Quantum Mechanics in Three dimensions

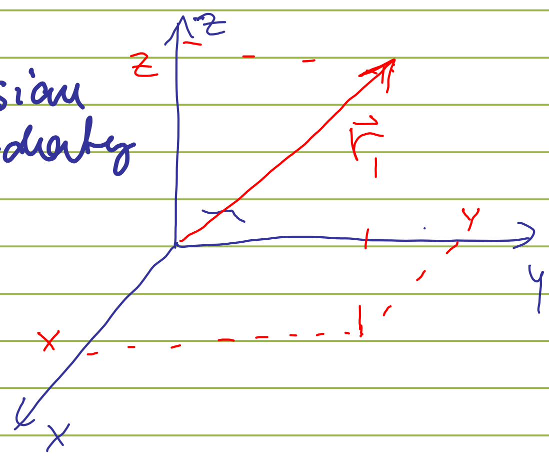
So far, we dealt with quantum systems we could approximate as one dimensional.

A general problem:

quantum particle in 3d potential

$$V = V(x, y, z) = V(\vec{r})$$

Cartesian coordinates



$$\vec{r} = (x, y, z)$$

Classically:

$$H = \frac{p^2}{2m} + V(\vec{r})$$

$$p^2 = p_x^2 + p_y^2 + p_z^2 = \vec{p}\cdot\vec{p}$$

where $\vec{p} = (p_x, p_y, p_z)$

Quantum particle:

A physical state

$$\psi(x,y,z,t) = \psi(\vec{r},t)$$

is a solution to Schroedinger equation

$$i\hbar\frac{\partial}{\partial t}\psi = \hat{H}\psi$$

where

$$\hat{H} = \frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} + V(\hat{x},\hat{y},\hat{z})$$

and $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$, $\hat{p}_y = -i\hbar\frac{\partial}{\partial y}$, $\hat{p}_z = -i\hbar\frac{\partial}{\partial z}$

Combine

$$\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) = \vec{\nabla}$$

Then

$$\hat{\vec{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z) = -i\hbar \vec{\nabla}$$

and $\hat{\vec{p}}$ operator is a 3d vector

$$\hat{p}^2 \equiv \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2 = -\hbar^2 \nabla^2$$

$\hat{p}^2$ is a 3d scalar.

where

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

is the Laplacian, in Cartesian coordinates.

3d Schroedinger Eqn

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

Want normalizable states

$$\int d^3\vec{r}\, |\Psi(\vec{r},t)|^2 = 1$$

Solution with definite energy

E :

$$\Psi(\vec{r},t) = \psi_E(\vec{r})\, e^{-iEt/\hbar}$$

since

$$i\hbar\frac{\partial}{\partial t}\Psi(\vec{r},t) = E\,\Psi(\vec{r},t)$$

$\Psi(\vec{r},t)$ solves

$$i\hbar \frac{\partial}{\partial t} \Psi = \hat{H} \Psi$$

provided ψ_E solves

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

or

Time-indep. S.E.

$$\boxed{-\frac{\hbar^2}{2m} \nabla^2 \psi_E(\vec{r}) + V(\vec{r}) \psi_E(\vec{r}) = E \psi_E(\vec{r})}$$

General state

$$\psi(\vec{r}, t) = \sum_{\text{allowed } E} c_E \, \psi_E(\vec{r}) \, e^{-iEt/\hbar}$$

Ex 1

3d Harmonic oscillator:

$$V_{osc}(\vec{r}) = \frac{1}{2}\left(k_x x^2 + k_y y^2 + k_z z^2\right)$$

this is an approximation to an arbitrary 3d potential near a minimum where

$$\vec{\nabla} V = 0 \Rightarrow \frac{\partial}{\partial x} V = 0 = \frac{\partial}{\partial y} V = \frac{\partial}{\partial z} V$$

The second derivative matrix

$$\frac{\partial}{\partial r_i}\frac{\partial}{\partial r_j} V$$

is symmetric, and can always be diagonalized. Above, x, y, z are coordinates in corresponding coordinates.

$$\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z$$

$$\hat{H}_i = \frac{\hat{p}_i^2}{2m} + \frac{1}{2} k_i \hat{r}_i^2$$

where $i = x, y, z$ and

$r_x = x$, $r_y = y$, $r_z = z$.

Note

$$[\hat{r}_i, \hat{p}_j] = i\hbar \delta_{ij}$$

$$\hat{r}_i = (r_x, r_y, r_z)$$

$$\hat{p}_j = (p_x, p_y, \hat{p}_z)$$

Try

$$\psi(x, y, z) = \psi_{n_x}(x)\, \psi_{n_y}(y)\, \psi_{n_z}(z)$$

Eigenstate of H_x

Eigenfunction of H_i.

$$H_i \psi_{n_i} = \underbrace{\left(n_i + \tfrac{1}{2}\right)\omega_i \hbar}_{E_i} \psi_{n_i}$$

where $\omega_i = \sqrt{k_i/m}$

$\psi_{n_i} \equiv \psi_{n_i}(r_i) = n_i$'th eigenfunction.

Then

$$\psi_E(\vec{r}) = \psi_{n_x}(x)\, \psi_{n_y}(y)\, \psi_{n_z}(z)$$

is Eigenfn of

$$\hat{H} = \hat{H}_x + \hat{H}_y + \hat{H}_z$$

acts only on

w/ energy

$$E = E_x + E_y + E_z$$

$$= \hbar\omega_x\left(n_x + \tfrac{1}{2}\right) + \hbar\omega_y\left(n_y + \tfrac{1}{2}\right) + \hbar\omega_z\left(n_z + \tfrac{1}{2}\right)$$

Note:

- For:

$\omega_x \neq \omega_y \neq \omega_z$

no symmetry & no degeneracy

- For $\omega_x = \omega_y \neq \omega_z$:

Axial symmetry (rot. about z-axis)

Degeneracy: states

ψ_{n_x, n_y, n_z} , $\psi_{n_x' n_y' n_z'}$

Have same energy if

$n_x + n_y = n_x' + n_y'$

$n_z = n_z'$

- For $\omega_x = \omega_y = \omega_z$:

Spherical symmetry.

Same energy if

$n_x + n_y + n_z = n_x' + n_y' + n_z'$.

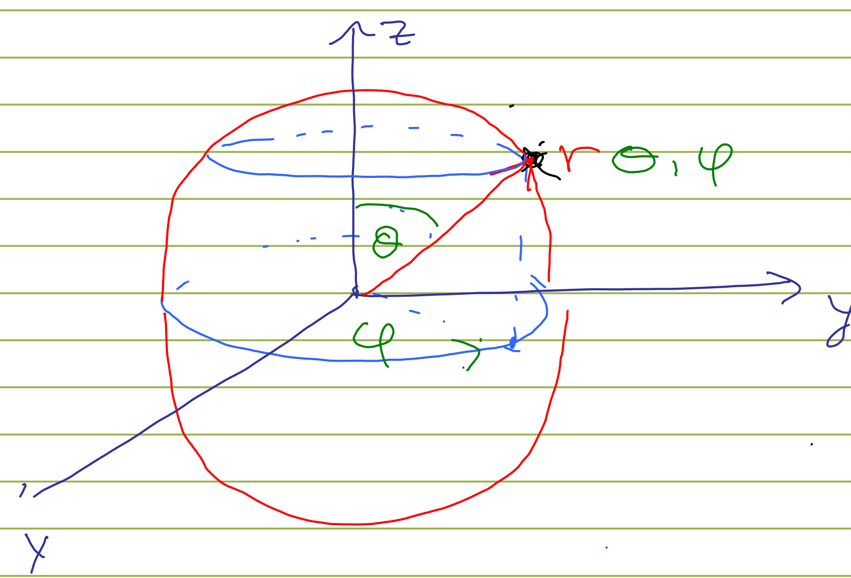
Spherically symmetric potential

$$V(\vec{r}) = V(r)$$

where $r = \sqrt{x^2+y^2+z^2}$

depends only on distance from origin. Useful to use coordinates that make use of spherical symmetry!

Change to "spherical coordinates"



r - radius

θ - polar angle

φ - azymuthal angle

$$r = \sqrt{x^2+y^2+z^2}$$

$$\theta = \cos^{-1}\left(\frac{z}{\sqrt{x^2+y^2+z^2}}\right)$$

$$\phi = \tan^{-1}(y/x)$$

Change to polar coordinates in SE

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

In these coordinates

$$\nabla^2\psi$$

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{(\partial\varphi)^2} \right] \quad (*)$$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial\varphi} \quad (**)$$

are angular momentum operators

where:

$\vec{L} = \vec{r} \times \vec{p}$ ← classical angular momentum

$= (L_x, L_y, L_z)$

and

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

equals

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

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

$$\left.+\frac{1}{\sin\theta^2}\frac{\partial^2}{\partial\varphi^2}\psi\right]$$

Since $\hat{p}^2\psi = -\hbar^2\nabla^2\psi$

this says

$(\text{radial momentum})^2$

$$\hat{p}^2\psi = -\frac{\hbar^2}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\psi\right)$$

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

$$\left.+\frac{-\hbar^2}{\sin\theta^2}\frac{\partial^2}{\partial\varphi^2}\psi\right]$$

angular momentum

Separation of variables:

Suppose

$$\psi(r,\theta,\varphi) = R(r)\, Y(\theta,\varphi)$$

Then T.I.S.E:

$$Y\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\left(\frac{\partial}{\partial r}R(r)\right) + V(r)R(r) - E R(r)\right]$$

$$= \frac{R}{r^2}\left[-\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}Y\right) - \frac{\hbar^2}{\sin\theta^2}\frac{\partial^2}{\partial\varphi^2}Y\right]$$

OR:

$$\frac{r^2}{R}\left[-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}R\right) + VR - ER\right]$$

$$= \frac{1}{Y}\left[-\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}Y\right) - \frac{\hbar^2}{\sin\theta^2}\frac{\partial^2}{\partial\varphi^2}Y\right]$$

* For $\psi(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi)$

to solve eqn, need

$$-\frac{\hbar^2}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}Y\right) - \frac{\hbar^2}{\sin\theta^2}\frac{\partial^2}{\partial\varphi^2}Y = \Lambda Y$$

For some constant Λ.

Ie

$$\hat{L}^2 Y = \Lambda Y$$

$Y = Y(\theta,\varphi)$ has to be eigfn

of angular momentum squared operator.

Later: Spectrum of $\hat{L}^2$ is discrete. Allowed values of Λ are

$$\Lambda = \hbar^2 \ell(\ell+1)$$

where

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

and degenerate

$$Y_{\ell, m}$$

$$m = \underbrace{-\ell, -\ell+1, \ldots, -1, 0, 1, \ldots, \ell}_{2\ell+1}$$

all have same L^2 eigenvalue. They are distinguished by

$$\hat{L}_z Y_{\ell m} = \hbar m Y_{\ell m}$$

where

$$\hat{L}_z Y_{\ell m} = -i\hbar \frac{\partial}{\partial \varphi} Y_{\ell m},$$

Then, $R(r)$ solves

$$-\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{d}{dr}\left(r^2 \frac{d}{dr} R\right)$$

$$+\left[\frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} + V(r)\right] R$$

$$= E R(r)$$

Angular equation

$$-\hbar^2 \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial\theta} Y\right)$$

$$-\frac{\hbar^2}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} Y = \Lambda Y$$

Try separation of variables

$$Y(\theta,\varphi) = \Theta(\theta)\,\Phi(\phi)$$

$\Rightarrow$ $\Phi(\phi)$ must solve

$$-\hbar^2 \frac{\partial^2}{\partial\phi^2}\Phi/\Phi = \text{const}$$

or Φ is eigenfunction of

$$\hat{L}_z^2 = -\hbar^2 \frac{\partial^2}{\partial\phi^2}.$$

Solution $\Phi = e^{im\phi}$.

where $\hat{L}_z^2 \Phi = + m^2 \hbar^2 \Phi$

Then $\Theta(\theta)$ solves

$$-\hbar^2 \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} \Theta$$

$$+ \frac{m^2 \hbar^2}{\sin^2\theta} \Theta = \Lambda \Theta$$

Let $x = \cos\theta$. Then

$$\frac{\partial}{\partial x} = \frac{\partial\theta}{\partial x} \frac{\partial}{\partial\theta} = \frac{1}{\sin\theta} \frac{\partial}{\partial\theta}$$

So, in terms of x:

$$-\hbar^2 \frac{\partial}{\partial x} \cdot \left[(1-x^2) \frac{\partial}{\partial x} \Theta(x) \right]$$

$$+ \frac{m^2 \hbar^2}{1-x^2} \Theta = \Lambda \Theta$$

$\Rightarrow \quad \Lambda = \hbar^2 \ell(\ell+1) \quad , \quad \ell = 0, 1, 2, \ldots$

where

$$\Theta(\theta) = A\, P_\ell^m(\cos\theta)$$

where

$$P_\ell^m(x) \equiv (1-x^2)^{\frac{|m|}{2}} \left(\frac{d}{dx}\right)^{|m|} P_\ell(x)$$

$$P_\ell(x) = \frac{1}{2^\ell \ell!} \left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell$$

$P_\ell(x)$ = Legendre polynomial

Note:

$P_\ell^m = 0$ unless $|m| \leq \ell$

or $m = -\ell, \ldots, -1, 0, 1, \ldots, \ell$

$$P_0(x) = 1$$

$$P_1(x) = x$$

$$P_2(x) = \frac{1}{2}(3x^2 - 1)$$

$P_\ell^m(x)$ depends only on m^2.

$$P_\ell^0(x) = P_\ell(x)$$

$$P_\ell^{\pm 1}(x) = (1-x^2)^{1/2} \frac{d}{dx} P_\ell(x)$$

$$Y_{\ell,m}(\theta) = \underset{\substack{\uparrow \\ \text{normalization}}}{A_{\ell m}} P_\ell^m(\theta)\, e^{im\phi}$$

The Radial Eqn

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}R\right) + \left[V(r) + \frac{\hbar^2}{2mr^2}\ell(\ell+1)\right]R = ER$$

$$V_{eff}(r) = V(r) + \underbrace{\frac{\hbar^2}{2mr^2}\, l(l+1)}_{\text{centrifugal Term}}$$

$l \neq 0 \Rightarrow$ repels particle from $r=0$

Simplifies if:

$$R(r) \equiv \frac{u(r)}{r}$$

Then

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{d}{dr} R\right) = \frac{1}{r^2}\frac{d}{dr}\left(r \frac{d}{dr} u - u\right)$$

$$= \frac{1}{r^2} \cdot r \frac{d^2}{dr^2} u = \frac{1}{r}\frac{d^2}{dr^2} u$$

$\Rightarrow u$ solves

$$\frac{1}{r} \times \left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} u + V_{eff}(r)\, u = E u \right]$$

Soln to T.I.S.E

For fixed E, l, m

$$\psi_{E,l,m}(\vec{r}) = \frac{u_{E,l}(r)}{r} Y_{l,m}(\theta,\varphi)$$

Normalization

$$\int d^3\vec{r} \, |\psi_{E,l,m}(\vec{r})|^2 = 1$$

$$\int d^3\vec{r} = \int r^2 \sin\theta \, dr \, d\theta \, d\varphi$$

Ex 3d Harmonic oscillator w/

$$\omega_x = \omega_y = \omega_z = \omega$$

in spherical coordinates:

$$V = \frac{1}{2} m \omega^2 (x^2 + y^2 + z^2) = \frac{1}{2} m \omega^2 r^2$$

$$V_{eff} = \frac{1}{2} m \omega^2 r^2 + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}$$

For $l=0$ $\Rightarrow$ $u(r)$ happens to solve 1D Harmonic oscillator eqn

$$-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} u + \frac{1}{2} m \omega^2 r^2 u = E u$$

$l=0$ spectrum

$$E = \hbar \omega \left(n + \frac{1}{2}\right)$$

$$u_n(r) = A_n\left(\hbar\frac{d}{dr} + \omega m r\right)^n u_0(r)$$

$$u_0(r) = A\, e^{-\frac{m\omega}{2\hbar} r^2}$$

$$r^2 = x^2 + y^2 + z^2$$

$$R_n(r) = \frac{u_n(r)}{r}$$

Allowed values $n = \cancel{0}, 1, 2, 3, \ldots$

since $\lim_{r \to 0}$ of $R_n(r)$ does not exist

Comparing w/

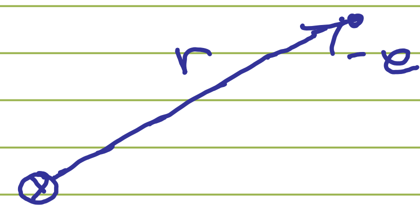
$$E = \hbar\omega\left(n_x + n_y + n_z + \frac{3}{2}\right)$$

$$\Rightarrow \quad n = n_x + n_y + n_z + 1$$

(Note: $\ell = 0$ is a unique state among a space of states w/ same energy and different (n_x, n_y, n_z))

4.2 The Hydrogen Atom

Hydrogen :



Heavy Nucleus $\qquad m_p \gg m_e$

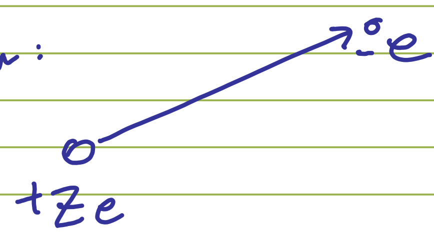
essentially motionless

$$m \approx m_e \qquad \left(m = \frac{m_p m_e}{m_e + m_p} \right)$$

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0} \times \frac{1}{r}$$

Get for free :

1 electron Ion :



Z = # of protons

Want: Spectrum of allowed energies.

$\Rightarrow$ Lead us to d

Solve effective 1 dim problem

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + V_{eff}(r)\right] u_{E,\ell}(r) = E\, u_{E,\ell}(r)$$

$$V_{eff}(r) = -\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2\,\ell(\ell+1)}{2mr^2}$$

Rewrite

$$-\frac{d^2}{dr^2} + \left[-\underbrace{\boxed{\frac{Ze^2 m}{4\pi\varepsilon_0\,\hbar^2}}}_{\frac{Z}{a}}\cdot\frac{2}{r} + \frac{\ell(\ell+1)}{r^2}\right] u$$

$$= \frac{2mE}{\hbar^2} u$$

$$\left[-\frac{d^2}{dr^2} + \left(-\frac{2Z}{a}\cdot\frac{1}{r} + \frac{\ell(\ell+1)}{r^2}\right)\right] u$$

$$= -\frac{2mE}{\hbar^2} u$$

$$a \equiv \frac{4\pi\varepsilon_0 \hbar^2}{e^2 \cdot m} \leftarrow \text{Bohr radius.}$$

$$a = 0.529 \times 10^{-10}\,m$$

Could solve for u, looking for series solutions, regular as

$$r \to 0, \quad r \to \infty$$

Near $r \to 0$

$$\left(-\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2} \right) u_{E,\ell} \propto 0$$

$$u_{\ell,E}(r) \propto \begin{cases} r^{\ell+1}, \\ \cancel{r^{-\ell}}, \end{cases} \qquad \frac{\chi_\ell}{r} \to \infty \text{ as } r \to 0$$

Near $r \to \infty$

$$-\frac{d^2}{dr^2} u \propto \frac{2mE}{\hbar^2} u$$

$$u_{E,\ell}(r) \propto e^{-\kappa r}, \quad \kappa^2 = -\frac{2mE}{\hbar^2} > 0$$

Bound states.

General solution for a radial wave fn

$$u_{E,\ell}(r) = r^{\ell+1} e^{-kr} \left(c_0 + c_1 r + c_2 r^2 + \dots + c_{n'} r^{n'}\right)$$

all behave as $r^{\ell+1}$ for small r
and as e^{-kr} for large r.

Expect: for each fixed ℓ:

Wave function with

$n' = 0, 1, 2 \dots$

$n' = \#$ of nodes

($n' \Leftrightarrow j_{max}$ in BOOK)

More nodes $\Leftrightarrow$ Higher energy.

Let

$$n \equiv n' + \ell + 1$$

# of nodes

$n' = 0, 1, \dots$

angular momentum

$\ell = 0, 1, \dots$

Nodeless wave fn

$$n' = 0 \iff n = l+1$$

$$u_{nl}(r) = A_0\, r^{l+1} e^{-\kappa r}$$

$$\frac{d}{dr} u = \left[\frac{(l+1)}{r} - \kappa\right] u$$

$$\frac{d^2}{dr^2} u = \left[\frac{[l+1]\cdot l}{r^2} - 2\,\frac{\kappa_{nl}(l+1)}{r} + \kappa_{nl}^2\right] u$$

This solves:

$$-\frac{d^2}{dr^2} u + \left[-\frac{2Z}{a_0}\cdot\frac{1}{r} + \frac{l(l+1)}{r^2}\right] u = -\kappa^2 u$$

provided:

$$2\kappa(l+1) = \frac{2Z}{a}$$

$$\Rightarrow \quad \kappa = \frac{Z}{(l+1)a} = \frac{Z}{na}, \quad \text{for } n = l+1,\ n' = 0$$

More generally:

$$u_{n,l}(r) = r^{l+1} e^{-\kappa_n r} \cdot v_{n,l}(r)$$

where

$$v_{n,l}(r) = \sum_{j=0}^{n'} c_j r^j \quad , \quad n = l+1+n'$$

Eqn must hold for all coefficients of r^j separately.

$$-k^2 u =$$

$$-\frac{d^2}{dr^2} u + \left[-\frac{2Z}{a_0} \cdot \frac{1}{r} + \frac{l(l+1)}{r^2} \right] u$$

$$-k^2 c_j r^{l+1+j}$$

$$= \Big[l(l+1) c_{j+2} - \frac{2Z}{a} c_{j+1}$$

$$- (l+1+j+2)(l+1+j+1) c_{j+2}$$

$$+2k(l+j+2) c_{j+1} \qquad - k^2 c_j \Big] r^{l+1+j}$$

$$\Rightarrow \left[l(l+1) - (l+j+3)(l+j+2)\right] C_{j+2}$$

$$= \left[\frac{2Z}{a} - 2k(l+j+2)\right] C_{j+1}$$

determines C_{j+2} in terms of C_{j+1}

$$C_{n'+1} = 0 \quad C_{n'} \quad C_{n'-1} \quad \cdots \quad C_1 \quad C_0$$

$\Rightarrow$ Coefficient of $C_{n'}$ has to $= 0$

$$0 = \frac{2Z}{a} - 2k(l+n'+1)$$

$$\Rightarrow \quad k = \frac{Z}{a \cdot (n'+l+1)} = \frac{Z}{a \cdot n}$$

$$E_{n,l} = -\frac{\hbar^2 k_{n,l}^2}{2m}$$

$$= -\frac{\hbar^2}{2ma^2} \frac{Z^2}{n^2}$$

$v_{n,\ell}(r)$ = polynomial of degree n in r

"Associated Laguerre polynomial"

$$\boxed{\begin{aligned} E_n &= -\frac{Z^2\hbar^2}{2m\cdot a^2}\cdot\frac{1}{n^2} \\ &= +\frac{Z^2}{n^2}\cdot E_1 \end{aligned}}$$

depends only on $n = n' + \ell + 1$ and not ℓ, n' separately

where $$\boxed{E_1 = -\frac{\hbar^2}{2ma^2} = -13.6\ \mathrm{eV}}$$

Stationary state:

$$\psi_{n,\ell,m}(r,\theta,\varphi) = A_{n,\ell,m} R_{n\ell}(r) Y_{\ell,m}(\theta,\varphi)$$

$$= A_{n,\ell,m}\, r^{\ell} e^{-k_{n\ell} r} v_{n,\ell}(r)\, Y_{\ell,m}$$

$$n \equiv n' + l + 1$$

is "principal quantum number" since it determines energy

$$\boxed{E_n = \frac{Z^2}{n^2} E_1 \qquad E_1 = -\frac{\hbar^2}{2ma^2}}$$

Bohr formula guessed in 1913 (S.E derivation) 1924

Degeneracy:

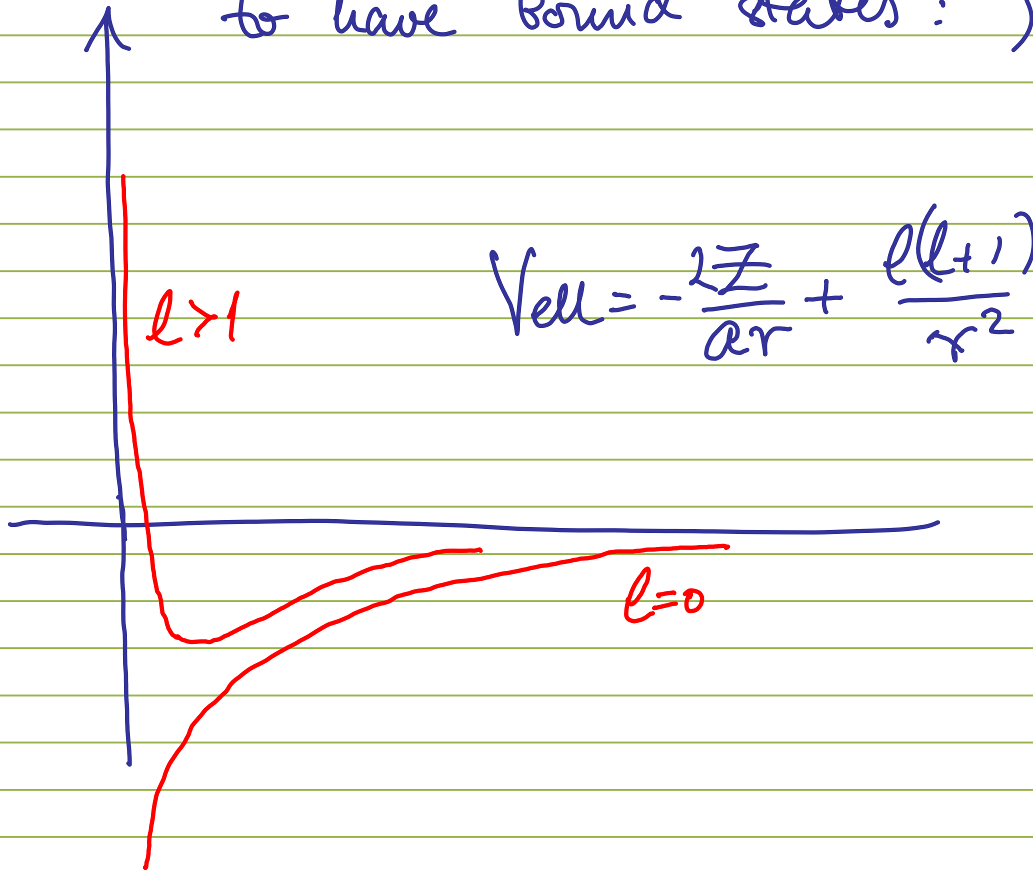
- For each fixed n, values of l allowed are

$$l = 0, \ldots, n-1$$

too shallow

(For l too high, well becomes V

to have bound states :)



* For fixed ℓ, there are arbitrarily many states of higher and higher energy,

w/ $\quad n' = n - (\ell+1)$

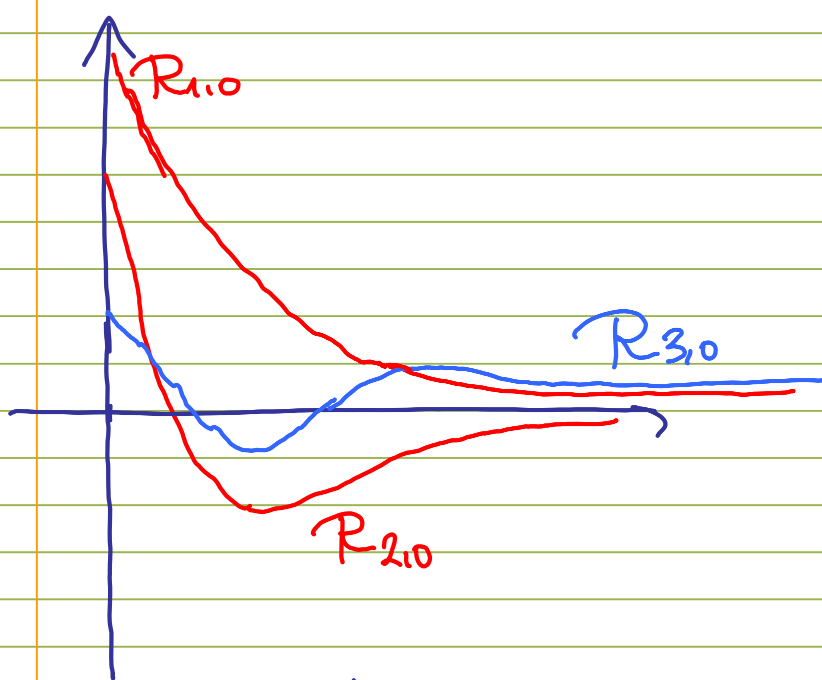
nodes

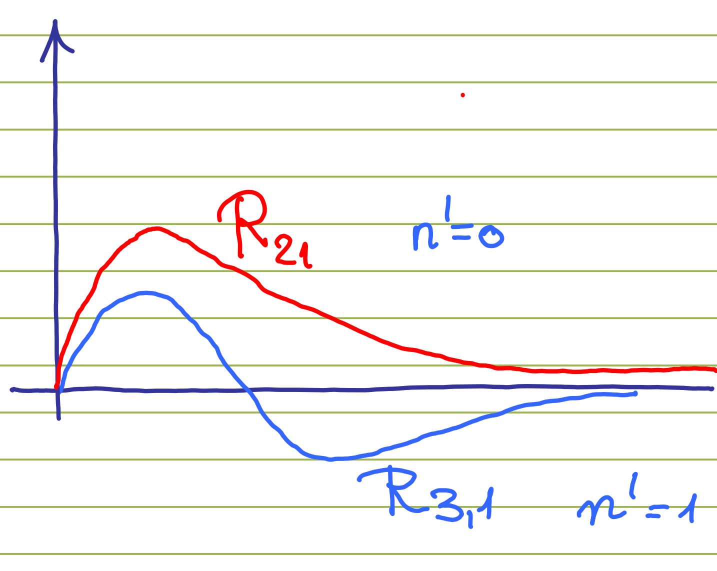
$$R_{1,0} = A_{1,0}\, e^{-r}$$

$$R_{2,1} = A_{2,1}\, r\, e^{-r/2a}$$

$$R_{2,0} = A_{2,0}\left(1 - \frac{1}{2} r/a\right) e^{-r/2a}$$

$$R_{3,2} = A_{3,2}\, r^2\, e^{-r/3a}$$





For $\ell > 0$, wave-fn vanishes at $r=0$.

(A particle can't have any angular momentum at $r=0$!)

- To find degeneracy of states recall:

  - at fixed ℓ, have $2\ell+1$ states with

L_z eigenvalues $\hbar m$.

$$m = -\ell, -\ell+1, \ldots, -1, 0, 1, \ldots, \ell$$

$$d(n) = \sum_{\ell=0}^{n-1} (2\ell+1)$$

$$= 2 \cdot \frac{n(n-1)}{2} + n = n^2$$

Wave functions are orthonormal

$$\int d^3\vec{r}\ \psi^*_{n,m,\ell}(\vec{r})\ \psi_{n',m',\ell'}(\vec{r})$$
$$= \delta_n^{n'}\ \delta_\ell^{\ell'}\ \delta_m^{m'}$$

We saw:

$$\int d^3\vec{r} = \int r^2 dr\ \sin\theta\, d\theta\, d\varphi$$

$$\int \sin\theta\, d\theta\, d\varphi\ Y^*_{\ell,m}(\theta,\varphi)\ Y_{\ell' m'}(\theta,\varphi)$$
$$= \delta_\ell^{\ell'}\delta_m^{m'}$$

and
$$\int r^2 dr\ R_{n,\ell}(r)\, R_{n'\ell'}(r)$$
$$= \int dr\ u_{n,\ell}(r)\ u_{n'\ell'}(r) = \delta_n^{n'}\delta_\ell^{\ell'}$$

E

$Z=1 \Leftrightarrow$ Hydrogen Atom

$n=4$ 4s $n'=3$ 4p $n'=2$ 4d $n'=1$ 4f $n'=0$

$n=3$ 3s $n'=2$ 3p $n'=1$ 3d $n'=0$

$n=2$ 2s $n'=1$ 2p $n'=0$

$n=1$ 1s $n'=0$

$\ell=0$ $\ell=1$ $\ell=2$ $\ell=3$

s orbital p orbital d orbital f

1-fold degenerate 3-fold degenerate 5-fold 7-fold

The energy levels are exact to 0.01 %.

Missing effects

* relativistic
* non-coulomb nucleus-electron interactions.

-

This gives also a fair first approximation to energy levels of multi-electron ions..

.. But for this we must include spin.

Hydrogen emission spectra

Suppose you have an atom in some state

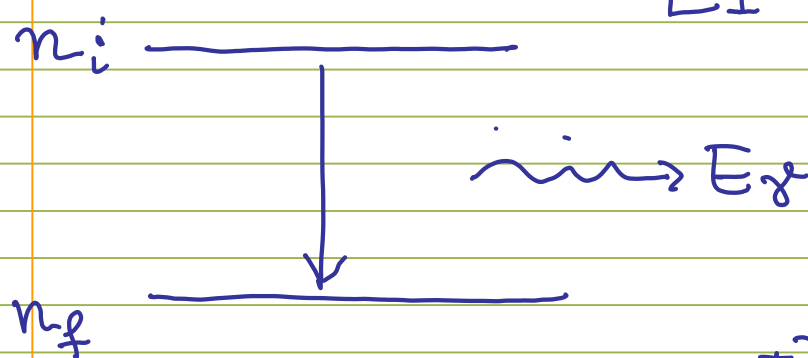
$$\psi_{n,l,m}$$

Strictly, it should stay there forever. However, in reality electron is coupled to electro-magnetic field... this is true even in vacuum. This coupling allows electron to transition between the states by emitting

* Emitting a photon of energy

$$E_\gamma = E_i - E_f$$

$$= E_1\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$



≥ 0 if $n_f < n_i$ since

$$E_1 = -\frac{\hbar^2}{2ma^2} \sim -13.6\,eV$$

Energy of a photon

$$E_\gamma = h\nu \quad \left(= \hbar\omega, \; \omega = 2\pi\nu \right)$$

In terms of frequency

$$\nu = \frac{1}{T}$$

or, in terms of

$$\frac{1}{\lambda} = \frac{\nu}{c}$$

$$E_\gamma = \frac{hc}{\lambda}$$

So

$$\frac{1}{\lambda_\gamma} = \frac{E_1}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

wavelength
of emitted photon

$$R \equiv \left| \frac{E_1}{hc} \right|$$ Rydberg constant

$$\simeq 1.097 \times 10^{7}\ \mathrm{m}^{-1}$$

First discovered by matching to observation. "Explained" by Bohr.

Better understood by QM, and better still by

QED ← Relativistic effects

(computed to 11 digits!)

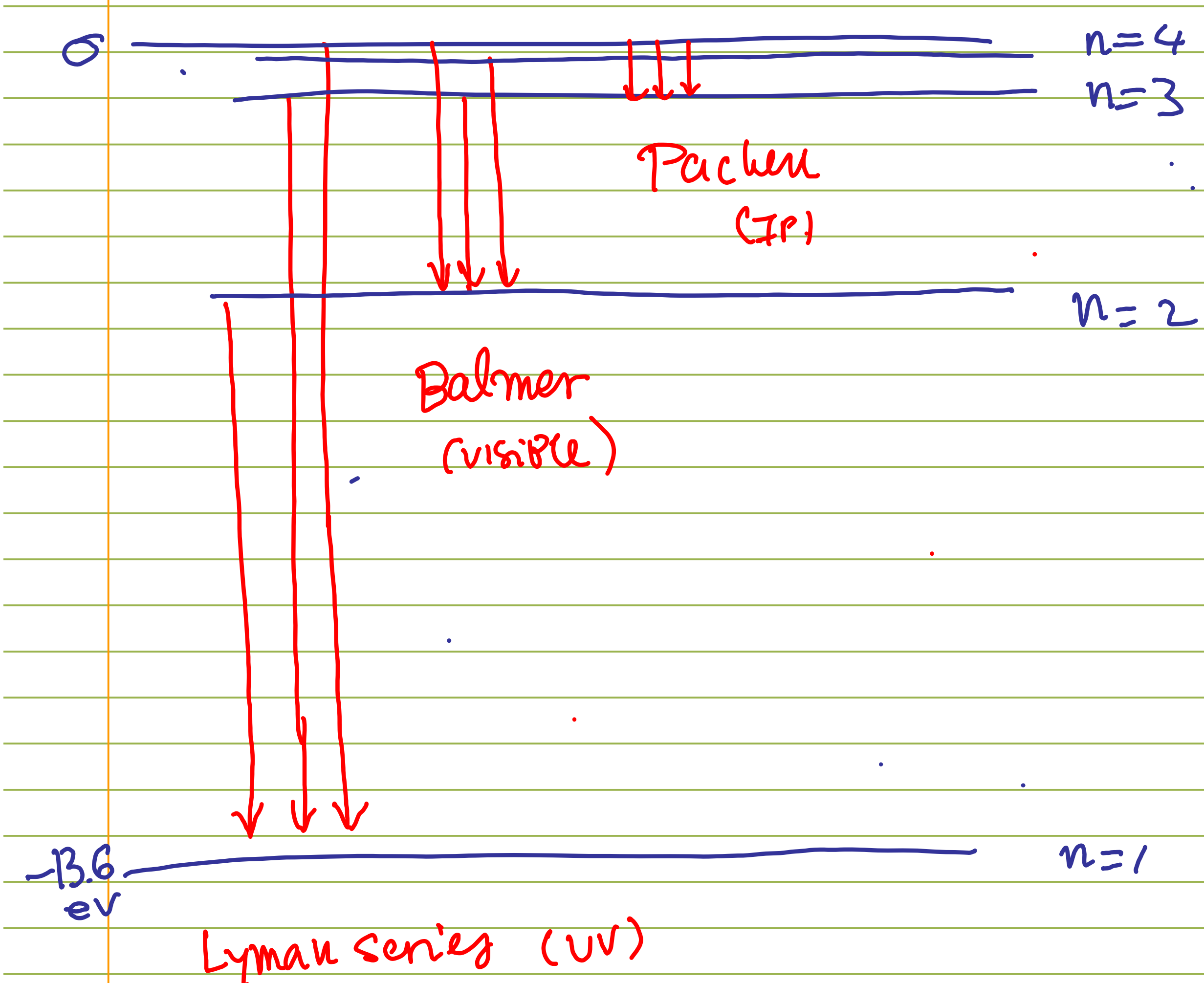
$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$R > 0$$

$$R = \frac{\hbar^2}{2ma^2} \times \frac{1}{hc}$$

$$= \frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \times \frac{1}{\underset{\overset{\parallel}{2\pi\hbar}}{hc}}$$

$$= \frac{m}{4\pi\hbar^3 c}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$$



Lyman
$n_f = 1$: $\frac{1}{\lambda} = R\left(1 - \frac{1}{n_i^2}\right)$

Balmer
$n_f = 2$ $\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n_i^2}\right)$

Pachen $\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n_i^2}\right)$

Angular Momentum

Classically, in a spherically symmetric potential

$$E, \quad \vec{L} = \vec{r} \times \vec{p}$$

are conserved

$$\frac{d}{dt} E = 0 = \frac{d}{dt} \vec{L}$$

In components

$$\vec{L} = (L_x, L_y, L_z)$$

where
$$L_x = y p_z - z p_y$$
$$L_y = z p_x - x p_z$$
$$L_z = x p_y - y p_x$$

In QM, these observables get promoted to operators

$$E \to \hat{H}$$
$$\vec{L} \to \hat{\vec{L}}$$
$$\vec{p} \to \hat{\vec{p}} =$$

For e.g

$$p_x \to \hat{p}_x = -i\hbar \frac{\partial}{\partial x}$$

$$L_x \to \hat{L}_x = y\left(-i\hbar\frac{\partial}{\partial z}\right) - z\left(-i\hbar\frac{\partial}{\partial y}\right)$$

acting on fn's of x, y, z.

The fact that $\vec{L}$ is conserved

$$\Leftrightarrow [\hat{\vec{L}}, \hat{H}] = 0$$

since

$$\frac{d}{dt}\hat{Q} = \frac{i}{\hbar}[\hat{H}, \hat{Q}] + \frac{\partial}{\partial t}\hat{Q}$$

for any operator $\hat{Q}$.

One can show, by direct calculation that for

$$\hat{H} = \frac{\hat{\vec{p}}^2}{2m} + V(r) \leftarrow \text{indep of } \theta, \varphi$$

$$[\hat{H}, \hat{L}] = 0 \quad \checkmark$$

Other commutators:

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$$

and cyclic perm. $x \to y \to z$

What does this mean?

Recall for any $\hat{A}, \hat{B}$

$$[\hat{A}, \hat{B}] \neq 0$$

means we cannot find states where $\hat{A}, \hat{B}$ are definite simultaneously, as in any state:

$$\sigma_A \cdot \sigma_B \geq \left| \frac{1}{2i} \langle [A, B] \rangle \right|$$

So, no common eigenfunctions of L_x, L_y, L_z!

Fortunately

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

commutes with all

$$[L^2, L_x] = 0 = [L^2, L_y]$$
$$= [L^2, L_z]$$

So, we <u>can</u> find common eigenfunctions of

$$H, L^2, L_z.$$

(or L_x, L_y).

$\rightsquigarrow$ These where

$$\psi_{E,\ell,m} = R_{E,\ell}(r)\, Y_{\ell,m}(\theta, \varphi)$$

$L^2 \rightarrow$ $\leftarrow L_z$

One can show, in spher. coord

$$L_z = x p_y - y p_x = -i\hbar \frac{\partial}{\partial \varphi}$$

$$\left(\begin{array}{l} x = r \sin\theta \cos\varphi \\ y = r \sin\theta \sin\varphi \end{array} \right)$$

$$L^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin\theta^2} \frac{\partial^2}{\partial\varphi^2} \right]$$

$\rightsquigarrow$

$$L^2 Y_{l,m}(\theta,\varphi) = \hbar^2 (l+1) l \, Y_{l,m}$$

$$L_z Y_{l,m}(\theta,\varphi) = \hbar m \, Y_{l,m}$$

It turns out that to derive spectr. of L^2 we do <u>not</u> need explicit formulas for eigenfn's, only commutation rels!

Suppose we try to find f

$$L^2 f = \lambda f, \quad L_z f = \mu f$$

Let $\quad L_\pm = L_x \pm i L_y$

Then

$$[L_z, L_\pm]$$
$$= [L_z, L_x \pm i L_y]$$
$$= i\hbar (L_y \mp i L_x)$$
$$= \pm \hbar (L_x \pm i L_y)$$
$$= \pm \hbar L_\pm$$

This means that

L_+ increases L_z eigenvalue by $\hbar$ and L_- decreases it

$$L_z(L_+ f) = (L_+ L_z + \mu L_+) f$$

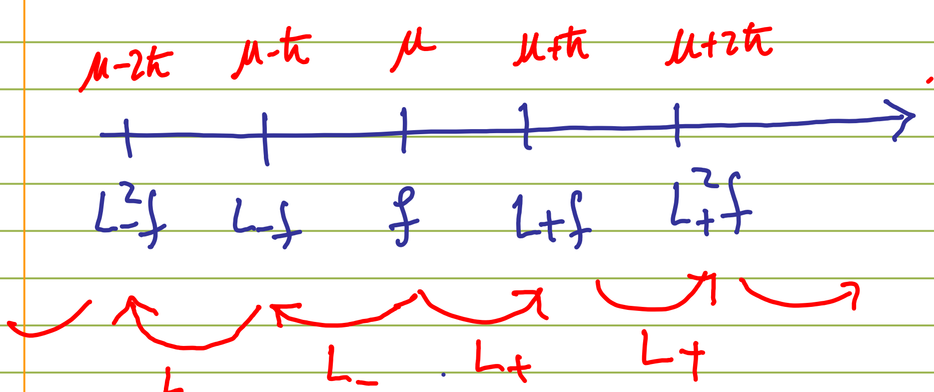
$$= (\mu + \hbar) L_+ f .$$

New eigenfn., new L_z eigenvalue

$$L^2 (L_+ f) = L_+ L^2 f .$$

$$= \lambda L_+ f$$

New eigenf. same L^2



This can't go on forever, as

no eigenvalue of L_z can

be bigger, in absolute

value, than λ since

L^2, L_x, L_y, L_z are

hermitian and in any state

$$\langle L^2 \rangle = \langle L_x^2 \rangle + \langle L_y^2 \rangle + \langle L_z^2 \rangle \geq \langle L_z^2 \rangle$$

$\Rightarrow$ there must be a top

$$\mu_{max} \equiv \hbar l$$

and states

$$|f_{max}\rangle \quad , \quad |f_{min}\rangle$$

such that

$$L_+ |f_{max}\rangle = 0 = L_- |f_{min}\rangle$$

Let $$L_z|f_{max}\rangle = \hbar \ell |f_{max}\rangle$$
$$L_z|f_{min}\rangle = \hbar \bar{\ell} |f_{min}\rangle$$

What are $\ell, \bar{\ell}$?

Since
$$L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z$$

we have
$$L^2|f_{max}\rangle = \lambda|f_{max}\rangle$$
$$= (L_- L_+ + L_z^2 + \hbar L_z)|f_{max}\rangle$$
$$= (0 + \hbar^2 \ell^2 + \hbar^2 \ell)|f_{max}\rangle$$
$$= \hbar^2 \ell(\ell+1)|f_{max}\rangle$$

Similarly
$$L^2|f_{min}\rangle = \lambda|f_{min}\rangle$$
$$= \hbar^2 \bar{\ell}(\bar{\ell}-1)|f_{min}\rangle$$

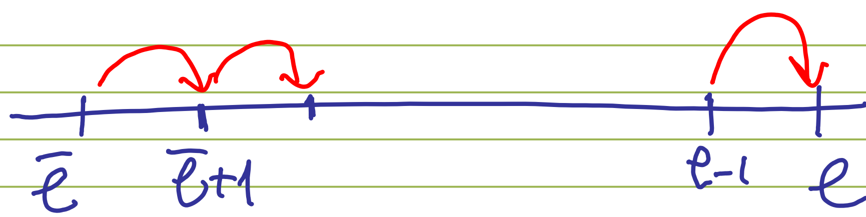
So $$\hbar^2 l(l+1) = \lambda = \hbar^2 \bar{l}(\bar{l}-1)$$

$l, \bar{l}$ are not necessarily integers

But $$l - \bar{l} = \# \text{ of step up's} \equiv L$$

is an integer ≥ 0.

$$L = \# \text{ of steps} = l - \bar{l}$$



$$\hbar^2 l(l+1) = \lambda = \hbar^2 \bar{l}(\bar{l}-1)$$

$$= \hbar^2 (l-L)(l-L-1)$$

or $$2l(L+1) = L(L+1)$$

since $L+1 \neq 0 \Rightarrow$

$$l = L/2 = -\bar{l}$$

$L = 0, 1, 2, \ldots$

- Eigenvalues of L^2 are

$$\hbar^2 \ell(\ell+1)$$

where $\underbrace{\ell = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, 2, \ldots}_{\text{either integer or half integer } \geq 0}$

- Eigenvalues of L_z are

$$-\ell, -\ell+1, \quad\quad , \ell-1, \ell$$

Gives us allowed eigenvalues,

without needing eigenfunctions.

* For $\ell = 0, 1, 2, \ldots$

Eigenfunctions are

$$Y_{\ell,m}(\theta, \varphi)$$

we wrote down before

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

Associated Legendre Polynomial

* What about

$$\ell = \frac{1}{2}, \frac{3}{2}, \ldots$$

This type of angular momentum does not have anything to do with where the particle is.

Instead it corresponds to

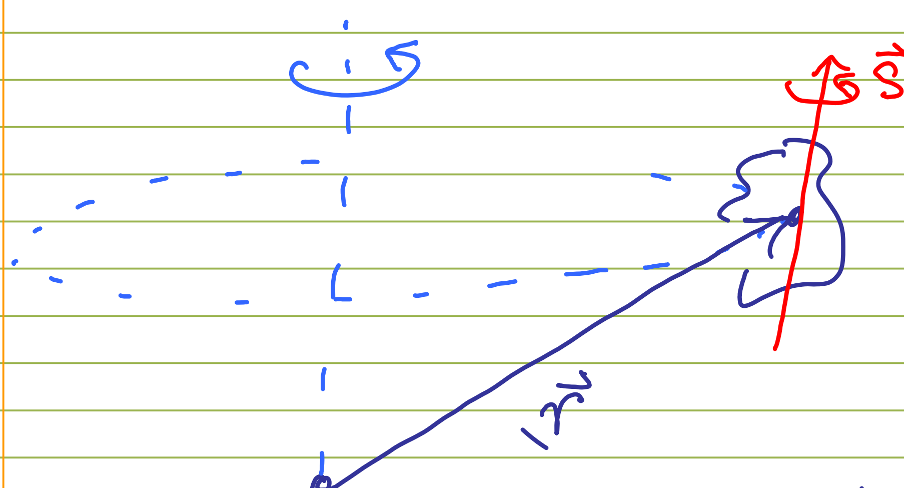
an Internal degree of freedom.

"Spin".

4.4 Spin

In Classical mechanics ..

two kinds of angular momentum



orbital ang. momentum

$\vec{L} = \vec{r} \times \vec{p}$ ← motion of center of mass

$\vec{S}$ = motion about center of mass

$\vec{S}$

Behaves exactly like L

$$[S_x, S_y] = i\hbar S_z \quad + \text{ given}$$

$\Rightarrow$ particles can be common eigst.

of $\quad S^2 = \vec{S}\cdot\vec{S}$

and $\quad S_z$ say

$$S^2 |s\, m\rangle = \hbar^2 s(s+1)\, |s\, m\rangle$$

$$S_z |s, m\rangle = \hbar m\, |s\, m\rangle$$

$$m = -s, -s+1 \quad , s$$

It turns out electrons, quarks, all carry an intrinsic spin, which is a property of the particle.

Electrons $\quad s = \frac{1}{2}, \quad m = +\frac{1}{2}$ or $-\frac{1}{2}$

Photons $\quad s = 1; \quad m = +1, 0$ or -1

Gravitons $\quad s = 2; \quad m = +2, +1, 0, -1,$ or -2

↑

Even though they are pointlike particles so nothing is really spinning about c.o.m.

Electrons in atom have both spin and orbital angular momentum ℓ.

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

Total angular momentum

$$\vec{J} = \vec{L} + \vec{S}$$

orbital or extrinsic — spin or intrinsic

where

$$[\vec{L}, \vec{S}] = 0$$

$\Rightarrow$

Total electron wave fn:

$$\psi_{n,\ell,m}(r,\theta,\varphi) \times \left|\tfrac{1}{2}, \pm\tfrac{1}{2}\right\rangle$$

(See Ch 6 or 137 b)

- - - - - - - - -

Spin 1/2

$$|s\, m\rangle = \begin{cases} \left|\tfrac{1}{2}, \tfrac{1}{2}\right\rangle \equiv |\uparrow\rangle \text{ up} \\ \left|\tfrac{1}{2}, -\tfrac{1}{2}\right\rangle \equiv |\downarrow\rangle \text{ down} \end{cases}$$

This abstract representation of states is all we can ask for since internal spin $\vec{S}$ of a point particle has nothing to do with positions x, y, z.

Still... we can get from it all we need.

Lets write down

$$S^2, \; S_z, \; S_+, \; S_-$$

in $|\uparrow\rangle, |\downarrow\rangle$

Basis.

$$S_z|\uparrow\rangle = \frac{\hbar}{2}|\uparrow\rangle$$

$$S_z|\downarrow\rangle = -\frac{\hbar}{2}|\downarrow\rangle$$

$\Rightarrow$

$$S_z = \begin{array}{c c} & \begin{array}{cc} |\uparrow\rangle & |\downarrow\rangle \end{array} \\ \begin{array}{c} |\uparrow\rangle \\ |\downarrow\rangle \end{array} & \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} \end{array} \hbar$$

In Basis where

$$|\uparrow\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |\downarrow\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Check:

$$S_z|\uparrow\rangle = \begin{pmatrix} \hbar/2 & 0 \\ 0 & -\frac{\hbar}{2} \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$= \frac{\hbar}{2}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{\hbar}{2}|\uparrow\rangle$$

Similarly

$$S^2 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} * \frac{3}{4}\hbar^2$$

since

$$S^2 |\uparrow\rangle = \hbar^2 s(s+1) |\uparrow\rangle$$
$$= \hbar^2 \cdot \frac{3}{4} |\uparrow\rangle$$

Recall

$$S_+ | s, m\rangle \propto | s, m+1\rangle$$

$$S_- | s, m\rangle \propto | s, m-1\rangle$$

One can show:

$$S_{\pm} |s, m\rangle = \hbar \sqrt{s(s+1) - m(m \pm 1)}\, |s, m \pm 1\rangle$$

So, $s=\frac{1}{2}$

$$S_+|\uparrow\rangle = 0 \quad , \quad S_+|\downarrow\rangle = \frac{\hbar}{2}|\uparrow\rangle$$

$s=\frac{1}{2}, m=-\frac{1}{2}$

$$S_-|\uparrow\rangle = \hbar|\downarrow\rangle \quad , \quad S_-|\downarrow\rangle = 0$$

$$S_+ = \begin{pmatrix} 0 & \hbar \\ 0 & 0 \end{pmatrix} \quad , \quad S_- = \begin{pmatrix} 0 & 0 \\ \hbar & 0 \end{pmatrix}$$

Since

$$S_\pm = S_x \pm i S_y$$

$$S_x = \frac{1}{2}\left(S_+ + S_-\right)$$

$$= \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$S_y = \frac{1}{2i}\left(S_+ - S_-\right)$$

$$= \frac{\hbar}{2}\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}$$

spin $\frac{1}{2}$ matrices

These play such an important role; one defines

$$S_x = \frac{\hbar}{2}\sigma_x, \quad S_y = \frac{\hbar}{2}\sigma_y, \quad S_z = \frac{\hbar}{2}\sigma_z$$

Pauli spin ($\frac{1}{2}$) matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Example

Find a state $|\psi\rangle$ such that measurement of S_z gives:

$S_z = \frac{1}{2}$ w/ prob. $|a|^2$

$S_z = -\frac{1}{2}$ w/ prob $|b|^2$

$|a|^2 + |b|^2 = 1$

In the same state, find probability to measure

$$S_x = \frac{\hbar}{2} \quad \text{and} \quad S_x = -\frac{\hbar}{2}$$

Let $|\uparrow_z\rangle$, $|\downarrow_z\rangle$ be eigenvectors of S_z

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} = |\uparrow_z\rangle \qquad \left(S_z = +\frac{\hbar}{2} \right)$$

$$\begin{pmatrix} 0 \\ 1 \end{pmatrix} = |\downarrow_z\rangle \qquad \left(S_z = -\frac{\hbar}{2} \right)$$

Then

$$\text{Prob}\left(S_z = +\frac{\hbar}{2} \right) = \left| \langle \uparrow_z | \psi \rangle \right|^2 = |a|^2$$

$$\text{Prob}\left(S_z = -\frac{\hbar}{2} \right) = \left| \langle \downarrow_z | \psi \rangle \right|^2 = |b|^2$$

Since $\langle \uparrow | \uparrow \rangle = 1 = \langle \downarrow | \downarrow \rangle$

$\langle \uparrow | \downarrow \rangle = 0 = \langle \downarrow | \uparrow \rangle$

$$|\psi\rangle = a|\uparrow\rangle_z + b|\downarrow\rangle_z = \begin{pmatrix} a \\ b \end{pmatrix}$$

(a, b determined up to a phase)

Similarly:

$$\text{Prob}\left(S_x = \frac{\hbar}{2}\right) = \left|\langle \uparrow_x | \psi \rangle\right|^2$$

$$\text{Prob}\left(S_x = -\frac{\hbar}{2}\right) = \left|\langle \downarrow_x | \psi \rangle\right|^2$$

To find these we need to know

$|\uparrow\rangle_x$, $|\downarrow\rangle_x$ $\Leftrightarrow$ Eigenvectors of S_x

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \text{in basis}$$

$$|\uparrow_z\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |\downarrow_z\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Its eigenvectors are

$$|\uparrow_x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \qquad S_x = +\frac{\hbar}{2}$$

$$|\downarrow_x\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \qquad S_x = -\frac{\hbar}{2}$$

$$\left(\langle \uparrow_x | \uparrow_x \rangle = 1 = \langle \downarrow_x | \downarrow_x \rangle \right)$$

So $\text{Prob}(\uparrow_x) = |\langle \uparrow_x | \psi \rangle|^2$

$$= \left| \frac{1}{\sqrt{2}} (1 \;\; 1) \begin{pmatrix} a \\ b \end{pmatrix} \right|^2$$

$$= \left| \frac{a+b}{\sqrt{2}} \right|^2$$

$$\text{Prob}(\downarrow_x) = \left| \frac{a-b}{\sqrt{2}} \right|^2$$

E.g.: $a=1, b=0$ $\Leftrightarrow$ electron is in state $|\uparrow_z\rangle$. If we measure S_z get $\hbar/2$ w/ 100% certainty. But for S_x 50-50 to get $S_x = \pm \frac{\hbar}{2}$

$a=b=1$ $\Leftrightarrow$ get $S_x = \frac{\hbar}{2}$ w/ 100% certainty $\Leftrightarrow$ electron is in eigenstate of S_x.

Example:

Find $\langle S_x \rangle$, $\langle S_y \rangle$, $\langle S_z \rangle$

in state $|\psi\rangle = a|\uparrow_z\rangle + b|\downarrow_z\rangle$:

$$|\psi\rangle = \begin{pmatrix} a \\ b \end{pmatrix}, \quad \langle\psi| = \begin{pmatrix} a^* & b^* \end{pmatrix}$$

So

$$\langle S_z \rangle = \langle\psi| S_z |\psi\rangle$$

$$= \begin{pmatrix} a^* & b^* \end{pmatrix} \begin{pmatrix} \frac{\hbar}{2} & 0 \\ 0 & -\frac{\hbar}{2} \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix}$$

$$= \frac{\hbar}{2}\left(|a|^2 - |b|^2\right)$$

$$\langle S_x \rangle = \begin{pmatrix} a^* & b^* \end{pmatrix} \begin{pmatrix} 0 & \frac{\hbar}{2} \\ \frac{\hbar}{2} & 0 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix}$$

$$= \begin{pmatrix} \frac{\hbar}{2} b^* & \frac{\hbar}{2} a^* \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix}$$

$$= \frac{\hbar}{2}\left(ab^* + ba^*\right)$$

$$\langle S_y \rangle = \frac{\hbar}{2}\left(iab^* - ba^*\right)$$

Electron in Magnetic Field

How do we measure spin?

Spinning charge has magnetic dipole moment

$\gamma =$ property of particle

$$\vec{\mu} = \gamma \vec{S}$$

gyro-mag. ratio

Spin angular momentum

It behaves like a little magnet which likes to align w/ magnetic field $\vec{B}$

$$H = -\vec{\mu} \cdot \vec{B} = -\gamma \vec{S} \cdot \vec{B}$$

Pick "z" axis along $\vec{B}$:

$$H = -\gamma S_z \cdot B$$

(This focuses only on spin contribution)

$$H|\uparrow_z\rangle = -\gamma B_0 S_z|\uparrow_z\rangle = \underbrace{-\frac{\hbar\gamma B_0}{2}}_{E_+}|\uparrow_z\rangle$$

$$H|\downarrow_z\rangle = \underbrace{+\frac{\hbar\gamma B_0}{2}}_{E_-}|\downarrow_z\rangle$$

In magnetic field

$$|\psi\rangle = a|\uparrow_+\rangle + b|\uparrow_-\rangle$$

Become time dependent as

$$|\uparrow_+\rangle \to e^{-iE_+t/\hbar}|\uparrow_+\rangle$$

$$|\downarrow_-\rangle \to e^{-iE_-t/\hbar}|\downarrow_-\rangle$$

So

$$|\psi(t)\rangle = \underbrace{a e^{-iE_+t/\hbar}}_{a(t)}|\uparrow\rangle + \underbrace{b e^{-iE_-t/\hbar}}_{b(t)}|\downarrow\rangle$$

Corresponding

$$\langle S_z\rangle = \hbar\frac{|a(t)|^2 - |b(t)|^2}{2} = \frac{|a|^2 - |b|^2}{2}\hbar$$

$$\langle S_x\rangle = \frac{\hbar}{2}\,\frac{b(t)^* a(t) + a(t)^* b(t)}{2}$$

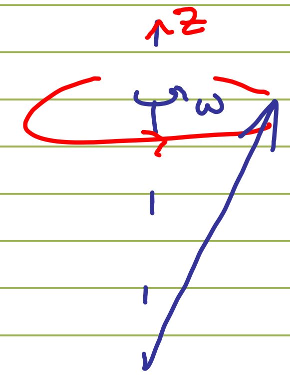
Choose $a = \cos\frac{\alpha}{2}$, $b = \sin\frac{\alpha}{2}$

$$\langle S_z \rangle = \frac{\hbar}{2}\cos\alpha$$

$$\langle S_x \rangle = \frac{\hbar}{2}\cos(\gamma B_0 t)\cdot\sin\alpha$$

$$\langle S_y \rangle = -\frac{\hbar}{2}\sin(\gamma B_0 t)\cdot\sin\alpha$$

→



$\langle \vec{S} \rangle$ precesses about z-axis w/ frequency

$$\omega = \gamma B_0$$

Larmor frequency

Since $\omega = \gamma B_0$ does not depend on $\hbar$, one should see same precession classically.

Classical particle in mag. field

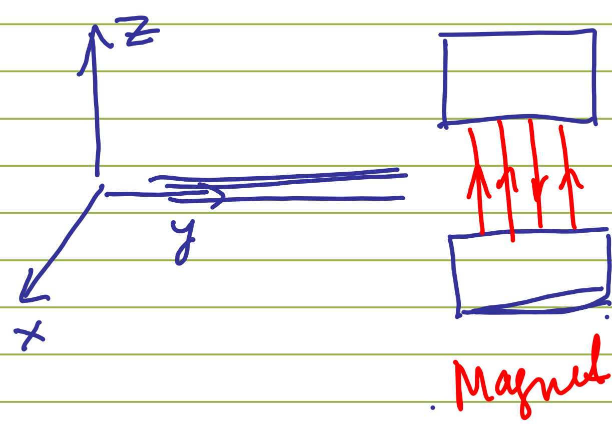
$$\frac{d}{dt}\vec{S} = \underbrace{\vec{\mu} \times \vec{B}}$$

torque on particle due to magnetic moment.

$\Rightarrow$ same precession frequency

Stern - Gerlach Expt

Place a beam of electrons in inhomogeneous magnetic field



Electrons in Beam experience

$$\vec{B} = (B_0 + \alpha z)\hat{z} ; \quad 0 \le t \le T$$

(need x. component as well, but will ignore)

For short time while they travel

through magnet

$$|\psi(t)\rangle = a|\uparrow_z\rangle e^{-iE_+t/\hbar} + b|\downarrow\rangle_z e^{-iE_-t/\hbar}$$

$$0 \le t \le T$$

No time dependence Before or

after

For $t < 0$

$$|\psi(t)\rangle = a\,|\uparrow_z\rangle + b\,|\downarrow_z\rangle$$

For $t > T$, electron emerges

in time indep. state:

$$|\psi(t)\rangle = a e^{-\frac{iE_+T}{\hbar}} |\uparrow_z\rangle + b e^{-\frac{iE_-T}{\hbar}} |\downarrow_z\rangle$$

$t > T$

Since

$$E_\pm = \mp \frac{\hbar}{2} \gamma B(z) = \mp \frac{\hbar}{2} \gamma (B_0 + \alpha z)$$

Spin up component of $|\psi(t)\rangle$

has momentum

$$p_z = -i\hbar \frac{\partial}{\partial z}$$

equal to

$$p_z = \begin{cases} \frac{\hbar}{2} B_0 \alpha T & \text{for } |\uparrow_z\rangle \\ -\frac{\hbar}{2} B_0 \alpha T & \text{for } |\downarrow_z\rangle \end{cases}$$

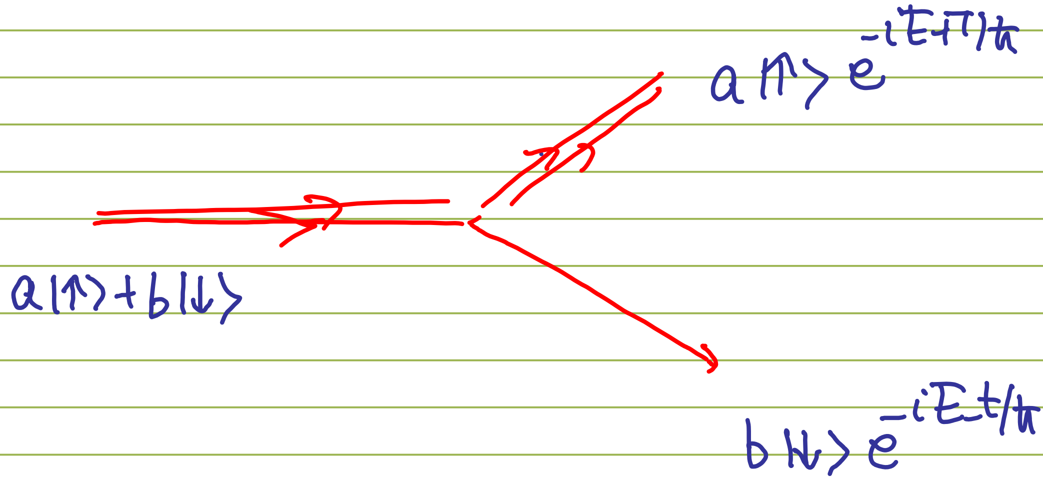
components

⇒ Leads to splitting of beam

⇒ produces from a state

$$\psi(t \leq 0) = a\,|\uparrow_z\rangle + b\,|\downarrow_z\rangle$$

with no definite spin, a state w/ definite spin.



spin ↑ w/ probability

$$|a|^2$$

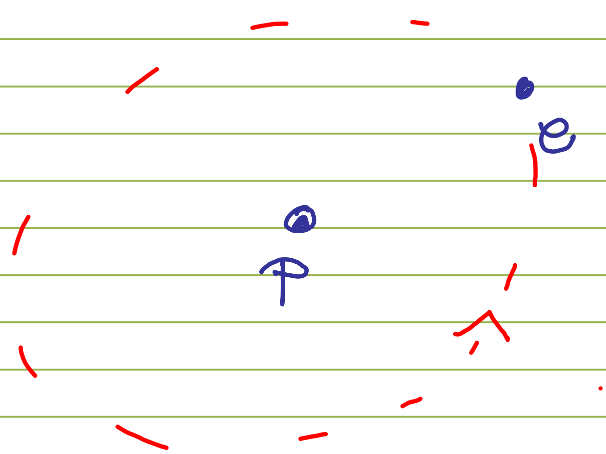
in initial beam, and

1 or 0 in two emerging beams.

Addition of Angular Momentum

Suppose you have two particles with spin:

E.g. Hydrogen atom, in ground state.



Both proton and electron are spin $\frac{1}{2}$ particles. Total spin of atom

$$\vec{S} = \underbrace{\vec{S}_p}_{\text{proton spin}} + \underbrace{\vec{S}_e}_{\text{electron spin}}$$

4 possible states

	m_p	m_e	m_p+m_e $\parallel$ m
$\vert\uparrow_p, \uparrow_e\rangle$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+1$
$\vert\uparrow_p, \downarrow_e\rangle$	$+\frac{1}{2}$	$-\frac{1}{2}$	0
$\vert\downarrow_p, \uparrow_e\rangle$	$-\frac{1}{2}$	$+\frac{1}{2}$	0
$\vert\downarrow_p, \downarrow_e\rangle$	$-\frac{1}{2}$	$-\frac{1}{2}$	-1

Claim: The 4 states correspond to total spin:

$S=1$ $\qquad\qquad\qquad$ $S=0$

$\underbrace{m=1,0,-1}_{\text{three states}}$ $\qquad\qquad$ $\underbrace{m=0}_{\text{one state}}$

$$|S=1, m=1\rangle = |\uparrow_p \uparrow_e\rangle$$

$$|S=1, m=-1\rangle = |\downarrow_p \downarrow_e\rangle$$

Q: What is $|S=1, m=0\rangle$ state?

$$|S=1, m=0\rangle = S_- |S=1, m=1\rangle$$

or:

$$S_- |\uparrow_p \uparrow_e\rangle = (S_-^p + S_-^e) |\uparrow_p \uparrow_e\rangle$$

$$= |(S_-^p \uparrow_p), \uparrow_e\rangle$$

$$+ |\uparrow_p, S_-^e \uparrow_e\rangle$$

$$= \frac{1}{\sqrt{2}} \left(|\downarrow_p, \uparrow_e\rangle + |\uparrow_p, \downarrow_e\rangle \right)$$

$S=0, m=0$ state is linear comb. of $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$ orthogonal to it

$$|S=0, m=0\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow_p, \downarrow_e\rangle - |\downarrow_p, \uparrow_e\rangle \right)$$

Replace two spin $\frac{1}{2}$ particles with two particles of arbitrary spins

$$S_1 \text{ and } S_2$$

There are $(2S_1+1)\times(2S_2+1)$ possible states:

$$|S_1, m_1\rangle \otimes |S_2; m_2\rangle$$

$m_1 = -S_1, \dots, S_1$

$m_2 = -S_2, \dots, S_2$

These are eigenfn's of

$$S_1^2, \quad S_2^2, \quad S_1^z, \; S_2^z$$

But, they are <u>not</u> eigenfns of $\quad S^2 = (\vec{S}_1 + \vec{S}_2)^2$

Since

$$S^2 = \vec{S}\cdot\vec{S} = \vec{S}_1^{\,2} + \vec{S}_2^{\,2} + 2\vec{S}_1\cdot\vec{S}_2$$

$$= S_1^2 + S_2^2 + 2\vec{S}_1\cdot\vec{S}_2$$

So, while

$$[S^2, S_1^2] = 0 = [S^2, S_2^2]$$

but $$[S^2, S_{1,2}^z] \neq 0$$

Instead, we can look for basis of eigenstates of

$$S^2, \; S_1^2, \; S_2^2, \; S_z = S_{1,z} + S_{2,z}$$

Since they mutually commute.

$$|S, S_1, S_2, m\rangle \equiv |S, m\rangle$$

(Recall: S^2 commutes w/ S_x, S_y, S_z
but S_x, S_y, S_z do not commute w/ each other)

Claim: From

$$(2S_1+1)\times(2S_2+1)$$

states

$$|S_1,m_1\rangle\otimes|S_2,m_2\rangle$$

can obtain all eigenstates

$$|S,m\rangle$$

where

$$S = \underbrace{S_1+S_2}_{\text{max}},\ \ldots\ldots,\ \underbrace{|S_1-S_2|}_{\text{min}}$$

in integer steps.

E.g: $|S=S_1+S_2,\ m=S_1+S_2\rangle$

$$= |S_1, m_1=S_1\rangle\otimes|S_2, m_2=S_2\rangle$$

(Easy to check #'s of states add up!)

More generally:

$$|s, m\rangle = \sum_{m = m_1 + m_2} C^{s\,m}_{s_1 m_1, s_2 m_2} |s_1, m_1\rangle \otimes |s_2, m_2\rangle$$

$$C^{s\,m}_{s_1 m_1\, s_2 m_2} = \text{"Clebsch-Gordon coefficients"}.$$

E.g

$$C^{1\,1}_{\frac{1}{2}\frac{1}{2}\,\frac{1}{2}\frac{1}{2}} = 1$$

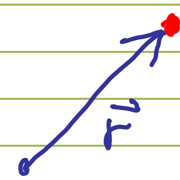
$$C^{1\,0}_{\frac{1}{2}-\frac{1}{2}\,\frac{1}{2}+\frac{1}{2}} = -\frac{1}{\sqrt{2}}$$

Identical particles

Single particle wave function

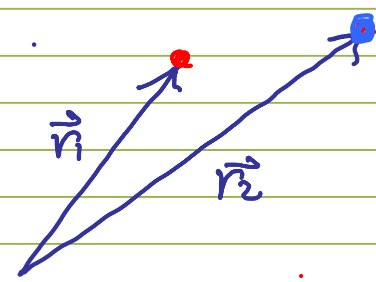
$\psi(\vec{r}, t)$

position of particle



Two particle wave fun

$\psi(\vec{r}_1, \vec{r}_2, t)$



$|\psi(\vec{r}_1, \vec{r}_2, t)|^2 =$ Probability density to find particle 1 at $\vec{r}_1$ and particle 2 at $\vec{r}_2$.

$= P(\vec{r}_1, \vec{r}_2, t)$

This is all well if particles
#1 and #2
are distinguishable.

However, QM is full of particles
which are <u>not</u> distinguishable.

E.g. Any two electrons
are exactly the same
(or protons, or photons....)

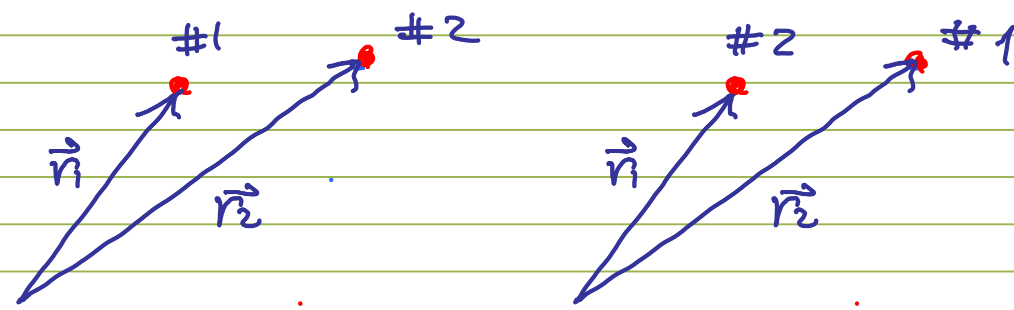
Then, it <u>has</u> to be true
that

$$p(\vec{r}_1, \vec{r}_2, t) = p(\vec{r}_2, \vec{r}_1, t)$$

Since we cannot distinguish

particle #1 at $\vec{r}_1$ & #2 at $\vec{r}_2$

From #2 at $\vec{r}_1$ & #1 at $\vec{r}_2$.



For Identical particles, Hamiltonian

$$H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V(\vec{r}_1, \vec{r}_2, t)$$

must have symetry

$$H(\vec{r}_1, \vec{r}_2, t) = H(\vec{r}_2, \vec{r}_1, t) \quad (*$$

(so, in particular, $m_1 = m_2 = m$).

Then, we can take its eigenf's to be either symmetric or anti-symmetric.

Let $P =$ exchange operator

$$P f(\vec{r}_1, \vec{r}_2) = f(\vec{r}_2, \vec{r}_1) \quad , \text{ for any } f.$$

Then, (*) is the same as

$$PHf = HPf$$

for any f, or.

$$[P, H] = 0$$

This means, we can find a basis of Hilbert space that consists of simultaneous eigenfunctions of H and P. Since

$$P^2 = 1,$$

its eigenvalues are

$$+1 \quad \text{or} \quad -1$$

symmetric fns   anti-sym. in fns

$$\psi(\vec{r}_1, \vec{r}_2) = \pm \psi(\vec{r}_2, \vec{r}_1)$$

So far, we only included spatial part of wave fns. In nature, we must also include spin.

E.g, wave fn of two distinct spin $\frac{1}{2}$ particles is of form

$\psi(\vec{r}_1, \vec{r}_2) \otimes$ element of 4-dim vector space spanned by $|\uparrow,\uparrow\rangle$, $|\uparrow,\downarrow\rangle$, $|\downarrow,\uparrow\rangle$, $|\downarrow,\downarrow\rangle$

For identical particles, total quantum state has to be symmetric or anti-symmetric.

Spin-Statistics Theorem

For identical particles of spins

the total quantum state, including spin, has to be

* anti-symmetric, if

$s = \frac{1}{2}, \frac{3}{2}, \ldots$ half-integer

* symmetric, if

$s = 0, 1, 2, \ldots$ integer

Particles w/ half-integer spin are called

"fermions"

(electrons, protons, neutrons are all fermions)

Particles w/ integer spin are called

"bosons"

(photons and Higgs particle are bosons)

E.g consider two electrons in ∞-square well. Assume particles are non-interacting.

Total quantum state

spatial $\times$ spin

is anti-symmetric if

symmetric $\times$ anti-symmetric

anti-sym $\times$ symmetric

Spatial wave fn is symmetric

$$\psi^{+}_{n_1,n_2}(x_1,x_2) = \frac{1}{\sqrt{2}}\left(\psi_{n_1}(x_1)\psi_{n_2}(x_2) + \psi_{n_1}(x_2)\psi_{n_2}(x_1)\right)$$

1-particle

$\psi_n(x)$ — n'th wave fn of ∞ square well

Anti-symmetric:

$$\psi^-_{n_1 n_2}(x_1 x_2) = \frac{1}{\sqrt{2}}\left(\psi_{n_1}(x_1)\,\psi_{n_2}(x_2) - \psi_{n_1}(x_2)\,\psi_{n_2}(x_1)\right)$$

Note: $\psi^-_{n_1 n_2}(x_1, x_2) = 0$ if $n_1 = n_2$

Spin wave fn's:

Symmetric:

$$S=1 \quad \begin{cases} |\uparrow\uparrow\rangle, & m=1 \\ \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right), & m=0 \\ |\downarrow\downarrow\rangle, & m=-1 \end{cases}$$

Anti-symmetric

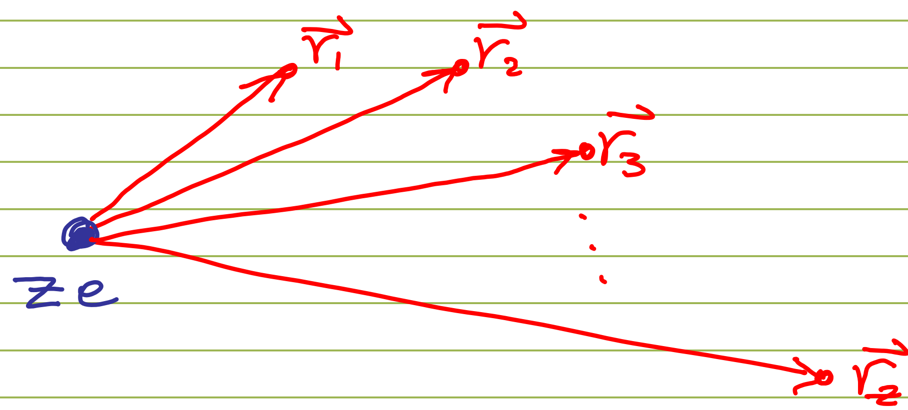
$$S=0 \qquad \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

$\Rightarrow$ Lowest energy state has $n_1 = n_2 = 1$ and $S = 0$.

Next level up has $n_1 = 1$, $n_2 = 2$ and $S = 0$ or $S = 1$.

Periodic Table

A neutral atom consists of heavy nucleus of charge $+Ze$ and Z electrons.



Hamiltonian (assuming $m_p \gg m_e = m$)

$$H = \underbrace{\sum_{j=1}^{Z} \left(-\frac{\hbar^2}{2m} \nabla_j^2 - \frac{1}{4\pi\varepsilon_0} Z \frac{e^2}{|r_j|} \right)}_{H_0 = \text{1 electron in field of nucleus}}$$

$$+ \underbrace{\frac{1}{2} \frac{1}{4\pi\varepsilon_0} \sum_{i \neq j = 1}^{Z} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{H_{int} \;\; \text{Coulomb repulsion of electrons}}$$

Stationary states

(1) $H \psi_E(\vec{r}_1, \vec{r}_2) = E \psi_E(\vec{r}_1, \vec{r}_2)$

Q: What is the ground state of H for $Z = 1, 2, \ldots$

$\Leftrightarrow$ which atoms exist in nature

Can derive from this the

Periodic Table of Elements!

Stationary states w/

$$E > E_{\text{ground state}}$$

$\Leftrightarrow$ excited states of the atom

Full quantum state is

$$\psi_E(\vec{r}_1, \quad, \vec{r}_2) \cdot \chi(\vec{s}_1, \quad, \vec{s}_2)$$

Total quantum state has to

be anti-symmetric

$$\psi(\vec{r}_2, \vec{r}_1, \vec{r}_3, \quad \ldots) \chi(\vec{s}_2, \vec{s}_1, \ldots, \vec{s}_z)$$

$$= -\psi(\vec{r}_1, \vec{r}_2, \ldots) \chi(\vec{s}_1, \vec{s}_2, \ldots, \vec{s}_z)$$

This can be achieved by taking

$$\begin{cases} \psi^{(+)}(\vec{r}_1, \vec{r}_2, \quad \vec{r}_Z) & \text{symm} \\ \times \\ \chi^{(-)}(\vec{r}_1, \vec{r}_2 \quad , \vec{r}_Z) & \text{anti-symm} \end{cases}$$

$$\begin{cases} \psi^{(-)}(\vec{r}_1, \vec{r}_2 \quad \vec{r}_Z) & \text{anti-sym} \\ \times \\ \chi^{(+)}(\vec{r}_1, \vec{r}_2, \quad) & \text{symm} \end{cases}$$

Getting a symm. or anti-symm. solution with the same energy from <u>any</u> soln to (1) is not difficult.

$\psi(\vec{r}_1, \quad , \vec{r}_Z)$ — arbitrary sol'n

Corresponding symm. sol'n:

$$\psi^{(+)}(\vec{r}_1, \quad , \vec{r}_Z) = \frac{1}{\sqrt{N!}} \Big(\psi(\vec{r}_1, \vec{r}_2, \quad , \vec{r}_Z) + \text{all permutations} \Big)$$

E.g for 2 particles

$$\psi^{(+)}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left(\psi(\vec{r}_1, \vec{r}_2) + \psi(\vec{r}_2, \vec{r}_1) \right)$$

Anti-symm:

$$\psi^{-}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left(\psi(\vec{r}_1, \vec{r}_2) - \psi(\vec{r}_2, \vec{r}_1) \right)$$

Q: Find general formula for

$$\psi^{(-)}(\vec{r}_1, \quad , \vec{r}_z)$$

in terms of sum over permutations w/ some signs. What should the signs be?

However, finding any exact solution to (1) is difficult. (One can find soln's numerically). Problem is the electron-repulsion part.

$$H_{int} = \sum_{i \neq j} \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

$$H = H_0 + H_{int} \approx H_0$$

Ground states can be deduced from Hydrogenic ones!

We can get a fairly good qualitative picture which atoms exist & derive essential features of Table of elements.

E.g $Z = 2$

$$\psi_E(\vec{r}_1, \vec{r}_2) \approx \psi_{n_1 \ell_1 m_1}(\vec{r}_1)\, \psi_{n_2 \ell_2 m_2}(\vec{r}_2)$$

$$E = \underset{Z^2}{\overset{\uparrow}{4}} \left(E_{n_1} + E_{n_2} \right)$$

$$E_n = -\frac{1}{n^2} \times \overbrace{13.6\,\text{eV}}^{\text{Bohr Energy}}$$

E.g ground state:

$$n_1 = n_2 = 1 \quad \Rightarrow \quad \ell_1 = \ell_2 = 0$$

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_{100}(\vec{r}_1)\, \psi_{100}(\vec{r}_2)$$

$$n_1 \quad \ell_1 \quad m_1$$

w/ energy

$$E = 4 \cdot 2 \cdot (-13.6\ \text{eV})$$
$$= -108.8\ \text{eV}$$

Exact

$$E = -79.0\ \text{eV}$$

Note: exact answer is higher in energy $\Leftrightarrow$ the term we neglected raises energy

In the ground-state

$$\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1)$$

is necessarily symmetric —
— the anti-symmetrized wave fn vanishes. So, the spin part

$$\chi(\vec{S}_1, \vec{S}_2) = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

has to be anti-symmetric. $\Leftrightarrow$ spin singlet: $s=0, m=0$.

Total He ground state:

$$\psi_{100}(\vec{r}_1)\,\psi_{100}(\vec{r}_2)\,\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

Periodic Table

Ground states of heavier atoms can be deduced similarly.

The lowest energy state corresponds to Z electrons

placed in lowest energy configuration subject to total anti-symmetry of wave function.

We worked out ground-states of

H $(Z=1)$

$n=1$ $\uparrow$

$l=0, \; s=\frac{1}{2}$

He $(Z=2)$

$n=1$ $\uparrow\downarrow$

$l=0, \; s=0$

"Pauli - exclusion principle"
prevents having more than
one electron in same state,
so for

$Z \geq 3$, have to start filling
up higher energy levels

Roughly, outer electrons being in
n-th shell $\Longleftrightarrow$
n-th row of periodic
table

$n=2$ level has room for 8
electrons, subject to Pauli
exclusion

	$m=0$	$m=1$	$m=0$	$m=-1$
$n=2$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
	$\ell=0$	$\ell=1$		

Filling all 8 spots with electrons gets us from

$Z=3$ to $Z=10$

Lithium Neon

States w/ lower ℓ have lower energy, since the electrons get closer to nucleus and see higher effective Z

$n=2$	$\uparrow$	$\uparrow\downarrow$
	Lithium	Beryllium
	Li	Be

Chemistry conventions

$\ell = 0 \iff$ s orbital

$\ell = 1 \iff$ p orbital

$\ell = 2 \iff$ d orbital

Element	Z	Electron conf.
H Hydrogen	1	$1s$
He Helium	2	$(1s)^2$
Li Lithium	3	$(1s)^2\, 2s$
Be Beryllium	4	$(1s)^2(2s)^2$
B Boron	5	$(1s)^2(2s)^2(2p)$
C Carbon	6	$(1s)^2(2s)^2(2p)^2$
N Nitrogen	7	$(1s)^2(2s)^2(2p)^3$

O Oxigen	8	$(1s)^2(2s)^2(2p)^4$
F Fluorine	9	$(1s)^2(2s)^2(2p)^5$
Ne Neon	10	$(1s)^2(2s)^2(2p)^6$

After Neon, $n=2$ level is filled and we have to go to $n=3$

We get 2 atoms filling up

3s $\qquad$ $(3s)^2$

$Z=11$, Na $\qquad$ $Z=12$ Mg

and 6 more

$(3s)^2(3p)$ $\qquad$ $(3s)^2(3p)^6$

$Z=13$ $\qquad$ $Z=18$

Al Aluminum $\qquad$ Ar Argon

After that ... it turns out

more energetically favorable to

go to $n=4$ shell

than fill up 3d shell...

so

$Z=19$	$Z=20$
K	Ca
Kalium	Calcium
4s	$(4s)^2$

The next 10 elements fill up

$(n=3, \ell=2)$

3d orbitals

$Z=21$ - - - - - $Z=30$

Sc Zn

Scandium Zinc

and following 6 go back to

$n=4 \quad \ell=1$

$Z=31$ - - - - $Z=36$

Ga Kr

Gallium Krypton

$(4p)$ $(4p)^6$

Full electron configuration

$Z=31$ Ga

$$\underbrace{(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^{10}(4s)^2}_{31 \text{ electrons}}4p$$