# Chapter 4 One-Electron Atoms

One-electron atoms: H, $He^{+}$, $Li^{2+}$, etc.

## 4-1 Quantum Theory of the One-electron Atom

$\hbar^2\nabla^2\Psi/2m+(E-V)\Psi=0$, where $V=-e^2/4\pi\varepsilon_0 r$

$$\Rightarrow \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\Psi}{\partial\phi^2}+\frac{2m}{\hbar^2}(E+\frac{e^2}{4\pi\varepsilon_0 r})\Psi=0$$

Let $\Psi(r,\theta,\varphi)=R(r)\Theta(\theta)\Phi(\varphi)$

$$\Rightarrow \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+[\frac{2m}{\hbar^2}(E_n+\frac{e^2}{4\pi\varepsilon_0 r})-\frac{l(l+1)}{r^2}]R=0\ldots(1),$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+[l(l+1)-\frac{m_l^{\,2}}{\sin^2\theta}]\Theta=0\ldots(2), \text{ and } \frac{d^2\Phi}{d\phi^2}+m_l^{\,2}\Phi=0\ldots(3)$$

$E_n$ is the eigenvalue of (1), and we can prove that $E_n=\dfrac{-me^4}{32n^2\pi^2\varepsilon_0^{\,2}\hbar^2}$, where $n$=1, 2, …

(**Principal quantum number**).

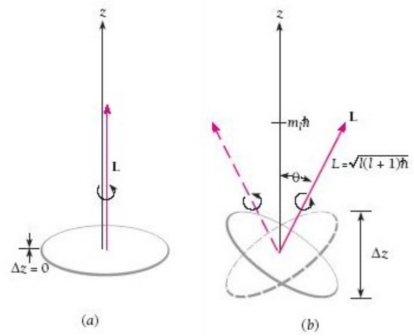
$l(l+1)$ is the eigenvalue of (2), and we can prove that $l$=0, 1, 2, …, $n$-1 (**Orbital quantum number**).

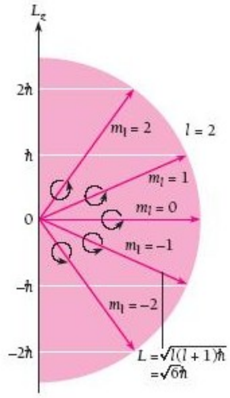
$m_l$ is the eigenvalue of (3), and we can prove that $m_l$=0, ±1, ±2, …, ±$l$ (**Magnetic quantum number**).

By (1): $\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}[(E_n-V)-\frac{\hbar^2 l(l+1)}{2mr^2}]R=0$, and set $E=K_{radial}+K_{orbital}+V$.

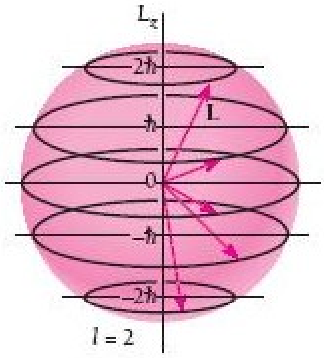
If $K_{orbital}=\frac{\hbar^2 l(l+1)}{2mr^2}$, then (1)$\Rightarrow \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}K_{radial}R=0$ is dependent on only $r$ and the energy of radial motion. It is in agreement with the physical depiction.

$\therefore$ $K_{orbital}=\frac{\hbar^2 l(l+1)}{2mr^2}=\frac{(mvr)^2}{2mr^2}=\frac{L^2}{2mr^2}$ $\Rightarrow$ Angular momentum of an electron is $L=\sqrt{l(l+1)}\hbar$.

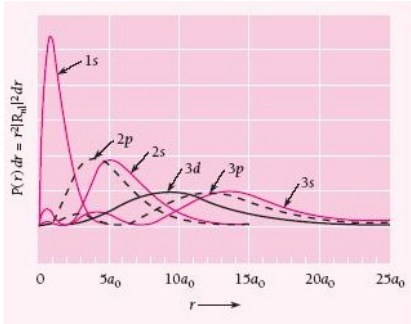




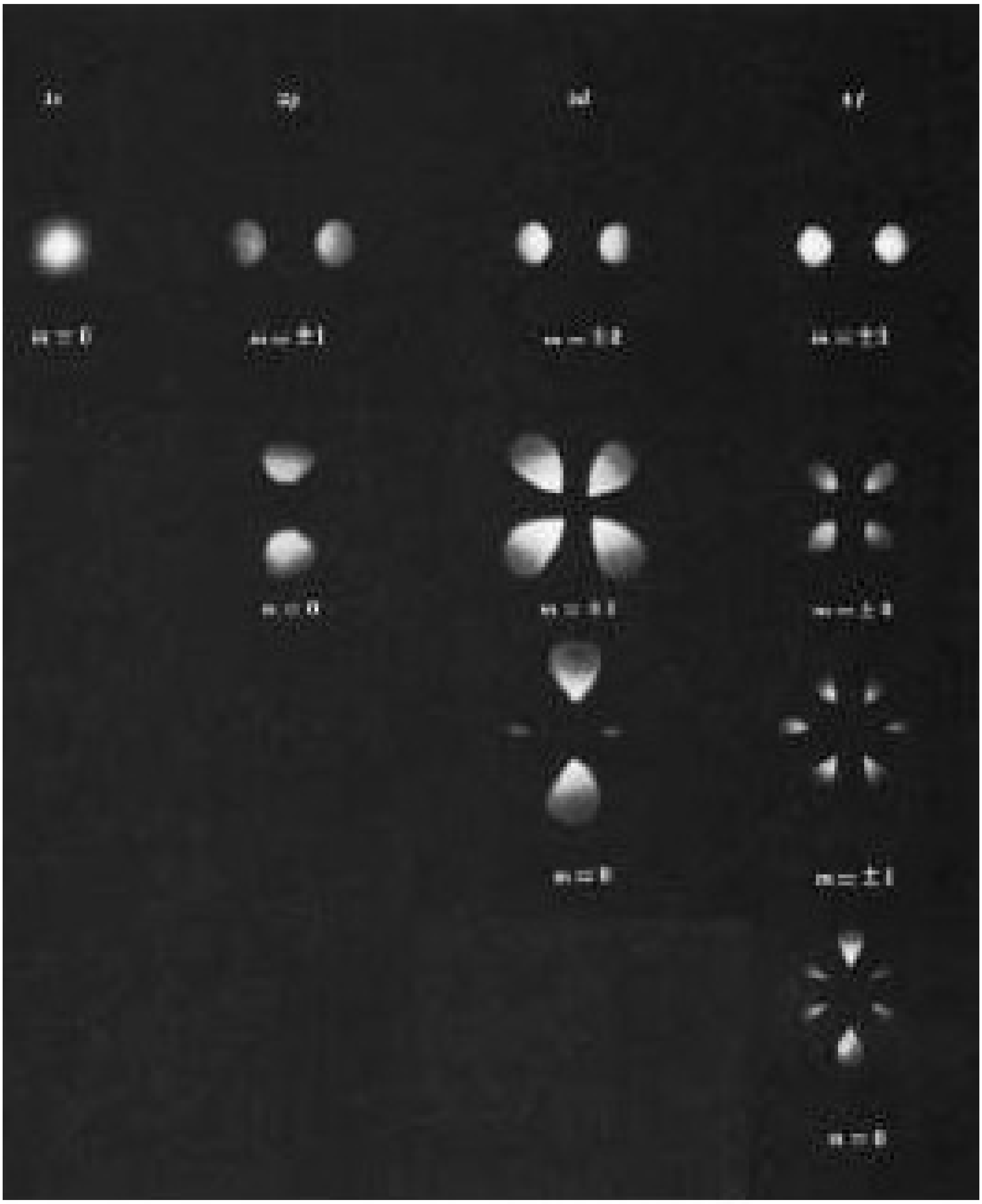
$L_z$
$2\hbar$
$\hbar$
0
$-\hbar$
$-2\hbar$
$m_l = 2$
$l = 2$
$m_l = 1$
$m_l = 0$
$m_l = -1$
$m_l = -2$
$L = \sqrt{l(l+1)}\hbar$
$= \sqrt{6}\hbar$

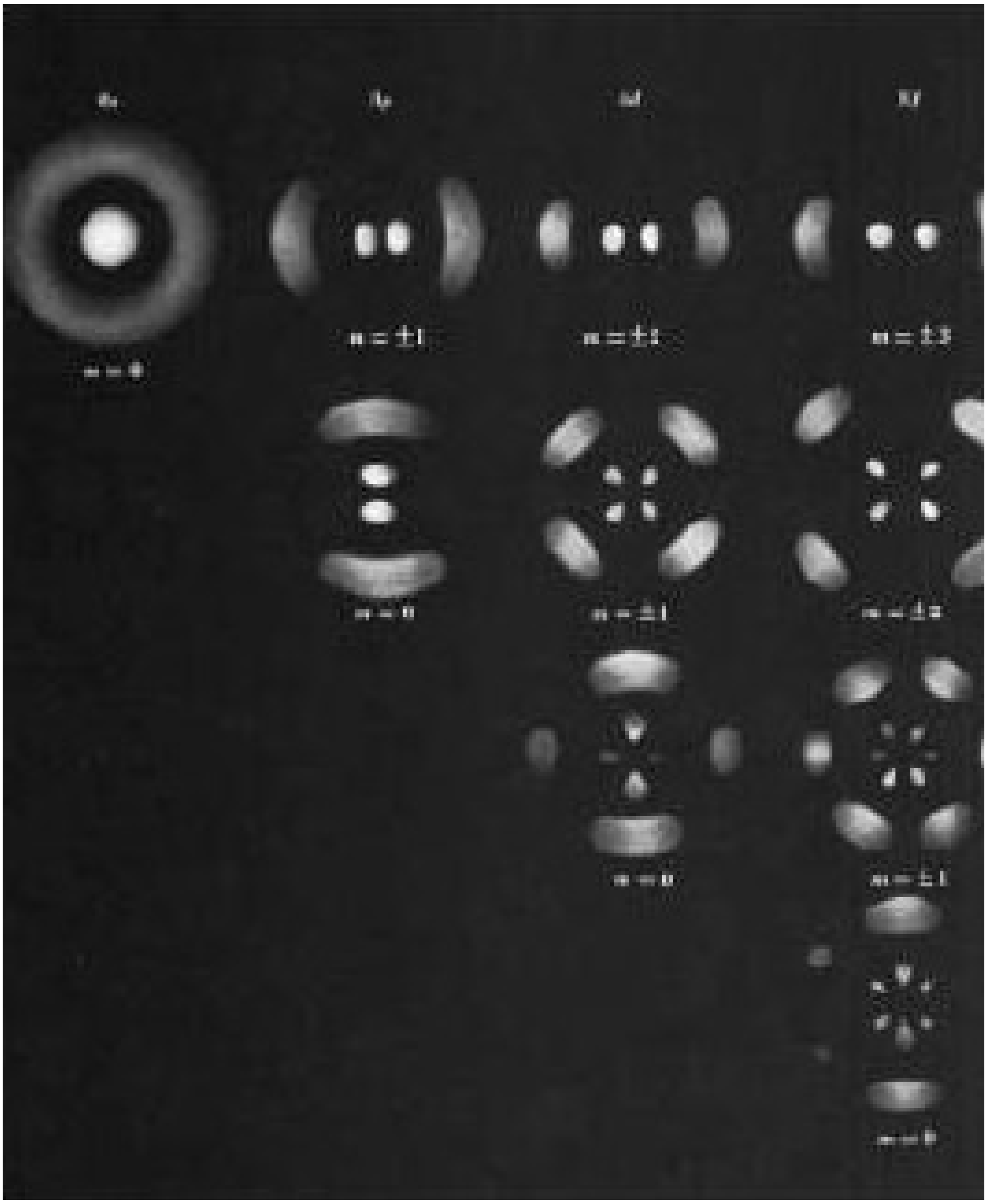
$L_z$
$2\hbar$
$\hbar$
L
0
$-\hbar$
$-2\hbar$
$l = 2$

$P(r)\,dr = r^2|R_{nl}|^2\,dr$
1s
2p
2s
3d
3p
3s
0
$5a_0$
$10a_0$
$15a_0$
$20a_0$
$25a_0$
$r$

m = ±1
m = 0

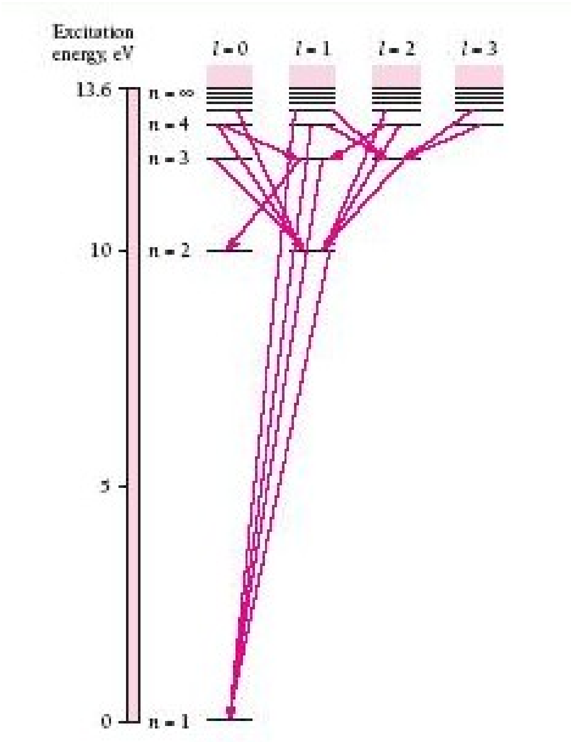


**Eg. The wave function of a 1s electron is $\Psi = \frac{e^{-\frac{r}{a_0}}}{\sqrt{\pi}\,a_0^{\frac{3}{2}}}$. Please find the average of 1/r for an electron in the hydrogen atom. [台大電研]**

: Normalized Wave Functions of the Hydrogen Atom for $n = 1, 2,$ and 3*

| $n$ | $l$ | $m_l$ | $\Phi(\phi)$ | $\Theta(\theta)$ | $R(r)$ | $\psi(r, \theta, \phi)$ |
|---|---|---|---|---|---|---|
| 1 | 0 | 0 | $\frac{1}{\sqrt{2\pi}}$ | $\frac{1}{\sqrt{2}}$ | $\frac{2}{a_0^{3/2}}e^{-r/a_0}$ | $\frac{1}{\sqrt{\pi}\,a_0^{3/2}}e^{-r/a_0}$ |
| 2 | 0 | 0 | $\frac{1}{\sqrt{2\pi}}$ | $\frac{1}{\sqrt{2}}$ | $\frac{1}{2\sqrt{2}\,a_0^{3/2}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$ | $\frac{1}{4\sqrt{2\pi}\,a_0^{3/2}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$ |
| 2 | 1 | 0 | $\frac{1}{\sqrt{2\pi}}$ | $\frac{\sqrt{6}}{2}\cos\theta$ | $\frac{1}{2\sqrt{6}\,a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$ | $\frac{1}{4\sqrt{2\pi}\,a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}\cos\theta$ |
| 2 | 1 | ±1 | $\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$ | $\frac{\sqrt{3}}{2}\sin\theta$ | $\frac{1}{2\sqrt{6}\,a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$ | $\frac{1}{8\sqrt{\pi}\,a_0^{3/2}}\frac{r}{a_0}e^{-r/2a_0}\sin\theta\, e^{\pm i\phi}$ |
| 3 | 0 | 0 | $\frac{1}{\sqrt{2\pi}}$ | $\frac{1}{\sqrt{2}}$ | $\frac{2}{81\sqrt{3}\,a_0^{3/2}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right)e^{-r/3a_0}$ | $\frac{1}{81\sqrt{3\pi}\,a_0^{3/2}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right)e^{-r/3a_0}$ |
| 3 | 1 | 0 | $\frac{1}{\sqrt{2\pi}}$ | $\frac{\sqrt{6}}{2}\cos\theta$ | $\frac{4}{81\sqrt{6}\,a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$ | $\frac{\sqrt{2}}{81\sqrt{\pi}\,a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\cos\theta$ |
| 3 | 1 | ±1 | $\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$ | $\frac{\sqrt{3}}{2}\sin\theta$ | $\frac{4}{81\sqrt{6}\,a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$ | $\frac{1}{81\sqrt{\pi}\,a_0^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}\sin\theta\, e^{\pm i\phi}$ |
| 3 | 2 | 0 | $\frac{1}{\sqrt{2\pi}}$ | $\frac{\sqrt{10}}{4}(3\cos^2\theta-1)$ | $\frac{4}{81\sqrt{30}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$ | $\frac{1}{81\sqrt{6\pi}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}(3\cos^2\theta-1)$ |
| 3 | 2 | ±1 | $\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$ | $\frac{\sqrt{15}}{2}\sin\theta\cos\theta$ | $\frac{4}{81\sqrt{30}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$ | $\frac{1}{81\sqrt{\pi}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin\theta\cos\theta\, e^{\pm i\phi}$ |
| 3 | 2 | ±2 | $\frac{1}{\sqrt{2\pi}}e^{\pm 2i\phi}$ | $\frac{\sqrt{15}}{4}\sin^2\theta$ | $\frac{4}{81\sqrt{30}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$ | $\frac{1}{162\sqrt{\pi}\,a_0^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin^2\theta\, e^{\pm 2i\phi}$ |

*The quantity $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 5.292 \times 10^{-11}$ m is equal to the radius of the innermost Bohr orbit.




**Selection rules of transitions:** If $\int\Psi_n{}^*x\Psi_m dr\neq0$, the electron can transfer from quantum state $\Psi_m$ (energy level $E_m$) to state $\Psi_n$ (energy level $E_n$).

(Proof) Consider a composite wavefunction $\Psi=a\Psi_n+b\Psi_m$, where $\Psi_n=\mathit{\Psi}_n e^{-i(2\pi E_n/h)t}$, $\Psi_m=\mathit{\Psi}_m e^{-i(2\pi E_m/h)t}$, and $|a|^2+|b|^2=1$.

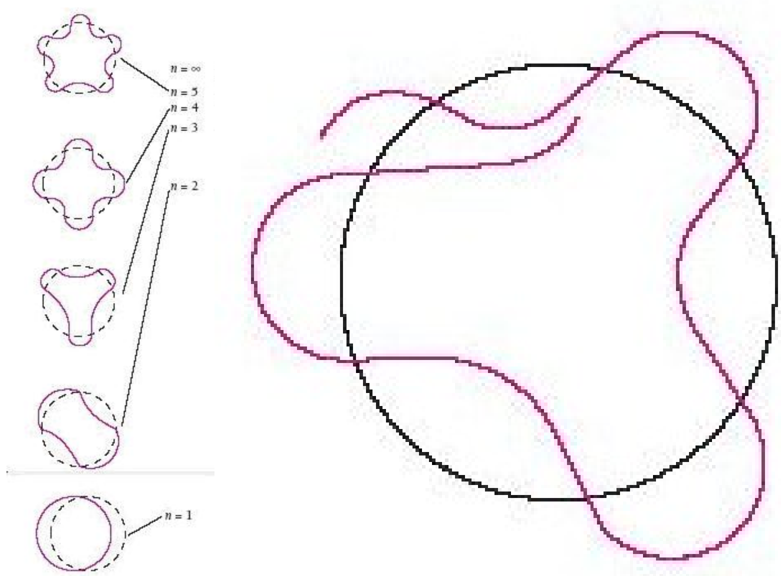
$\langle x\rangle=\int\Psi^*x\Psi dr=a^2\cdot\int x|\Psi_n|^2dr+b^2\cdot\int x|\Psi_m|^2dr+2a^*b\cos(2\pi\nu t)\cdot\int\Psi_n{}^*x\Psi_m dr$, where $\nu=(E_n-E_m)/h$

If $\int\Psi_n{}^*x\Psi_m dr=0$, the average electron position $\langle x\rangle$ is independent of $t$. Therefore, it is a forbidden transition.

∴ Transition from quantum state $\Psi_m$ to state $\Psi_n$ is allowed if $\int\Psi_n{}^*x\Psi_m dr\neq0$.

For hydrogen, selection rules are $\triangle l=l'-l=\pm1$ and $\triangle m_l=m_l'-m_l=0, \pm1$ if an electron is transferred from $\Psi_{n,l,ml}$ to $\Psi_{n',l',ml'}$.

**4-2 Bohr's Model of One-electron Atoms**




For a one-electron atom, the stability conditions of orbit are $\begin{cases} n\lambda = 2\pi r_n \\ \lambda = \dfrac{h}{mv} \\ \dfrac{mv^2}{r_n} = \dfrac{1}{4\pi\varepsilon_0}\cdot\dfrac{Ze^2}{r_n^{\ 2}} \end{cases}$,

where $n$=1, 2, 3, …, and $Z$ is atomic number. We can solve the above equations an obtain $v=\dfrac{\sqrt{Z}e}{\sqrt{4\pi\varepsilon_0 m r_n}}$, $\lambda=\dfrac{h}{e}\cdot\sqrt{\dfrac{4\pi\varepsilon_0 r_n}{mZ}}$, $r_n=\dfrac{n^2h^2\varepsilon_0}{Z\pi me^2}$, $n$=1, 2, 3, …

**Total energy:** $E_n=K+V=mv^2/2-Ze^2/4\pi\varepsilon_0 r_n=Ze^2/8\pi\varepsilon_0 r_n-Ze^2/4\pi\varepsilon_0 r_n=-Ze^2/8\pi\varepsilon_0 r_n$ $=-mZ^2e^4/8n^2h^2\varepsilon^2=-E_1Z^2/n^2$, where $E_1=13.6eV$

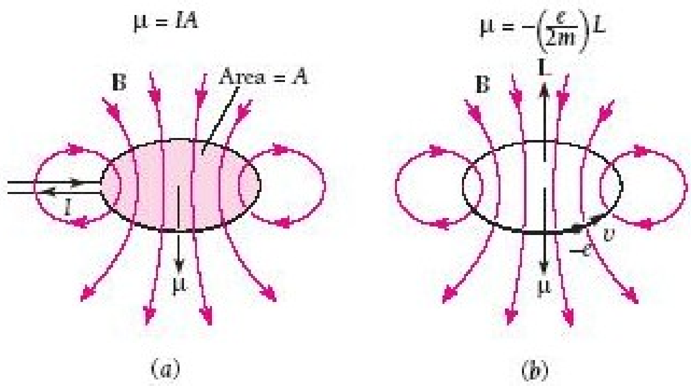
**Eg. (a) An electron of H atom drops from the second excited state to the ground state, how much energy does it lose? (b) For He$^+$ atom, repeat the calculation.**

(Sol.) (a) $n$: 3→1, $E_1$-$E_3$=-13.6(1/1$^2$-1/3$^2$)=-12.08eV

(b) -12.08×2$^2$=-48.355eV

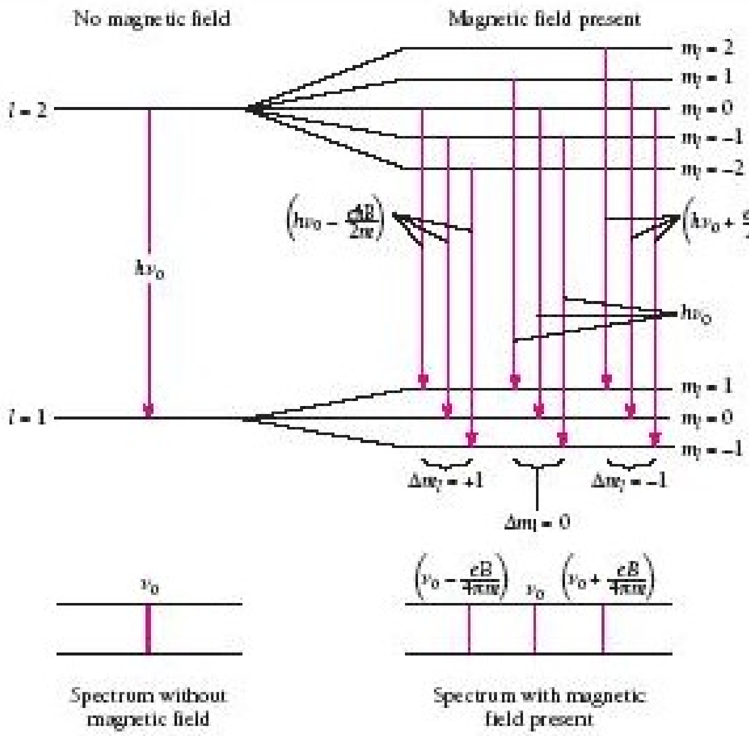
### 4-3 Zeeman Effect

The torque $\tau$ on a magnetic dipole $\mu=IA=-eL/2m$ of an orbiting electron in $B$: $\tau=\mu\times B=\mu B\sin\theta$. Hence the potential energy is $U_m=\int\mu d\theta=-\mu B\cos\theta=eLB\cos\theta/2m$. And utilizing $\cos\theta=\dfrac{m_l}{\sqrt{l(l+1)}}$ and $L=\sqrt{l(l+1)}\hbar$, we have $U_m=m_lB(e\hbar/2m)$, where $\mu_B=e\hbar/2m$ is called Bohr's magneton.




(*a*) Magnetic moment of a current loop enclosing area *A*. (*b*) Magnetic moment of an orbiting electron of angular momentum L.

**Normal Zeeman effect:** $\nu_1=\nu_0-\mu_B B/h=\nu_0-eB/4\pi m$, $\nu_2=\nu_0$, $\nu_3=\nu_0+\mu_B B/h=\nu_0+eB/4\pi m$.




In the normal Zeeman effect a spectral line of frequency $\nu_0$ is split into three components when the radiating atoms are in a magnetic field of magnitude *B*. One component is $\nu_0$ and the others are less than and greater than $\nu_0$ by $eB/4\pi m$. There are only three components because of the selection rule $\Delta m_l = 0, \pm 1$.