Chapter 8

The time-dependent wave equation of a particle in a three dimensional box (L, L, L) is

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t) + U(\vec{r})\psi(\vec{r}) = i\hbar\frac{\partial\psi(\vec{r},t)}{\partial t}$$

Laplacian ; $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

for stationary states $\psi(\vec{r},t) = \psi(\vec{r})\,e^{-i\omega t}$

$\Rightarrow$ time-independent S.E. is

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\vec{r})\right]\psi(\vec{r}) = E\,\psi(\vec{r})$$

Hamiltonian operator

energy observable

$\psi(\vec{r}) = \psi(x)\cdot\psi(y)\cdot\psi(z)$ in Cartesian Coordinates

In this case $\psi(x) = \sqrt{\frac{2}{L}}\,\sin\left(n_1\frac{\pi}{L}x\right)$

$$\psi(y) = \sqrt{\frac{2}{L}}\,\sin\left(n_2\frac{\pi}{L}y\right)$$

$$\psi(z) = \sqrt{2/L}\,\sin\left(n_3\,\pi/L\,z\right)$$

So
$$E = \frac{\pi^2 \hbar^2}{2mL^2}\left(n_1^2 + n_2^2 + n_3^2\right)$$

and
$$\psi(x,y,z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_1 \pi}{L} x\right) \sin\left(\frac{n_2}{L}\pi y\right) \sin\left(\frac{n_3 \pi}{L} z\right)$$

with
$n_1 = 1, 2, \ldots$
$n_2 = 1, 2, \ldots$
$n_3 = 1, 2, \ldots$

Degenarcy appears when different states have the same energy!

Example

n_1	n_2	n_3
1	1	2
1	2	1
2	1	1

$$\rightarrow \psi_{112} = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{\pi}{L} y\right) \sin\left(\frac{2\pi}{L} z\right)$$

$$\rightarrow \psi_{121} = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{2\pi y}{L}\right) \sin\left(\frac{\pi}{L} z\right)$$

$$\rightarrow \psi_{211} = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{2\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right) \sin\left(\frac{\pi}{L} z\right)$$

Three different state having the same energy

$$E_{112} = E_{121} = E_{211} = \frac{6\pi^2 \hbar^2}{2mL^2}$$

In the case of central forces acting on a particle we use spherical spherical coordinates for the Laplacian.

Schrodinger equation is

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial\psi}{\partial\theta}$$

$$+\frac{2\mu}{\hbar^2}\left[E-U\right]\psi=0 \quad -(1)$$

The wave function $\psi(r,\theta,\phi) = R(r)\,\Theta(\theta)\,\Phi(\phi)$

This leads to three differential equations

$$\frac{d^2\Phi}{d\phi^2}+m_\ell^2\,\Phi=0 \quad -(2)$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left[\ell(\ell+1)-\frac{m_\ell^2}{\sin^2\theta}\right]\Theta=0 \quad -(3)$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}\left[E-U-\frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]R=0 \quad -(4)$$

Solving the Schrodinger equation (1) means solving the above three equations.

Solution of equation (2) is $\Phi(\phi) = e^{im_\ell\phi}$

Solution of equation (3) are the "associated Legendre polynomials". See Table 7.2 in your textbook. They are called $P_\ell^{m_\ell}(\cos\theta)$

The product $\Theta(\theta)\,\Phi(\phi)$ specify the full angular dependence of the central force wavefunction and are know as "spherical harmonics", denoted $Y_\ell^{m_\ell}(\theta,\phi)$. See Table 7.3 in your text book.

In our case $|\vec{L}|$, L_z and E are sharp observables.

$$|\vec{L}| = \sqrt{\ell(\ell+1)}\,\hbar \qquad \ell = 0, 1, 2, \ldots$$

$$L_z = m_\ell \hbar \qquad -\ell \le m_\ell \le \ell$$

ℓ: "orbital quantum number"

m_ℓ: "magnetic quantum number"

"Angular momentum and its z-component are QUANTIZED"

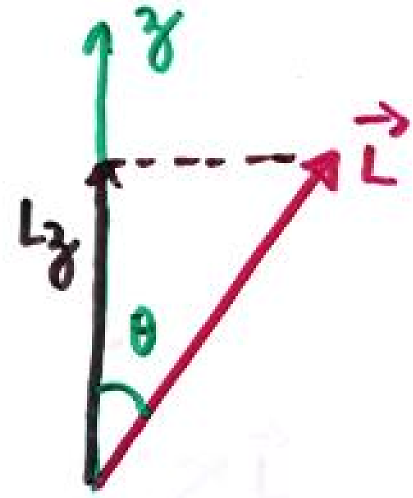
So: $$\psi_{n\ell m_\ell}(\vec{r}) = R_{n\ell}(r)\, Y_\ell^{m_\ell}(\theta,\phi)$$

Total wavefunction

radial wave

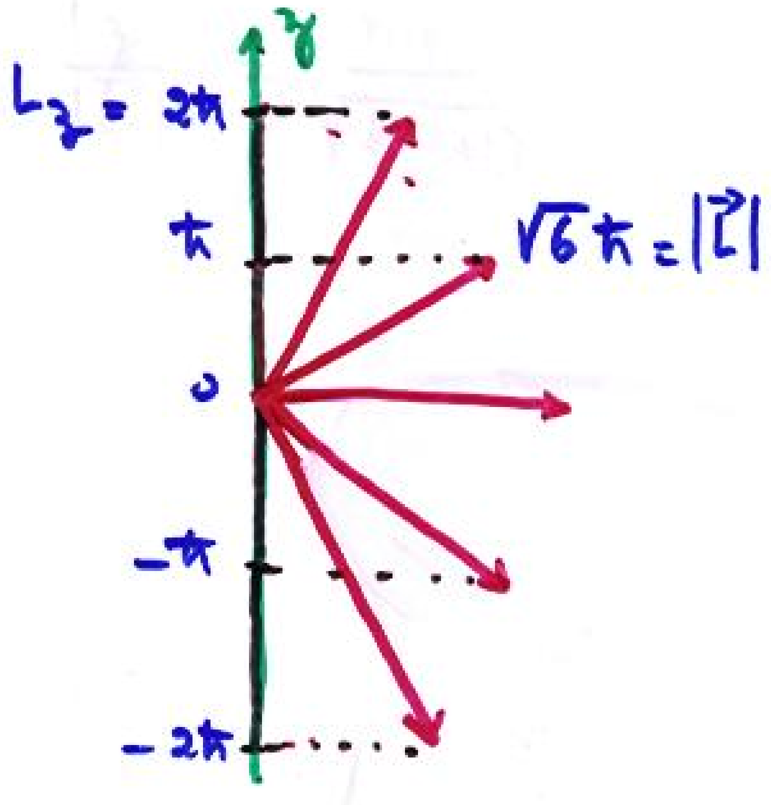
angular wave

In quantum mechanics, space is "quantized". That is the angular momentum can take only specific directions with respect to the z-axis



$$\cos\theta = \frac{L_z}{|\vec{L}|} = \frac{m_\ell}{\sqrt{\ell(\ell+1)}} \qquad -\ell \le m_\ell \le \ell$$

For example: $\ell = 2 \Rightarrow m_\ell = -2, -1, 0, 1, 2.$



For hydrogen and hydrogen-Like ions

The allowed energies are

$$E_n = -\frac{13.6\,Z^2}{n^2} \qquad n = 1, 2, 3, \ldots.$$

n is the "principle quantum number".

and the wavefunctions are

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

given in Table 7.4 for n = 1, 2 and 3.
(your textbook)

For example

when $n = 1 \Rightarrow \ell = 0$ and $m_\ell = 0$

$$\psi_{100} = R_{10}(r)\, Y_0^0(\theta, \phi) \Leftarrow$$ ground state wavefunction

$$E_1 = -13.6\,Z^2 \Leftarrow$$ ground state energy

From Tables $\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}}$

For hydrogen atom: $Z = 1$

For helium He^+ ion: $Z = 2$ etc..

n	shell symbol	ℓ	subshell symbol
1	K	0	s
2	L	1	p
3	M	2	d
4	N	3	f
⋮	⋮	⋮	⋮

If $n = 3$ $\quad \ell = 0 \leftarrow$ 3s state

$\ell = 1 \leftarrow$ 3p state

$\ell = 2 \leftarrow$ 3d state

Always remember

$n = 1, 2, 3, \ldots$

$\ell = 0, 1, 2, \ldots (n-1)$

$-\ell \leq m_\ell \leq \ell$

For $n = 2$ $\quad l = 0 \quad m_l = 0 \rightarrow \psi_{200}$

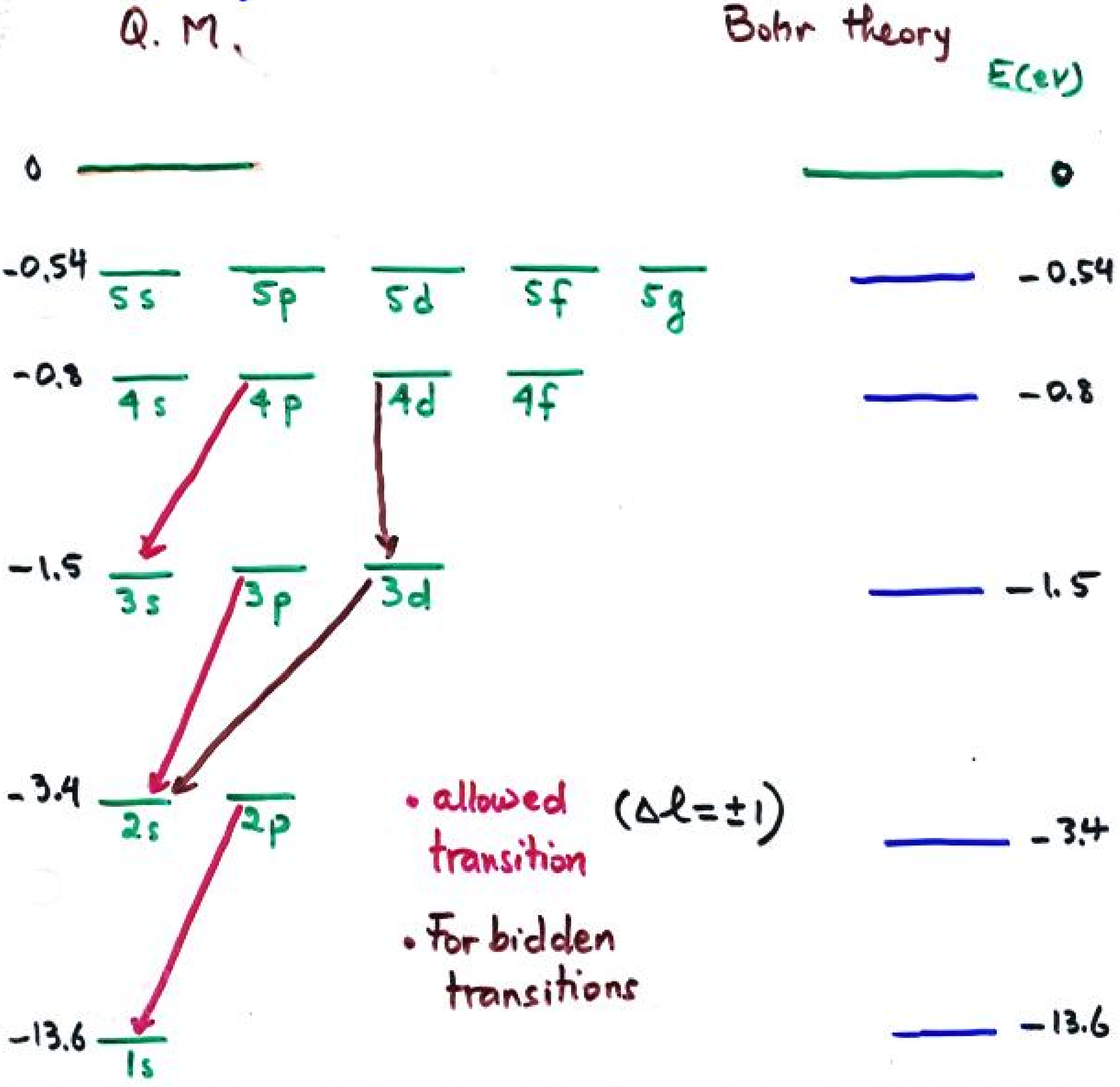
$\qquad\qquad\quad l = 1 \quad m_l = -1 \rightarrow \psi_{21-1}$

$\qquad\qquad\qquad\qquad m_l = 0 \rightarrow \psi_{210}$

$\qquad\qquad\qquad\qquad m_l = 1 \rightarrow \psi_{211}$

$$E_2 = -\frac{13.4}{4} Z^2 = -3.4 Z^2 \text{ (ev)}$$

For hydrogen atoms



- The ground state of the hydrogen and hydrogen like atoms will have quantum numbers:

$n = 1 \quad l = 0 \quad m_l = 0$

$$E_1 = -13.6\, Z^2 \ (eV)$$

$$\psi_{100} = R_{10} Y_0^0 = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}}$$

ψ_{100} does not depend on θ and ϕ and is spherically symmetric so are all $l=0$ (s-states).

The radial probability density for <u>ANY</u> state is

$P(r) = r^2 |R(r)|^2$

$R(r)$ is the radial wavefunction.

also $\displaystyle\int_0^\infty P(r)\, dr = 1$ and $\displaystyle\langle r \rangle = \int_0^\infty r P(r)\, dr$

average distance of the electron from the nucleus.

- The excited states of hydrogen like atoms are

$n = 2$

$l = 0 \quad m_l = 0 \qquad E_2 = -3.4\, Z^2 \ (eV)$

$l = 1 \quad m_l = 1, 0, -1$

$$\psi_{200} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{3/2}\left(1-\frac{Zr}{2a_0}\right)e^{-\frac{Zr}{2a_0}}$$

$$\psi_{211} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{8a_0}\right)e^{-\frac{Zr}{2a_0}}\sin\theta\, e^{i\phi}$$

$$\psi_{210} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{3/2}\left(\frac{Zr}{2a_0}\right)e^{-\frac{Zr}{2a_0}}\cos\theta$$

$$\psi_{21-1} = -\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{8a_0}\right)e^{-\frac{Zr}{2a_0}}\sin\theta\, e^{-i\phi}$$

The level E_2 is 4-fold degenerate.