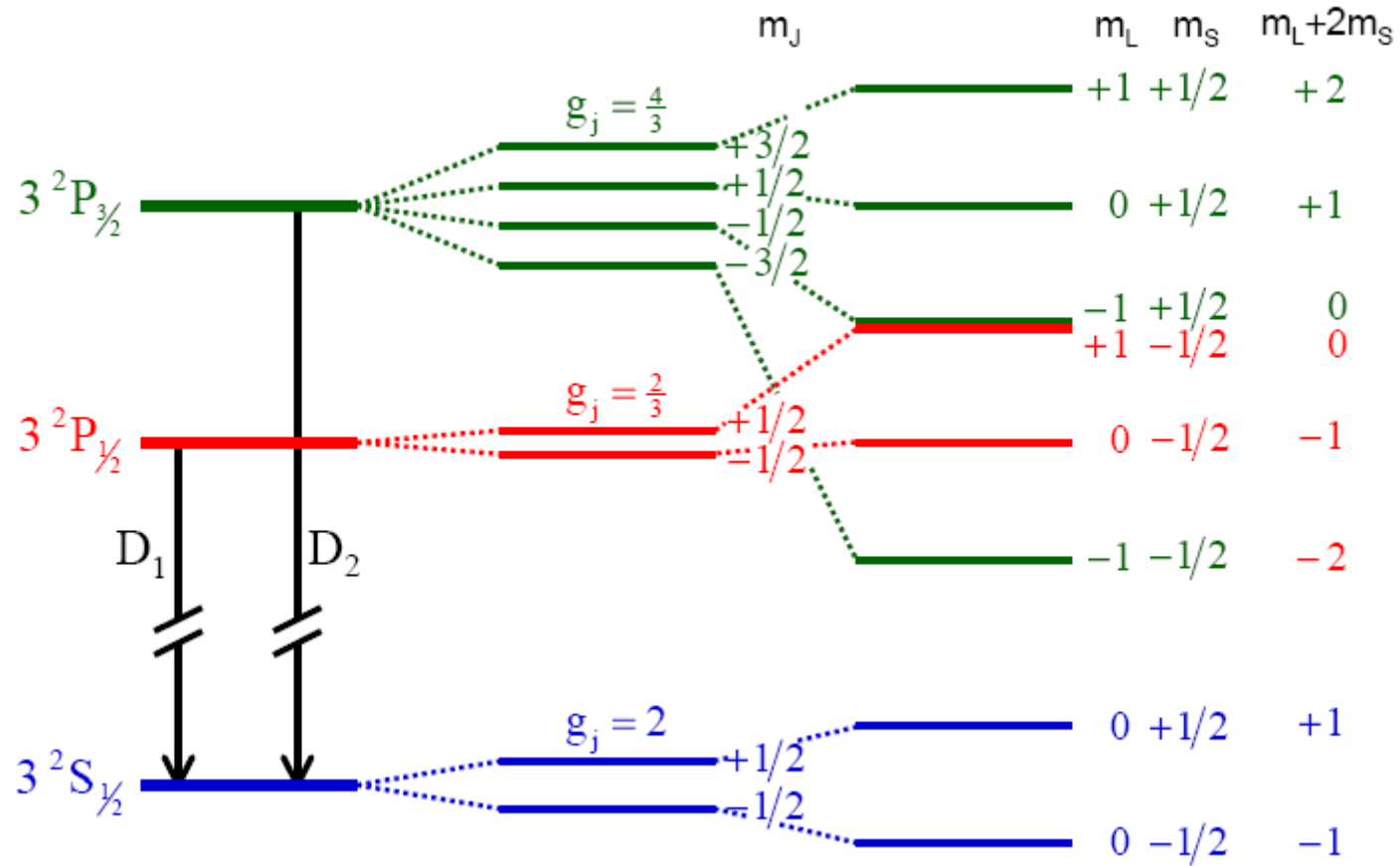
考虑LS耦合

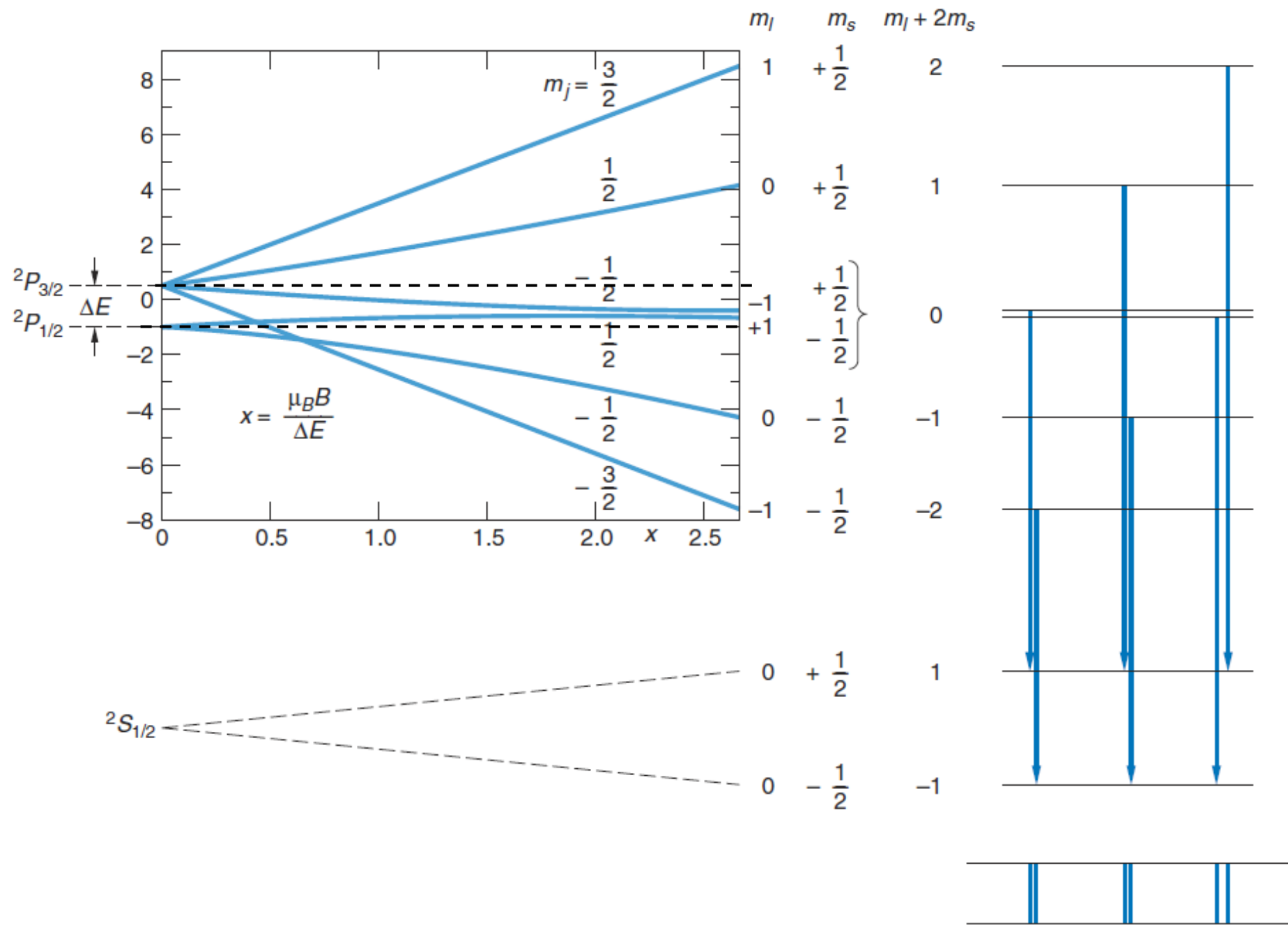
不考虑LS耦合

强外磁场中

弱磁场

强磁场

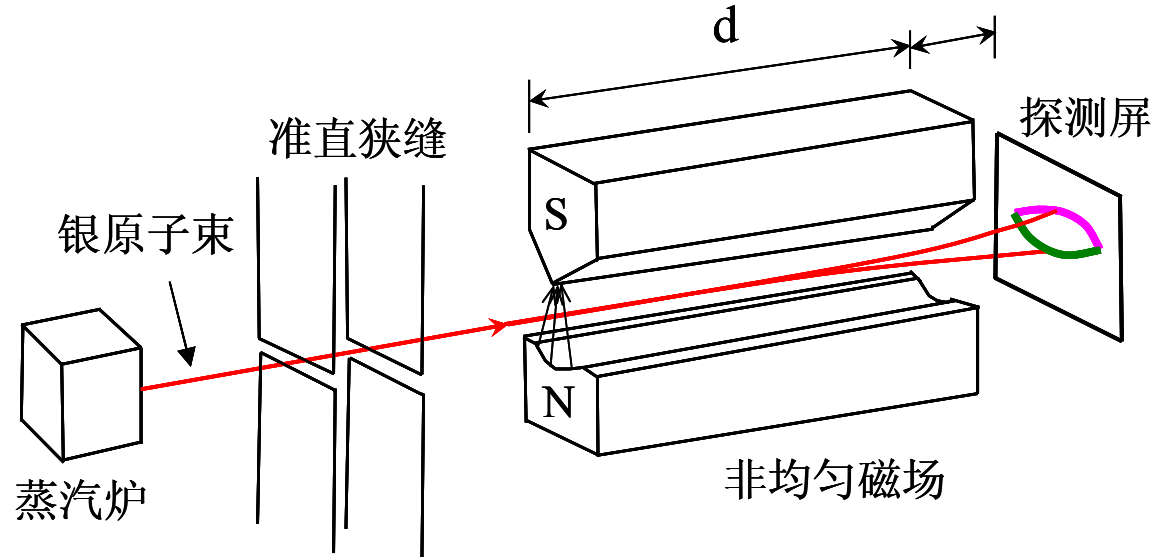




## 4.1.4 斯特恩—盖拉赫实验的再讨论

计入自旋-轨道相互作用后，原子在非均匀外磁场中受到的作用力

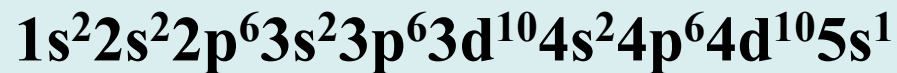
$$F_z = \mu_z \frac{\partial B}{\partial z} = -m_j g_j \mu_B \frac{\partial B}{\partial z}$$



例4.1.4 斯特恩-盖拉赫实验中所用的原子为银原子，银原子蒸汽炉的加热温度为1320K。不均匀磁场区的长度 $d$ 为0.1m，磁场梯度 $dB/dZ=2300 T/m$ 。如果冷凝屏放在磁场的末端，那么银原子在冷凝屏上两条斑纹的间距为多少？

解：

银原子基态的电子组态为：



$$g_j = 1 + \frac{\frac{1}{2} \times \frac{3}{2} + \frac{1}{2} \times \frac{3}{2} - 0 \times 1}{2 \times \frac{1}{2} \times \frac{3}{2}} = 2$$

$$\mu_{j_z} = -m_j g_j \mu_B = \pm \mu_B$$

$$v = \sqrt{\frac{4kT}{M}}$$

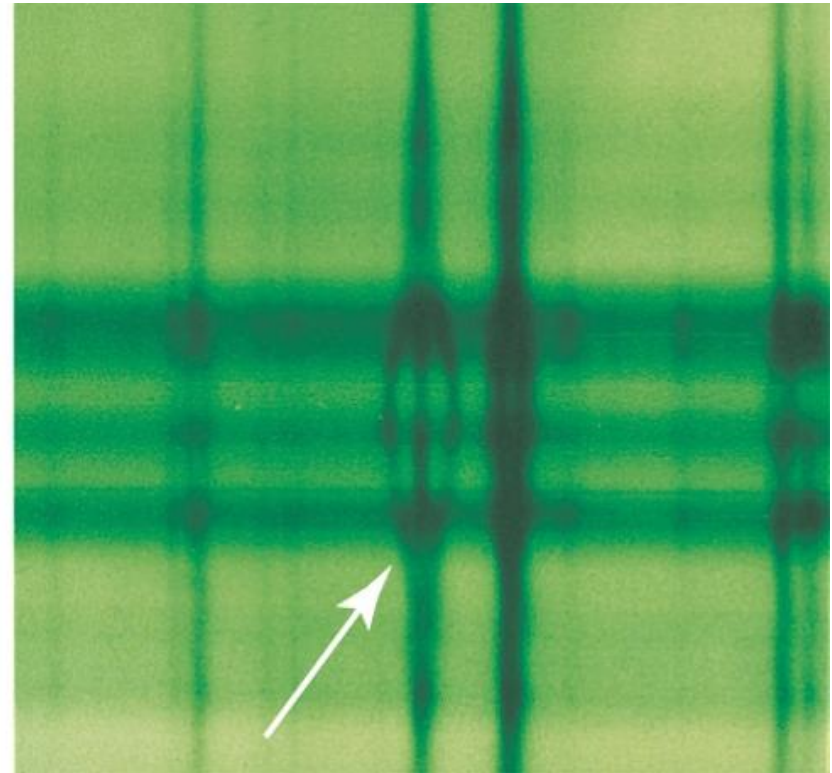
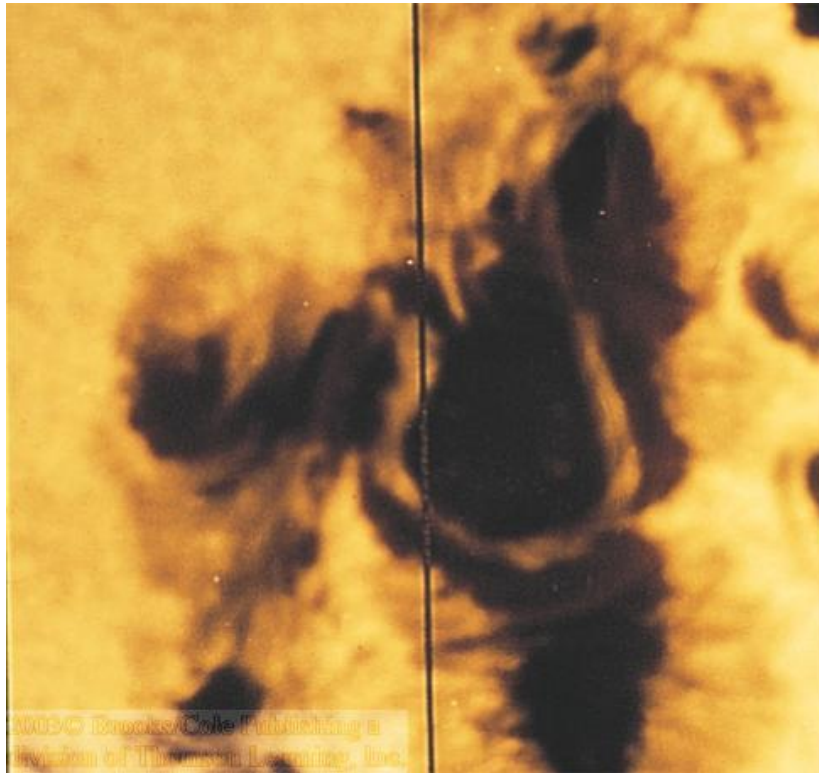
$$S = \frac{1}{2} at^2 = \frac{1}{2} \frac{F_z}{M} \left(\frac{d}{v}\right)^2$$

$$= \frac{1}{2} \left(\mu_z \frac{dB}{dz}\right) \frac{d^2}{4kT} = 0.0015m$$

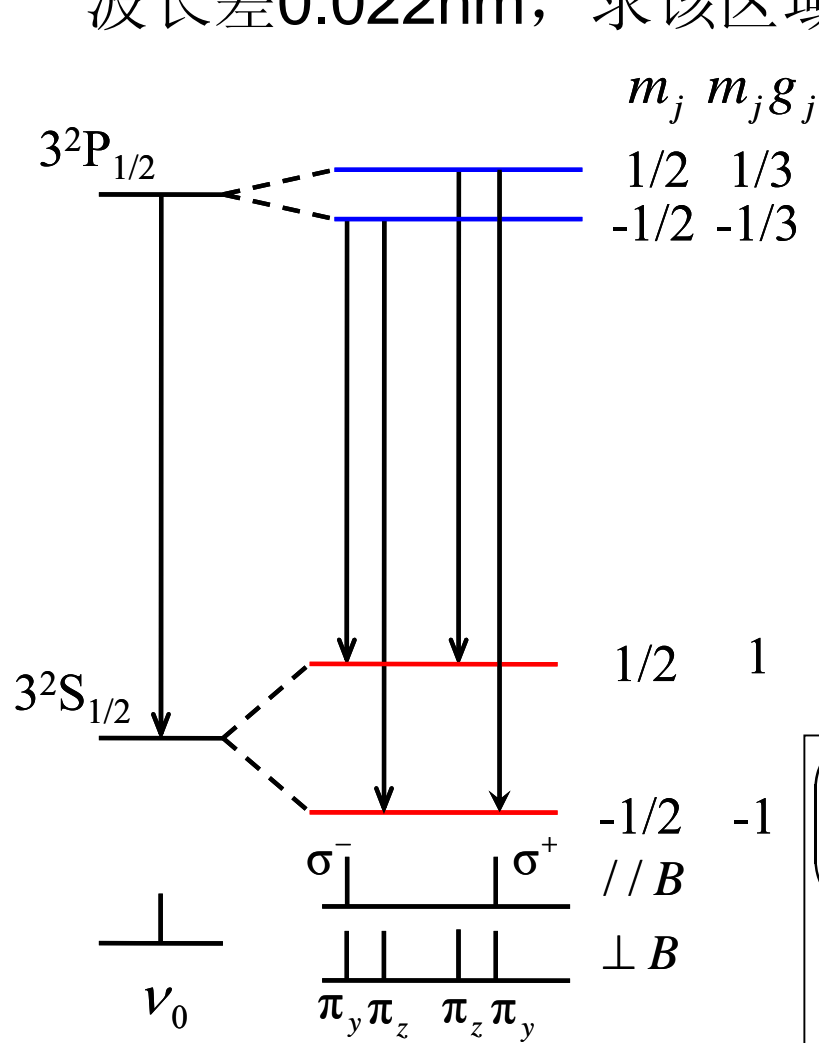
$$L = 2S = 3mm$$

## 太阳黑子中磁场

通过塞曼效应测量磁场



探测从太阳某一区域发射的钠黄光D1线，发现最短波长和最长波长差0.022nm，求该区域太阳的磁场



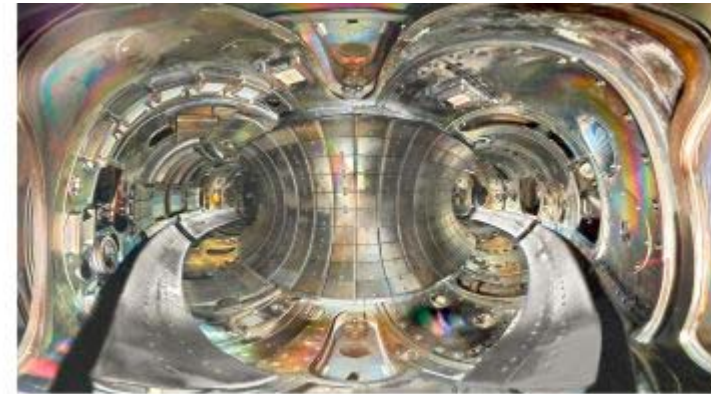
$$\frac{1}{\lambda} - \frac{1}{\lambda_0} = \left\{ \begin{array}{c} -\frac{4}{3} \\ -\frac{2}{3} \\ \frac{2}{3} \\ \frac{4}{3} \end{array} \right\} \mathcal{L}$$

$$\left( \frac{1}{\lambda} - \frac{1}{\lambda_0} \right)_{\max} - \left( \frac{1}{\lambda} - \frac{1}{\lambda_0} \right)_{\min} = \frac{\Delta\lambda}{\lambda_0^2} = \frac{8}{3} \times 0.466 B / cm$$

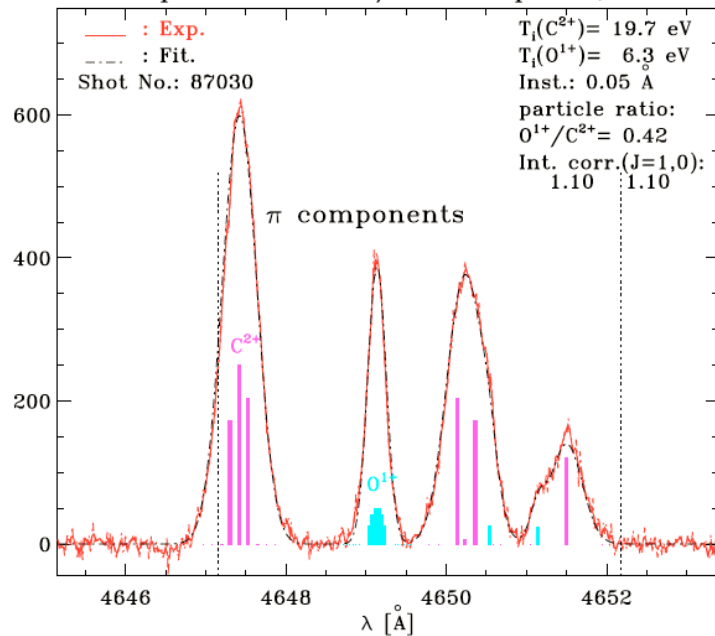
$$B = \frac{\Delta\lambda}{\lambda_0^2} \times \frac{3}{8} \times 0.466 / cm = 0.51T = 5100 gauss$$

# 托克马克塞曼谱

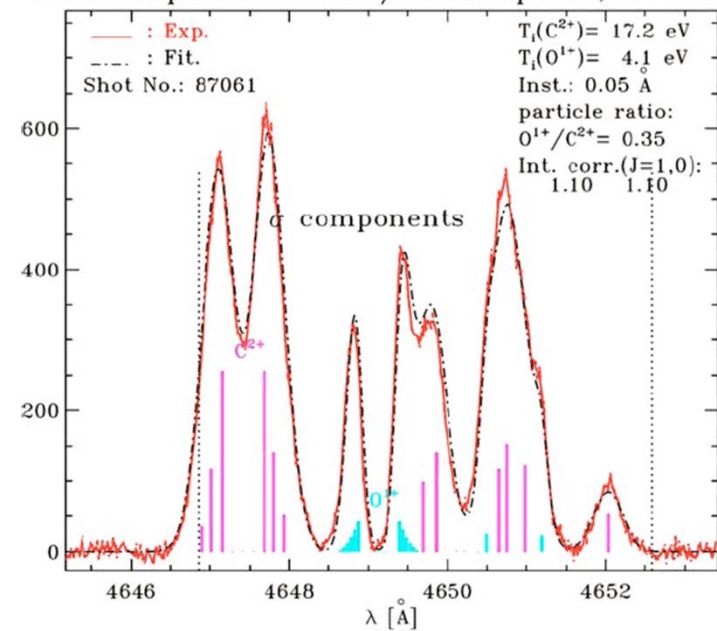
Ion	Transition	$J$	$J'$	$\lambda$ (Å)
C III	$2s3p\ ^3P^o \rightarrow 2s3s\ ^3S$	0	1	4651.47
		1	1	4650.25
		2	1	4647.42
O II	$2p^2(^3P)3p\ ^4D^o \rightarrow 2p^23s\ ^4P$	$\frac{1}{2}$	$\frac{1}{2}$	4650.84
		$3\frac{1}{2}$	$2\frac{1}{2}$	4649.13
C III	$2p(^2P^o)3p\ ^3P \rightarrow 2p3s\ ^3P^o$	1	0	4652.05
		2	1	4651.02
O III	$2s^22p(^2P^o)5s\ ^3P^o \rightarrow 2s^22p4p\ ^3P$	1	1	4649.97



Zeeman Spectrum of CIII/OII Multiplet 1, B= 2.23 T



Zeeman Spectrum of CIII/OII Multiplet 1, B= 2.60 T



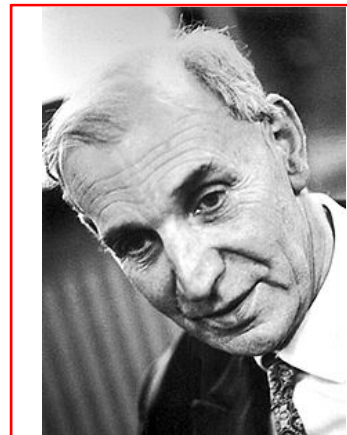


## 4.2 磁共振技术

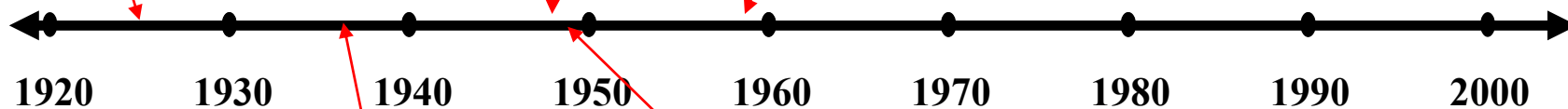
电子自旋  
的提出



库什, 1955



卡斯特勒, 1966



1920

1930

1940

1950

1960

1970

1980

1990

2000

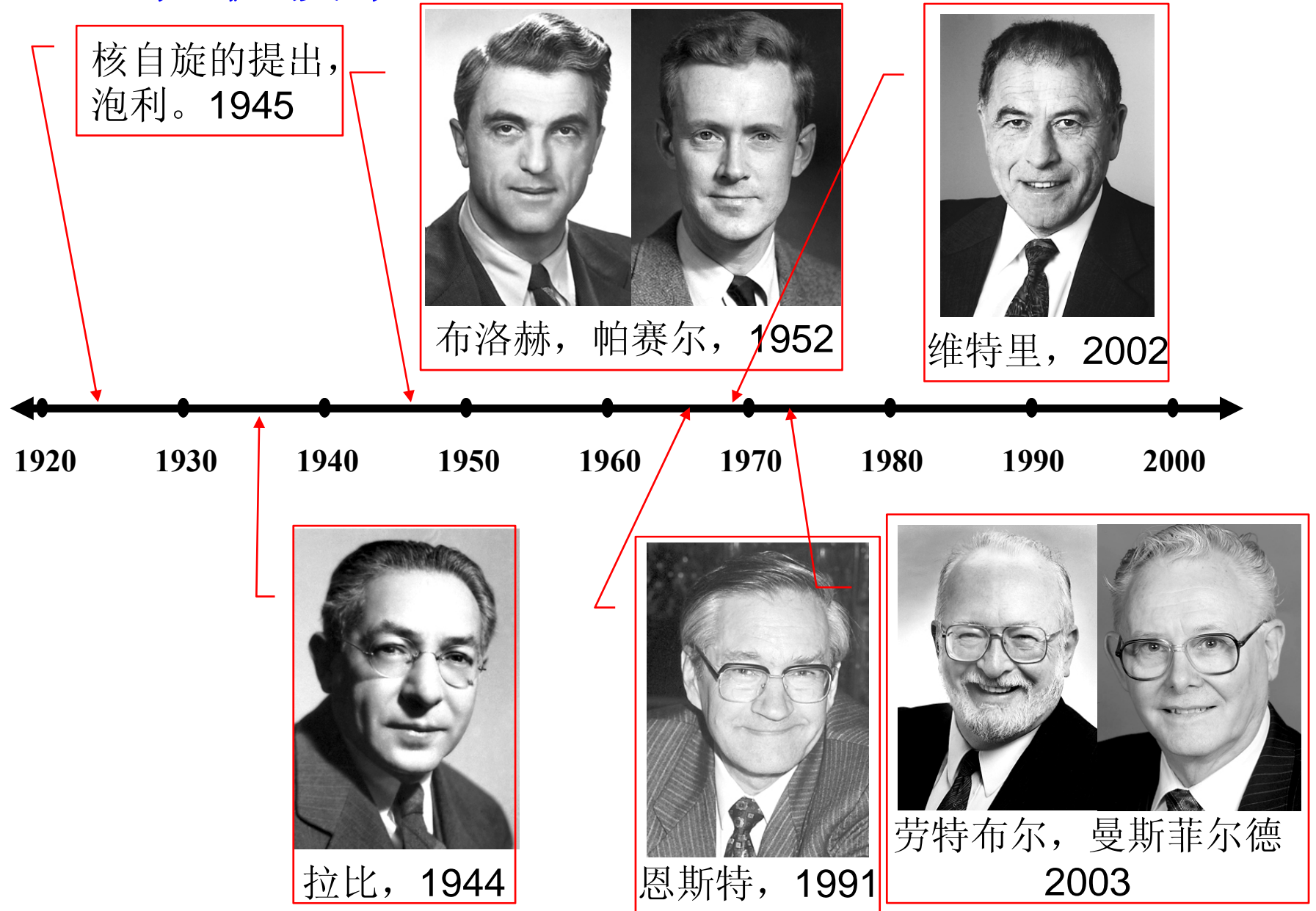


拉比, 1944

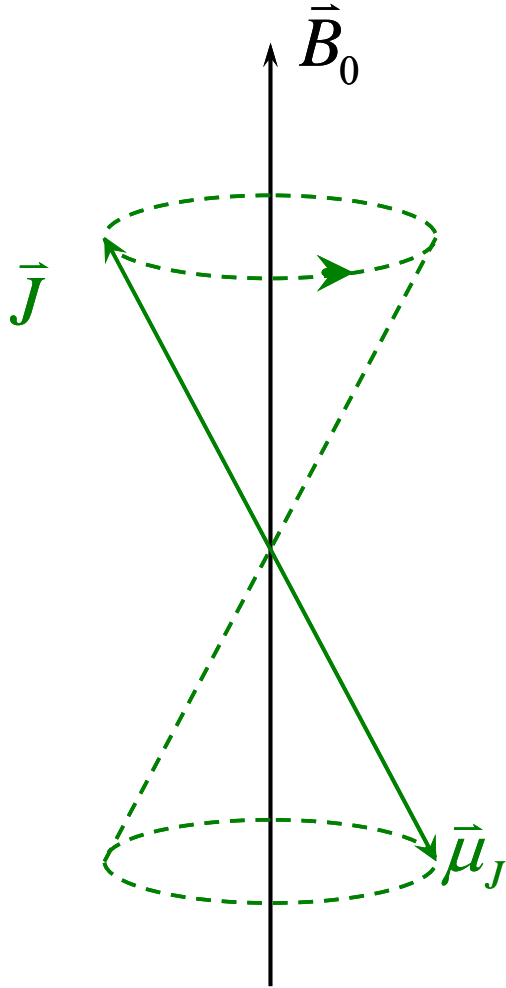


拉姆齐, 1989

## 4.2 磁共振技术



## 4.2.1 磁矩在外磁场中的运动



$$\vec{\tau} = \vec{\mu} \times \vec{B}$$

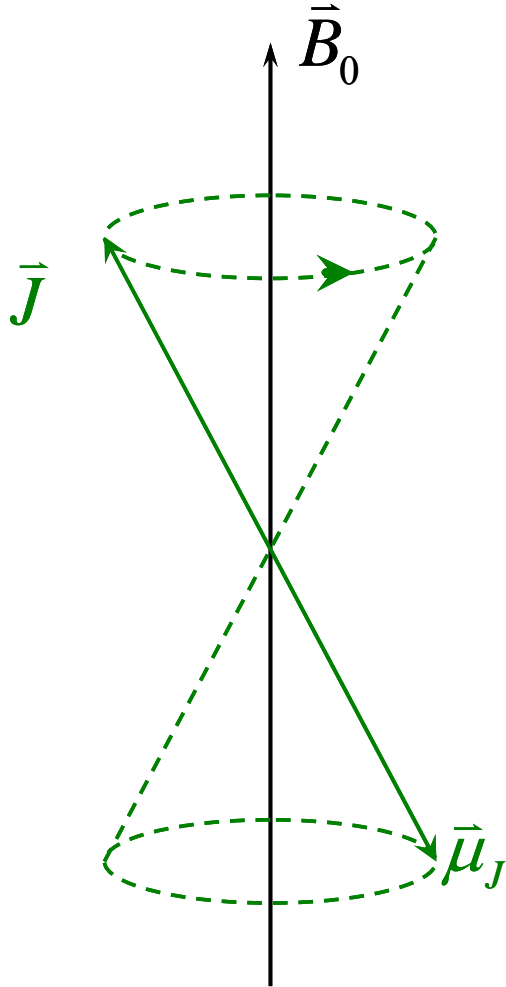
$$\frac{d\vec{J}}{dt} = \vec{\mu}_J \times \vec{B}_0$$

$$\frac{d\vec{J}}{dt} = -g_J \frac{\mu_B}{\hbar} \vec{J} \times \vec{B}_0 = \frac{g_J \mu_B}{\hbar} \vec{B}_0 \times \vec{J}$$

$$\vec{\omega} = \frac{g_J \mu_B}{\hbar} \vec{B}_0 = g_J \frac{e}{2m_e} \vec{B}_0$$

拉莫尔频率

## 4.2.1 磁矩在外磁场中的运动



$$\frac{d\vec{J}}{dt} = -g_J \frac{\mu_B}{\hbar} \vec{J} \times \vec{B}_0 = \frac{g_J \mu_B}{\hbar} \vec{B}_0 \times \vec{J}$$

$$\vec{\omega} = \frac{g_J \mu_B}{\hbar} \vec{B}_0 = g_J \frac{e}{2m_e} \vec{B}_0$$

拉莫尔频率

$$\gamma = \frac{\mu_J}{J} = -g_J \frac{e}{2m_e}$$

旋磁比

$$\vec{\omega} = -\gamma \vec{B}_0$$

弱磁场中:

$$U = -\vec{\mu}_J \cdot \vec{B} = -\mu_{Jz} B$$

$$U = m_J g_J \mu_B B$$

$$E'_J = E_J + m_J g_J \mu_B B$$

相邻能级间距对应的光子圆频率:

$$\omega = \Delta E / \hbar = g_J (e / 2m_e) B$$

与拉莫尔频率正好相等

$$M_J \rightarrow M_J + 1$$

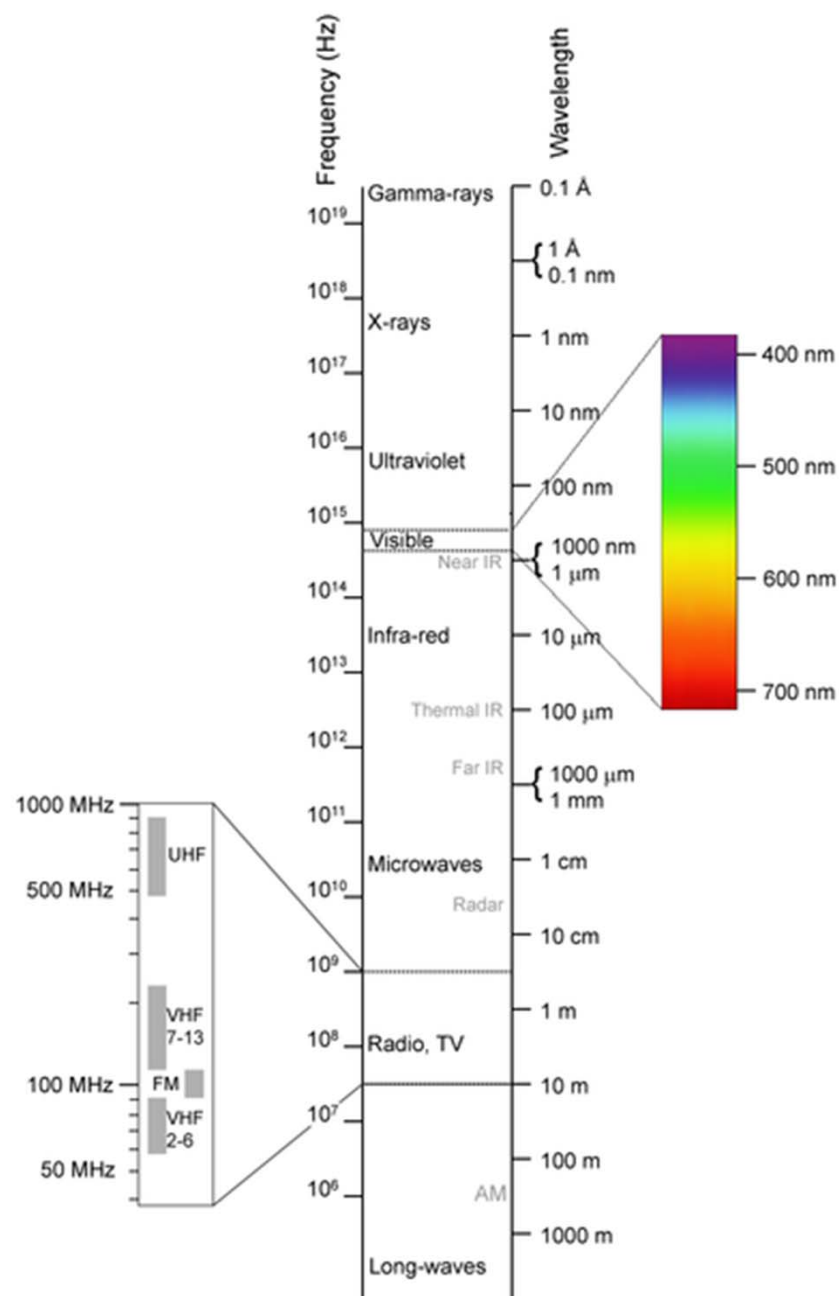
$$\Delta n = \Delta L = \Delta S = \Delta J = 0$$

电偶极禁戒！

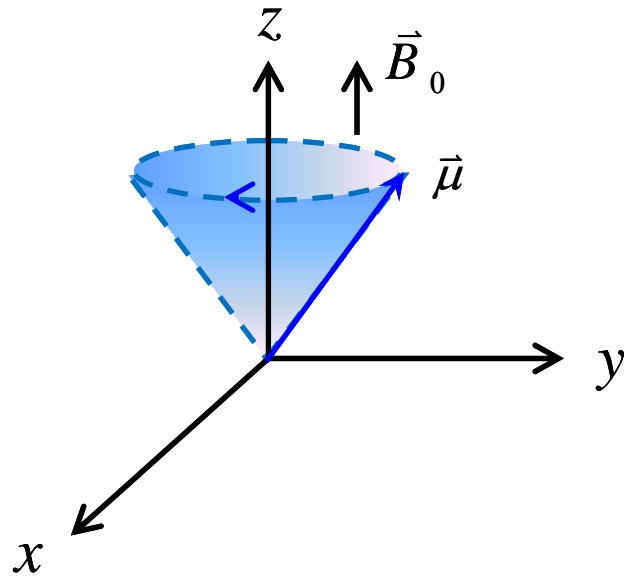
磁偶极允许！

涉及磁偶极吸收和发射的技术就是磁共振技术，  
它一般落在微波或射频波段。

CLASS	FREQUENCY	WAVELENGTH	ENERGY
Y	300 EHz	1 pm	1.24 MeV
HX	30 EHz	10 pm	124 keV
SX	3 EHz	100 pm	12.4 keV
SX	300 PHz	1 nm	1.24 keV
EUV	30 PHz	10 nm	124 eV
NUV	3 PHz	100 nm	12.4 eV
NIR	300 THz	1 $\mu$ m	1.24 eV
MIR	30 THz	10 $\mu$ m	124 meV
FIR	3 THz	100 $\mu$ m	12.4 meV
EHF	300 GHz	1 mm	1.24 meV
SHF	30 GHz	1 cm	124 $\mu$ eV
UHF	3 GHz	1 dm	12.4 $\mu$ eV
VHF	300 MHz	1 m	1.24 $\mu$ eV
HF	30 MHz	10 m	124 neV
MF	3 MHz	100 m	12.4 neV
LF	300 kHz	1 km	1.24 neV
VLF	30 kHz	10 km	124 peV
VF/ULF	3 kHz	100 km	12.4 peV
SLF	300 Hz	1 Mm	1.24 peV
ELF	30 Hz	10 Mm	124 feV
ELF	3 Hz	100 Mm	12.4 feV



## 4.2.2 磁共振技术的基本原理



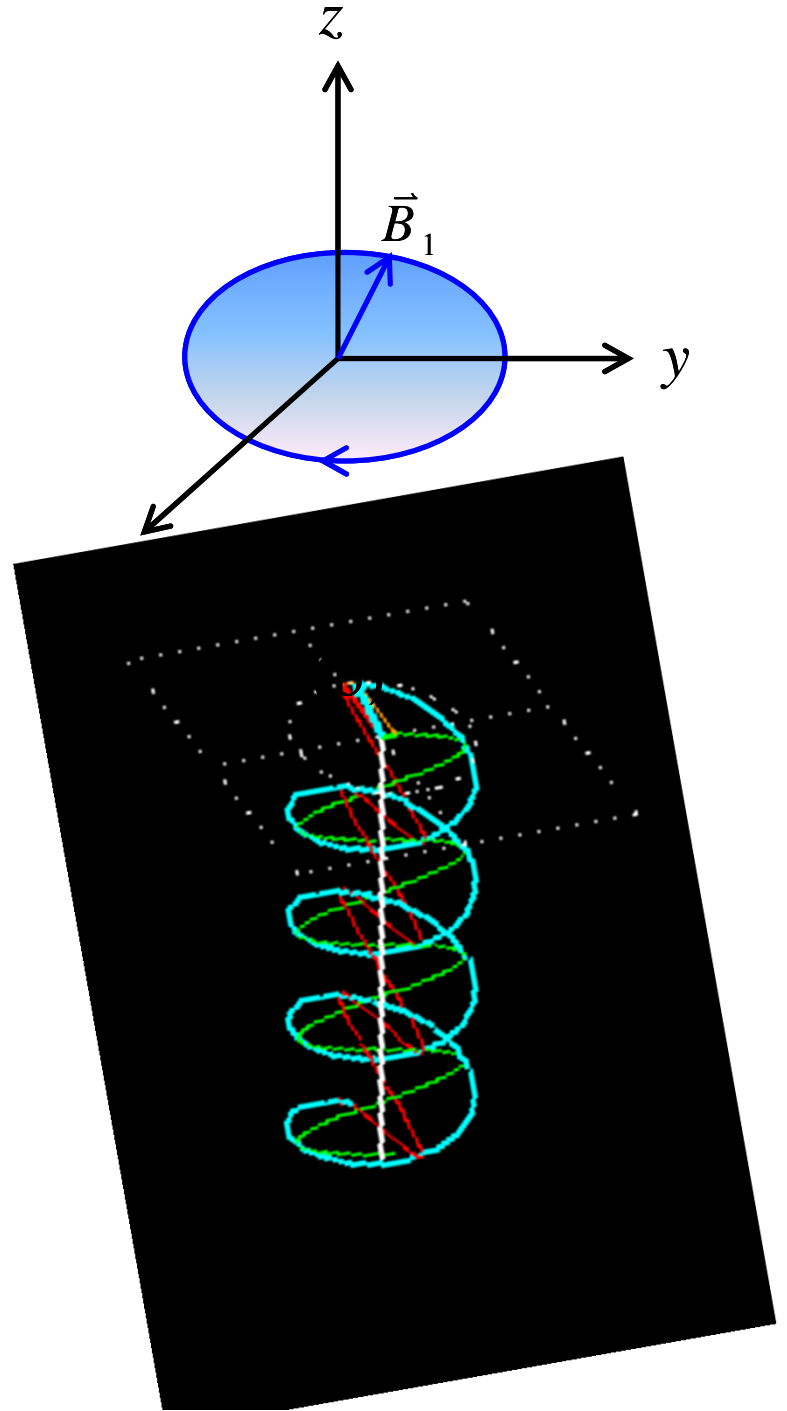
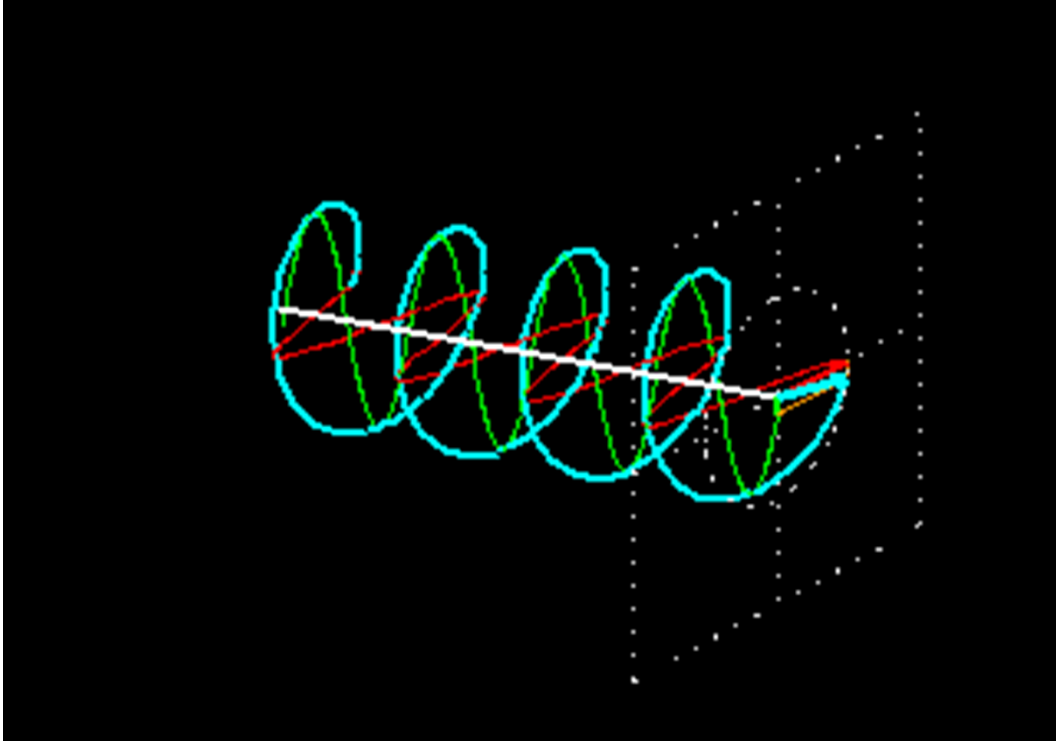
(a)

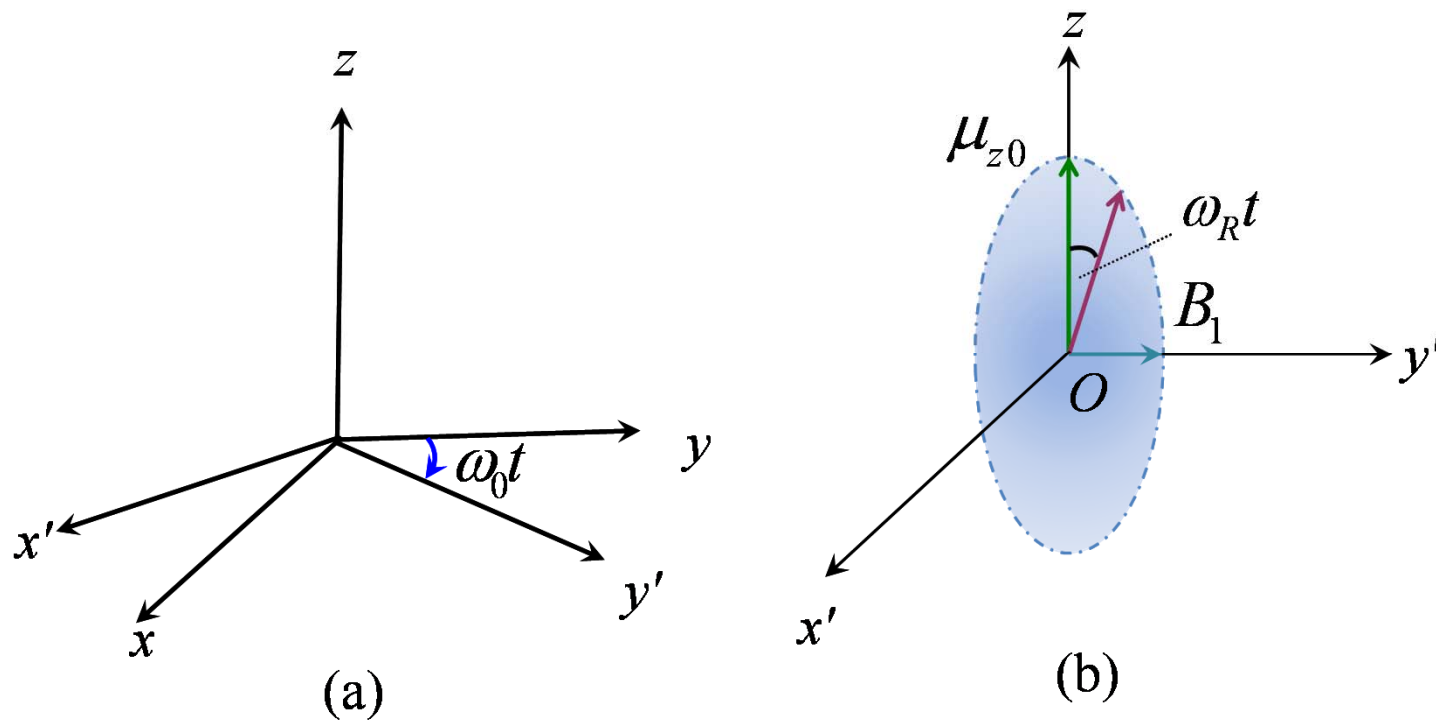
$$\frac{d\vec{J}}{dt} = -\gamma\vec{B}_0 \times \vec{J} = \vec{\omega}_0 \times \vec{J}$$

$$\vec{\mu}_J = -g_J \frac{\mu_B}{\hbar} \vec{J} = \gamma\vec{J}$$

$$\frac{d\vec{\mu}_J}{dt} = \gamma\vec{\omega}_0 \times \vec{J} = \vec{\omega}_0 \times \vec{\mu}_J$$



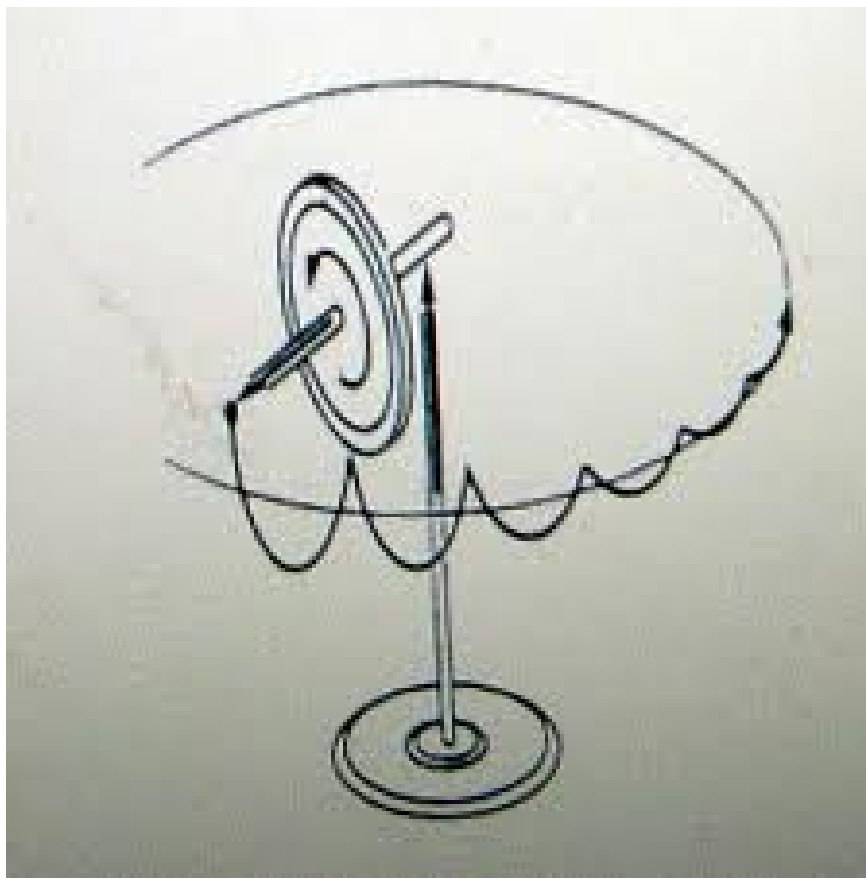




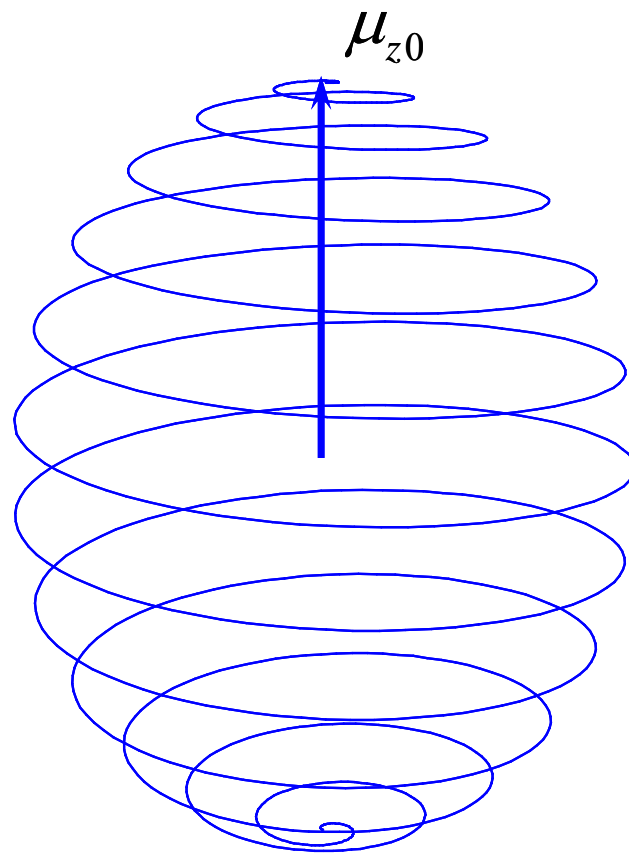
$$\omega_0 \gg \omega_R$$

$$\omega_R = -\gamma B_1$$

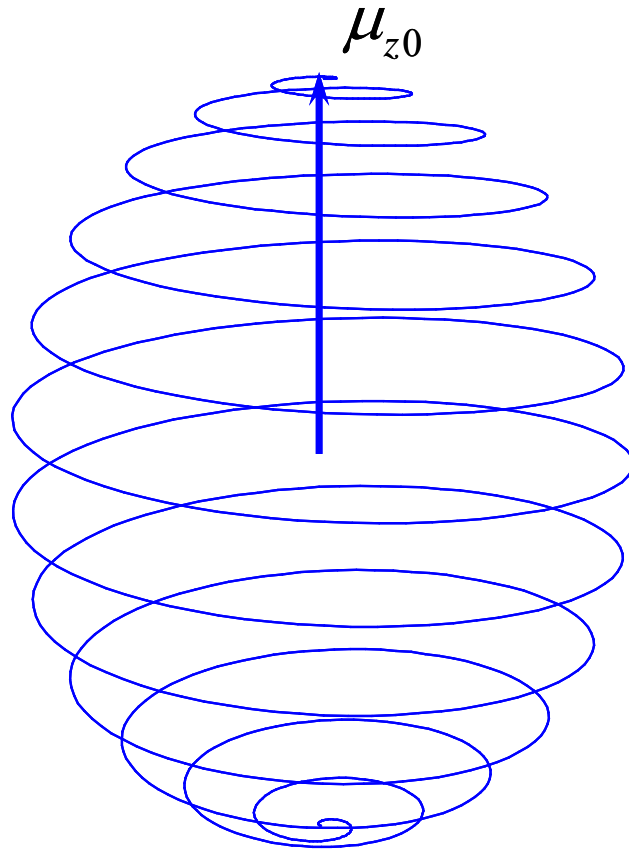
拉比频率



陀螺的进动与章动轨迹



磁共振中磁矩的运动轨迹



$$\mu_z = \mu_{z0} \cos \omega_R t$$

拉比频率 $\omega_R$ 与粒子处于  
高低能级的概率有关

磁共振中磁矩的运动轨迹

量子力学语言描述，拉比

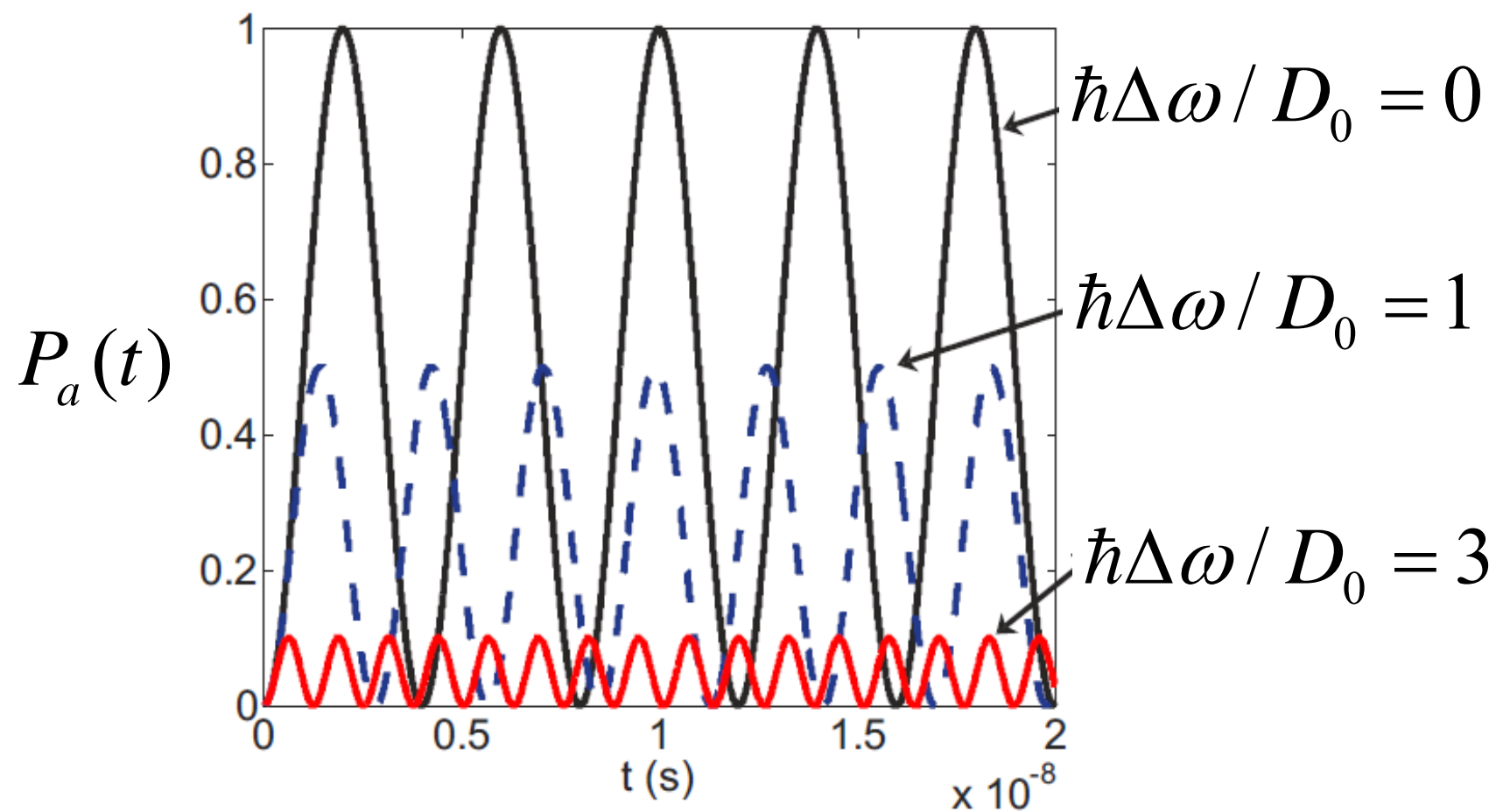
$$P_a(t) = \left( \frac{D_0}{\hbar \omega_R} \right)^2 \sin^2 \left( \frac{\omega_R t}{2} \right)$$

$$D_0 = g_J \mu_B B_1 \quad \omega_R = \sqrt{(\Delta\omega)^2 + (D_0 / \hbar)^2}$$

$$\Delta\omega = 0: \quad \omega_R = D_0 / \hbar = g_J \mu_B B_1 / \hbar = \gamma B_1$$

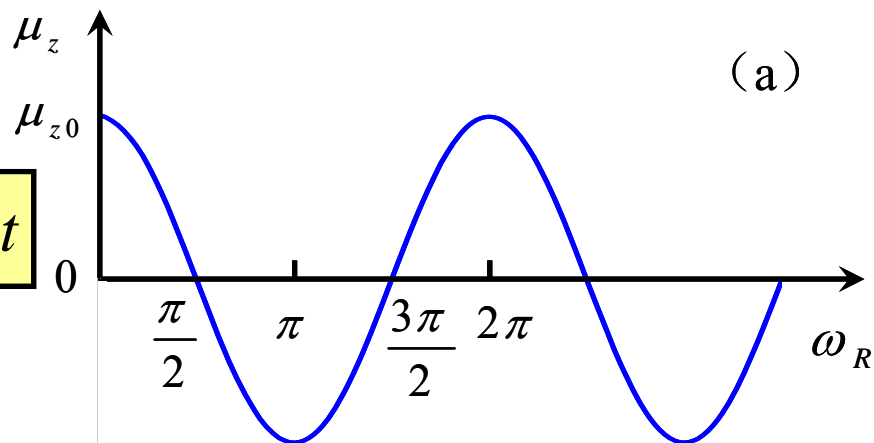
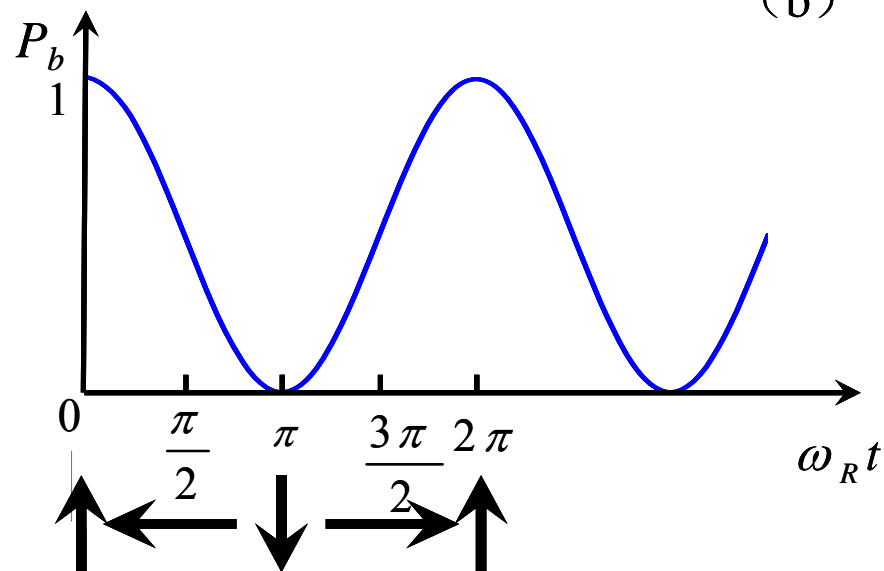
$$\Delta\omega \neq 0: \quad \omega_R \neq \gamma B_1 \quad \text{频率失谐量}$$

$$P_b(t) = 1 - P_a(t) = 1 - \left( \frac{D_0}{\hbar \omega_R} \right)^2 \sin^2 \left( \frac{\omega_R t}{2} \right)$$

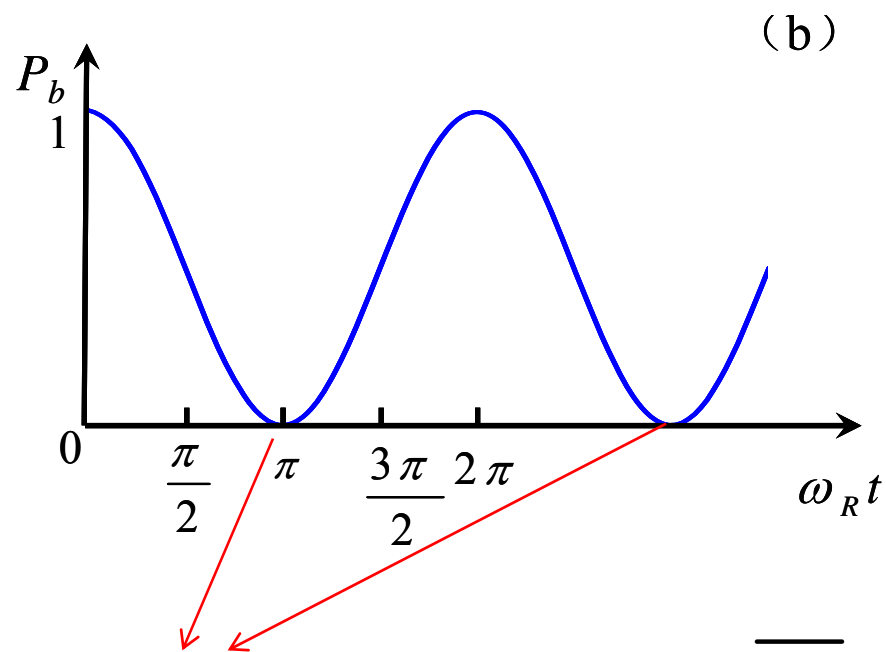


在共振情形下  $\Delta\omega = 0$   
 $\omega = \omega_0, \omega_R = \gamma B_1 = D_0 / \hbar$

$$\begin{cases} P_a = \sin^2\left(\frac{D_0}{2\hbar}t\right) \\ P_b = \cos^2\left(\frac{D_0}{2\hbar}t\right) \end{cases}$$



$$\overline{\mu_z} = \mu_{z0} P_b + (-\mu_{z0}) P_a = \mu_{z0} \cos \omega_R t$$

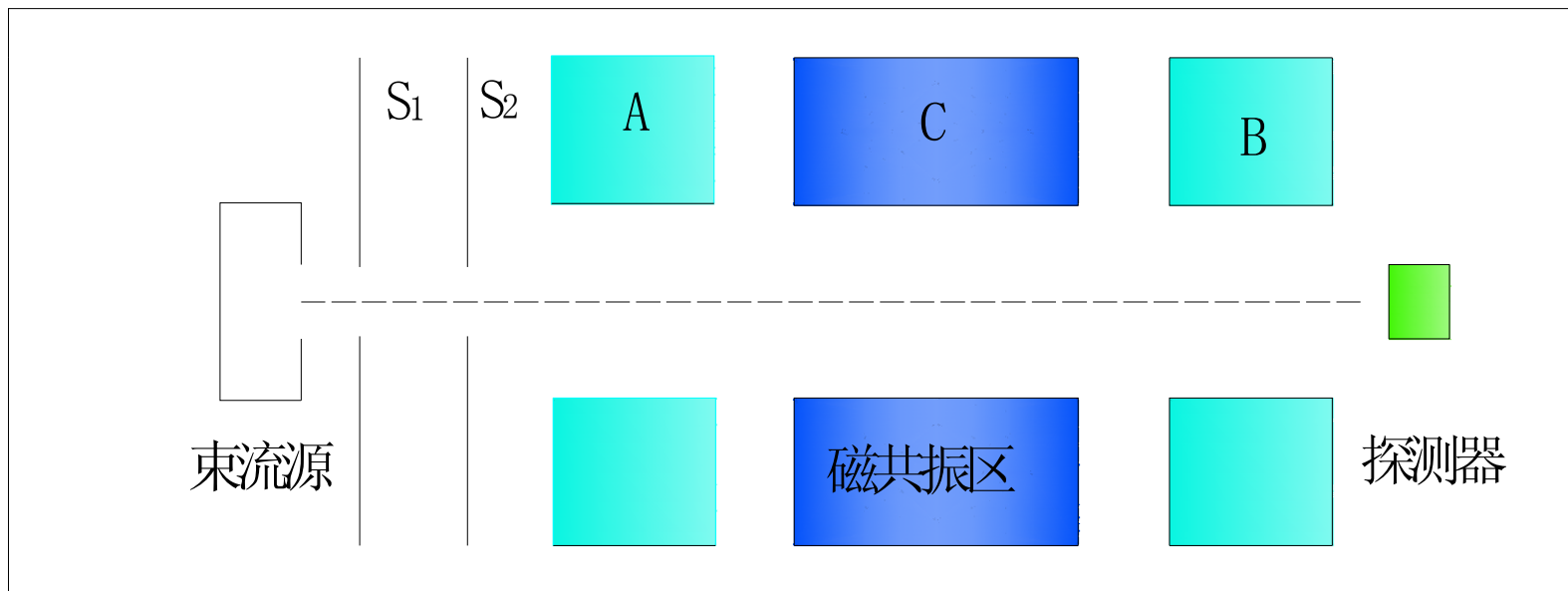


$$\delta t = (2n + 1)\pi / \omega_R \quad \mathbf{P_b=0} \quad \overline{\mu_z} = -\mu_{z0} \quad \pi \text{脉冲}$$

$$\delta t = (n + 1/2)\pi / \omega_R \quad \mathbf{P_b=1/2} \quad \overline{\mu_z} = 0 \quad \pi/2 \text{脉冲}$$

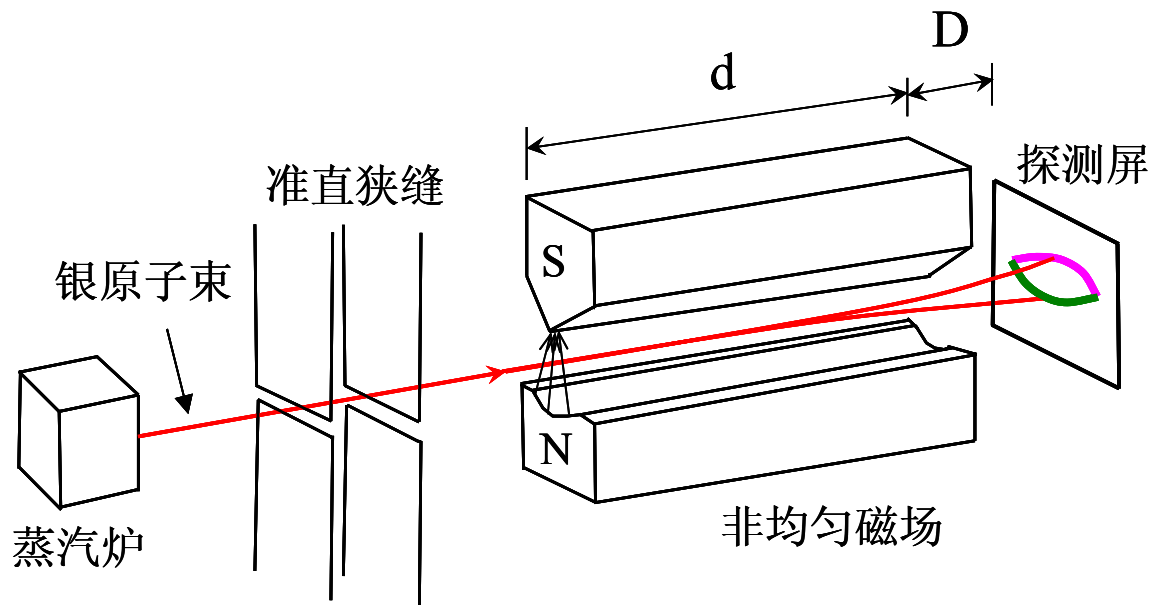


## 4.2.3 原子分子束磁共振技术



拉比的原子分子磁共振实验装置原理图

## 选态磁铁

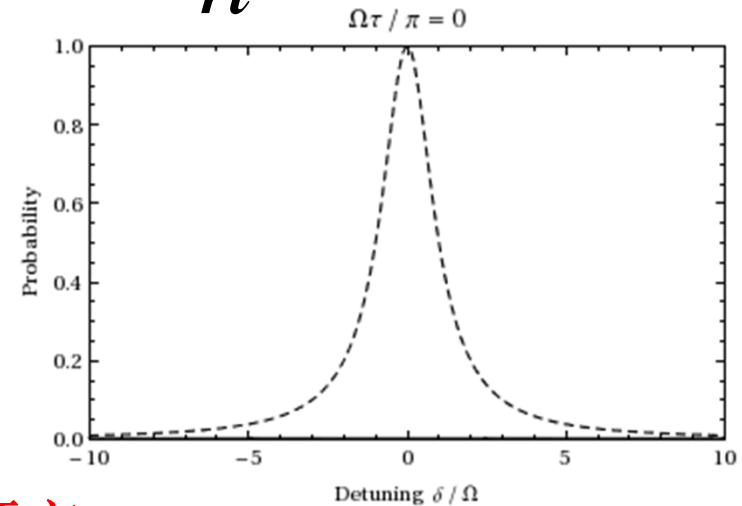


$$F_z = \mu_z \frac{\partial B}{\partial z} = -m_j g_j \mu_B \frac{\partial B}{\partial z}$$

不同磁矩态具有不同的运动轨迹

$$\omega_0 = \Delta E / \hbar = g_J \mu_B B_0 / \hbar = \frac{\mu_B}{\hbar} g_J B_0$$

共振条件:  $\omega = \omega_0$



1. 固定磁场强度，扫描射频场的频率 $\omega$
2. 固定射频场的频率 $\omega$ ，扫描磁场强度，进而扫描 $\omega_0$

可以测量 $\omega_0$ ，从而精确测量 $g$ 因子

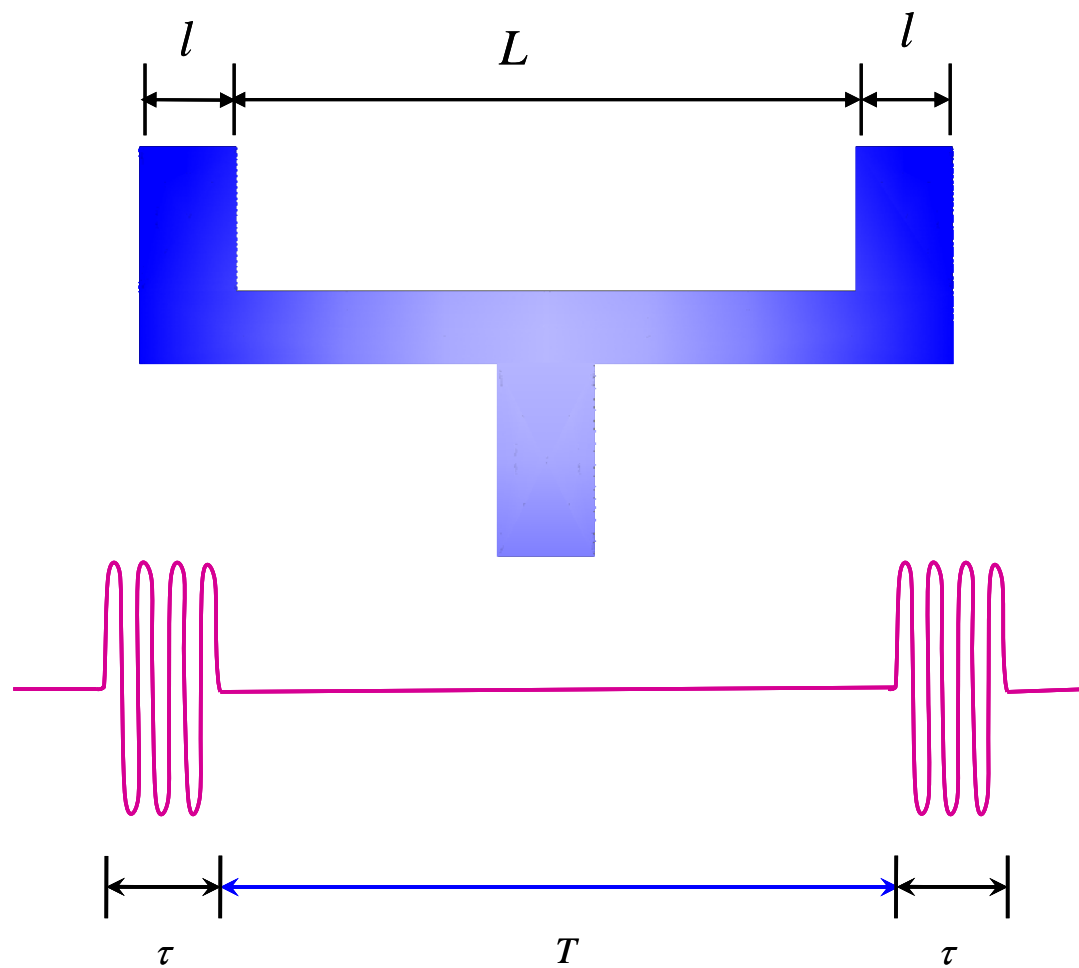
精度问题

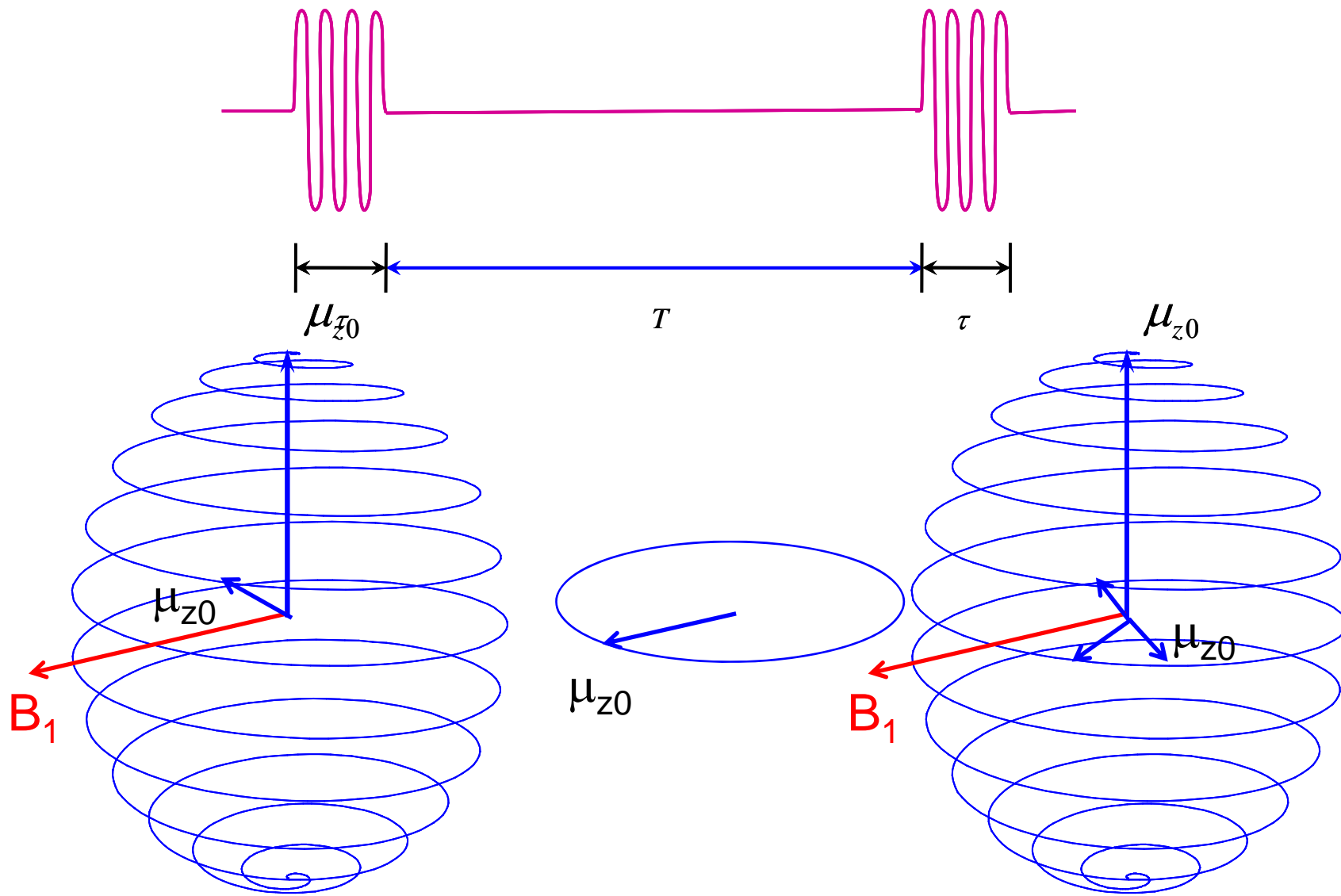
$$\Delta t = L / v_0$$

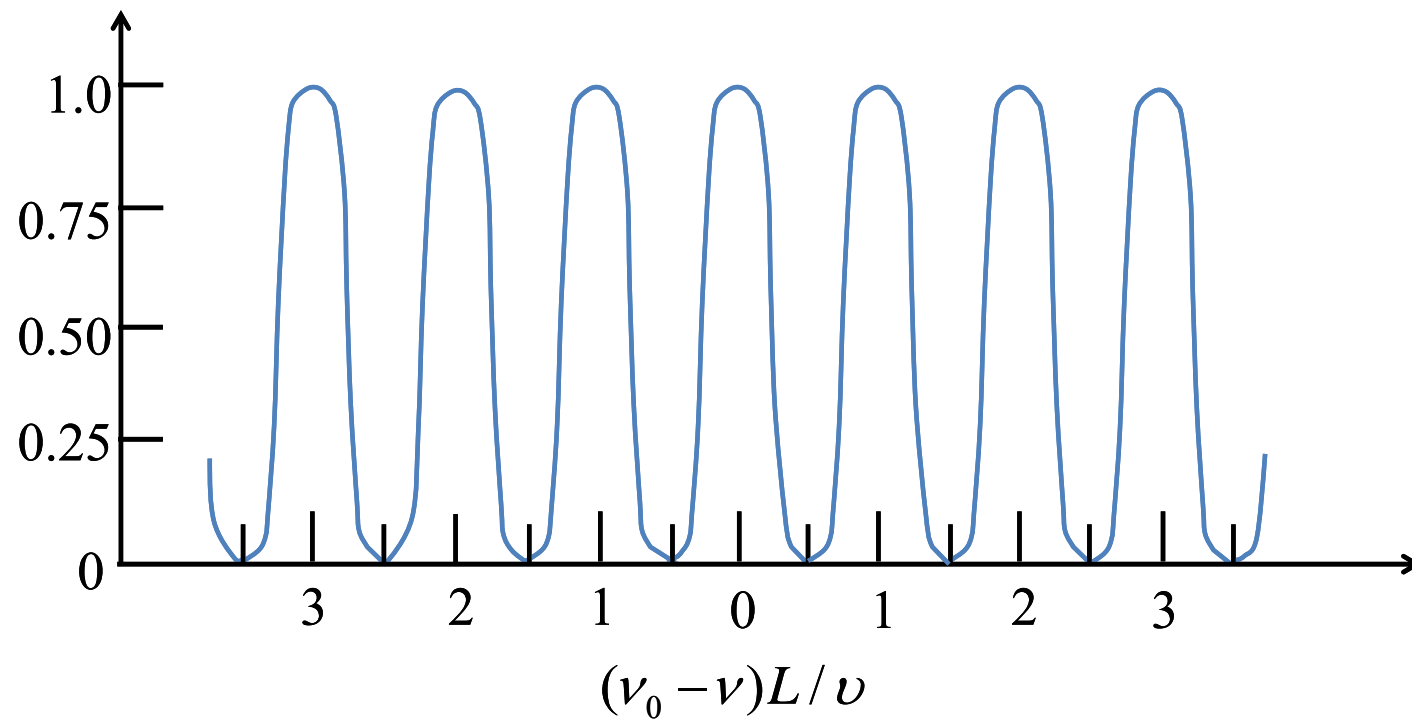
$$\Delta E \cdot \Delta t \geq \hbar / 2$$

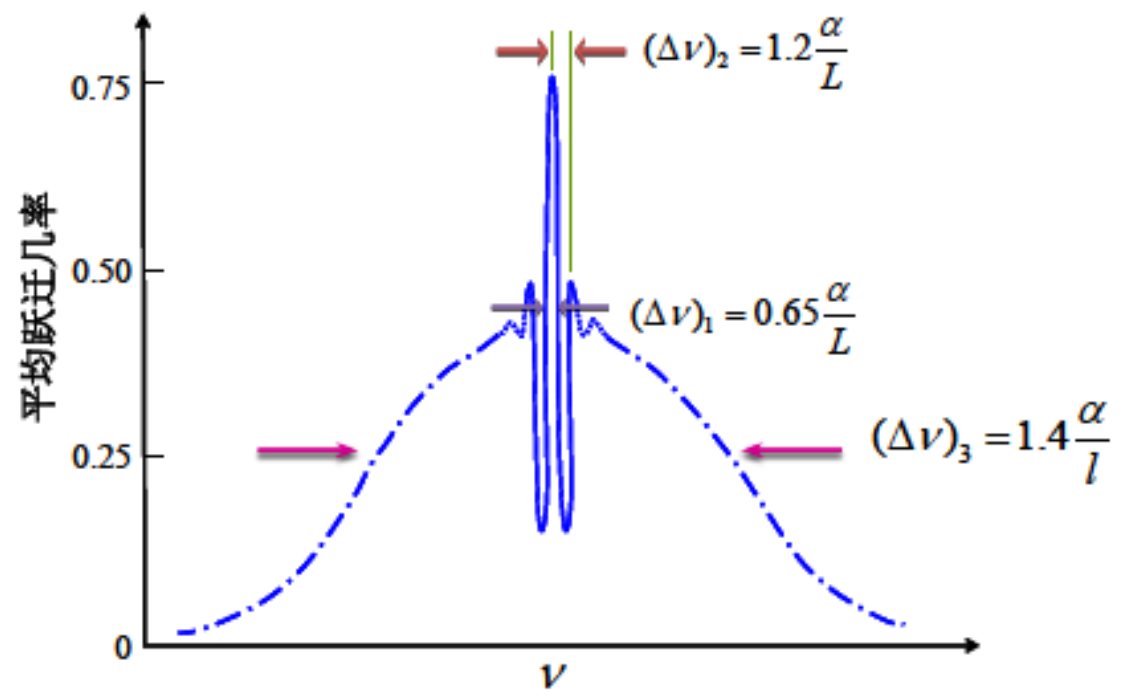
$$\Delta E \approx \hbar v_0 / 2L$$

# 拉姆齐，分离振荡场



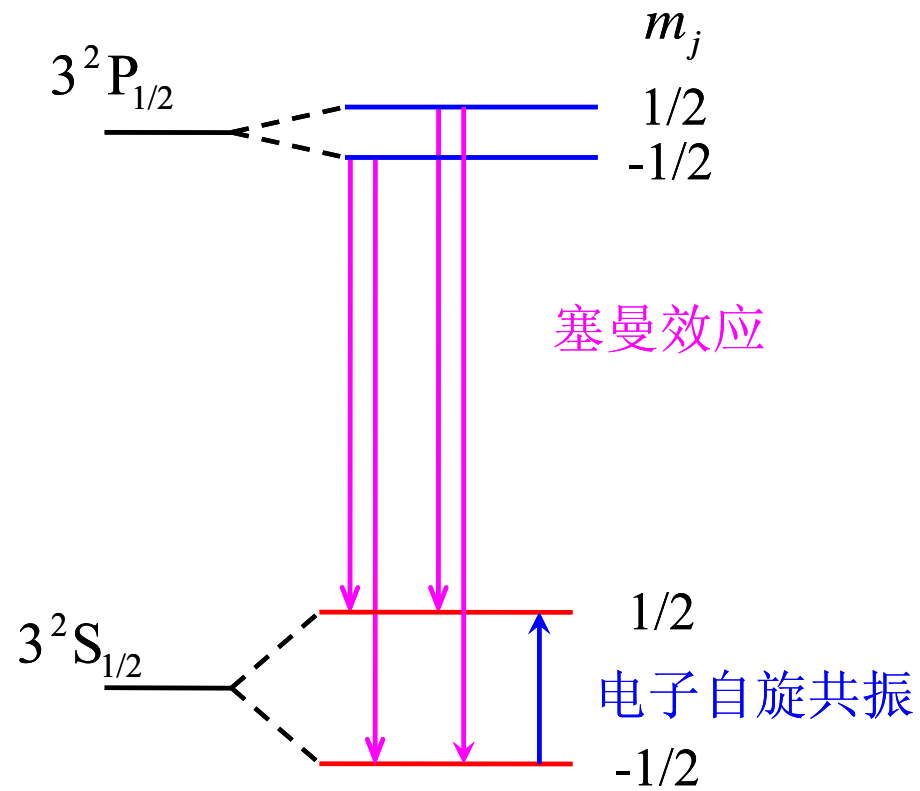




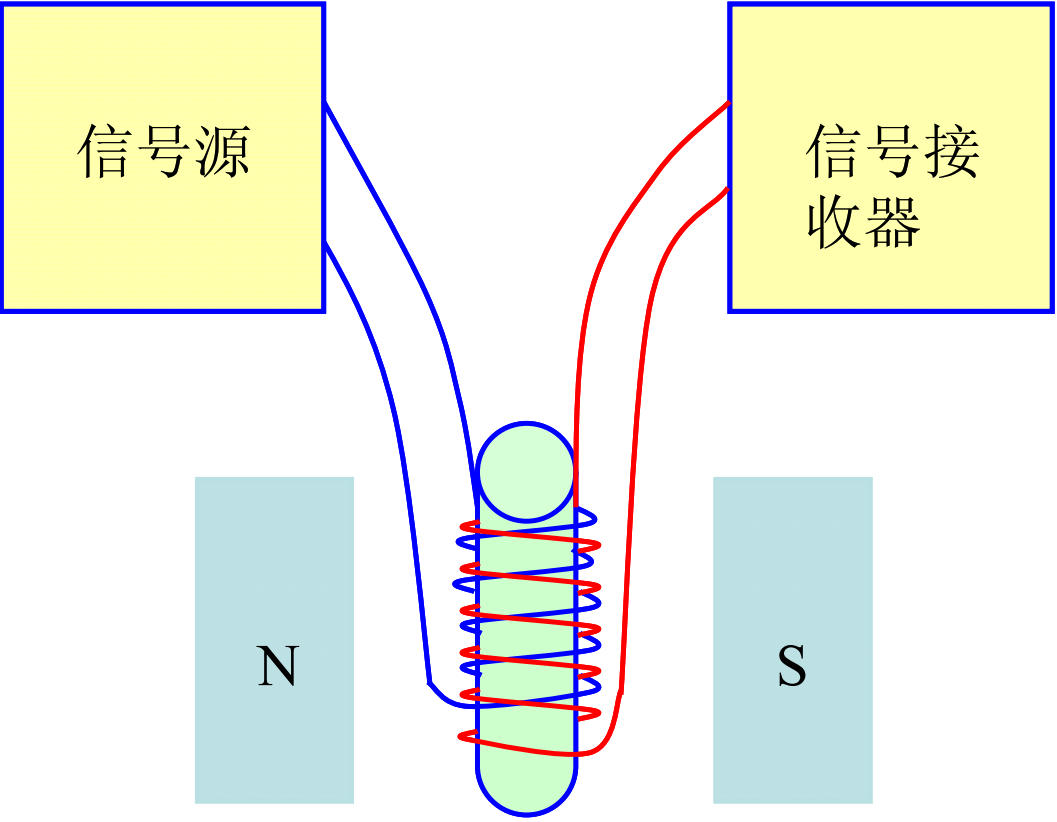




## 4.2.3 电子顺磁共振 (EPR)

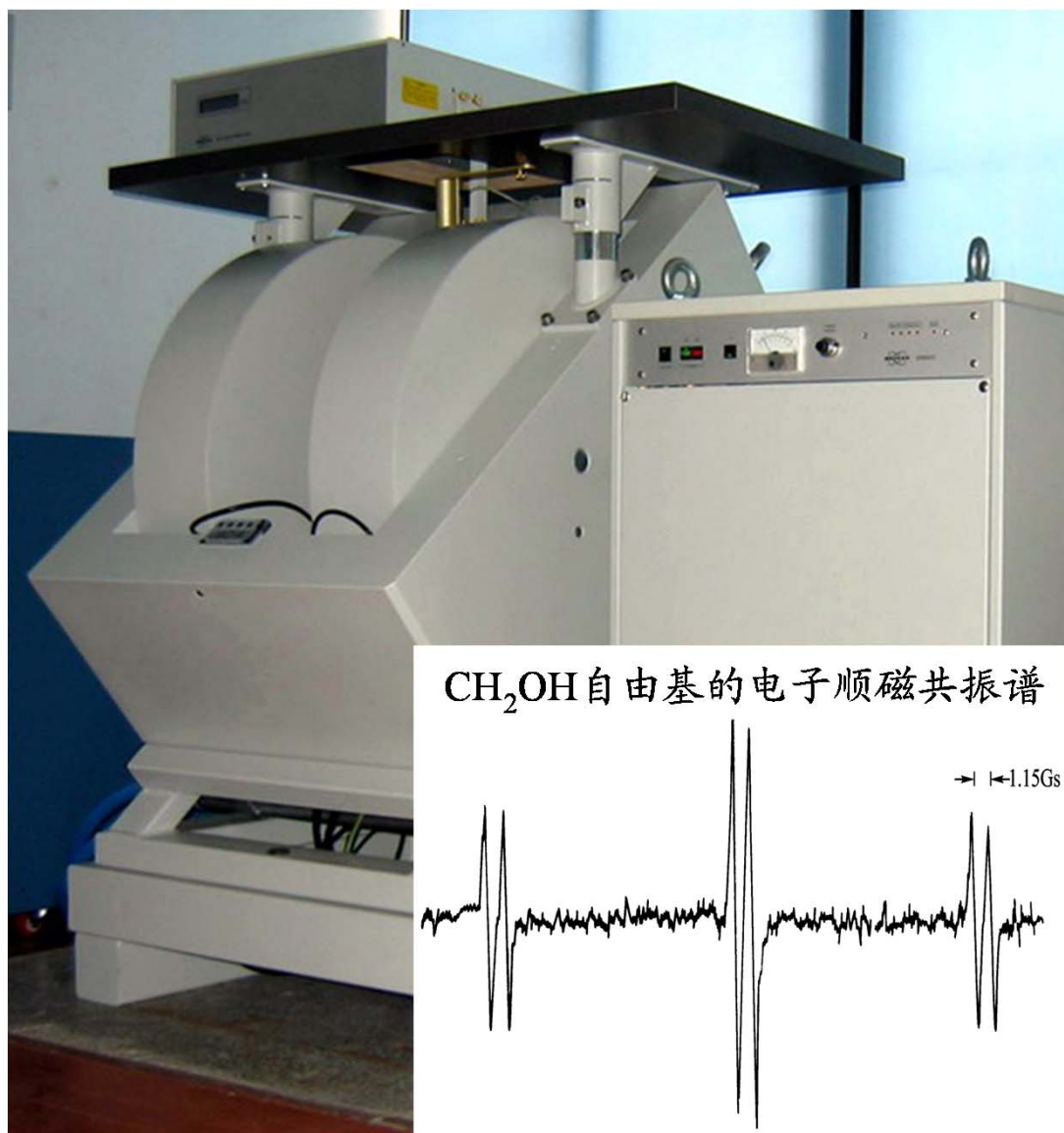


$$h\nu = g\mu_B B = g\mu_0\mu_B H$$



例4.2.1 Na原子处于磁场为**B**的微波谐振腔中，且  $\nu = 1 \times 10^{10} \text{ Hz}$   
试问**B**为何值时电磁波的能量能被吸收。

$$B = \frac{h\nu}{g\mu_B} = \frac{h\nu}{2\mu_B} = 0.36T$$



## 4.2.4 核磁共振 (NMR)

$$h\nu = g_N \mu_N B$$

$$\mu_N = e\hbar / 2m_p = 3.152451238 \times 10^{-8} \text{ eV} \cdot \text{T}^{-1}$$

电子顺磁共振

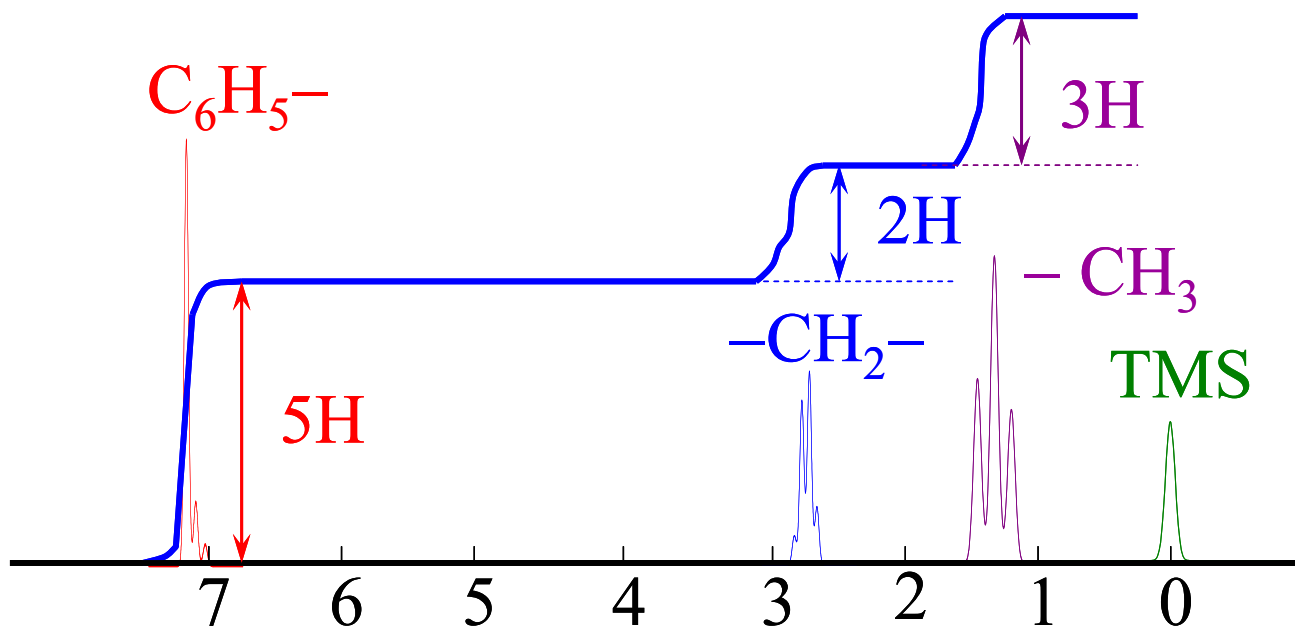
$$\frac{\nu}{B} = 14 g \text{ GHz/T}$$

核磁共振

$$\frac{\nu}{B} = 7.6 g_N \text{ MHz/T}$$

**$^1\text{H}$  (99.9844%) 、  $^{13}\text{C}$  (1.11%) 、  $^{17}\text{O}$ (0.038%)、  
 $^{19}\text{F}$ (40%)和 $^{31}\text{P}$  ( $\approx 100\%$ )**

$$B_{\text{外}} - \sigma B_{\text{外}} = (1 - \sigma) B_{\text{外}}$$



$$\delta = \frac{B_{\text{外标}} - B_{\text{外}}}{B_{\text{外标}}} \times 10^6 \text{ ppm}$$

**20世纪60年代**，恩斯特提出了一个设想来提高核磁共振的灵敏度和效率

技术核心有两条：

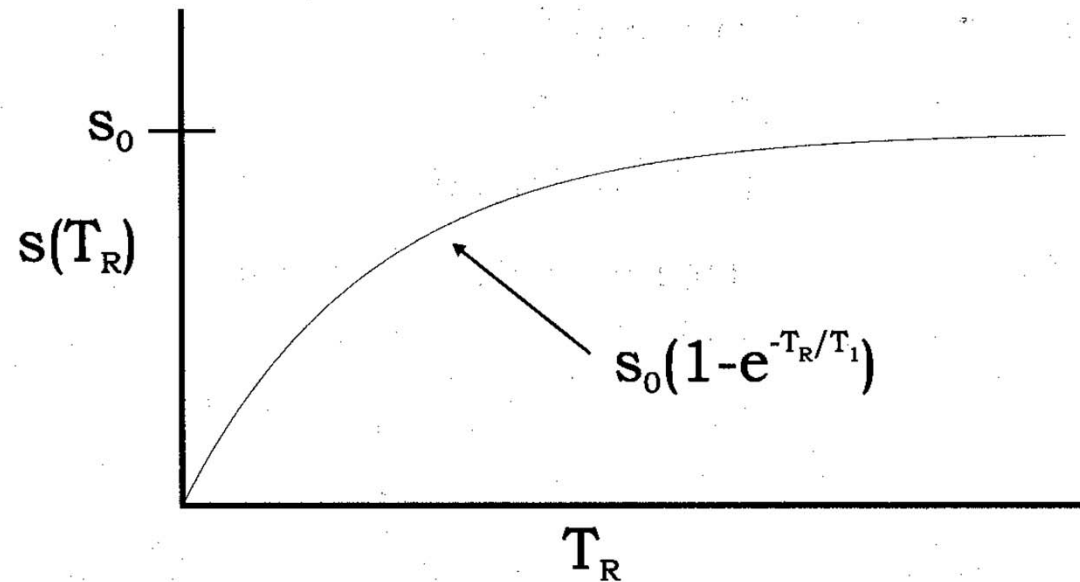
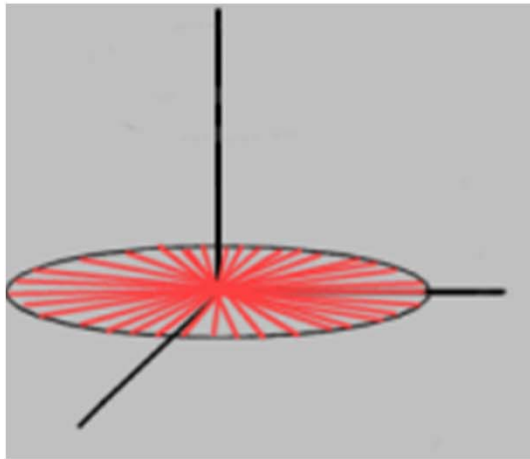
第一条是基于核磁矩在撤掉射频场后存在的弛豫现象；

第二条是短脉冲的射频信号具有频谱。



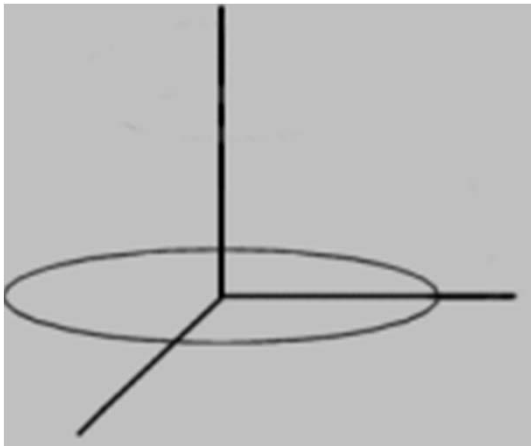
## T1弛豫

关闭射频信号后，处于非平衡自旋状态的核磁矩和与周围晶格之间互相交换能量，使核自旋状态演化为玻耳兹曼分布，这种弛豫称为纵向弛豫，又叫**T1弛豫**



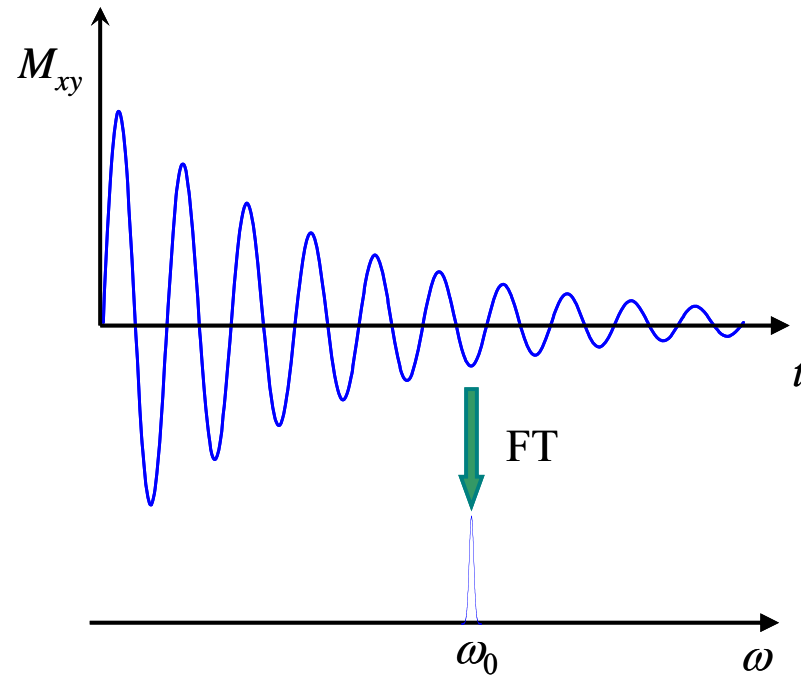
## T2弛豫

关闭射频信号后，由于核自旋之间的相互作用（所以横向弛豫也叫做自旋-自旋弛豫），也由于静磁场的非均匀性，导致各微观磁矩进动的相位逐渐变得不同步，并最终回到相位随机分布的平衡状态。

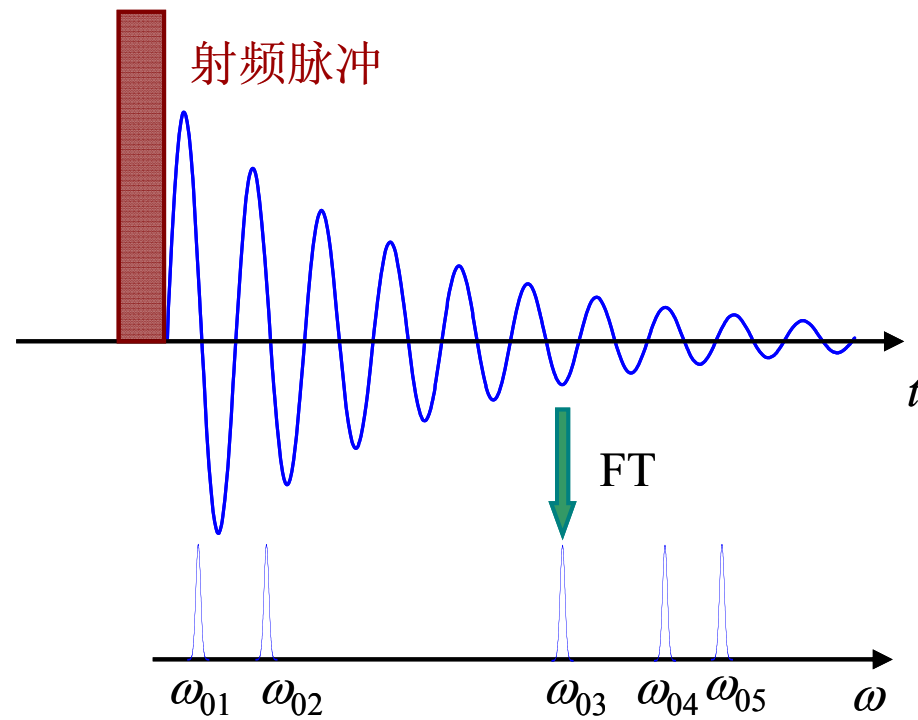


## T2弛豫

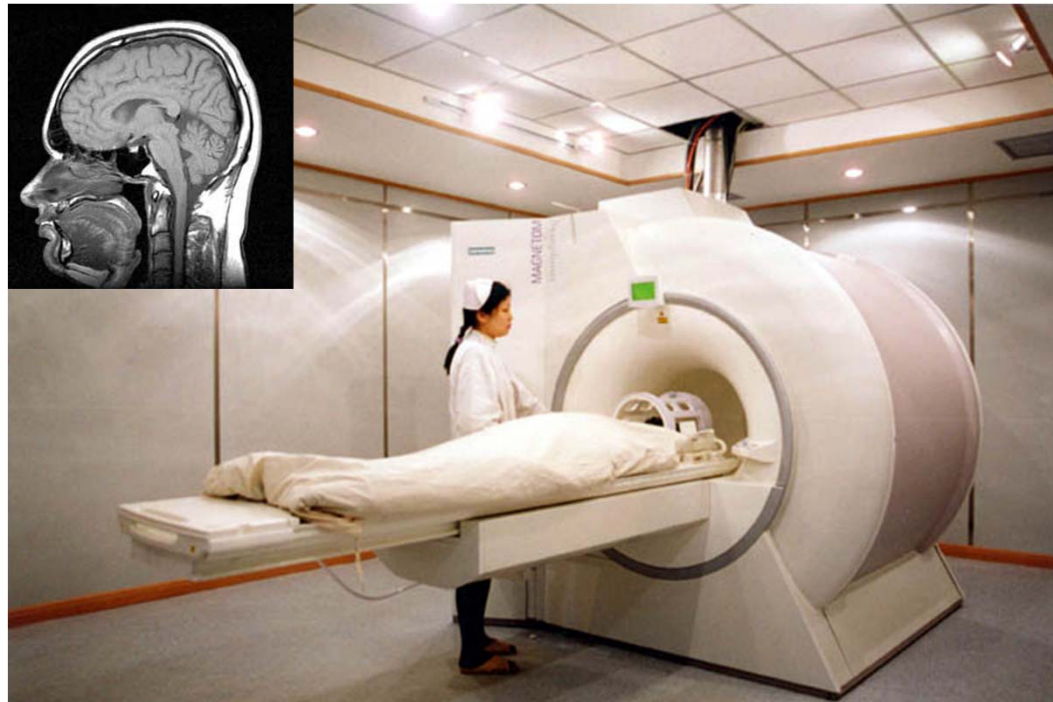
$$M_{xy} = M_{xy0} \sin \theta_0 \sin(\omega_0 t) \exp(-t / T_2)$$

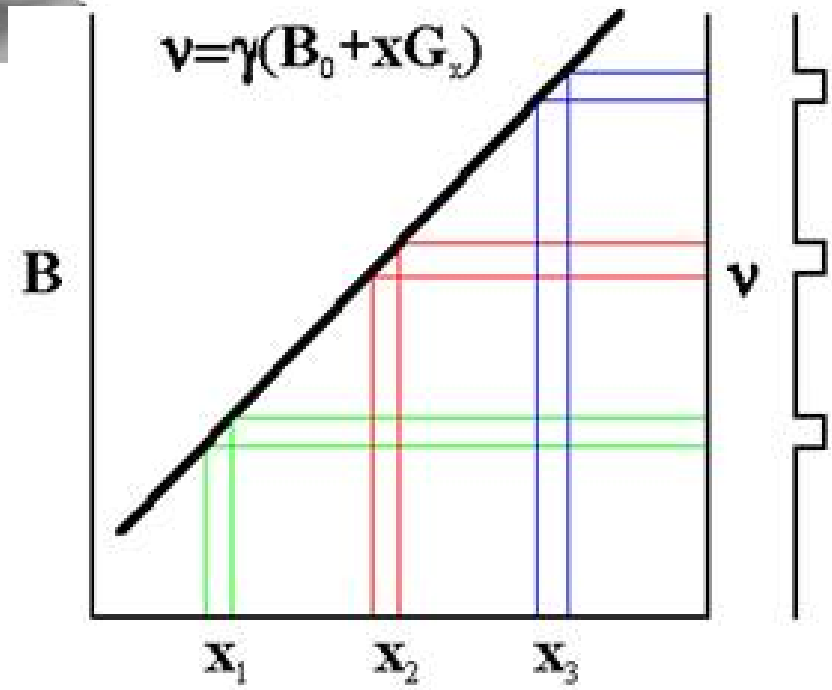


$$M_{xy} = \sum_i M_{xy}^0 \sin \theta_0 \sin \omega_0^i t \exp(-t / T_2^i)$$

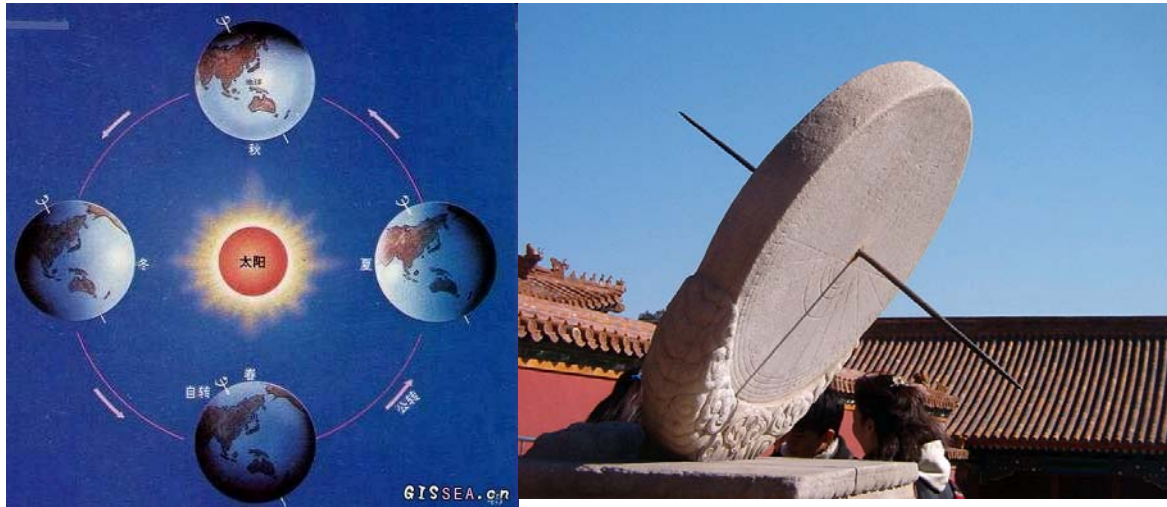


## 4.2.4 磁共振成像 (MRI)



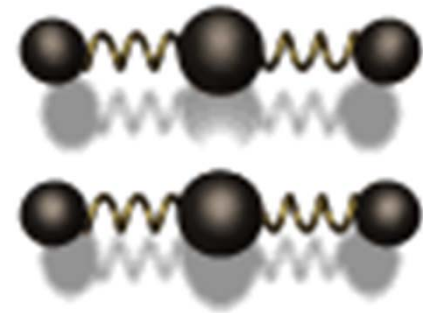
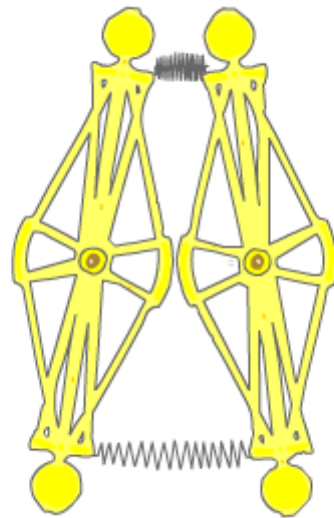
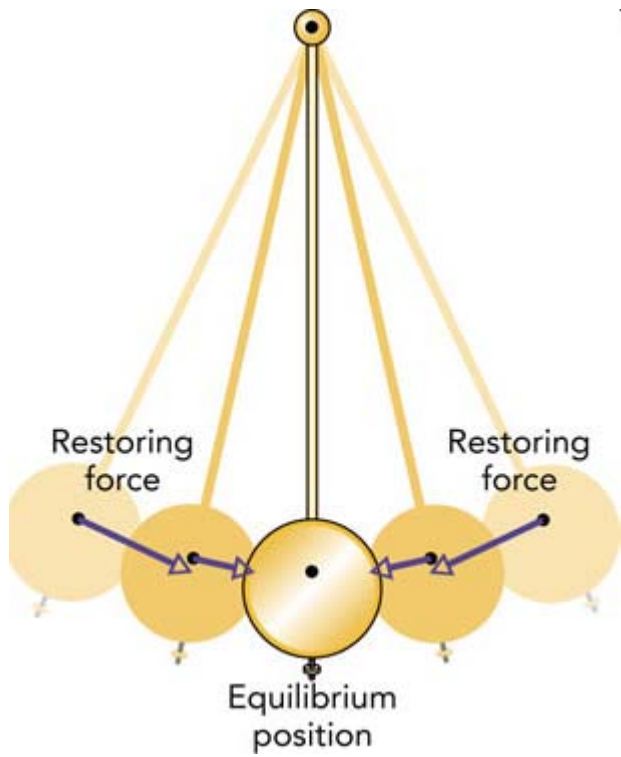


## 4.2 原子频标



1967年之前:

一个平太阳日的86400分之一为  
1秒, 相应的种被称为太阳钟





## 4.3.1 原子频标概述

### 时间标准

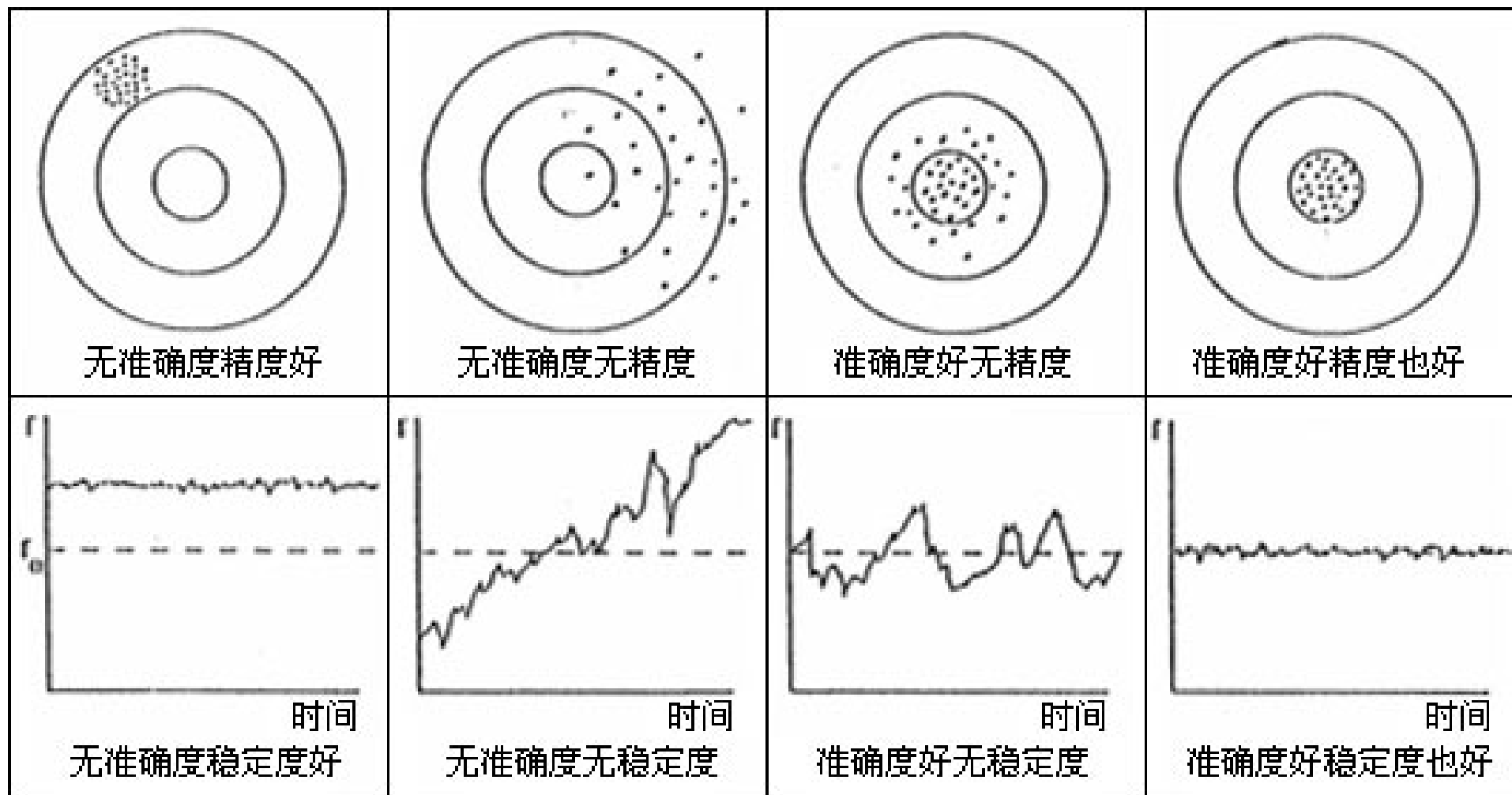
一秒到底是多少？

世界上没有任何一个单摆或者石英表是完全一样的

原子能级对应的电磁波频率？

利用原子的超精细能级间的跃迁频率来定义秒→原子频标

原子能级的典型特点是其稳定性、普适性和可重复性！



描述时间和频率的重要指标是准确度、精度、稳定度。对于守时和授时工作来说，原子钟的稳定度、准确度指标是工作关注的重点。

## 原子能级的典型特点是其稳定性、普适性和可重复性！

- ✓ 所有的同类原子，其能级结构都完全相同
- ✓ 与测量哪个原子无关
- ✓ 与测量环境无关
- ✓ 与测量时间无关
- ✓ 原子钟必然也具有相同的优点

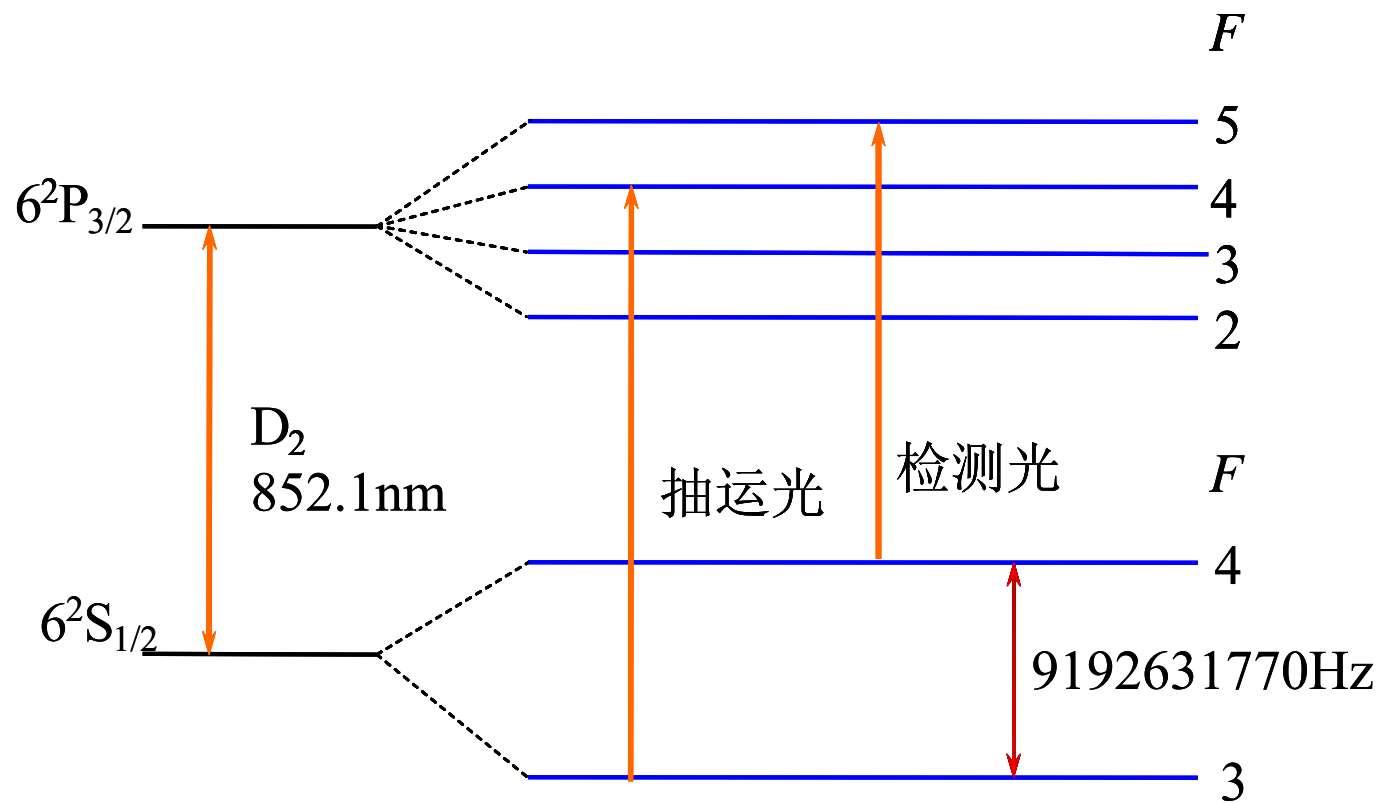
### 影响原子钟精度的内因：

- ✓ 与外磁场耦合塞曼效应引起的能级移动
- ✓ 与外电场耦合斯塔克效应引起的能级移动

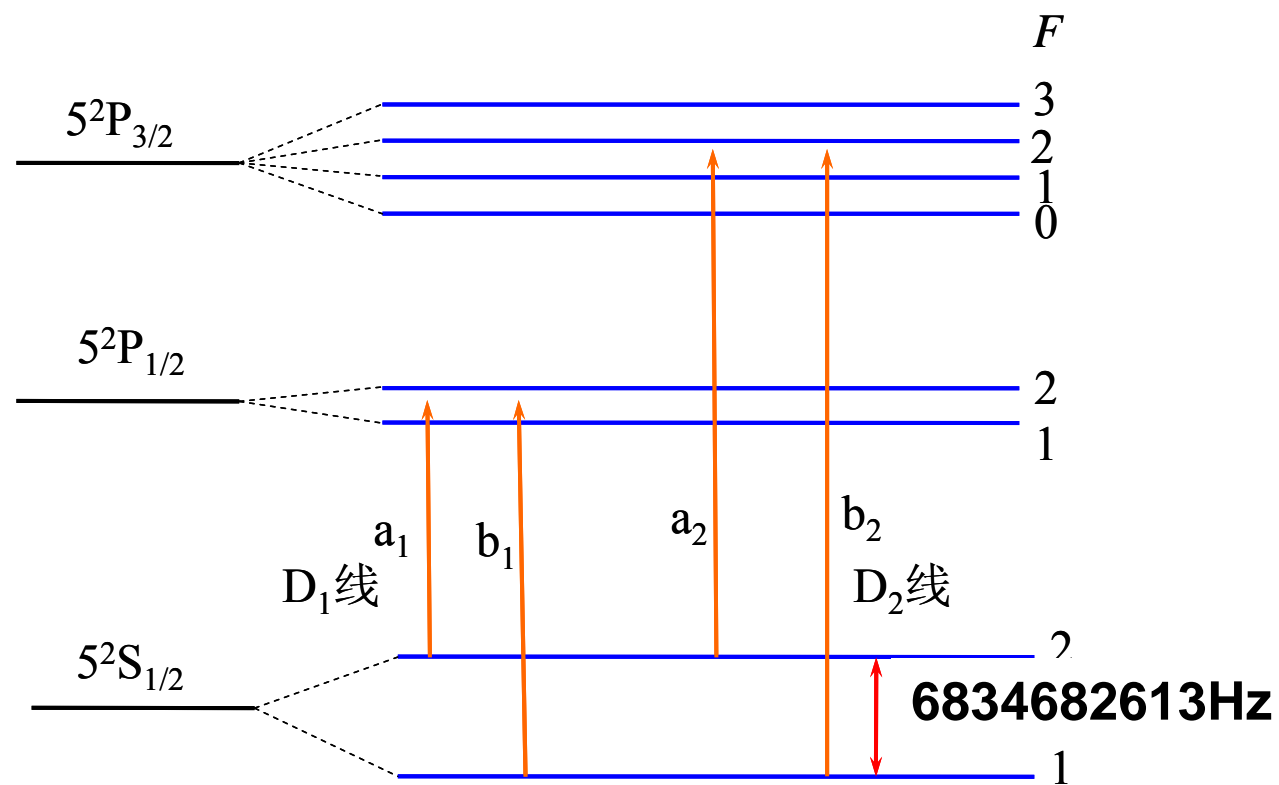
### 影响原子钟精度的外因：

- ✓ 多普勒增宽
- ✓ 渡越时间增宽

# 铯钟 ( $^{133}\text{Cs}$ ) :

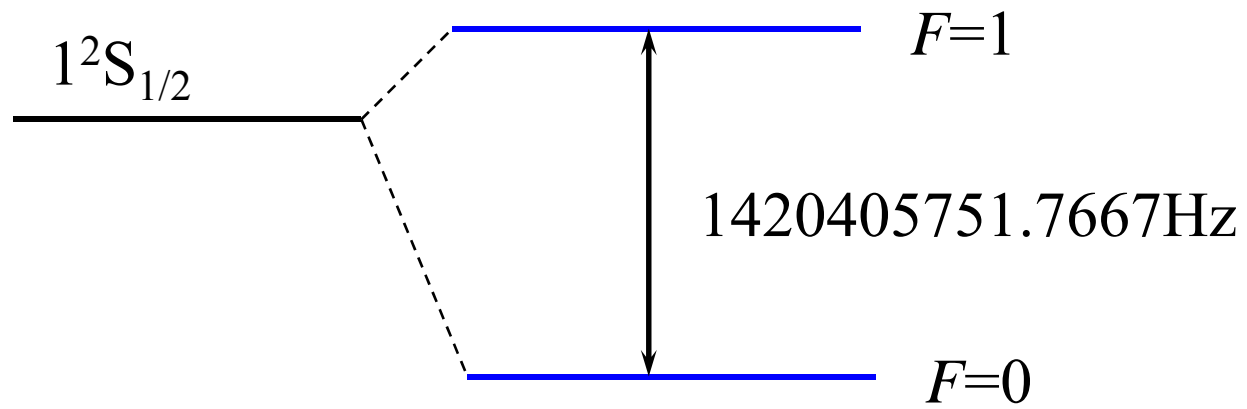


# 铷钟 ( $^{87}\text{Rb}$ ) :

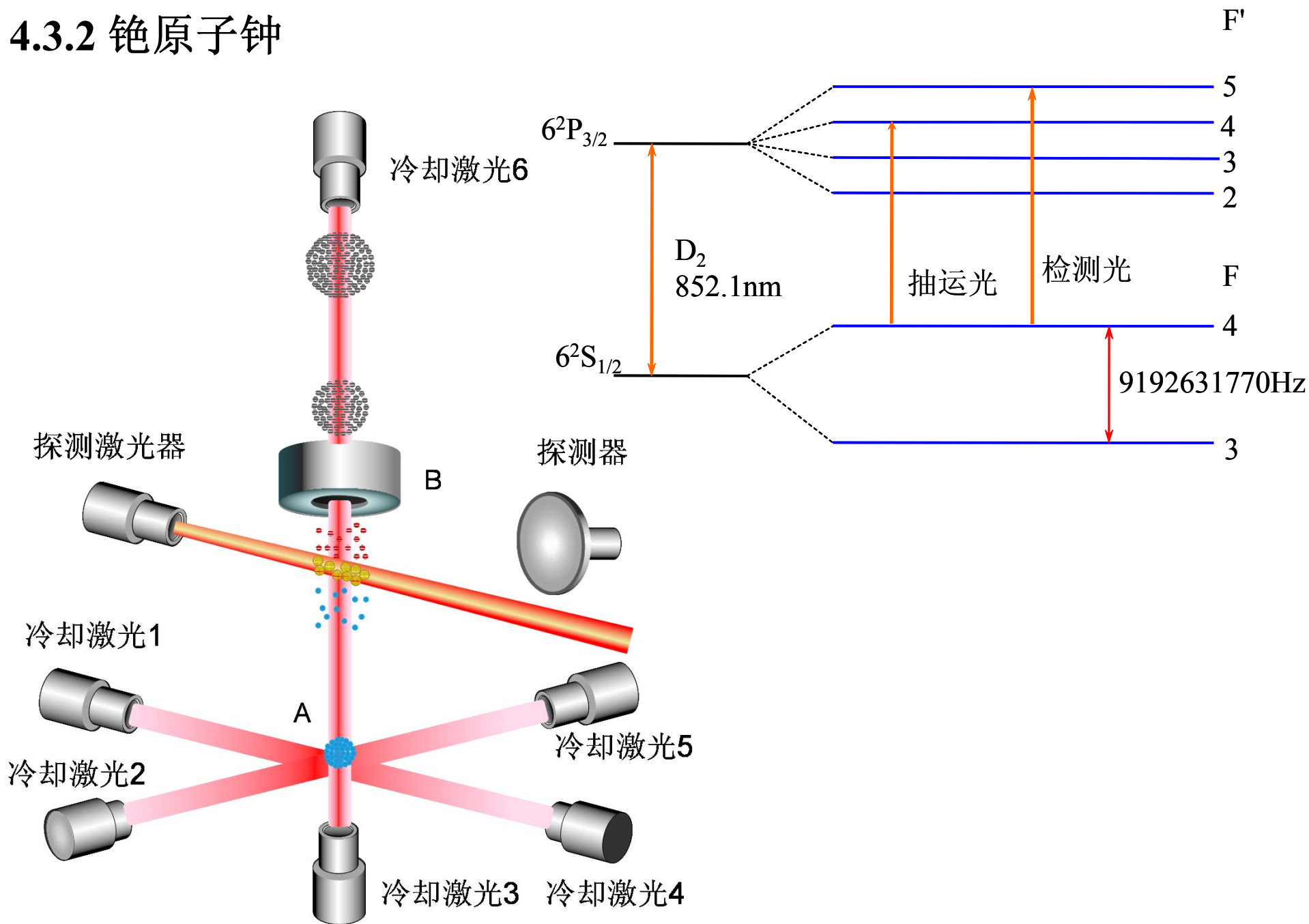


(a)  $^{87}\text{Rb}$ 能级图

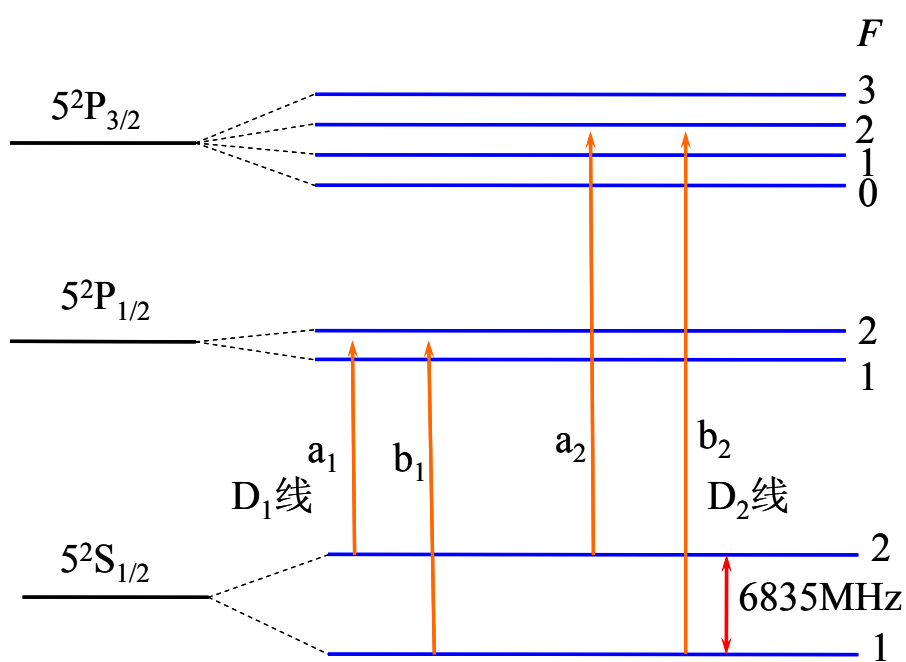
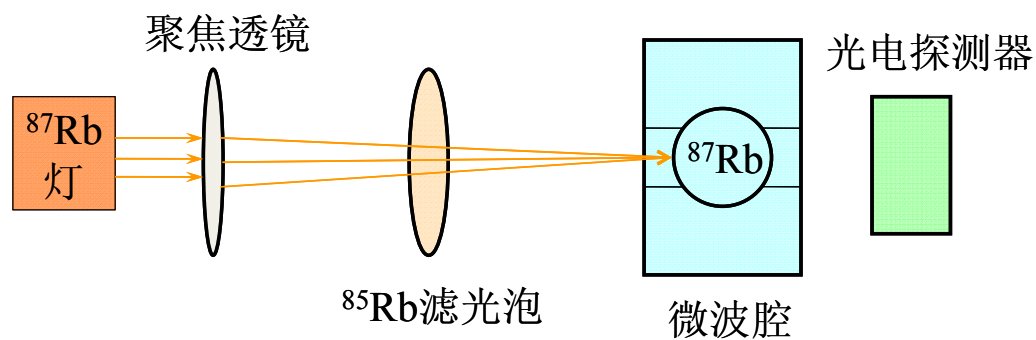
氢钟 ( $^1\text{H}$ ) :



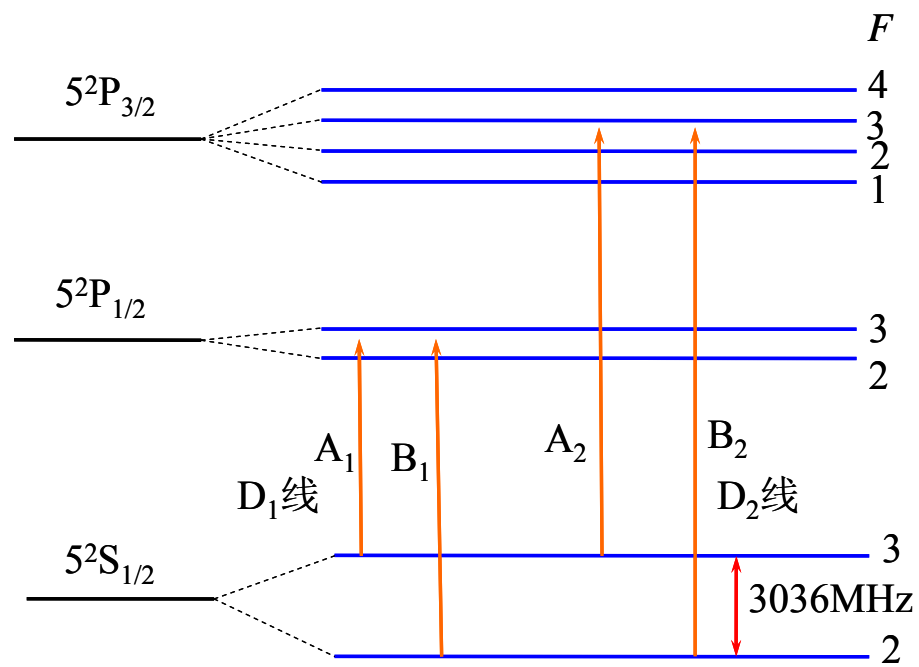
### 4.3.2 铯原子钟



### 4.3.3 铷原子钟



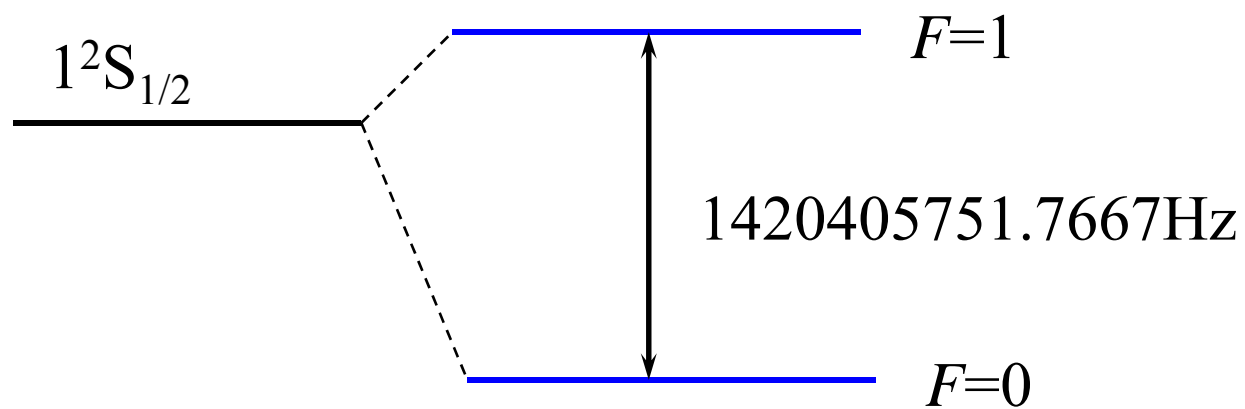
(a)  $^{87}\text{Rb}$ 能级图

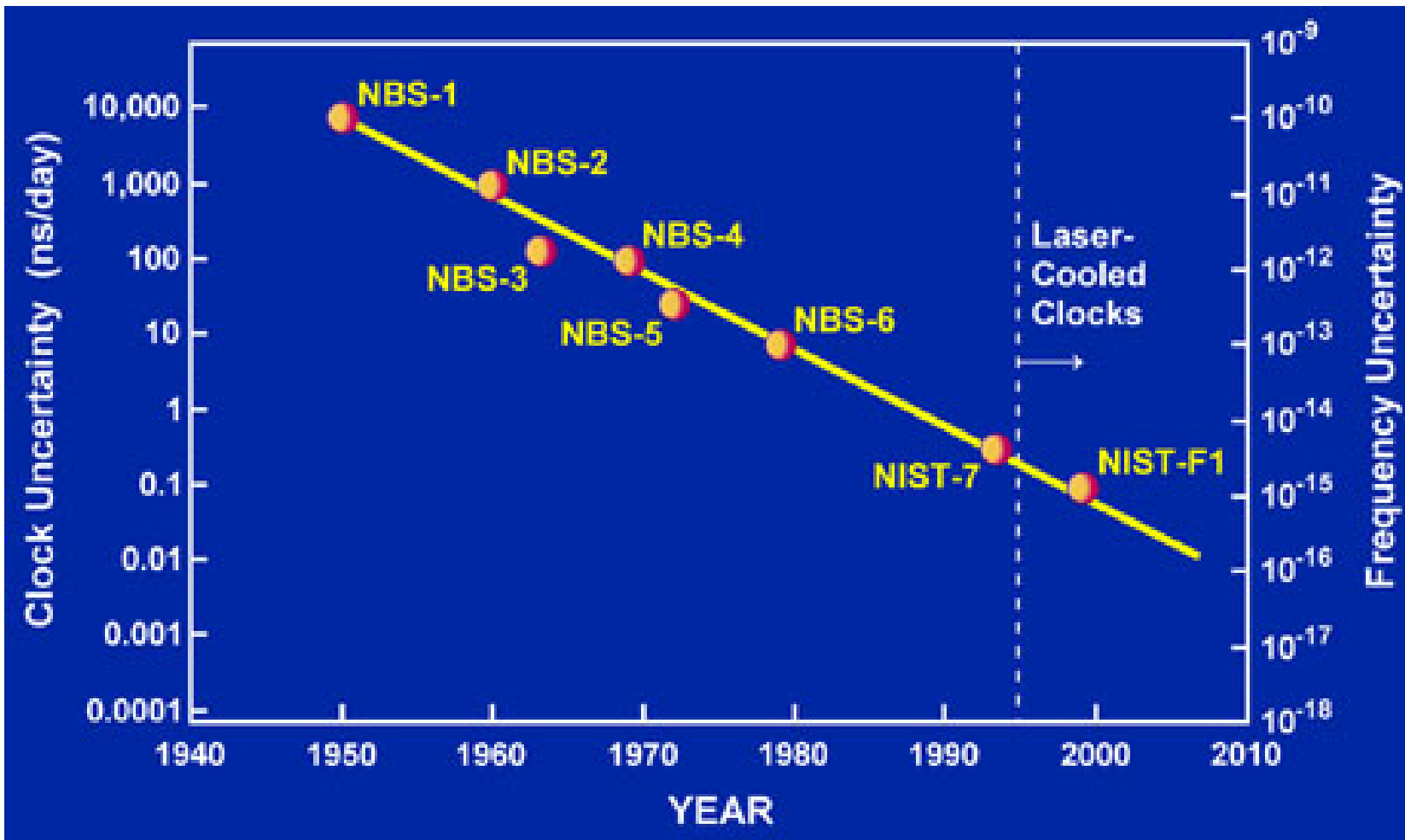


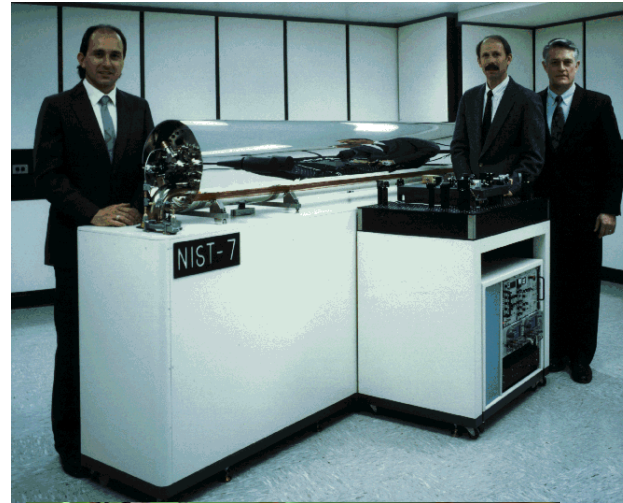
(b)  $^{85}\text{Rb}$ 能级图



## 4.3.4 氢原子钟







**NIST-7**



**NIST-F1**

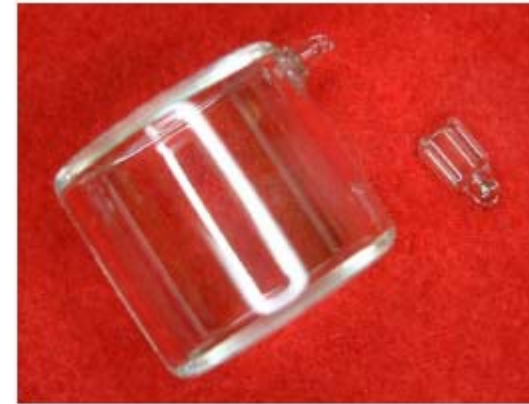


Volume  $\approx 125 \text{ cm}^3$

Power  $\approx 8 \text{ W}$

Stability  $< 3 \times 10^{-11}$  @ 1 second

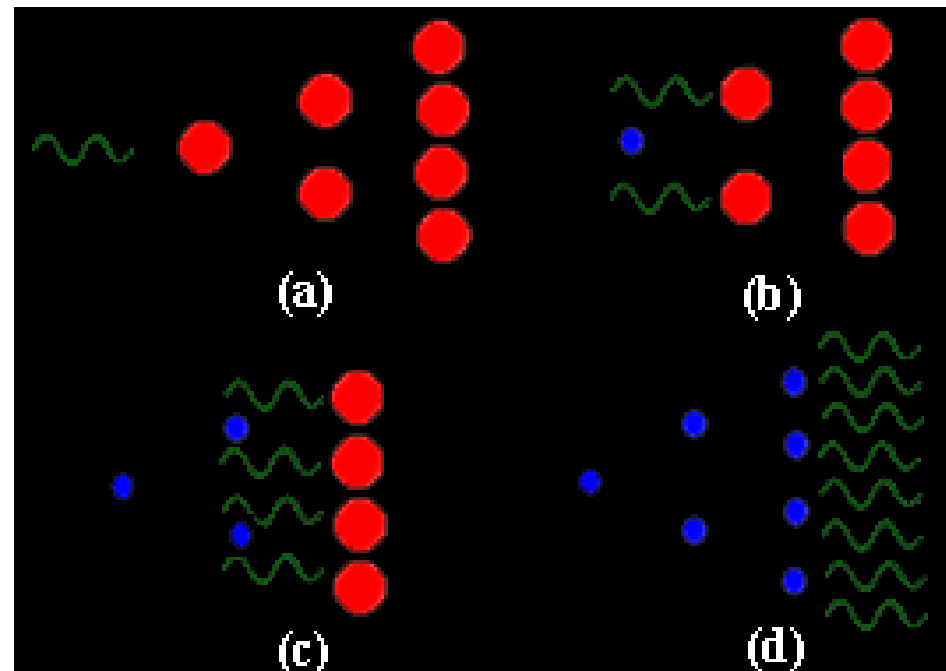
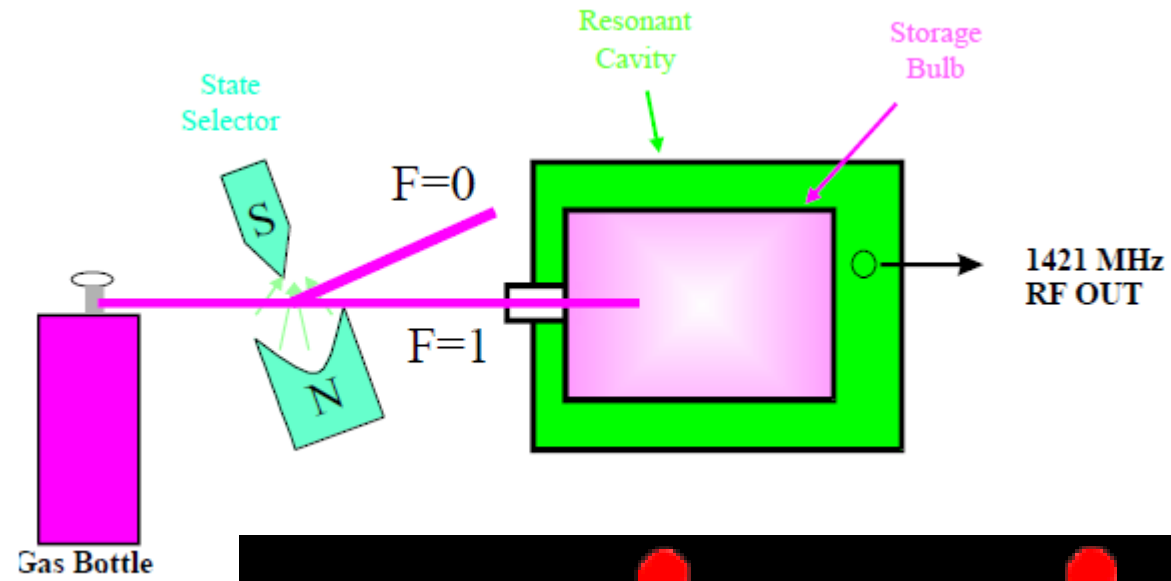
Drift  $< 5 \times 10^{-11}$ /month



LPRO and X72 Rb Cells



# 氢钟





**Symmetricom Model MHM2010**

# 商用原子钟



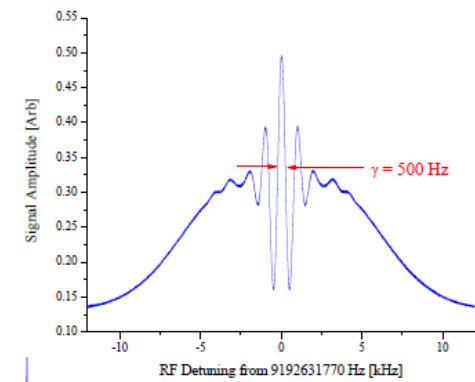
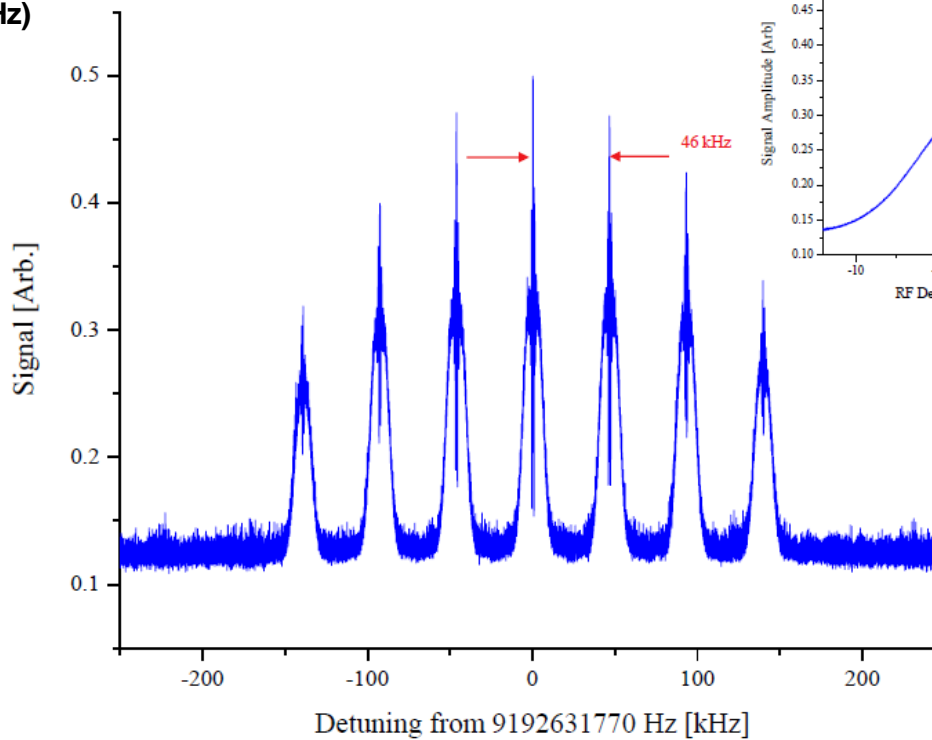
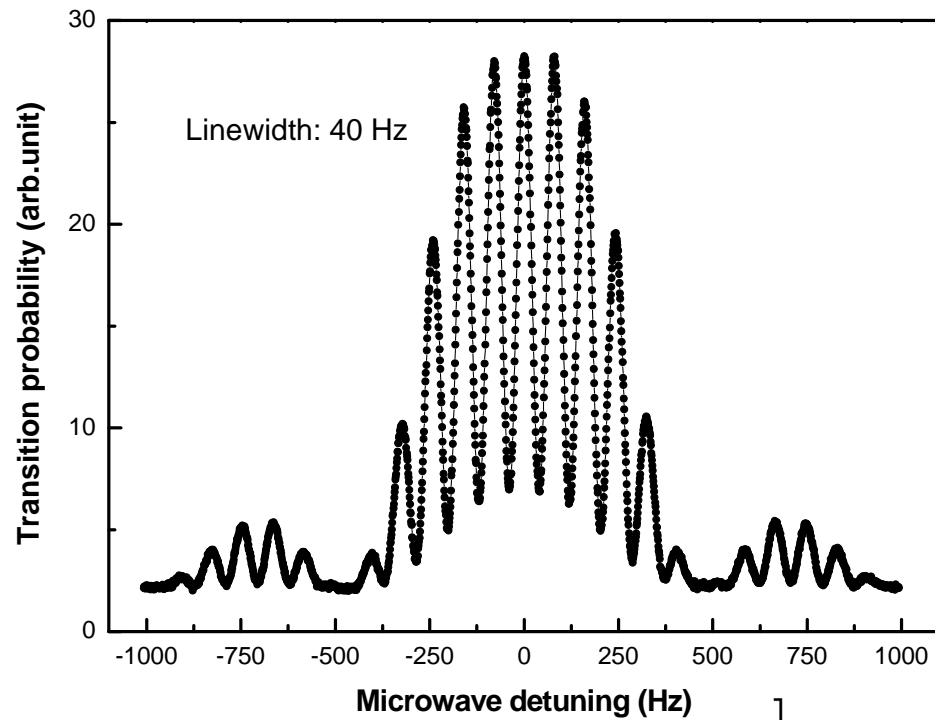
**Hydrogen maser**  
≈ \$250K  
≈ 100 W  
 $\sigma_y(1 \text{ sec}) \approx 2 \times 10^{-13}$   
Drift  $\approx 10^{-16}/\text{day}$



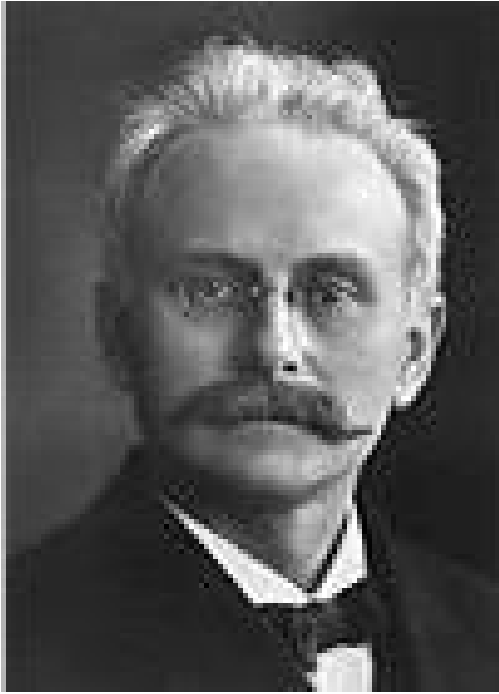
**Cesium Beam Frequency Standard**  
≈ \$50K  
≈ 30 W  
 $\sigma_y(1 \text{ sec}) \approx 10^{-11}$   
Drift  $\approx 0$



**Rubidium Oscillator**  
≈ \$2K  
≈ 10 W  
 $\sigma_y(1 \text{ sec}) \approx 10^{-11}$   
Drift  $\approx 10^{-12}/\text{day}$







**J. Stark, 1874-1957,**  
荣获**1919**年诺贝尔物  
理学奖

## 4.4 斯塔克效应

**1913**年，斯塔克在实验中发现，氢原子的巴耳末系，在电场中会发生劈裂，且此时谱线具有偏振性。这就是斯塔克效应，它是指原子和分子的能级和光谱在外加电场中的移动和分裂现象

- ✓ 一阶（线性）斯塔克效应：光谱分裂与电场强度呈线性关系
- ✓ 二阶（平方）斯塔克效应：电场强度呈二次方关系

## 4.4.1 线性斯塔克效应

电偶极矩在外电场中的能量:

$$U = -\vec{D} \cdot \vec{E}$$

原子的电偶极矩可写为:

$$\vec{D} = -\sum_{i=1}^N e\vec{r}_i$$

原子在外电场中引起的能量变化为:

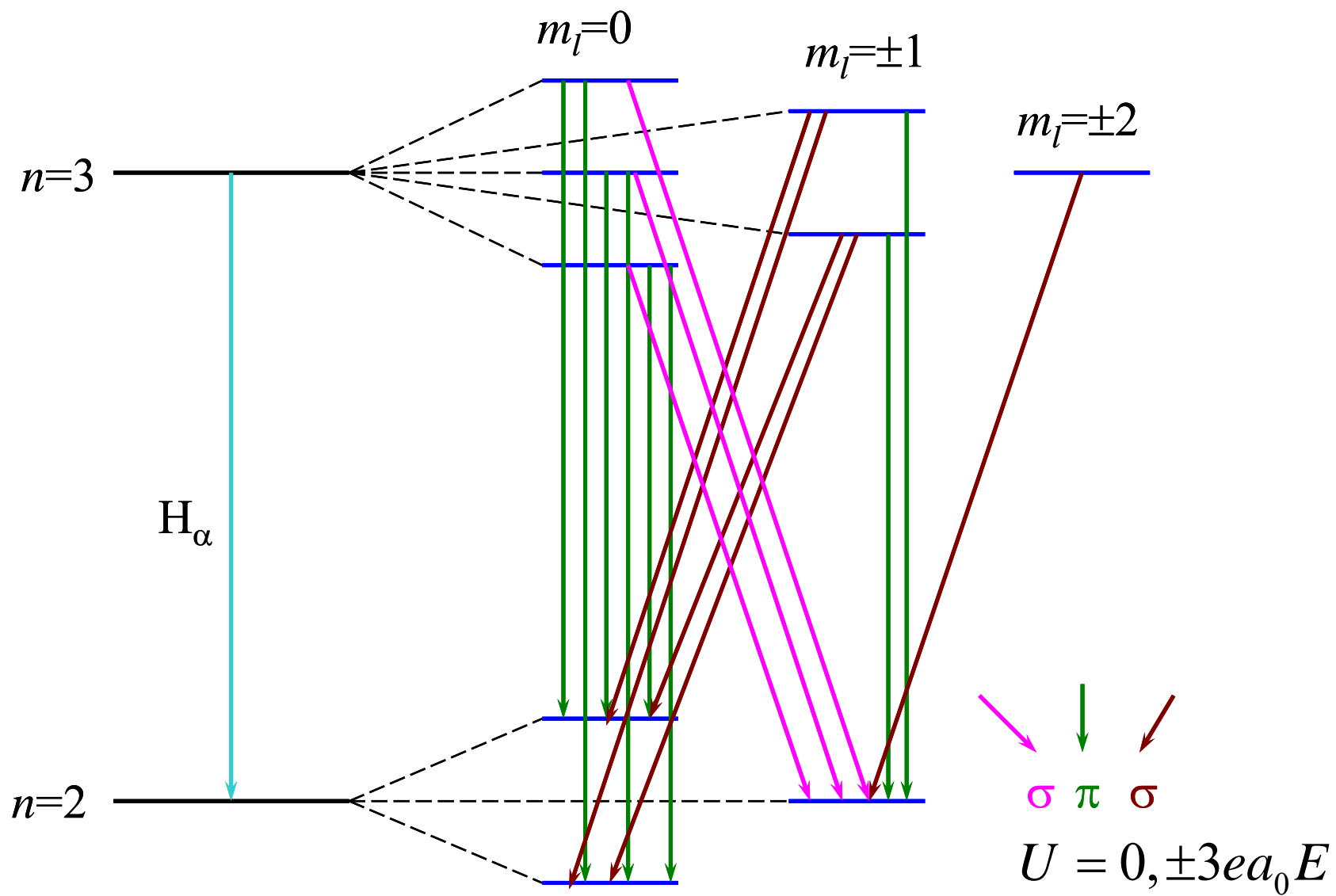
$$U = -(-e\vec{r}) \cdot \vec{E} = eEz$$

原子能级表现出的能量移动为:

$$U = eE \langle z \rangle$$

$$\langle z \rangle = \int \psi^* z \psi d\tau$$

任意一个具有确定角动量量子数  $l$  的状态, 其固有电偶极矩为 **0** !



氢原子  $n=3$  和  $n=2$  能级在外电场中的分裂和跃迁

例4.4.1 试计算氢原子 $n=2$ 的能级在外电场  $E=10^7$  V/m 时的能级分裂情况。

解：由公式 (4.4.6) 可知：

$$U = (0, \pm 3ea_0E) = (0, \pm 12.82) \text{cm}^{-1}$$

考虑到氢原子的精细结构移动约为  $0.46 \text{cm}^{-1}$ ，可知斯塔克分裂的间距远大于精细结构移动，在考虑斯塔克效应时认为氢原子的能量对  $l$  简并是有道理的。

## 4.4.2 平方斯塔克效应

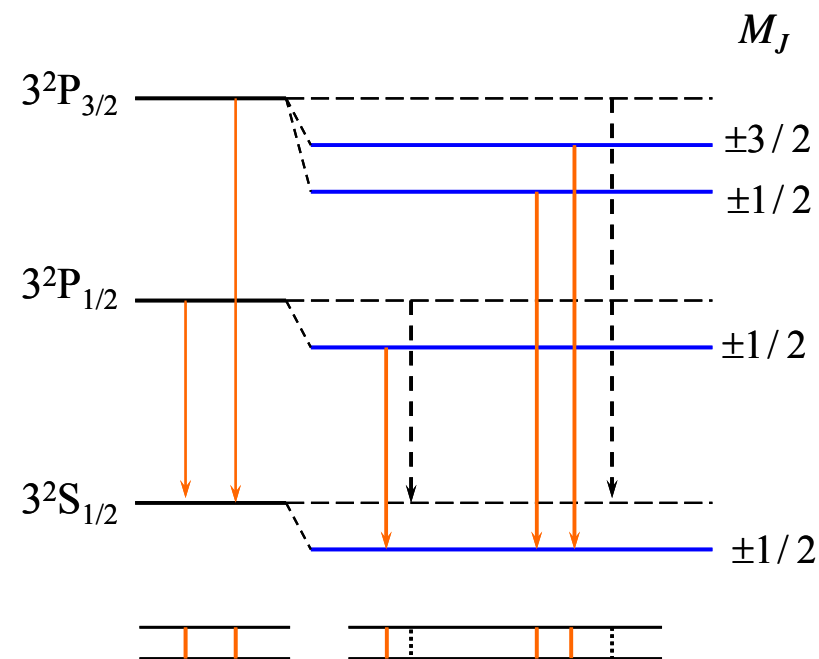
除氢以外，几乎所有原子都不存在线性斯塔克效应！

感生电偶极矩：

$$D' = \alpha E$$

感生电偶极矩引起的原子能级移动：

$$U = -\frac{1}{2} D' E = -\frac{1}{2} \alpha E^2$$



钠黄线的平方斯塔克效应

# 小结

## 一、原子磁矩

$$\vec{\mu}_J = -g_J \frac{\mu_B}{\hbar} \vec{J}$$

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad \text{朗德因子}$$

$$\mu_J = -g_J \sqrt{J(J+1)} \mu_B$$

$$\mu_{J_z} = -m_J g_J \mu_B \quad m_J = -J, -J+1, \dots, J-1, J$$

$3^2P_{1/2}$ :

$$g_{j_2} = 1 + \frac{\frac{1}{2} \times \frac{3}{2} + \frac{1}{2} \times \frac{3}{2} - 1 \times 2}{2 \times \frac{1}{2} \times \frac{3}{2}} = \frac{2}{3}$$

$3^2P_{3/2}$ :

$$g_{j_3} = 1 + \frac{\frac{3}{2} \times \frac{5}{2} + \frac{1}{2} \times \frac{3}{2} - 1 \times 2}{2 \times \frac{1}{2} \times \frac{3}{2}} = \frac{4}{3}$$

## 二、塞曼效应

弱磁场中：

$$U = -\vec{\mu}_J \cdot \vec{B} = -\mu_{Jz} B$$

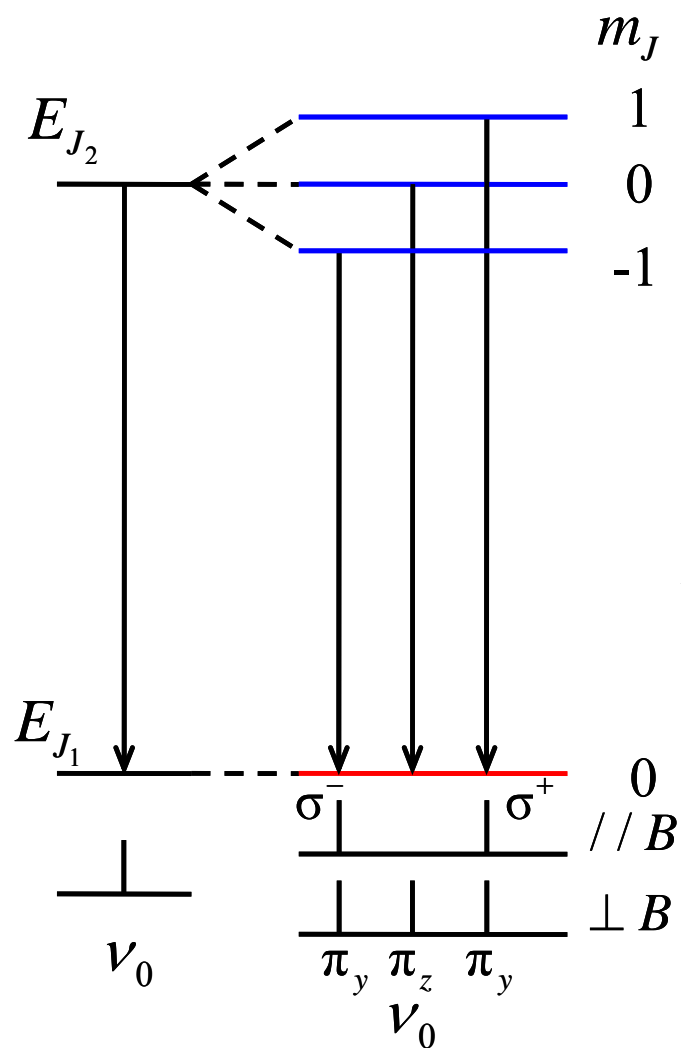
$$U = m_J g_J \mu_B B$$

$$E'_J = E_J + m_J g_J \mu_B B$$

无外磁场( $B \rightarrow 0$ )时，此 $2J+1$ 个态简并

有外磁场时，能级分裂为 $2J+1$ 条

$m_J$ ：磁量子数



$$\begin{aligned}
 h\nu &= E'_{J_2} - E'_{J_1} \\
 &= (E_{J_2} - E_{J_1}) + (m_{J_2}g_2 - m_{J_1}g_1)\mu_B B \\
 &= h\nu_0 + (m_{J_2}g_2 - m_{J_1}g_1)\mu_B B
 \end{aligned}$$

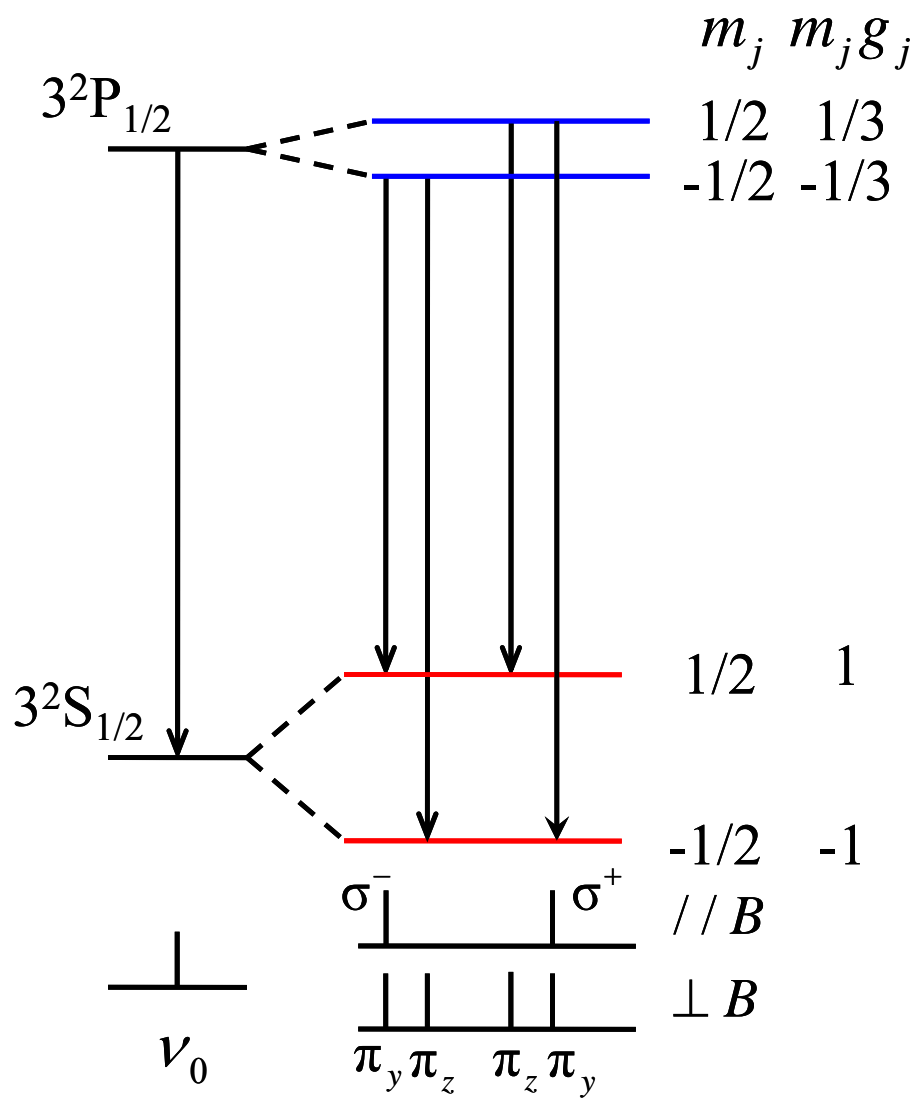
$$\frac{1}{\lambda} - \frac{1}{\lambda_0} = \frac{(m_{J_2}g_2 - m_{J_1}g_1)\mu_B B}{hc} = (m_{J_2}g_2 - m_{J_1}g_1)\mathcal{L}$$

$$\mathcal{L} = \frac{\mu_B B}{hc} = \frac{eB}{4\pi m_e c} \quad \text{洛伦兹单位}$$

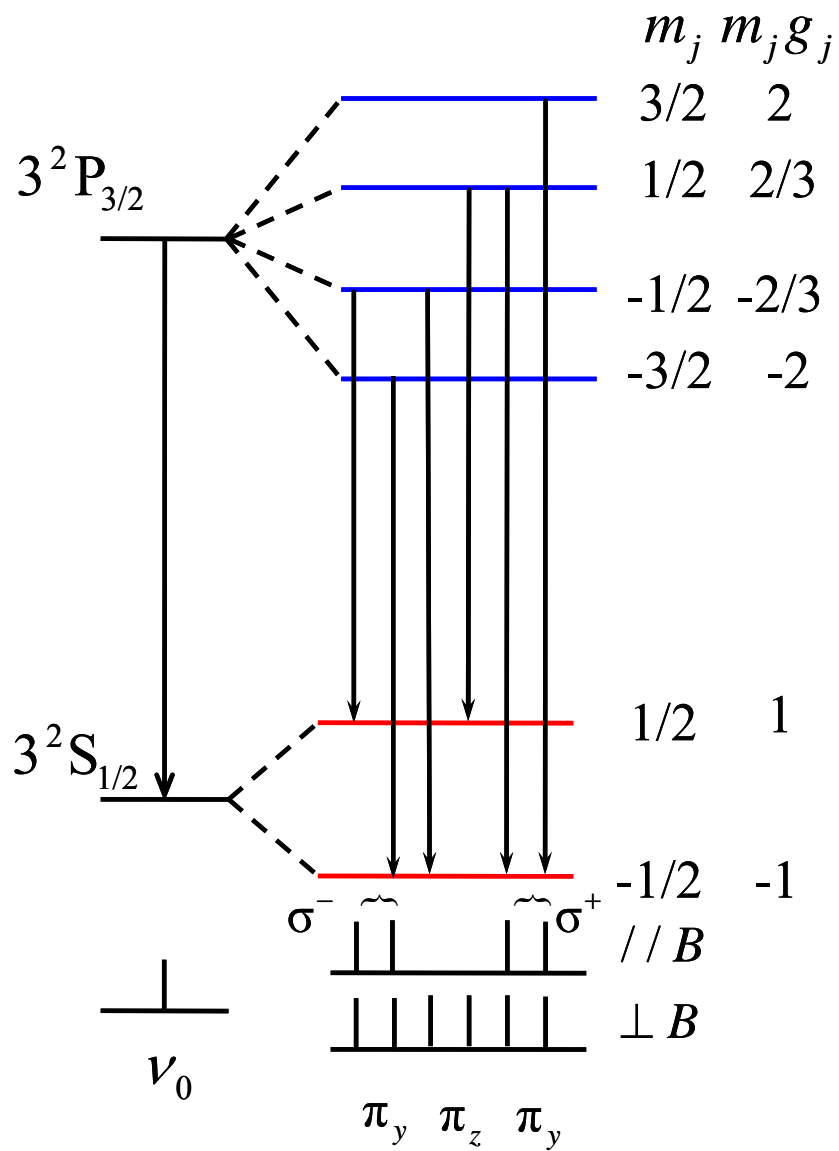
$$B=1\text{T时}, \mathcal{L}=0.466 \text{ cm}^{-1}$$

磁量子数选择定则:  $\Delta m = m_{J_2} - m_{J_1} = 0, \pm 1$  (当  $\Delta J = 0, 0 \not\leftrightarrow 0$ )





$$\frac{1}{\lambda} - \frac{1}{\lambda_0} = \left\{ \begin{array}{c} -\frac{4}{3} \\ -\frac{2}{3} \\ \frac{2}{3} \\ \frac{4}{3} \end{array} \right\} \mathcal{L}$$



$$\frac{1}{\lambda} - \frac{1}{\lambda_0} = \left\{ \begin{array}{c} -\frac{5}{3} \\ -1 \\ -\frac{1}{3} \\ \frac{1}{3} \\ 1 \\ \frac{5}{3} \end{array} \right\} \mathcal{L}$$

思考题：如何判断外磁场是强还是弱呢？

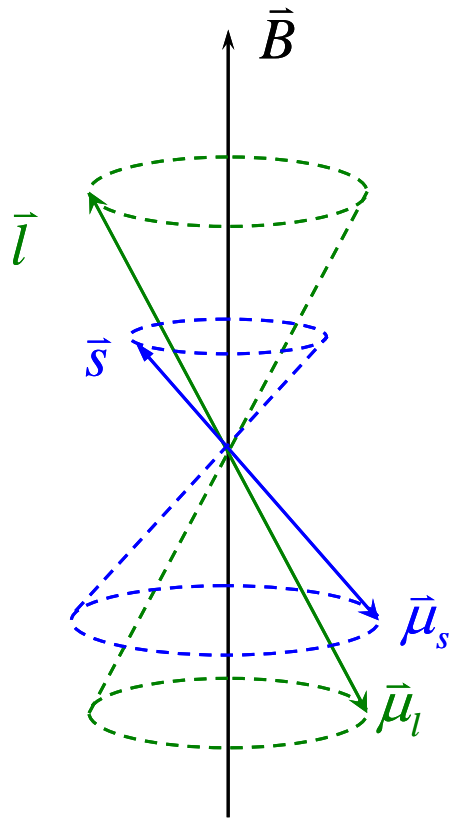
### 3.4节，第118页

碱金属原子最外层电子感受到的内磁场

原子	Li	Na	K	Rb	Cs
能级分裂 ( $\text{cm}^{-1}$ )	0.34	17.2	57.7	237.6	554.1
$B_{\text{内}}$ (T)	0.728	38.8	121	509.0	1187

### 三、帕邢—巴克效应

原子光谱在强外磁场中的分裂现象被称为帕邢-巴克效应



$$\vec{\mu} = \vec{\mu}_l + \vec{\mu}_s = -\frac{\mu_B}{\hbar} (g_l \vec{l} + g_s \vec{s})$$

$$\mu_z = -\frac{\mu_B}{\hbar} (g_l L_z + g_s S_z) = -(m_l + 2m_s) \mu_B$$

$$U = -\vec{\mu} \cdot \vec{B} = (m_l + 2m_s) \mu_B B$$

选择定则:

$$\begin{cases} \Delta m_s = 0 \\ \Delta m_l = 0, \pm 1 \end{cases}$$

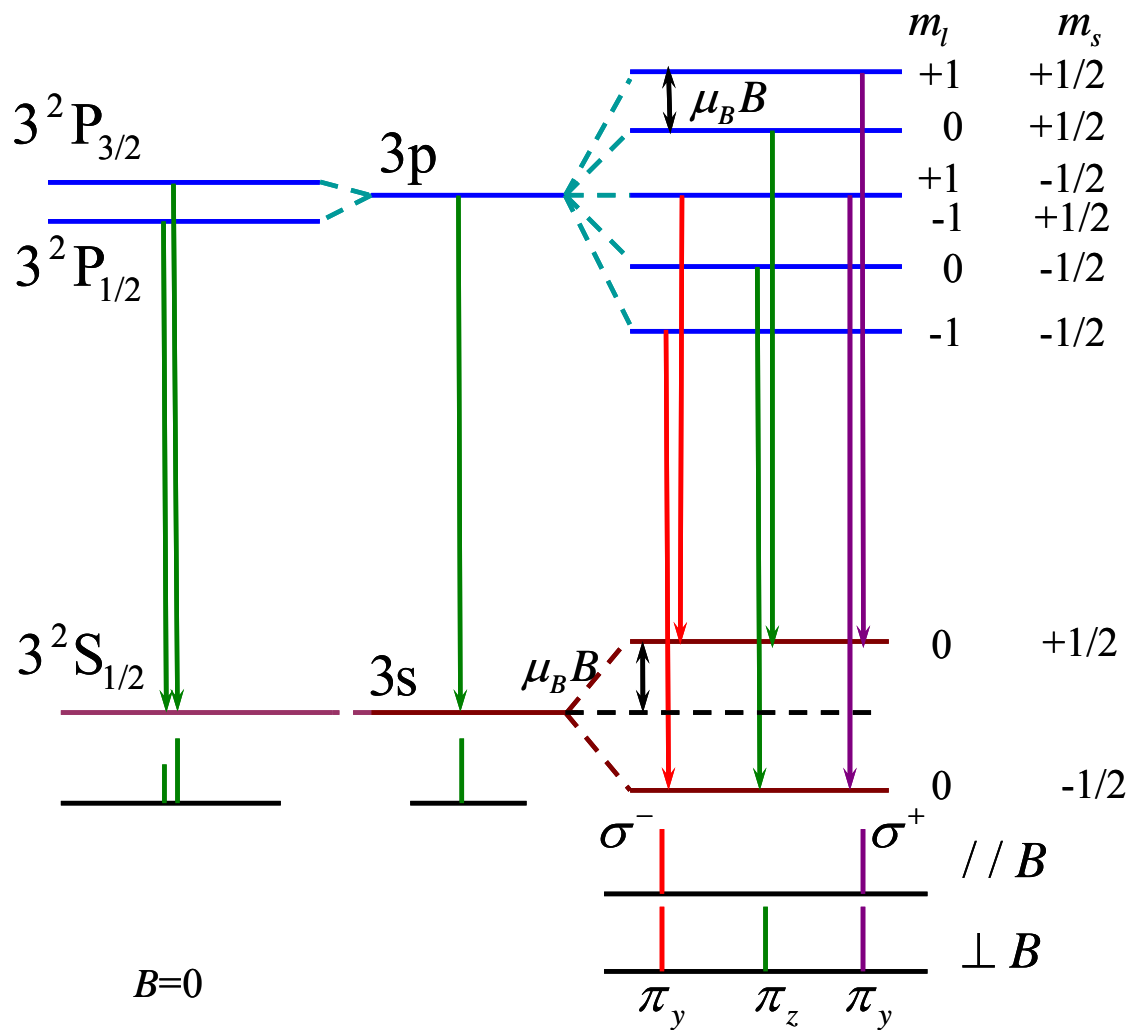
光谱分裂:

$$\begin{aligned} h\nu &= E_2' - E_1' \\ &= \left[ E_2 + (m_{l_2} + 2m_{s_2})\mu_B B \right] - \left[ E_1 + (m_{l_1} + 2m_{s_1})\mu_B B \right] \\ &= (E_2 - E_1) + (m_{l_2} - m_{l_1})\mu_B B \\ &= h\nu_0 + \Delta m_l \mu_B B \end{aligned}$$

三条谱线，表现为正常塞曼效应

### 例4.1.3 试分析强外磁场条件下钠原子 $3p \rightarrow 3s$ 跃迁的发射光谱。

解：



考虑LS耦合

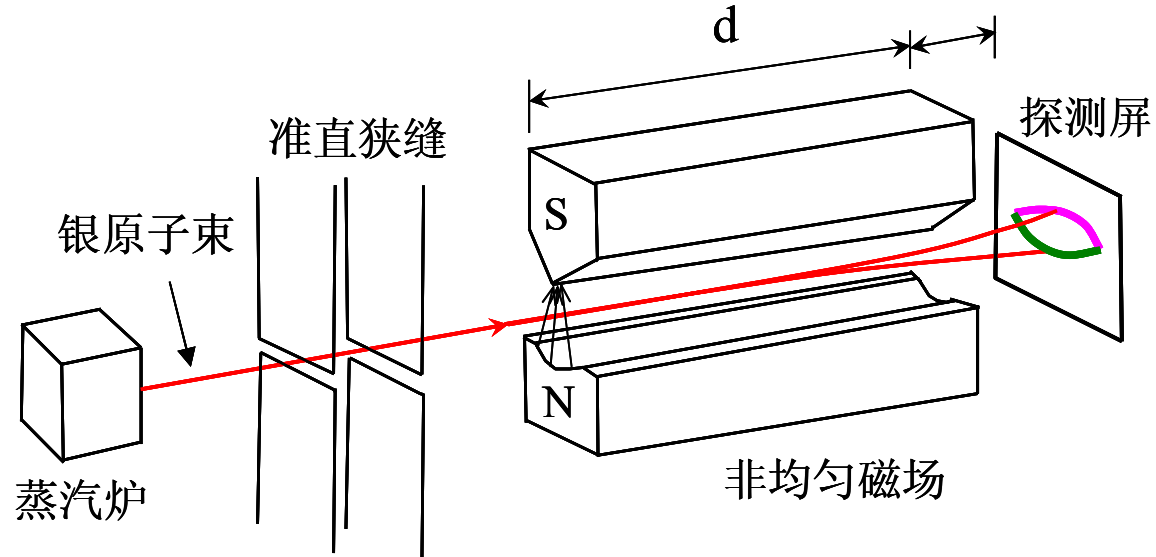
不考虑LS耦合

强外磁场中

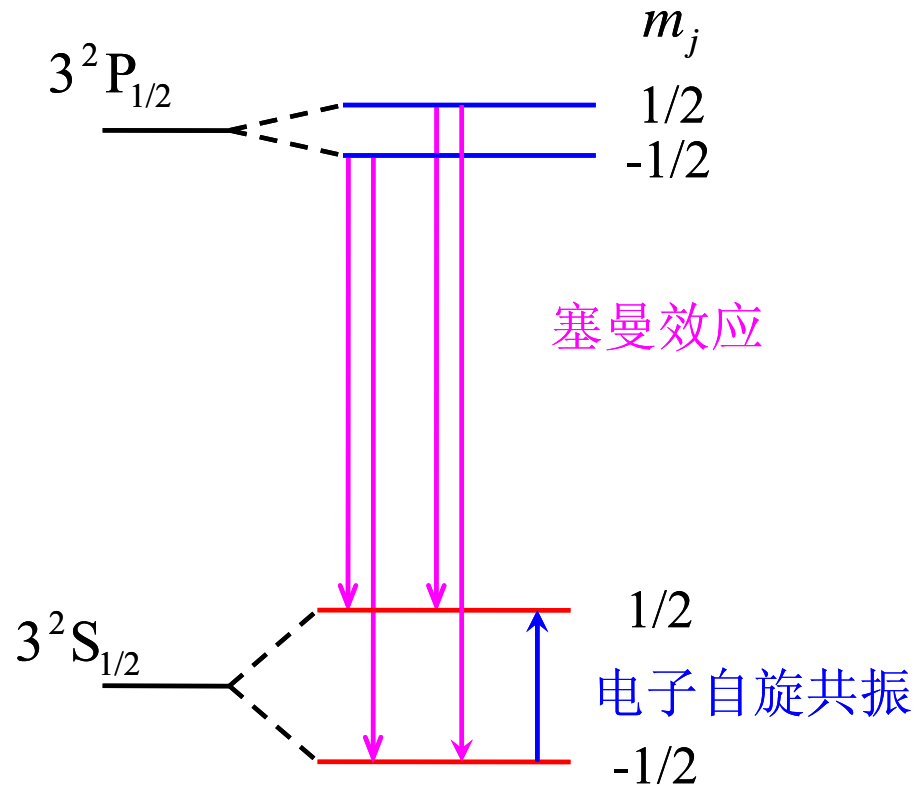
## 四、斯特恩—盖拉赫实验

计入自旋-轨道相互作用后，原子在非均匀外磁场中受到的作用力

$$F_z = \mu_z \frac{\partial B}{\partial z} = -m_j g_j \mu_B \frac{\partial B}{\partial z}$$



# 五、电子顺磁共振 (EPR)



$$h\nu = g\mu_B B = g\mu_0\mu_B H$$