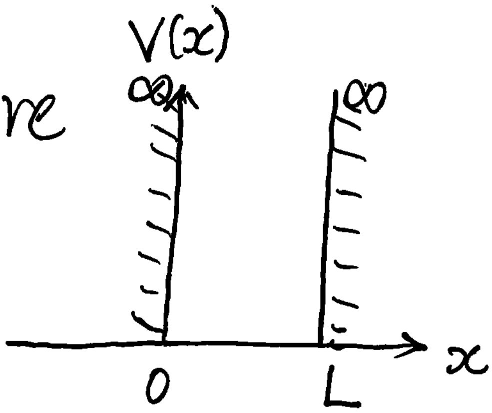
TISE

$$\hat{H}\psi_n = E_n\psi_n \qquad (1')$$

B. Standard Examples

(i) 1D particle-in-a-box [infinite potential well]

$$\underset{\substack{\uparrow\\ \text{potential energy function that goes into } \hat{H}}}{V(x)} = \begin{cases} 0 & 0<x<L \\ \infty & \text{elsewhere} \end{cases}$$



$$\psi(x) = 0 \quad \text{for} \quad x<0 \ \& \ x>L$$

Only need to solve TISE in well

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi + \underset{\substack{\shortparallel\\ 0}}{\cancel{V(x)\psi}} = E\psi$$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi \qquad \text{for} \quad 0 \leq x \leq L$$

$$\boxed{\begin{cases} E_n = \dfrac{n^2\pi^2\hbar^2}{2mL^2} & \text{after applying boundary conditions} \\ \psi_n = \sqrt{\dfrac{2}{L}}\sin\left(\dfrac{n\pi x}{L}\right) & ;\ \underset{\uparrow}{n}=1,2,3,\ldots \end{cases}} \qquad (9)$$

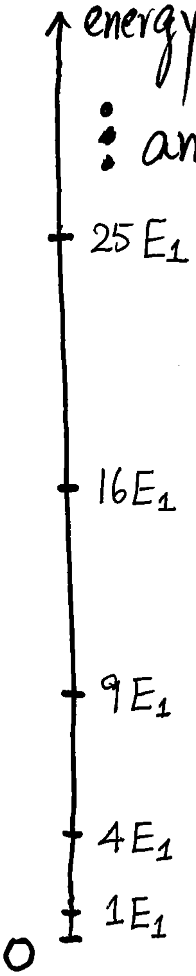
Note: starts from 1

relevant to:

- polymer chain
- Quantum wells formed by semiconductors

Allowed energies

1D infinite well



and so on (infinitely many)

[This picture is for the 1D case!]

(Quite different in 2D and 3D)

with $E_1 = \frac{\pi^2\hbar^2}{2mL^2}$

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2} \sim \frac{1}{L^2}$$

narrower well (more confinement) gives higher and farther apart energies

⇓

a handle to control allowed energies (engineering)

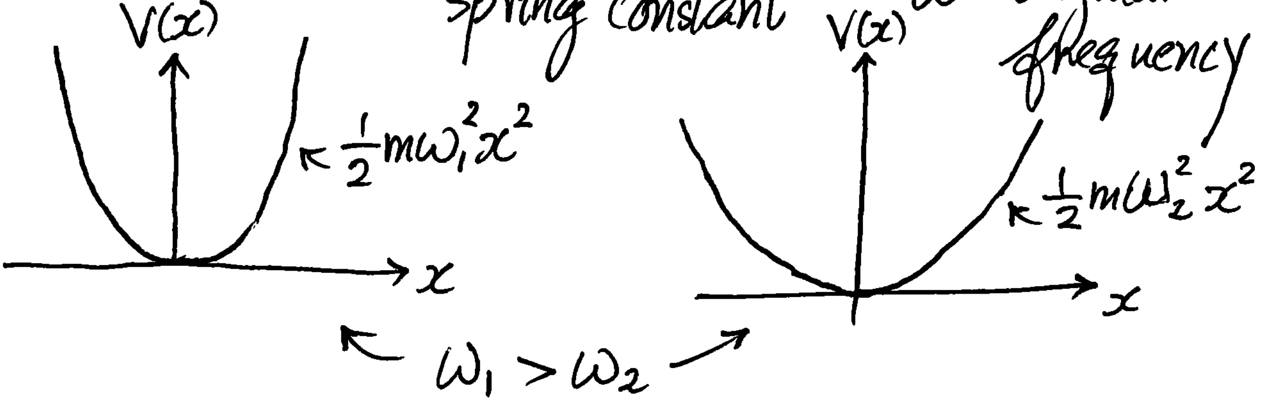
$E_n \sim \frac{1}{m}$ easier to see effects for particles of smaller mass

This simple result is at the heart of many ideas in nanoscience and technology!

- <u>infinitely many</u> eigenstates that are all <u>bound states</u>

(ii) <u>1D Harmonic Oscillator</u> (<u>most important problem in physics!</u>)

$$V(x) = \frac{1}{2}\underset{\substack{\uparrow\\ \text{"spring constant"}}}{k}x^2 = \frac{1}{2}m\underset{\substack{\uparrow\\ \omega = \text{angular frequency}}}{\omega^2}x^2 \quad \left[\omega^2 = \frac{k}{m}\right]$$



TISE
$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi + \frac{1}{2}m\omega^2x^2\psi = E\psi} \qquad (10)$$

- can be solved <u>exactly</u> [B.C.'s: $\psi \to 0$ as $|x| \to \infty$]
  [Series solution or operators method]
  (need mathematical skills & maturity!)

- $$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega = n\hbar\omega + \underbrace{\frac{1}{2}\hbar\omega}_{\text{zero-point/ ground state energy}}} \qquad (11)$$

$$n = \underset{\substack{\uparrow\\ \text{Note: starts from 0}}}{0}, 1, 2, \ldots$$

<u>Evenly spaced allowed energies</u>

- $\psi_n(x)$ are related to the special functions called the <u>Hermite polynomials</u>

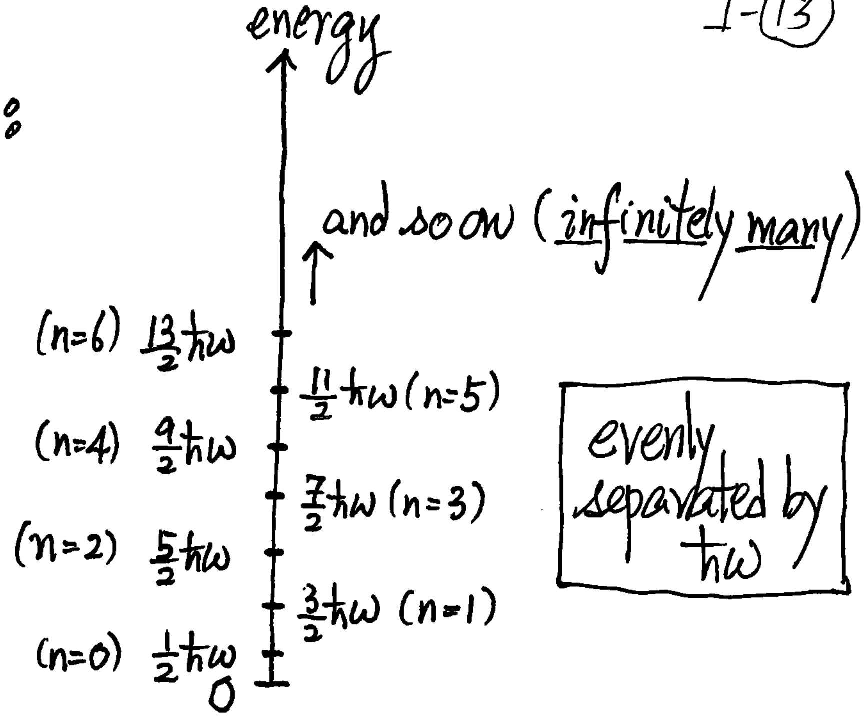
$$\psi_n(x) = \underbrace{\left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{1}{\sqrt{2^n n!}}}_{\text{normalization}}\ \underbrace{H_n\left(\sqrt{\frac{m\omega}{\hbar}}\,x\right)}_{\text{Hermite polynomial}}\ \underbrace{e^{-\frac{m\omega}{2\hbar}x^2}}_{\text{gaussian centered at } x=0}$$

	<u>About $x=0$</u>
$H_0(y) = 1$	even
$H_1(y) = 2y$	odd
$H_2(y) = 4y^2-2$	even
$H_3(y) = 16y^4 - 48y^2 + 12$	odd
$\vdots$	$\vdots$

Relevant to :

- Vibrational spectrum in molecular spectroscopy
- C(T) (heat capacity) of solids
- excitations of any binding
- What are photons? What are electrons? What are particles? (Quantum field theory)
- Bascially, everything that involves oscillations

Allowed energies:



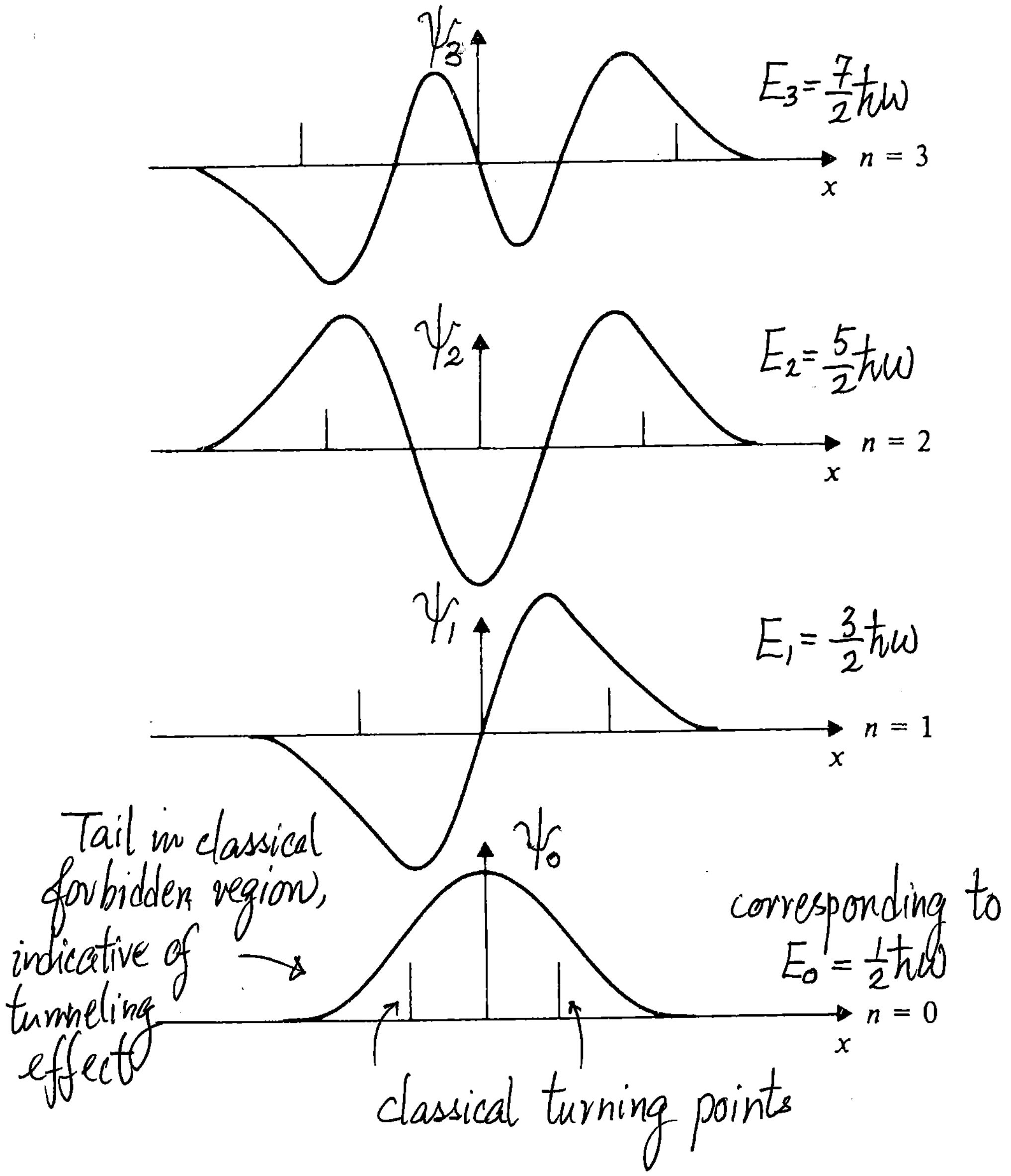
- n labels the eigenstates
- $n=0$ ground state with $\underbrace{E_0 = \frac{1}{2}\hbar\omega}$

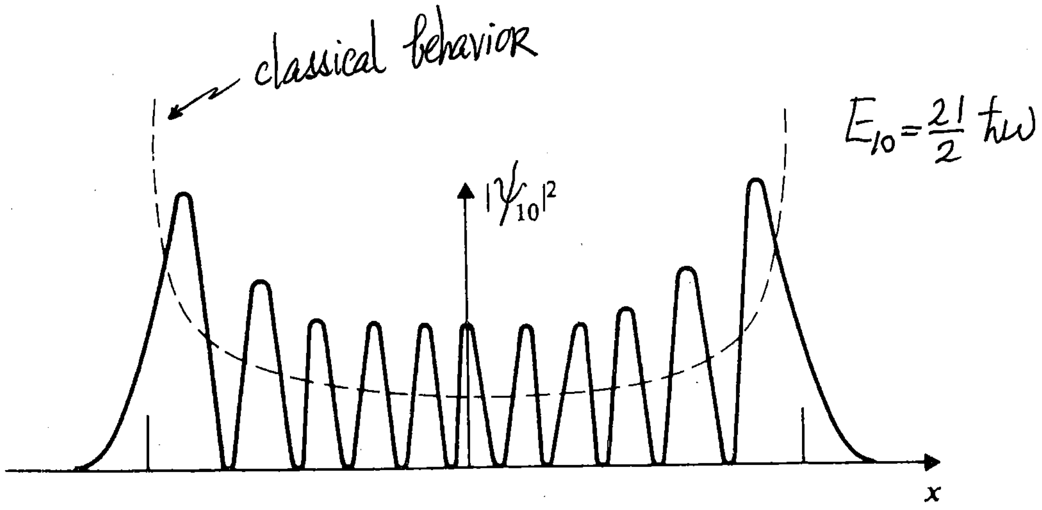
  "zero-point motion"
  [can't be at bottom of $V(x)$ due to uncertainty relation]
- $n = 1, 2, 3, \ldots$ label excited states
- n^{th} excited state with $E_n = (n+\frac{1}{2})\hbar\omega$

  can be regarded as having excited
  n units of the characteristic energy ($\hbar\omega$)
  over the ground state

  → an idea important to the modern view of what "particles" are!
- One can also introduce a^{+} and a to solve the problem

A few $\psi_n(x)$ for harmonic oscillator





[Taken from Rae, "Quantum Mechanics"]

(iii) 2D and 3D problems

- Select a convenient coordinate system (depending on $V(x,y)$ and $V(x,y,z)$)
- Try separating the variables

Hopefully, a problem in (x,y,z) becomes

$$\begin{cases} \text{a problem in } x & (\text{OR } r) \\ \text{a problem in } y & (\text{OR } \vartheta) \\ \text{a problem in } z & (\text{OR } \phi) \end{cases}$$

- Possible to have degenerate states

$$\text{different states} \begin{cases} \psi_i \longrightarrow E_i \\ \psi_j \longrightarrow E_j \end{cases} \text{but } E_i = E_j$$

(same eigen-energy)

  - Often due to symmetry of $V(\vec{r})$

    [eg. $V(\vec{r}) = V(r)$ gives $E_{n\ell}$ in general]

    $\overset{\uparrow}{n}$ principal quantum number; ("ℓ" in $Y_{\ell m}$)

  - Sometimes "accidental"

    [eg. $V(\vec{r}) = V(r) \propto \frac{-1}{r}$ gives $E_n = \frac{-13.6}{n^2}$ eV as in H-atom, even independent of ℓ]

Hydrogen atom

- In its simplest form[+], the hydrogen atom problem is

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r})\psi(\vec{r}) = E\psi(\vec{r}) \qquad \text{(TISE)}$$

with $\boxed{V(\vec{r}) = -\frac{e^2}{4\pi\varepsilon_0 r}}$ (12) where $r = |\vec{r}| = \sqrt{x^2+y^2+z^2}$

$\frac{1}{4\pi\varepsilon_0}$: SI units $\qquad$ $-e$ = electron charge

- $V(\vec{r})$ should be $V(r,\theta,\phi)$ in general
- But $V = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$ $\underbrace{\underline{\text{depends only on } r}}_{\text{"spherically symmetric" [central forces]}}$

$\Rightarrow$ use spherical coordinates (r,θ,ϕ)

- $\nabla^2\psi$ in spherical coordinates is:

$$\nabla^2\psi = \begin{cases} \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} \\ \frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} \end{cases} \qquad (13)$$

(either form will do)

[+] Meaning: Could be more complicated! E.g., simple correction using the reduced mass μ instead of m and complications due to spin-orbit coupling.

- Separation of Variables: $\psi(\vec{r}) = \psi(r,\theta,\phi) = \underbrace{R(r)}_{r\text{ only}}\ \underbrace{Y(\theta,\phi)}_{\text{angular part}}$
- $Y(\theta,\phi)$ satisfies

$$\boxed{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} = -\lambda Y} \qquad (14)$$

  - just another eigenvalue problem
  - Important: $\underbrace{\text{Eq.(14) does not carry } V(r)}$

$$\text{Meaning:}\left\{\begin{array}{l}\text{Same Eq.(14) for all } V(r) \\ \text{Solve it once and solutions} \\ \text{are good for all } V(r) \text{ problems}\end{array}\right.$$

$$\boxed{\begin{array}{l}\text{The solutions to Eq.(14) are called the} \\ \text{spherical harmonics } Y_{\ell,m}(\theta,\phi) \text{ or } Y_{\ell,m_\ell}(\theta,\phi). \\ \text{Boundary conditions are satisfied only when} \\ \boxed{\lambda = \ell(\ell+1)} \text{ and } \boxed{-\ell \le m_\ell \le +\ell}\end{array}} \quad (15)$$

- ℓ, m_ℓ become quantum numbers labeling hydrogen states. Boundary conditions lead to quantization.
- Eq.(14) is also useful in EM ($\because$ Laplace eq. of electric potential)

Summary: ϑ-ϕ equation

$$\boxed{\begin{gathered}\text{Solution:}\quad Y(\theta,\phi) \sim \underbrace{\Theta(\theta)}_{P_l^{m_l}(\cos\theta)} \cdot \underbrace{\Phi(\phi)}_{e^{im_l\phi}} \\ l = 0, 1, 2, \cdots \\ m_l = -l, \cdots, 0, \cdots, +l \quad [-l \leq m_l \leq l]\end{gathered}} \qquad (16)$$

Physically acceptable solution (B.C.)

$\Rightarrow$ λ in Eq.(14) must be $\boxed{\lambda = l(l+1)}$

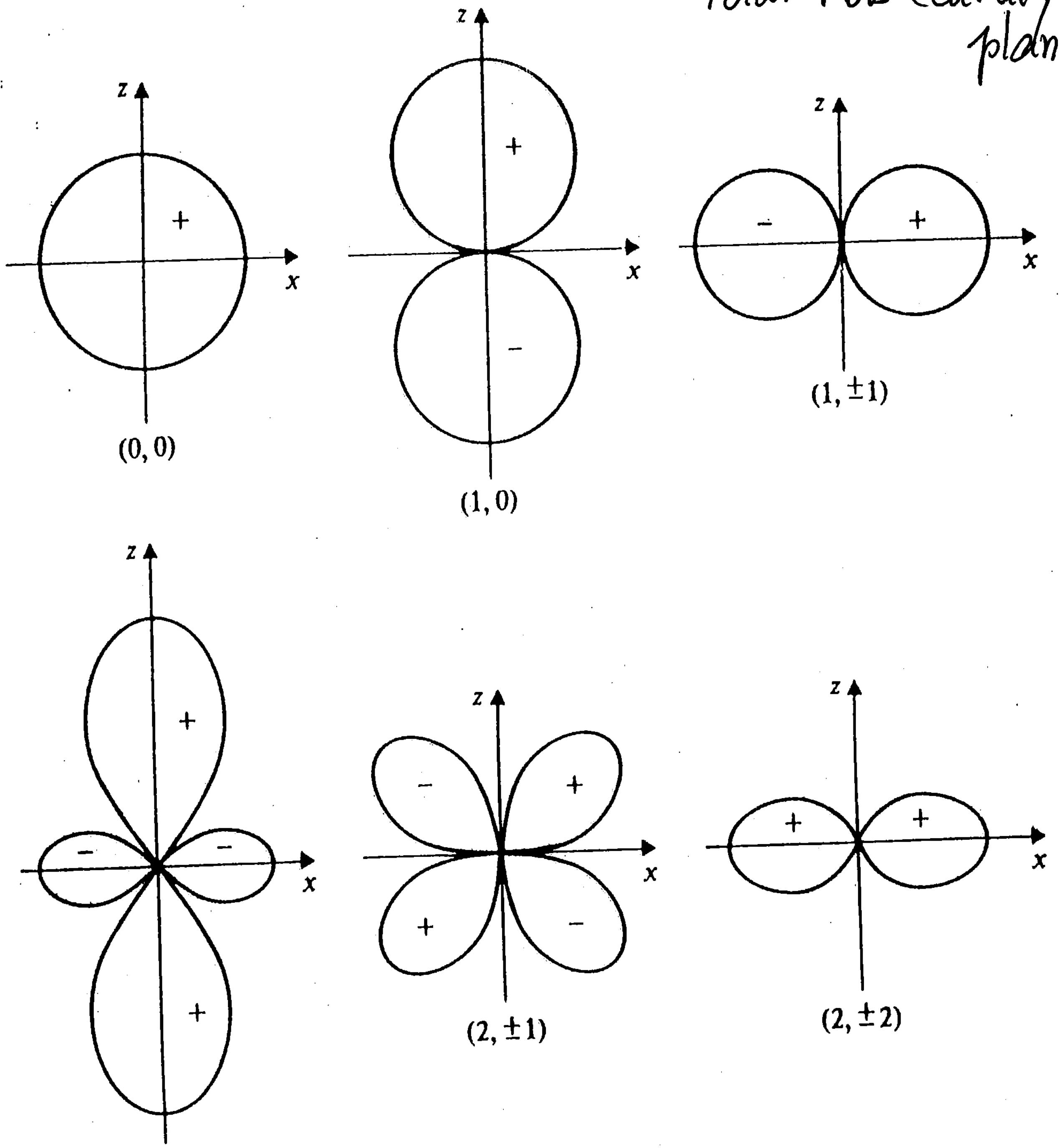
Following conventional notations, the solutions are written as:

$$\boxed{\begin{aligned} &Y_{l m_l}(\theta,\phi) = \text{Spherical Harmonics} \\ l=0:&\quad Y_{00} = \sqrt{\frac{1}{4\pi}} \\ l=1:&\quad Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta \;;\; Y_{1\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi} \\ l=2:&\quad Y_{20} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1) \\ &\quad Y_{2\pm1} = \mp\sqrt{\frac{15}{8\pi}}\cos\vartheta\,\sin\theta\, e^{\pm i\phi} \\ &\quad Y_{2\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta\, e^{\pm i2\phi} \\ &\vdots \end{aligned}} \qquad (17)$$

Good for all $V = V(r)$

The Spherical Harmonics $Y_{lm}(\theta,\phi)$

Polar Plots (Cut at y=0 plane)



(0,0) (1,0) (1,±1)

(2,0) (2,±1) (2,±2)

; Polar plots of the sections at $y = 0$ through the spherical harmonics with quantum numbers (l,m). The distance from the origin of a point on a curve is proportional to the magnitude of the function in that direction. The sign of the function in each region of space is also indicated.

x-z plane: $\phi = 0$ or π

- For $m_l = 0 \Rightarrow$ No ϕ-dependence in $Y_{lm_l}(\theta,\phi)$

$e^{im_l\phi} = 1$ $\Rightarrow$ Azimuthal symmetry

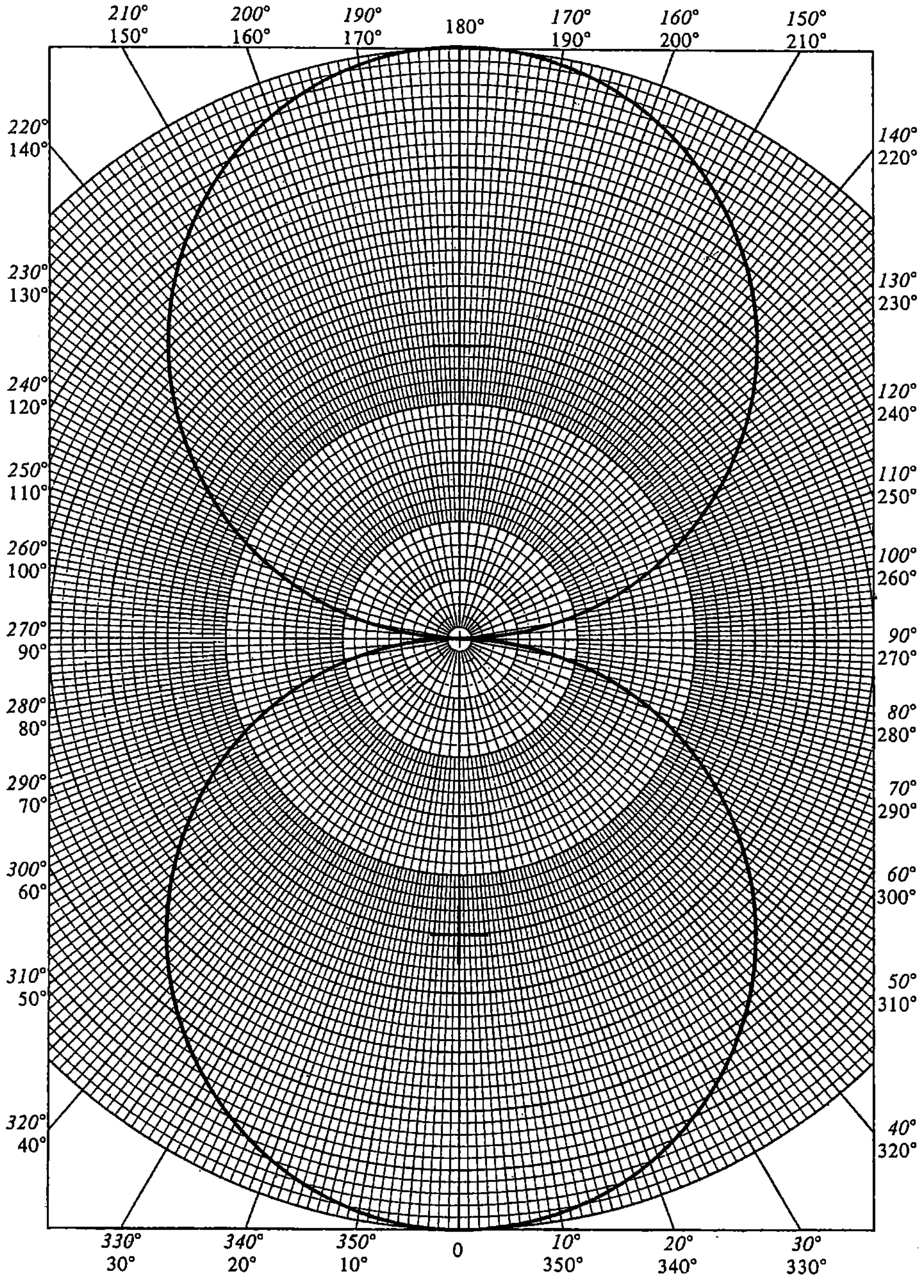
[whole picture: rotate about z-axis]

(true only for $m_l = 0$)

Aside: What are polar plots?

Example: $f(\theta) = \cos\theta$

- Want to plot $f(\theta)$ in a way that shows the angular dependence and the magnitude $|f(\theta)|$
  - a "polar plot graph paper"
  - given θ, find $f(\theta)$ and dot $|f(\theta)|$ from origin at θ
  - repeat for every θ



Of course, this can easily be done by computer or computer packages

A polar plot of $f(\theta) = \cos\theta$. To construct such a plot, mark off the distance $f(\theta)$ along the radial line labeled by the angle θ.

[Taken from D. McQuarrie, "Quantum Chemistry"]

$Y_{\ell m_\ell}(\theta,\phi)$ and "ℓ" and "m_ℓ" are important

Physical Meaning of ℓ

For a state with quantum number ℓ, the magnitude of the orbital angular momentum is $L = \sqrt{\ell(\ell+1)}\,\hbar$ (or $L^2 = \ell(\ell+1)\hbar^2$).

Since $\ell = 0, 1, 2, \cdots$, L is quantized.

- Operators for L^2 and L_z

Orbital angular momentum $\rightarrow$ $\vec{L} = \vec{r} \times \vec{p}$

$$\Rightarrow \begin{cases} \hat{L}_x = \frac{\hbar}{i}\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \\ \hat{L}_y = \frac{\hbar}{i}\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \\ \hat{L}_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \end{cases}$$

Transform to (r, θ, ϕ)

$$\hat{L}_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_y = i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$\boxed{\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}}$$ $\leftarrow$ particularly simple.

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

$$\hat{L}^2 = -\hbar^2 \underbrace{\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]}_{\text{Same as Eq.(14) LHS!}}$$

$$\therefore\ \hat{L}^2 Y_{l,m_l} = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y_{l,m_l}$$

$$= (-\hbar^2)\cdot(-l(l+1))\,Y_{lm_l}$$

$$\Rightarrow \boxed{\hat{L}^2 Y_{l,m_l} = \underbrace{l(l+1)\hbar^2}_{\text{eigenvalues of angular momentum squared}} Y_{lm_l}} \qquad (18)$$

$$\hat{L}_z Y_{l,m_l} = -i\hbar\frac{\partial}{\partial\phi}\underbrace{Y_{l,m_l}(\theta,\phi)}_{\sim e^{im_l\phi}}$$

$$\Rightarrow \boxed{\hat{L}_z Y_{l,m_l} = \underbrace{m_l\hbar}_{\text{eigenvalues of z-component of angular momentum}} Y_{lm_l}(\theta,\phi)} \qquad (19)$$

<u>Recall</u>: m_l takes on $\underbrace{-l, -l+1, \dots, 0, \dots, l-1, l}_{(2l+1)\text{ different values}}$

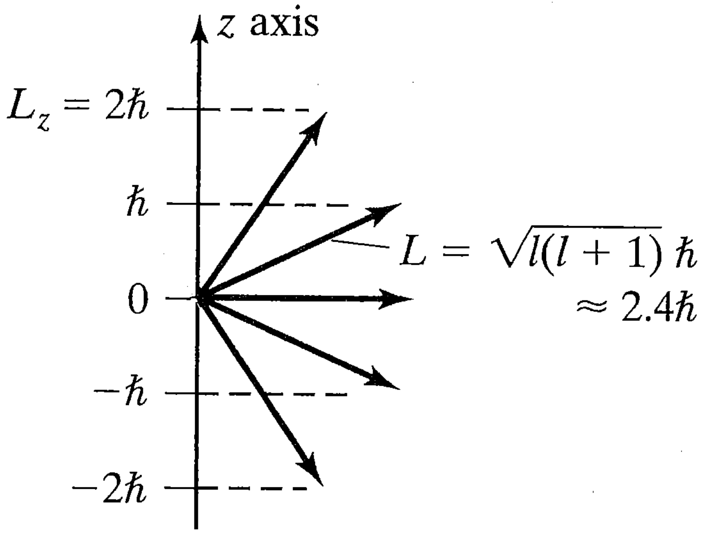
for a given l

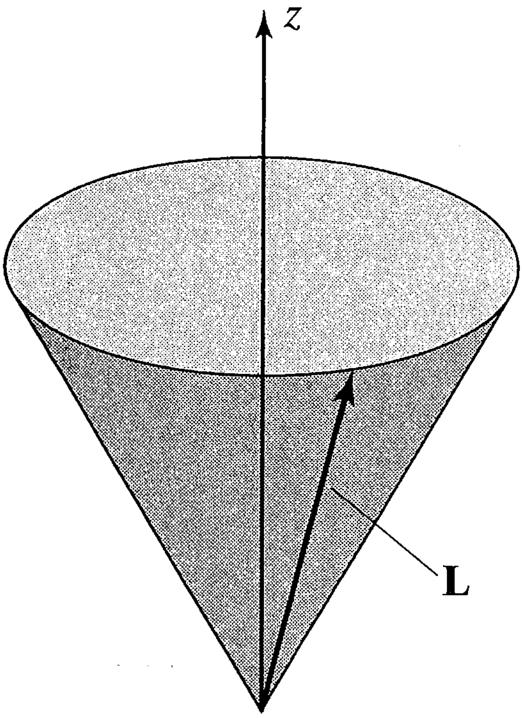
- Largest L_z is $l\hbar < \sqrt{l(l+1)}\,\hbar$
- Knowing L_z, cannot know L_x, L_y as $[\hat{L}_x, \hat{L}_z] \neq 0$
  $[\hat{L}_y, \hat{L}_z] \neq 0$

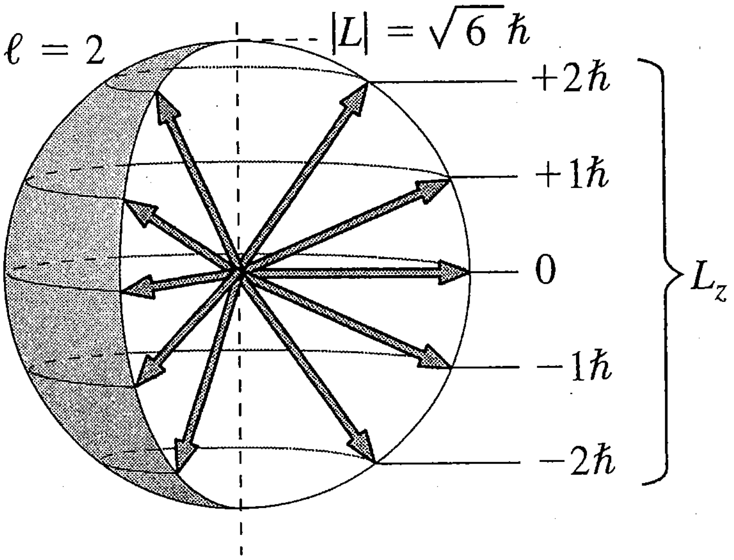
- Vector Model[†]: a model to think about $\hat{L}^2$ and $\hat{L}_z$ quantisation

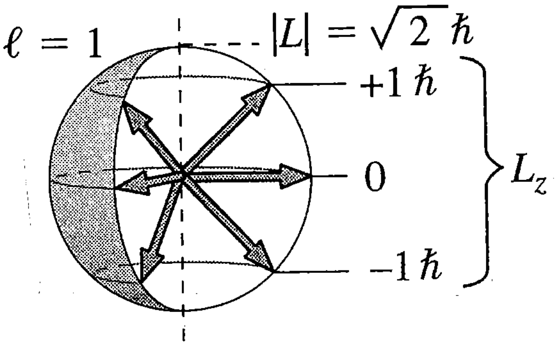
E.g. $l=2$, $L=\sqrt{2(3)}\,\hbar=\sqrt{6}\,\hbar\approx 2.4\hbar$

L_z can be $2\hbar, \hbar, 0, -\hbar, -2\hbar$









as L_x and L_y are not precisely known given that L_z is known

[Taken from Harris]

[†] Think of it as just a picture that summarizes QM results on orbital angular momentum. It is one of those very useful pictures/model. It can be used to interpret many results. However, one should not take it too far.

Radial Equation : Equation for $R(r)$

Recall: $\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$

The radial part $R(r)$ satisfies:

$$\boxed{\underbrace{-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r)}_{\text{k.e. (radial motion)}} + \underbrace{V(r)}_{V(r)\text{ comes in}}R(r) + \underbrace{\frac{l(l+1)\hbar^2}{2mr^2}R(r)}_{\text{k.e. (rotational motion)}} = E\,R(r) \qquad (20)}$$

c.f. $\frac{L^2}{2mr^2}$ term in central force problems in classical mechanics

- The equation for $R(r)$ for any given $V(r)$
- Just another eigenvalue equation (energy E)
- $\frac{l(l+1)\hbar^2}{2mr^2}R(r)$ term in Eq. (20) ⇒ plug in a value of l (e.g. $l=2$) gives an equation to solve

⇒ Many solutions labelled by "n"

⇒ Expect eigen-energies be labelled by E_{nl} (21)

n^{th} solution for the value of l

→ This is a general statement for any spherically symmetric $V(r)$

Recall: Given l, m_l takes on $\underbrace{-l, -l+1, \cdots, 0, \cdots, l-1, l}_{(2l+1) \text{ values}}$

But E_{nl} depends on n and l only

The solutions:
$$\psi(r,\theta,\phi) = R_{nl}(r) \cdot \left\{ \begin{array}{l} Y_{ll}(\theta,\phi) \\ Y_{l,l-1}(\theta,\phi) \\ \vdots \\ Y_{l,0}(\theta,\phi) \\ \vdots \\ Y_{l,-l+1}(\theta,\phi) \\ Y_{l,-l}(\theta,\phi) \end{array} \right.$$

all have the same energy E_{nl}

$$\boxed{\begin{array}{l} \therefore E_{nl} \text{ is } (2l+1)\text{-degenerated or} \\ \text{has a degeneracy of } (2l+1). \end{array}} \qquad (22)$$

This is due to the $\underbrace{\text{symmetry of } V(r)}_{\text{spherically symmetric (球性對稱)}}$

Key Points:

- $\underline{\text{Arbitrary}}$ $V(r)$ [spherically symmetric]
  - Energy eigenstates: $\psi_{nlm_l}(r,\theta,\phi) = R_{nl}(r)\, Y_{lm_l}(\theta,\phi)$ with energy E_{nl}
  - That is to say, for eigen-energy E_{nl}, there are $(2l+1)$ different $\psi_{nlm_l}(r,\theta,\phi)$ corresponding to $m_l = -l, \cdots, 0, \cdots, +l$. Thus, E_{nl} has a degeneracy of $(2l+1)$.

<u>Hydrogen atom</u> : $V(r) = \frac{-e^2}{4\pi\varepsilon_0} \cdot \frac{1}{r}$ (Coulombic)

- A <u>very special form</u> of $V(r) \sim -\frac{1}{r}$
- Solving Eq.(20) with $V(r) = \frac{-e^2}{4\pi\varepsilon_0}\frac{1}{r}$ gives $R_{nl}(r)$ as <u>associated Laguerre functions</u> (just another class of special functions) and the corresponding eigen-energies as:

$$\boxed{\begin{array}{c} E_n = \frac{-me^4}{32\pi^2\varepsilon_0^2\hbar^2} \cdot \frac{1}{n^2} \\ \text{where } n = 1, 2, 3, \ldots \\ \underline{\text{AND}} \quad n \geq l+1 \end{array}} \qquad (23)$$

- The pre-factor comes out to be ≈ −13.6 eV
- Eq.(23) is in good agreement with experimental data in the early 20th century! More accurate spectroscopic data later revealed more <u>fine</u> details, leading to further understanding of the physics inside an atom, e.g. how $\vec{L}$ and spin $\vec{S}$ interact.

- Eq. (23) gives E_n (depends on n only) but <u>not</u> the general form $E_{n,\ell}$

$\Rightarrow$ $E_n \approx -\frac{13.6}{n^2}$ eV energies have <u>higher degeneracy</u> than expected of $V(r)$

["<u>accidental</u>" due to the $-\frac{1}{r}$ form]

$$\text{degeneracy} = \underbrace{\sum_{\ell=0}^{n-1}}\underbrace{(2\ell+1)}_{\text{due to } (2\ell+1) \text{ different } m_\ell \text{ values}} = n^2 \quad (\text{ignored spin so far})$$

↑ values of ℓ for given n in E_n (as $n \geq \ell+1$)

↑ "<u>accidental</u>"

Degeneracy increasing with n (spin not included)

n	1	2				3								
ℓ	1s 0	2s 0	1 2p			3s 0	1 3p			2 3d				
m_ℓ	0	0	−1	0	+1	0	−1	0	+1	−2	−1	0	+1	+2
Degeneracy: Number of states	1	4				9								

With <u>spin</u> 2 8 18

start to look like the periodic table!

[Close, but <u>multi-electron atoms</u> require more physical consideration!]

A few hydrogen atom energy eigenstates:

$$\psi_{100} = \left(\frac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$$

"1s state"

$(n, l, m_l) = (1, 0, 0)$

$$a_0^{\dagger} \equiv \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2} = 0.529177 \times 10^{-10}\,\mathrm{m} \approx 0.53 \times \underbrace{10^{-10}\,\mathrm{m}}_{\text{Å}}$$

Bohr radius

$$\psi_{200} = \left(\frac{1}{8\pi a_0^3}\right)^{1/2} \left(1 - \frac{r}{2a_0}\right) e^{-\frac{r}{2a_0}}$$

"2s"

$$\psi_{210} = \left(\frac{1}{32\pi a_0^3}\right)^{1/2} \left(\frac{r}{a_0}\right) \cos\theta \; e^{-\frac{r}{2a_0}}$$

"$2p_z$"

$$\left.\begin{aligned} \psi_{211} &= -\left(\frac{1}{\pi a_0^3}\right)^{1/2} \left(\frac{r}{8a_0}\right) \sin\theta \; e^{i\phi} \; e^{-\frac{r}{2a_0}} \\ \psi_{21-1} &= \left(\frac{1}{\pi a_0^3}\right)^{1/2} \left(\frac{r}{8a_0}\right) \sin\theta \; e^{-i\phi} \; e^{-\frac{r}{2a_0}} \end{aligned}\right\}$$

linearly combine to give $2p_y$ and $2p_x$

$\vdots$

These solutions are needed in perturbative calculations.

[†] The Bohr radius a_0 is also written as a_B.

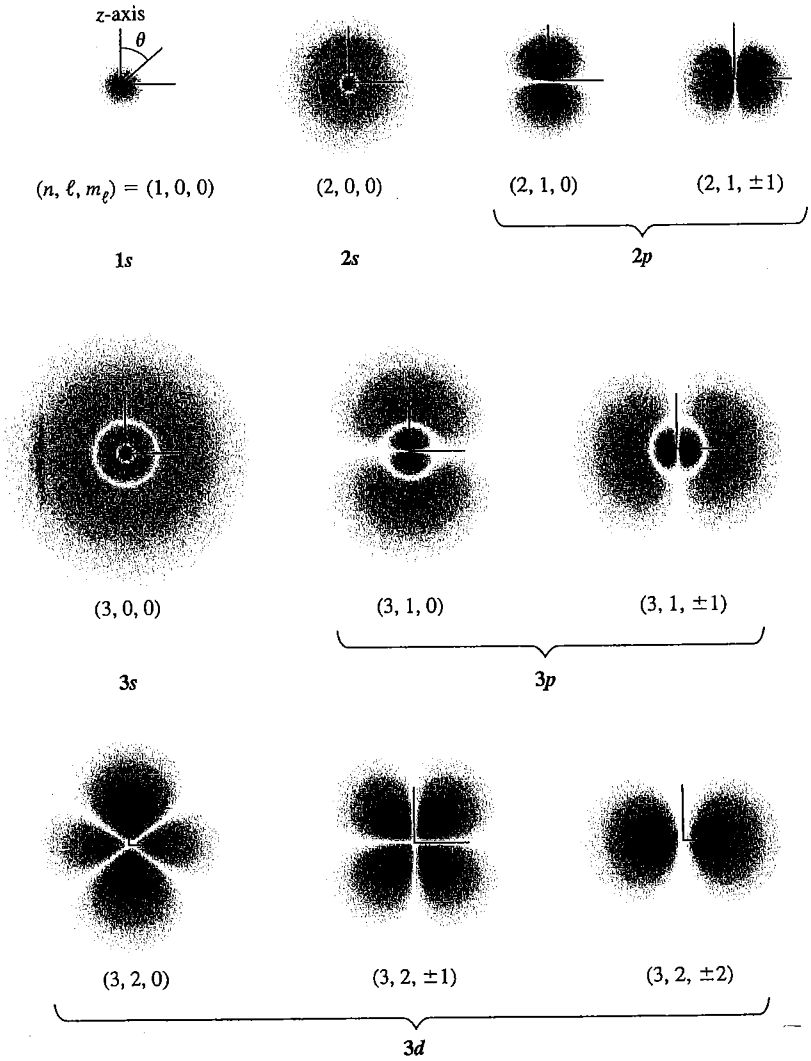
- Born's interpretation of $|\psi(r,\theta,\phi)|^2$

$$|\psi(r,\theta,\phi)|^2 \underbrace{d^3r}_{\substack{\text{volume}\\ \text{element at}\\ (r,\theta,\phi)}} = \underbrace{R^2(r)\,|Y_{\ell,m_\ell}(\theta,\phi)|^2}_{|\psi(r,\theta,\phi)|^2}\ \underbrace{r^2\sin\theta\,dr\,d\theta\,d\phi}_{\substack{\text{volume}\\ \text{element } d^3r}}$$

$$= R^2(r)\,\Theta^2(\theta)\cdot\overbrace{r^2\sin\theta\,dr\,d\theta\,d\phi}$$

(∵ $Y_{\ell m_\ell} \sim e^{im_\ell\phi}$, $|Y_{\ell,m_\ell}|^2$ does <u>not</u> depend on ϕ)

$$\overbrace{\qquad R^2(r)\,\Theta^2(\theta)\qquad}$$



- given (r,θ)

Evaluate $\underbrace{R^2(r)\,\Theta^2(\theta)}$

bigger value: Darker dot

smaller value: Lighter dot

- ψ_{210} certainly looks like $2p_z$
- But where are p_x and p_y?

Consider $n=2$, $\underbrace{\ell=1}_{p}$, $m_\ell=+1,-1$

$$\left.\begin{aligned} \psi_{211} &\sim \frac{r}{a_B}\sin\theta\, e^{+i\phi}\, e^{-\frac{r}{2a_B}} \\ \psi_{21-1} &\sim \frac{r}{a_B}\sin\theta\, e^{-i\phi}\, e^{-\frac{r}{2a_B}} \end{aligned}\right\} \text{apart from a constant}$$

- Form two linear combinations:

$$\left.\begin{aligned} \psi_{2p_x} &\sim \psi_{211}+\psi_{21-1} \\ \psi_{2p_y} &\sim \frac{1}{i}\left(\psi_{211}-\psi_{21-1}\right) \end{aligned}\right\} \underline{\text{Key Point!}}$$

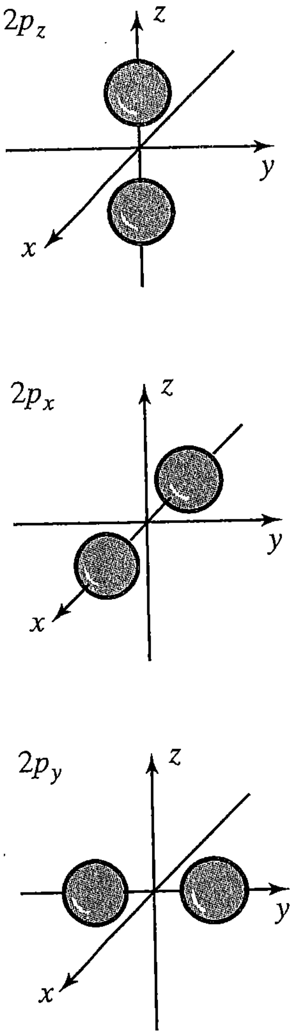
- $$\psi_{2p_x} \sim r\sin\theta\,\underbrace{\cos\phi}_{\frac{1}{2}(e^{i\phi}+e^{-i\phi})}\, e^{-\frac{r}{2a_B}} \sim x\,e^{-r/2a_B}$$

$$\psi_{2p_y} \sim r\sin\theta\,\sin\phi\, e^{-\frac{r}{2a_B}} \sim y\,e^{-r/2a_B}$$

Recall: $$\psi_{210} \sim r\cos\theta\, e^{-\frac{r}{2a_B}} \sim \underbrace{z\,e^{-r/2a_B}}_{\text{same form}} \sim \psi_{2p_z}$$

Contour plot of 75% of the highest value of $R^2(r)\,\Theta^2(\theta)$

ψ_{2p_z} is ψ_{210}



Perspective views of the 75% contours of $|\psi|^2$ for the $2p_z$, $2p_x$, and $2p_y$ wave functions.

ψ_{2p_x} and ψ_{2p_y} are linear combinations of ψ_{211} and ψ_{21-1}

Think like a physicist

- Why should an atom care about which directions being the x-direction, y-direction, z-direction?

- $\underbrace{\text{Schrödinger (1926)}}$ vs $\underbrace{\text{Bohr (1913)}}$

Schrödinger (1926):

- fundamental principle is a new equation (TISE) for matter wave + boundary conditions from physical consideration
- E_n and $R_{n\ell}(r) \cdot Y_{\ell m_\ell}(\theta, \phi)$

Bohr (1913):

- imposed ad hoc rule that $L = n\hbar$
- Classical mechanics plus ad hoc rule gives E_n
- orbits of radii $n^2 \underset{\uparrow}{a_B}$

Bohr radius

- In Schrödinger's first QM paper[†] in 1926, he wrote (translated into English)

> In this paper I wish to consider, first, the simple case of the hydrogen atom (non-relativistic and unperturbed), and show that, the customary conditions [Bohr postulates] can be replaced by another postulate, in which the notion of "whole numbers", merely as such, is not introduced. Rather when integralness does appear, it arises in the same natural way as it does in the case of the node-numbers of a vibrating string.

"Bohr postulates" ⇒ $L = \underbrace{n\hbar}$

which is <u>not</u> right as $L = \underbrace{\sqrt{\ell(\ell+1)}}_{\text{not an integer!}}\hbar$

L is quantized

[but Bohr is good at getting the $\underbrace{\text{key idea}}$]

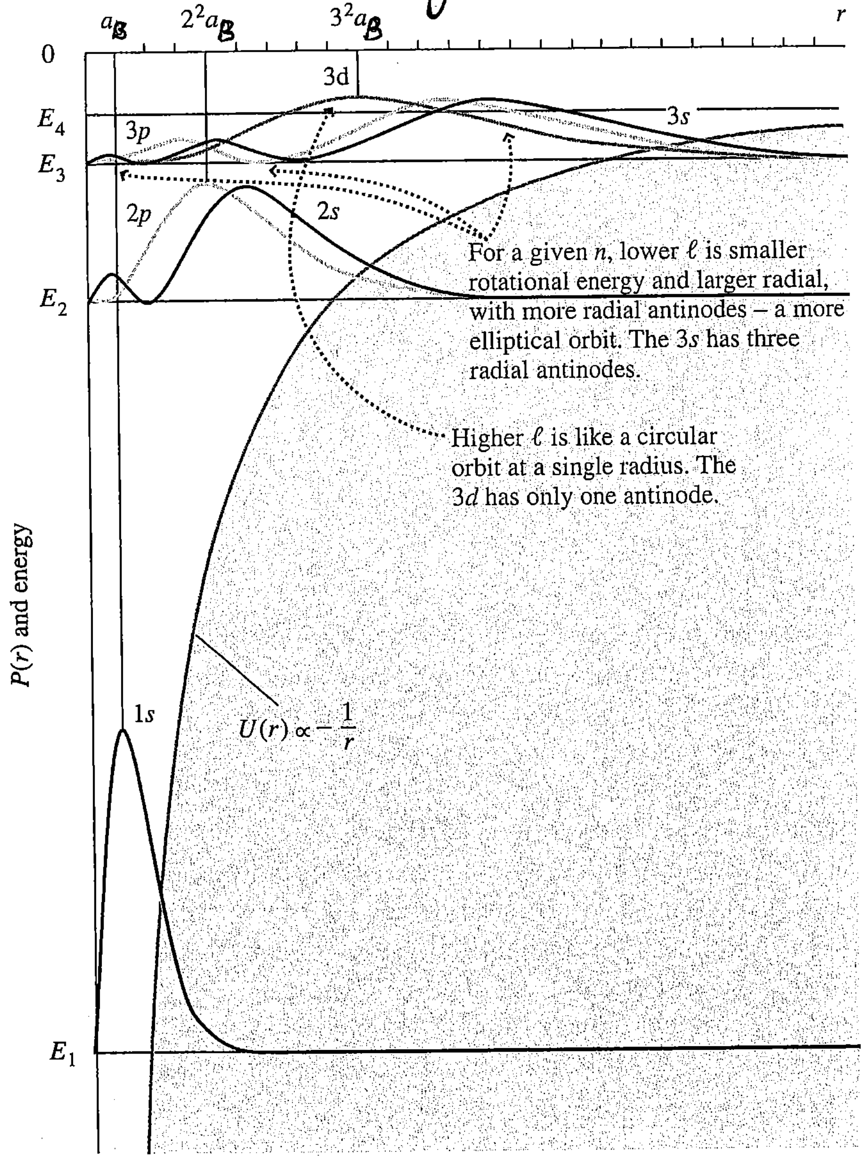
[†] Schrödinger published 5 papers in 1926, what a year!

Radial Probability

$$P(r) = R^2(r)\cdot r^2$$

Meaning: $P(r)dr = r^2R^2(r)dr$ = Prob. of finding particle between r and $r+dr$ from the origin, regardless of angles

Plots of P(r)



For a given n, lower ℓ is smaller rotational energy and larger radial, with more radial antinodes – a more elliptical orbit. The 3s has three radial antinodes.

Higher ℓ is like a circular orbit at a single radius. The 3d has only one antinode.

- Show structure of shells
- But shells are not sharp
- P(r) of 1s peaks at a_B
- P(r) of 2p (but not 2s) peaks at $4a_B$
- P(r) of 3d (but not 3s and 3p) peaks at $9a_B$

- Get a sense of P(r). It is important for understanding why atoms come together to form chemical bonds and molecules (and even solids).

Summary

- 1D, 2D, 3D infinite wells, harmonic oscillator, rotor, V(r) problems, hydrogen atom are the essential QM for us to move on.
- At the basic level, you should know the key features of the allowed energies and the eigenfunctions. They provide the basis to "think about"...
  - fine details in atomic spectrum
  - why chemical bonds are formed
  - directional character of bonding in e.g. benzene, diamond, graphene, ...
  - typical energies in atomic, molecular, and nuclear physics
  - nuclear structure
  - How big is a proton
  - nuclear decay

⋮

- Solutions to these <u>solvable problems</u> also form the basis of perturbation (approximation) calculations

- You are encouraged to review how the solutions are obtained mathematically (see QMI), although having a sense of the solutions is the first priority.