Chap 7

The hydrogen atom

- Angular momentum, spherical harmonics
- Schrödinger equation and the H atom
- Quantum numbers
- Electron distribution
- Zeeman effect
- Selection rule
- Electron spin

Central force problem

First, recall that in classical mechanics

Angular momentum

$$\vec{L} = \vec{r} \times m\vec{v} = mr^2\dot{\phi}\hat{z}$$

Planetary motion

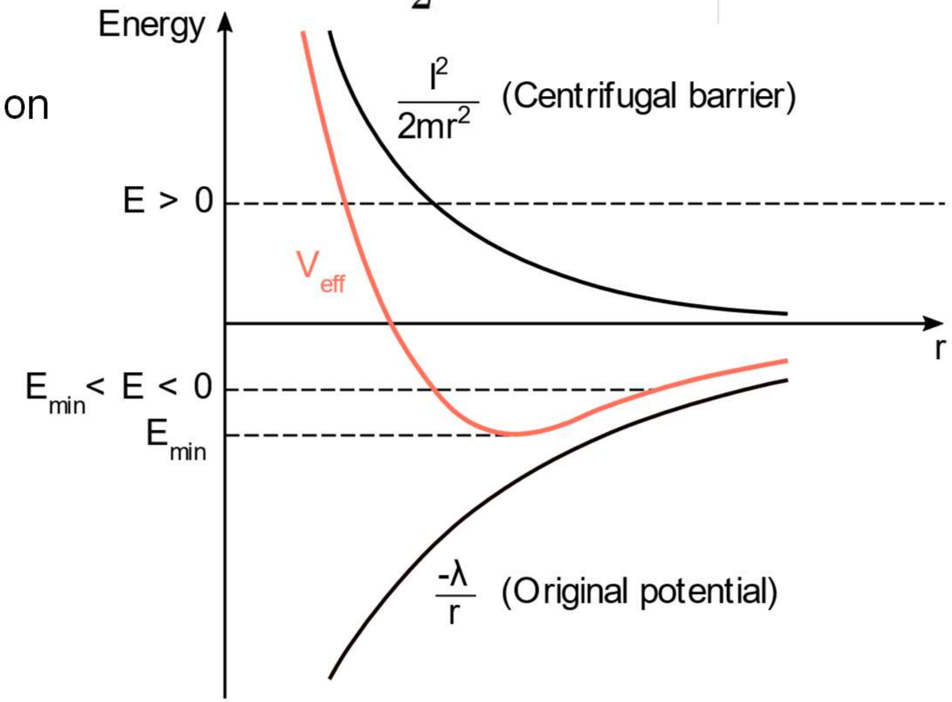
- Velocity $\dot{\vec{r}} = \dot{r}\hat{r} + r\dot{\phi}\hat{\phi}$
- Energy

$$E_{\text{tot}} = \frac{1}{2}m\dot{r}^2 + \frac{1}{2}mr^2\dot{\varphi}^2 + U(r) = \frac{1}{2}m\dot{r}^2 + \boxed{\frac{L^2}{2mr^2} + U(r)}$$

$$= \frac{1}{2}m\dot{r}^2 + U_{\text{eff}}(r)$$

Effective potential for radial motion

$$U_{\text{eff}}(r) = \boxed{U(r) + \frac{L^2}{2mr^2}}$$

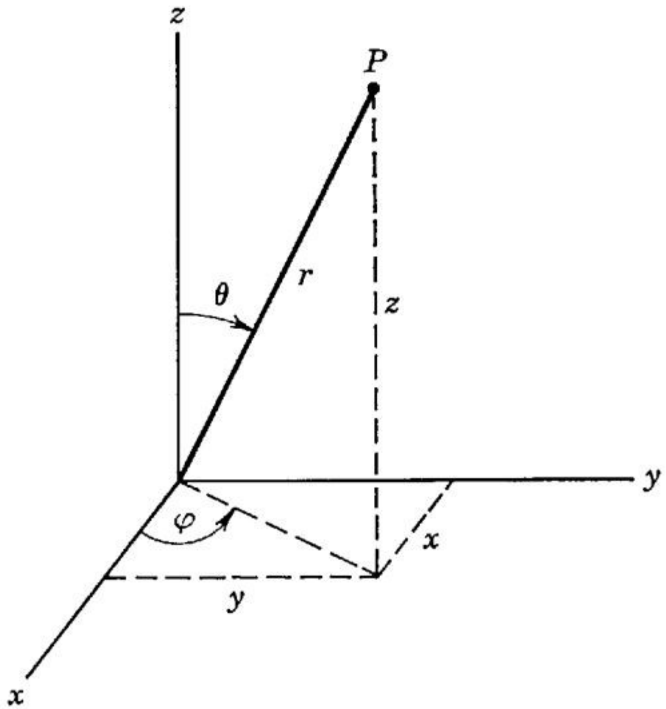


Orbital angular momentum operator

- Cartesian coordinate

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \qquad \begin{cases} L_x = yp_z - zp_y \\ L_y = zp_x - xp_z \\ L_z = xp_y - yp_x \end{cases} \Rightarrow \begin{cases} L_{x_{op}} = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ L_{y_{op}} = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ L_{z_{op}} = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{cases}$$

- Spherical coordinate



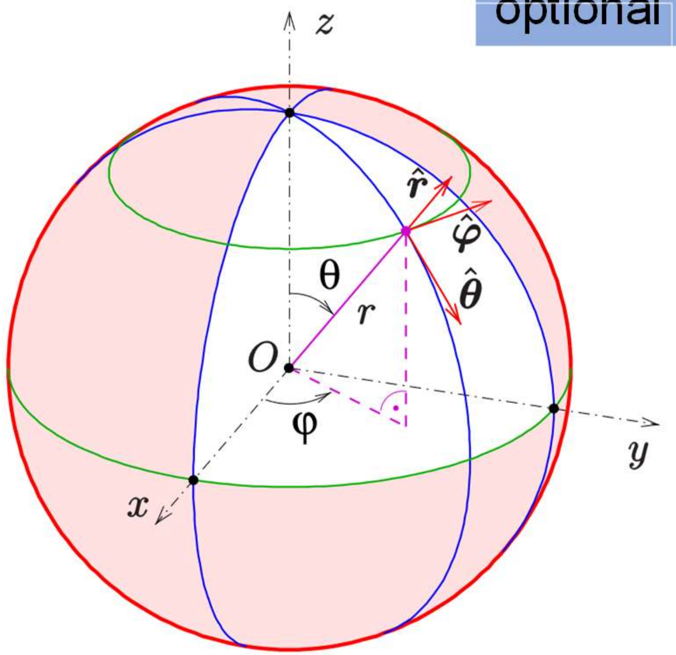
$$\begin{cases} L_{x_{op}} = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right) \\ L_{y_{op}} = i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right) \\ L_{z_{op}} = -i\hbar\frac{\partial}{\partial\varphi} \end{cases}$$

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

$$\Rightarrow \boxed{\mathbf{L}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)}$$

optional

$$\begin{cases} \hat{x} = \hat{r}\sin\theta\cos\varphi + \hat{\theta}\cos\theta\cos\varphi - \hat{\varphi}\sin\varphi \\ \hat{y} = \hat{r}\sin\theta\sin\varphi + \hat{\theta}\cos\theta\sin\varphi + \hat{\varphi}\cos\varphi, \\ \hat{z} = \hat{r}\cos\theta - \hat{\theta}\sin\theta. \end{cases}$$



$$\hat{\vec{L}} = \hat{\vec{R}} \times \hat{\vec{P}} = (-i\hbar r)\hat{r} \times \vec{\nabla}$$

$$= (-i\hbar r)\hat{r} \times \left[\hat{r}\frac{\partial}{\partial r} + \frac{\hat{\theta}}{r}\frac{\partial}{\partial\theta} + \frac{\hat{\varphi}}{r\sin\theta}\frac{\partial}{\partial\varphi}\right]$$

$$= -i\hbar\left(\hat{\varphi}\frac{\partial}{\partial\theta} - \frac{\hat{\theta}}{\sin\theta}\frac{\partial}{\partial\varphi}\right)$$

$$\begin{cases} \hat{L}_x = \hat{x}.\vec{L} = i\hbar\left(\sin\varphi\frac{\partial}{\partial\theta} + \cot\theta\cos\varphi\frac{\partial}{\partial\varphi}\right) \\ \hat{L}_y = i\hbar\left(-\cos\varphi\frac{\partial}{\partial\theta} + \cot\theta\sin\varphi\frac{\partial}{\partial\varphi}\right) \\ \hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}. \end{cases}$$

Quantum mechanics, by Zettili

Schrödinger eq $\hat{H}\psi(\vec{r}) = E\psi(\vec{r})$

- Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} + V(\vec{r}) = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})$

- Laplacian in spherical coordinate

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \boxed{\frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}}$$

however $$\mathbf{L}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

therefore $$\hat{H} = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + V(\vec{r}) + \frac{\hat{L}^2}{2mr^2}$$

This applies to **all** central force problems.

- What's the eigenfunctions of L^2?

➡ Spherical harmonics $Y_\ell^m(\theta,\phi)$

Review:
Spherical harmonics

associated Legendre polynomials

$$Y_\ell^m(\theta, \phi) = N P_\ell^m(\cos\theta) e^{im\phi}$$

$\ell = 0, 1, 2, \cdots$

$m = \ell, \ell - 1, \cdots, -\ell$

TABLE 6.2

The first few associated Legendre functions $P_l^{|m|}(x)$

$$P_0^0(x) = 1$$

$$P_1^0(x) = x = \cos\theta$$

$$P_1^1(x) = (1 - x^2)^{1/2} = \sin\theta$$

$$P_2^0(x) = \tfrac{1}{2}(3x^2 - 1) = \tfrac{1}{2}(3\cos^2\theta - 1)$$

$$P_2^1(x) = 3x(1 - x^2)^{1/2} = 3\cos\theta\sin\theta$$

$$P_2^2(x) = 3(1 - x^2) = 3\sin^2\theta$$

$$P_3^0(x) = \tfrac{1}{2}(5x^3 - 3x) = \tfrac{1}{2}(5\cos^3\theta - 3\cos\theta)$$

$$P_3^1(x) = \tfrac{3}{2}(5x^2 - 1)(1 - x^2)^{1/2} = \tfrac{3}{2}(5\cos^2\theta - 1)\sin\theta$$

$$P_3^2(x) = 15x(1 - x^2) = 15\cos\theta\sin^2\theta$$

$$P_3^3(x) = 15(1 - x^2)^{3/2} = 15\sin^3\theta$$

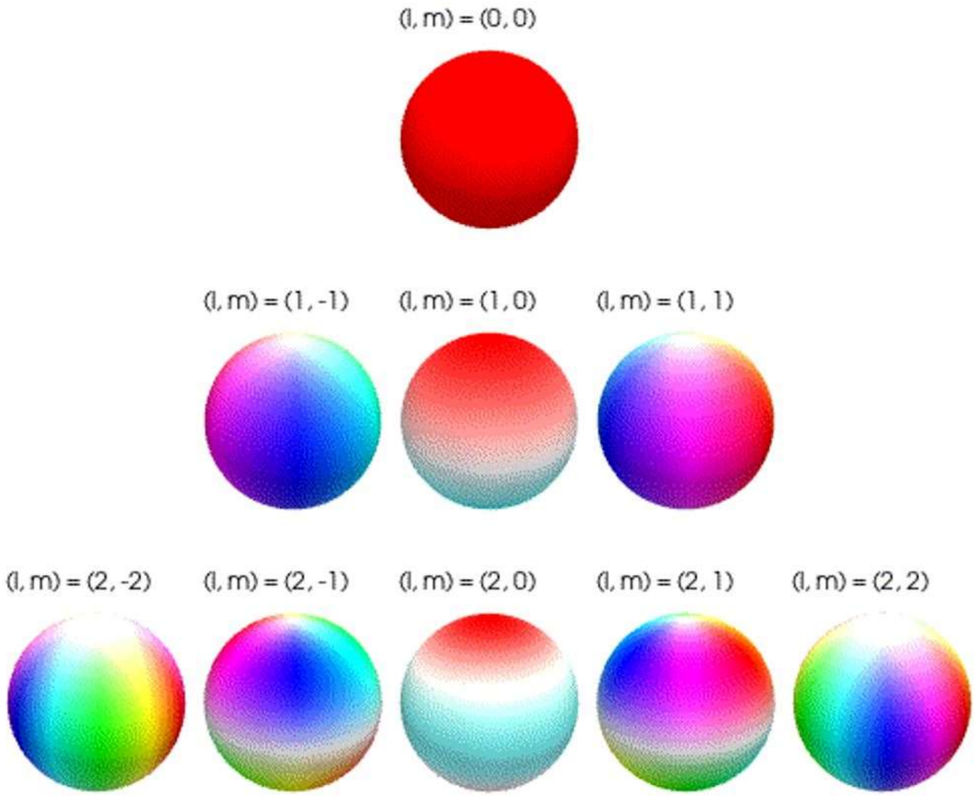


Table 7.2 Normalized Spherical Harmonics $Y(\theta, \phi)$

ℓ	m_ℓ	$Y_{\ell m_\ell}$
		$\frac{1}{2\sqrt{\pi}}$
		$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
		$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{\pm i\phi}$
		$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
		$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$
		$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{\pm 2i\phi}$

wiki

Ex 7.1: Show that the spherical harmonic function $Y_{11}(\theta, \phi)$ satisfies the angular Equation

$$\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)Y_1^1=-2Y_1^1$$

Solution

$$Y_{11}(\theta, \phi) = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\ e^{i\phi}$$

……

$$\Rightarrow\quad -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)Y_1^1=2\hbar^2Y_1^1$$

In general, $\hat{L}^2Y_\ell^m=\ell(\ell+1)\hbar^2Y_\ell^m$

also $\hat{L}_zY_\ell^m=\frac{\hbar}{i}\frac{\partial}{\partial\phi}P_\ell^m(\cos\theta)e^{im\phi}=m\hbar Y_\ell^m$

Spherical harmonics are eigenstates of L^2 and L_z

$$\begin{cases} \hat{L}^2 Y_\ell^m(\theta,\phi) = \ell(\ell+1)\hbar^2 Y_\ell^m(\theta,\phi) \\ \hat{L}_z Y_\ell^m(\theta,\phi) = m\hbar Y_\ell^m(\theta,\phi) \end{cases}$$

eigenvalues

Angular momentum quantum numbers:

$\ell = 0,1,2,\cdots$

$m = \ell, \ell-1, \cdots, -\ell$

- Why $L^2 = \ell(\ell+1)\hbar^2$?

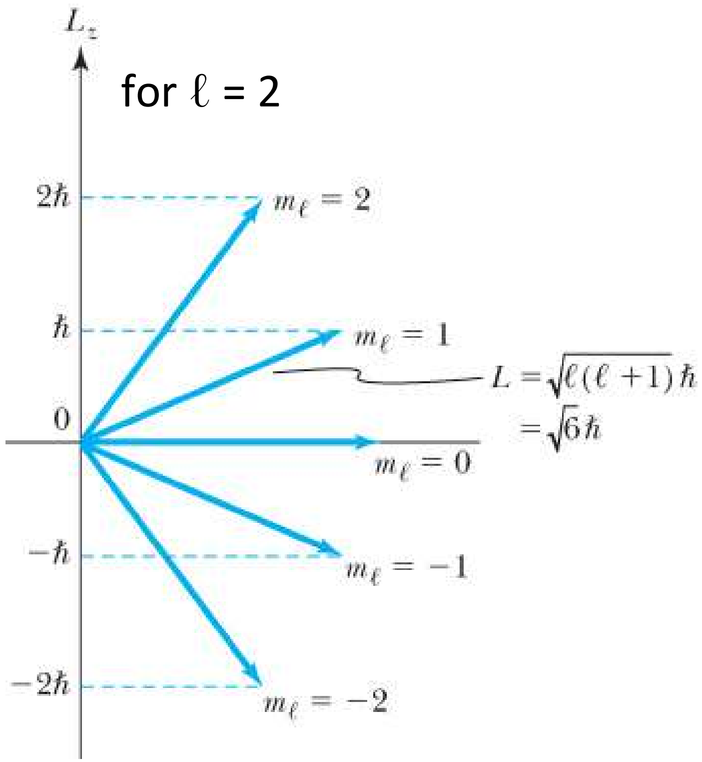
A heuristic explanation (Thornton and Rex):

We expect the average of the angular momentum components squared to be $\langle L_x{}^2 \rangle = \langle L_y{}^2 \rangle = \langle L_z{}^2 \rangle$.

$$\Rightarrow \langle L^2 \rangle = 3\langle L_z{}^2 \rangle = \frac{3}{2\ell+1}\sum_{m=-\ell}^{\ell} m^2\hbar^2 = \ell(\ell+1)\hbar^2$$

$$\sum_{k=1}^{n} k^2 = \frac{n(n+1)(2n+1)}{6}$$

Cf: Bohr model: $L = n\hbar$



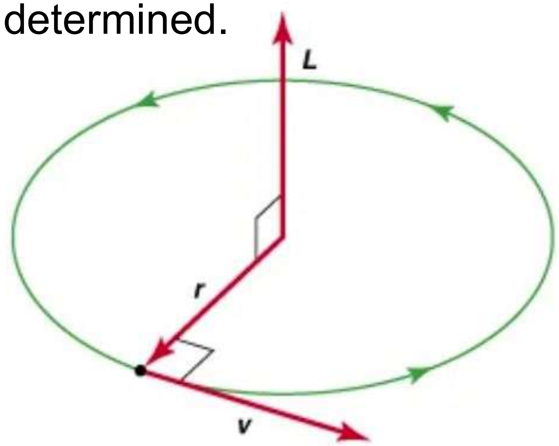
Called ‘space quantization”, or “azimuthal quantization”

- The choice of the z axis is arbitrary unless there is an external magnetic field *B* to define a preferred direction. It is customary to choose the z axis to be along ***B***. This is why *m* is called the *magnetic quantum number* (Thornton).

- How about the values of L_x and L_y?

After knowing L^2 and L_z, if we also know L_x, then L_y can be determined. This would violate the uncertainty principle:

If ***L*** is certain, then the electron is confined to a plane. The electron's momentum component along ***L*** is *exactly* zero. This simultaneous knowledge of *z* and p_z is forbidden.



optional

Commutation relations:

$$[L_x, L_y] = i\hbar L_z, \quad [L_y, L_z] = i\hbar L_x, \quad [L_z, L_x] = i\hbar L_y,$$

$$[L^2, L_x] = [L^2, L_y] = \boxed{[L^2, L_z] = 0.}$$

Compatible observables
(→ can have simultaneous eigenstates)

QuBear: 當物理學家迷失方向 - 用量子力學告訴你座標系自旋上、下

Back to the Schrödinger eq for hydrogen atom

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r})$$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + V(\vec{r}) + \frac{\hat{L}^2}{2mr^2}$$

Use separation of variables

$$\psi(\vec{r}) = R(r)Y_\ell^m(\theta,\phi)$$

It is known that $\hat{L}^2 Y_\ell^m(\theta,\phi) = \ell(\ell+1)\hbar^2 Y_\ell^m(\theta,\phi)$

➡ **Radial equation**

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{2m}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} + E\right) - \frac{l(l+1)}{r^2}\right]R = 0$$

Special case: ground state of H atom

Assume the ground state has $\ell = 0$ and this requires $m = 0$

$$\Rightarrow \quad \frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr} + \frac{2\mu}{\hbar^2}\left(E + \frac{e^2}{4\pi\varepsilon_0 r}\right)R = 0$$

μ: reduced mass

For the ground state, try

$$R = Ae^{-r/a_0}$$

A is a normalization constant.
a_0 is a constant with the dimension of length.

$$\Rightarrow \quad \left(\frac{1}{a_0^2} + \frac{2\mu}{\hbar^2}E\right) + \left(\frac{2\mu e^2}{4\pi\varepsilon_0\hbar^2} - \frac{2}{a_0}\right)\frac{1}{r} = 0$$

two expressions in parentheses need to be zero.

$$\Rightarrow \quad E = -\frac{\hbar^2}{2\mu a_0^2} = -E_0 = -13.6\ eV \qquad a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2} = 0.529\ \text{Å}$$

Ground state energy

Bohr radius

In general

- Eigenenergies $E_n = -\frac{E_0}{n^2}$ n=1,2,3, … (principle quantum number)

Note: for H atom, the eigenenergies do not depend on ℓ.
In general, for non-Coulomb central force system, the energy would depend on ℓ.

- Eigenstates $\psi_{n\ell m_\ell}(r,\theta,\phi) = R_{n\ell}(r) Y_\ell^{m_\ell}(\theta,\phi)$

For a given n, $\ell = 0,1,2,\cdots,n-1$

• Table 7 . 1 Hydrogen Atom Radial Wave Functions

n	ℓ	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right) \frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0} \frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$

Summary: the quantum states of Hydrogen atom are specified by 3 quantum numbers

Principal quantum number	$n = 1, 2, 3, \ldots$
Orbital quantum number	$l = 0, 1, 2, \ldots, (n-1)$
Magnetic quantum number	$m_l = 0, \pm 1, \pm 2, \ldots, \pm l$

spectroscopic notation:

$l =$ 0	1	2	3	4	5	6	...
s	*p*	*d*	*f*	*g*	*h*	*i*	...

Different eigenstates with the same eigenenergy

Degeneracy of eigenstates:

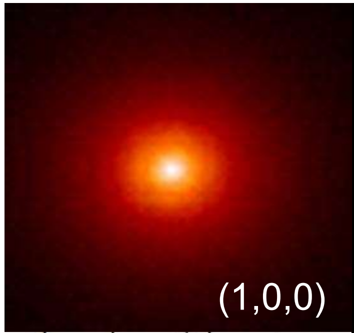
Table 6.2 Atomic Electron States

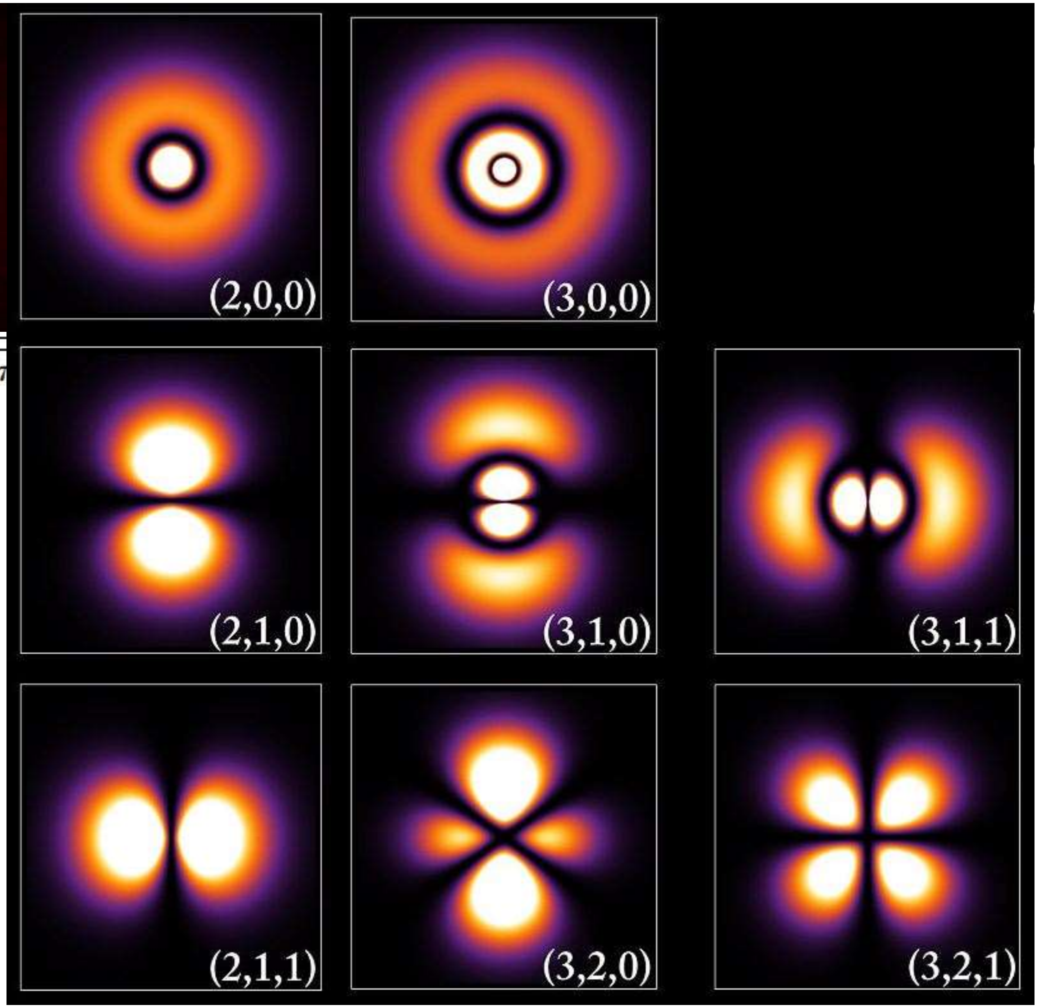
	$l = 0$	$l = 1$	$l = 2$	$l = 3$
$n = 1$	1*s*			
$n = 2$	2*s*	2*p*		
$n = 3$	3*s*	3*p*	3*d*	
$n = 4$	4*s*	4*p*	4*d*	4*f*
$n = 5$	5*s*	5*p*	5*d*	5*f*
$n = 6$	6*s*	6*p*	6*d*	6*f*

Table 6.1 Normalized Wave Functions of the Hydrogen Atom for $n = 1, 2$

$$\psi = R_{nl}\Theta_{lm_l}\Phi_{m_l}$$

n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}}e^{-r/a_0}$	$\frac{1}{\sqrt{\pi}\, a_0^{3/2}}e^{-r/a_0}$
						$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$
						$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}\cos\theta$
2	1	±1	$\frac{1}{\sqrt{2\pi}}$			$\frac{1}{8\sqrt{\pi}\, a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}\sin\theta\, e^{\pm i\phi}$





Ex 7.2: Show that the hydrogen wave function ψ_{211} is normalized.

$$\int \psi^*_{n\ell m_\ell}\psi_{n\ell m_\ell}\, d\tau = 1$$

Solution

$$\psi_{211} = R_{21}Y_{11} = \left[\frac{r}{a_0}\frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}\right]\left[\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{i\phi}\right]$$

$$\int \psi^*_{211}\psi_{211} r^2 \sin\theta\, dr\, d\theta\, d\phi$$

$$= \frac{1}{64\pi a_0^5}\int_0^\infty r^4 e^{-r/a_0}\, dr \int_0^\pi \sin^3 d\theta \int_0^{2\pi} d\phi$$

$$= \frac{1}{64\pi a_0^5}[24a_0^5]\left[\frac{4}{3}\right][2\pi]$$

$$= 1$$

Ex 7.12: Calculate the average orbital radius of a 1*s* electron in the hydrogen atom.

Solution

$$\langle r \rangle = \int \psi^*(r, \theta, \phi) r \psi(r, \theta, \phi)\, d\tau = \int r P(r)\, dr$$

$$= \int_0^\infty \frac{4}{a_0^3} e^{-2r/a_0} r^3\, dr$$

$$= \frac{4}{a_0^3} \frac{3a_0^4}{8} = \frac{3}{2} a_0$$

Example

Verify that the average value of $1/r$ for a 1*s* electron in the hydrogen atom is $1/a_0$.

Solution

$$\psi = \frac{e^{-r/a_0}}{\sqrt{\pi}\, a_0^{3/2}}$$

$$\left\langle \frac{1}{r} \right\rangle = \int_0^\infty \left(\frac{1}{r}\right) |\psi|^2\, dV$$

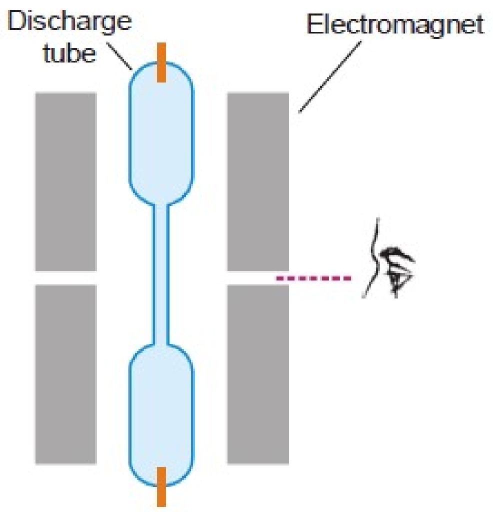
$$= \frac{1}{\pi a_0^3} \int_0^\infty r e^{-2r/a_0}\, dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi$$

$$= \left(\frac{1}{\pi a_0^3}\right)\left(\frac{a_0^2}{4}\right)(2)(2\pi) = \frac{1}{a_0}$$

- Angular momentum, spherical harmonics
- Schrödinger equation and the H atom
- Quantum numbers
- Electron distribution
- Zeeman effect
- Selection rule
- Electron spin

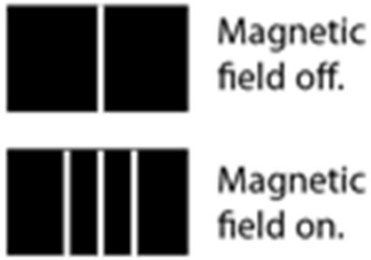
Magnetic Effects on Atomic Spectra

- 1845, Faraday found the connection between magnetic field and light
- Would the atomic spectrum be affected? With prism spectroscopy, Faraday failed to find any effect.
- 1896, with diffraction grating, Zeeman showed the spectral lines in a magnetic field split into multiple energy levels (called **Zeeman effect**).



Zeeman effect.

"Normal" Zeeman effect



Level splitting by B field

To understand this shift of energy levels using quantum mechanics, we need to consider the magnetic moment of a circulating electron.

Orbital magnetic moment

The circulating electron is similar to a current loop, which has a magnetic moment

$$\mu = IA = \frac{q}{T}A = \frac{(-e)\pi r^2}{2\pi r/v}$$

$$= \frac{-erv}{2} = -\frac{e}{2m}L$$

$$\Rightarrow \quad \vec{\mu} = -\frac{e}{2m}\vec{L}$$

$$\mu_z = -\frac{e}{2m}m_\ell \hbar = -\mu_B m_\ell$$

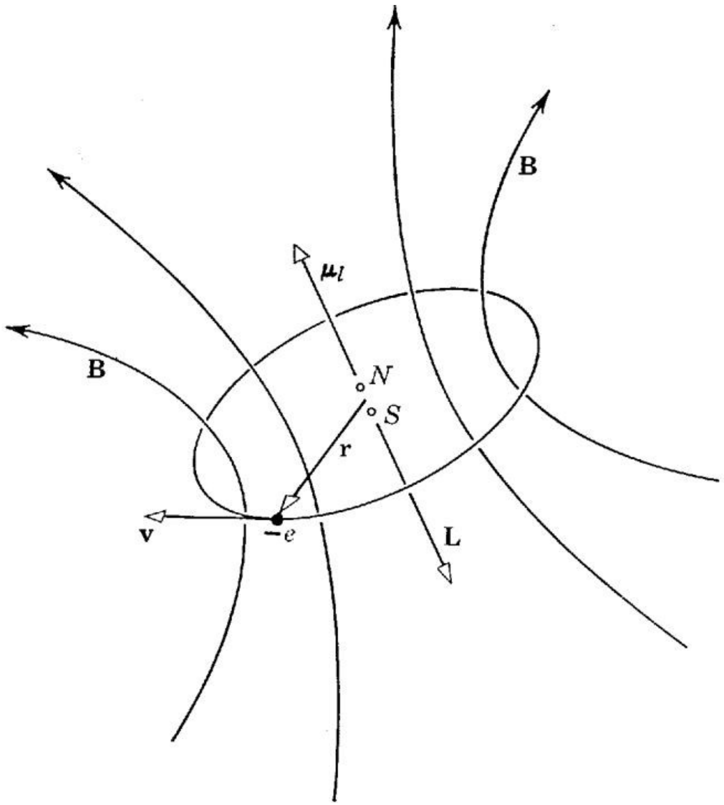
Bohr magneton

波耳磁元

$$\mu_b = \frac{e\hbar}{2m} = 0.927 \times 10^{-23} \text{ amp-m}^2$$

(or J/T)

$$= 0.058 \text{ meV/T}$$

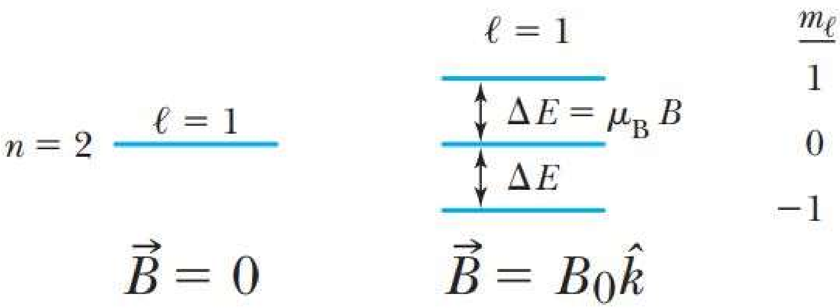


Tesla: an unit of magnetic field (proposed by Avčin at 1960).

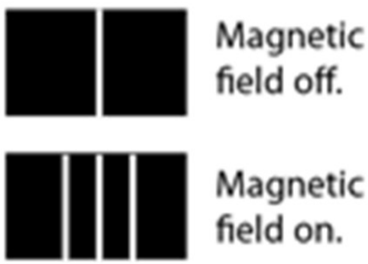
- The potential energy is quantized due to the magnetic quantum number *m*

$$V_B = -\mu_z B = +\mu_B m_\ell B$$

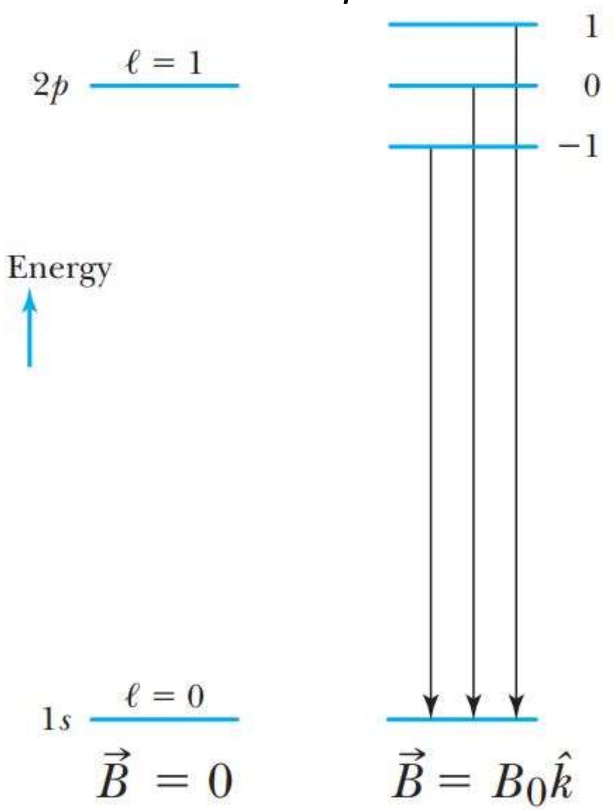
- For example, when a magnetic field is applied, the 2*p* level of hydrogen is split into 3 energy levels (if spin – to be introduced later – can be ignored)



Zeeman effect



transition from 2*p* to 1*s*



Ex 7.7: calculate the energy difference between the $m_\ell = 0$ and $m_\ell = +1$ components in the $2p$ state of atomic hydrogen placed in an external field of 2.00 T.

Solution

$$\Delta E = \mu_B B \, \Delta m_\ell$$

$$\Delta E = (9.27 \times 10^{-24}\ \text{J/T})(2.00\ \text{T}) = 1.85 \times 10^{-23}\ \text{J}$$

$$= 1.16 \times 10^{-4}\ \text{eV}$$

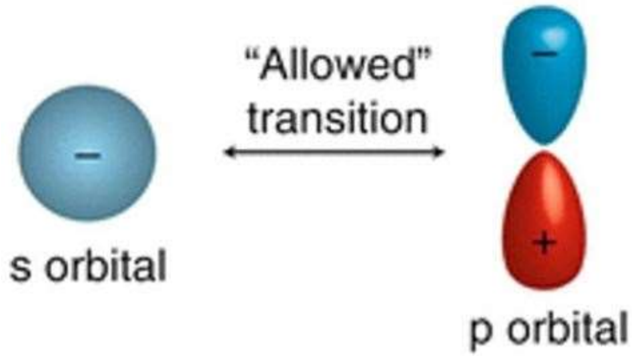
選擇定則 Selection rule in radiative transitions

(first found in observation)

Transition is allowed when

$$\Delta\ell = \pm 1$$

This is called selection rule



Explanation: the angular momentum of a photon is $\pm\hbar$, and total angular momentum has to be conserved,

optional

The transition probability is related to electric dipole moment

$$\Gamma_{i\to f} \propto \left|\int d^3v\,\psi_f^*(\vec{r})(-e\vec{r})\psi_i(\vec{r})\right|^2$$

Under space inversion:

$$Y_\ell^m(-\mathbf{r}) = (-1)^\ell Y_\ell^m(\mathbf{r}).$$

$\Rightarrow$ $\Gamma_{i\to f}=0$ if $\Delta\ell \neq \pm 1$

The transition is *forbidden*

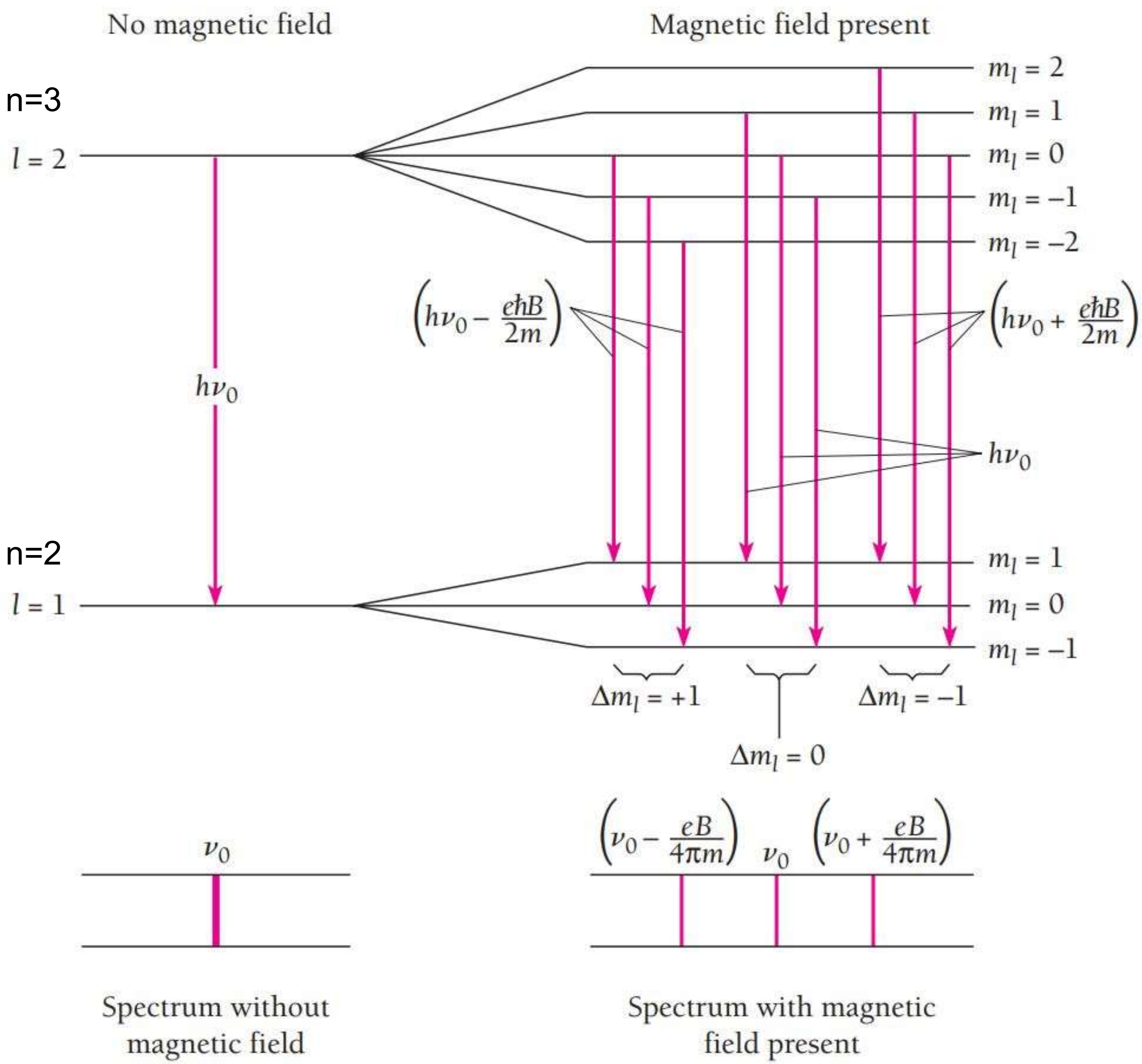
https://link.springer.com/referenceworkentry/10.1007/978-90-481-9751-4_30

Selection rule
(with magnetic field)

$$\Delta \ell = \pm 1$$
$$\Delta m_\ell = 0, \pm 1$$

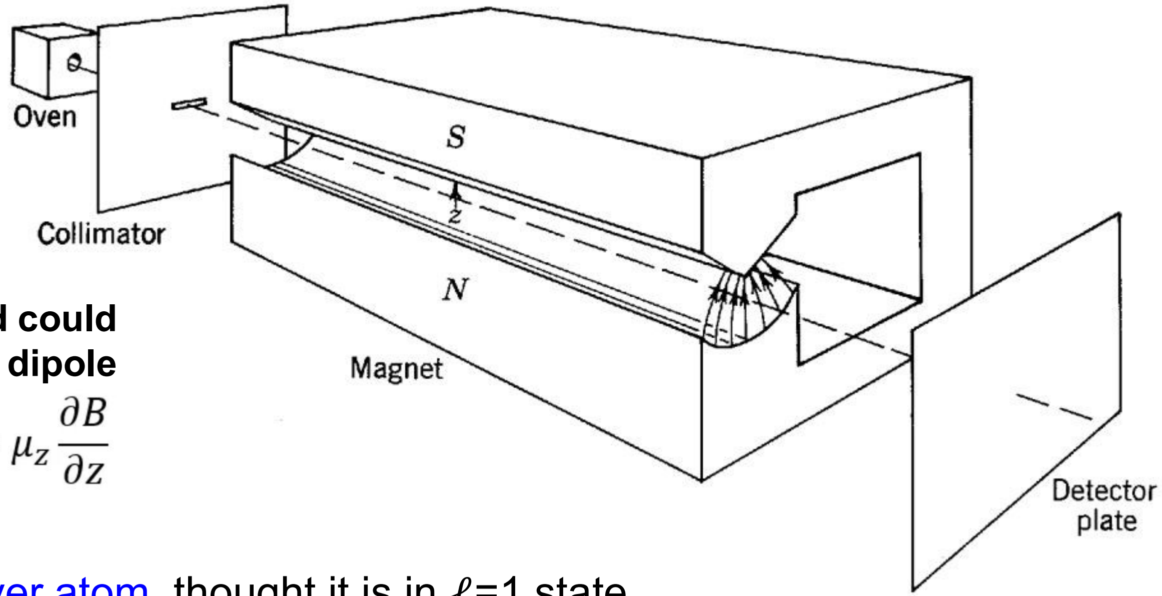
(no restriction on Δn)

Note: Other transitions are possible but with much smaller probabilities (magnetic dipole transitions 10^{-4}, electric quadrupole transitions 10^{-6} … etc)



In order to denounce the space quantization from *m,*

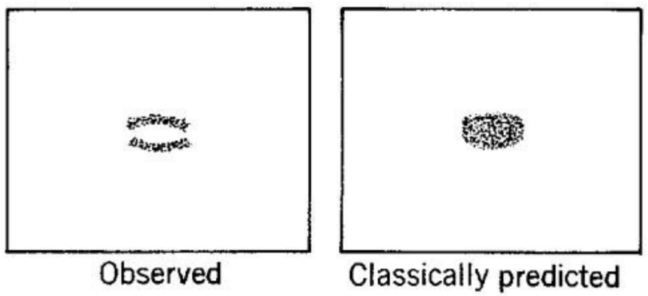
Stern and Gerlach carried out an experiment (1922)



Nonuniform B field could deflect a magnetic dipole

$$F_z = -\nabla(-\vec{\mu} \cdot \vec{B}) = \mu_z \frac{\partial B}{\partial z}$$

- They used silver atom, thought it is in ℓ=1 state, but observed just 2 lines.
- Ag[$4d^{10}5s^{1}$] atom is actually in ℓ=0 state. So what happened?
- Even though the azimuthal quantization is observed. Our understanding of quantum theory is incomplete.



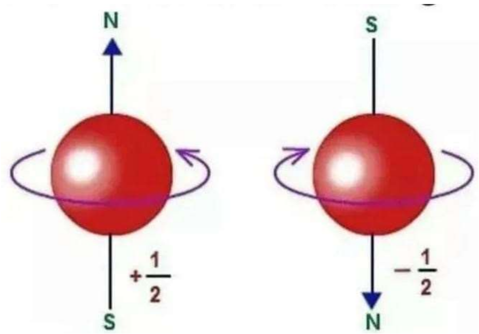
(independent of the choice of the z-direction)

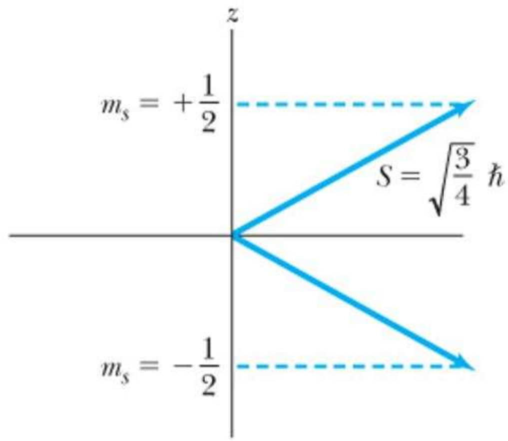
Uhlenbeck and Goudsmit's proposal (1925):

- In order to explain experimental data, they proposed that the electron must have the 4th quantum number (first suggested by Pauli) related to electron spin with spin quantum number $s = ½$.

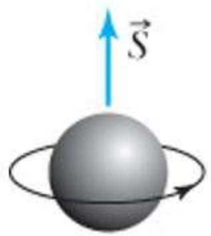
- The magnetic spin quantum number m_s has only two values, $m_s = \pm ½$.

$$S_z = m_s \hbar = \pm \tfrac{1}{2} \hbar$$





- However, electron radius r < Compton wavelength, so the surface of the spinning electron should be moving faster than the speed of light!



Qubear: 用量子力學大談奇異 Zeeman 效應⚡磁與電子自旋世界

- Magnitude of spin

$$\left|\vec{S}\right| = \sqrt{s(s+1)}\hbar = \sqrt{3/4}\hbar$$

$$S_z = m_s\hbar = \pm \tfrac{1}{2}\hbar$$

$$(s, m_s) = \left(\frac{1}{2}, \pm\frac{1}{2}\right)$$

- Recall that for orbital magnetic moment

$$\vec{\mu} = -\frac{e}{2m}\vec{L}$$

But for spin magnetic moment

(measured from SG experiment)

$$\vec{\mu}_S = -\frac{e}{m}\vec{S} = -g\frac{e}{2m}\vec{S}$$

i.e., gyromagnetic ratios *g*=2 (2.00231930436092(36) to be precise)

迴轉磁比

Q: Why not just choose *s*=1 ($s_z = \pm\hbar$, no 0), and g_s=1?

1. If s=1, then m_s would be $+1, 0, -1$ (3 levels)
2. Spin magnetic moment and spin angular momentum in principle can be measured independently
3. Later, Dirac's relativistic quantum mechanics would automatically give g_s=2

Ex 7.10:

Which of the following transitions for quantum numbers (n, ℓ, m_ℓ, m_s) are allowed for the hydrogen atom, and for those allowed, what is the energy involved?

(a) (2, 0, 0, 1/2) → (3, 1, 1, 1/2)
(b) (2, 0, 0, 1/2) → (3, 0, 0, 1/2)
(c) (4, 2, −1, −1/2) → (2, 1, 0, 1/2)

Solution

(a) $\Delta\ell = +1$, $\Delta m_\ell = 1$; allowed.

$$\Delta E = E_3 - E_2 = -13.6\ \text{eV}\left(\frac{1}{3^2} - \frac{1}{2^2}\right)$$

$= 1.89$ eV, corresponding to absorption of a 1.89-eV photon

(b) $\Delta\ell = 0$, $\Delta m_\ell = 0$; not allowed, because $\Delta\ell \neq \pm1$.

(c) $\Delta\ell = -1$, $\Delta m_\ell = 1$; allowed. Notice that $\Delta n = -2$ and $\Delta m_s = +1$ does not affect whether the transition is allowed.

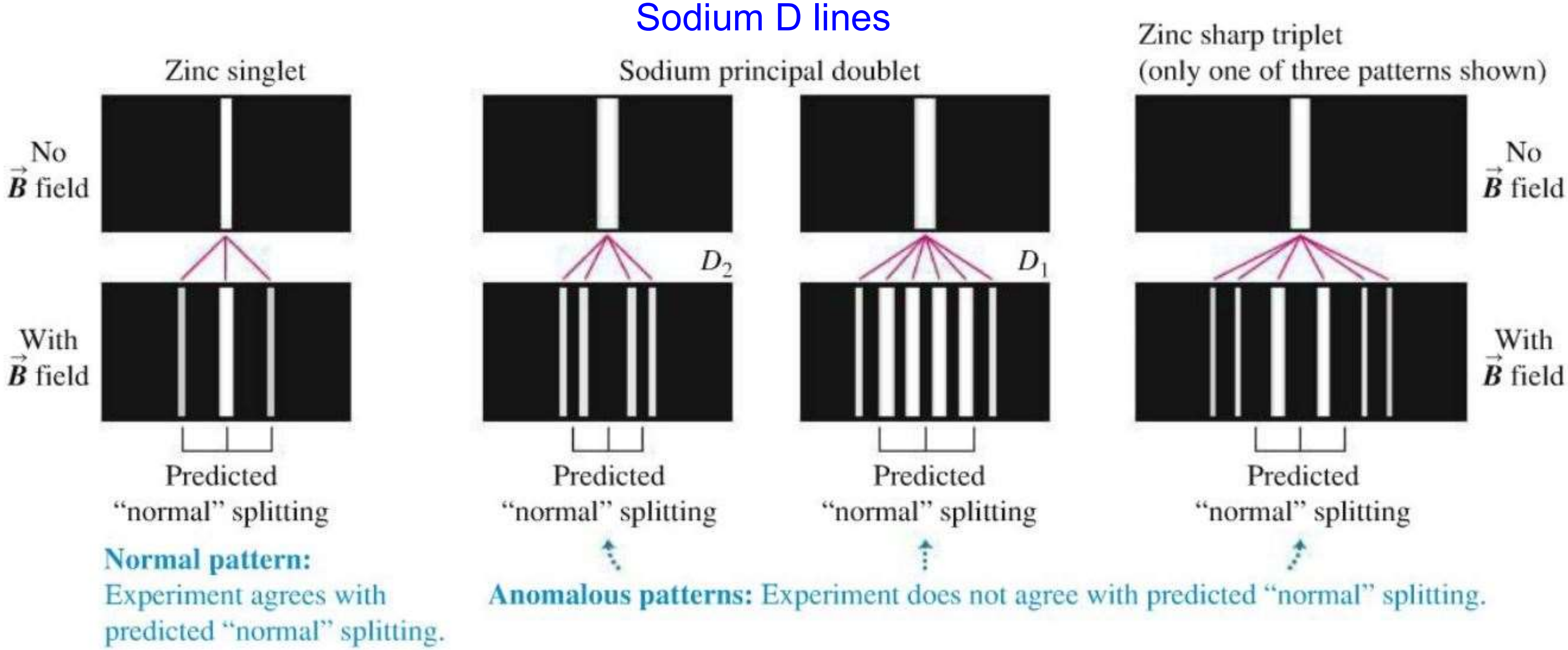
$\Delta m_s = 0$
hyperphysics

$$\Delta E = E_2 - E_4 = -13.6\ \text{eV}\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$= -2.55$ eV, corresponding to emission of a 2.55-eV photon

More on Zeeman splittings

Sodium D lines



Without spin

with spin

To explain it, we need to consider spin-orbit coupling (next Chap)