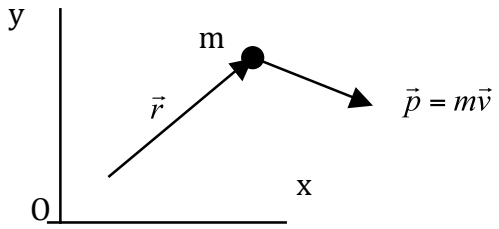
SJP QM 3220 3D 1

<u>Angular Momentum</u> (warm-up for H-atom)
Classically, angular momentum defined as (for a 1-particle system)

$$\vec{L} \equiv \vec{r} \times \vec{p} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$



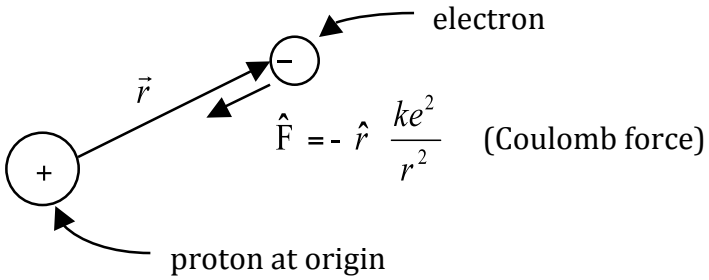
Note: $\vec{L}$ defined w.r.t. an origin of coords.

$$\vec{L} = \hat{x}\,(yp_z - zp_y) + \hat{y}\,(zp_x - xp_z) + \vec{z}\,(xp_y - yp_z)$$

(In QM, the operator corresponding to L_x is $\vec{L}_x = \hat{y}\,\hat{p}_z - \hat{z}\,\hat{p}_y$, $p_z = \frac{\hbar}{i}\frac{\partial}{\partial z}$, etc.
according to prescription of Postulate 2, part 3.)

Classically, torque defined as $\vec{\tau} \equiv \vec{r} \times \vec{F}$, and $\vec{\tau} = \frac{d\vec{L}}{dt}$ (rotational version of $\vec{F} = m\vec{a}$)
If the force is radial (central force), then $\vec{\tau} = \vec{r} \times \vec{F} = 0 \Rightarrow \vec{L} = const$.

H-atom:



In a multi-particle system, total average momentum:

$\vec{L}_{tot} = \sum_i \hat{L}_i$ is conserved for system <u>isolated</u> from <u>external</u> torques.
sum over particles

Internal torques can cause exchange of average momentum among particles, but $\vec{L}_{tot}$ remains constant.

In classical and quantum mechanics, only 4 things are conserved:
- energy
- linear momentum
- angular momentum
- electric charge

Back to QM. Define vector operator $\hat{\vec{L}}$

operator → $\hat{L}_x\hat{x} + \hat{L}_y\hat{y} + \hat{L}_z\hat{z}$ ← unit vector

$\hat{\vec{L}} = \hat{L}_x\hat{x} + \hat{L}_y\hat{y} + \hat{L}_z\hat{z}$

Recall $\frac{d\langle Q\rangle}{dt} = \frac{i}{\hbar}\left\langle \left[\hat{\mathcal{H}}, \hat{Q}\right]\right\rangle$

$$\Rightarrow \quad \underbrace{\frac{d\langle \hat{L}\rangle}{dt}} = \frac{i}{\hbar}\left\langle \left[\hat{\mathcal{H}}, \hat{\vec{L}}\right]\right\rangle$$

$$\frac{d<L_x>}{dt}\hat{x} + \frac{d<L_y>}{dt}\hat{y} + \ldots$$

Claim: for a central force such as in H-atom

$V = V(r) = -ke^2/r$, then $\left[\hat{\mathcal{H}}, \hat{L}\right] = 0$ (will show this later)

This implies $\frac{d\vec{L}}{dt} = 0$ (just like in classical mechanics)

Angular momentum of electron is H-atom is constant, so long as it does not absorb or emit photon. Throughout present discussion, we ignore interaction of H-atom w/photons.

Will show that for H-atom or for any atom, molecule, solid – any collection of atoms – the angular momentum is quantized in units of $\hbar$. $|\vec{L}|$ can only change by integer number of $\hbar$'s.

Units of $L = [L] = [\hbar]$

Note $[L] = [rp]$, $[p] = \left[\frac{\hbar}{r}\right]$ (since $p = \hbar k$)

$\Rightarrow [\mathrm{L}] = [r] \times \left[\frac{\hbar}{r}\right] = [\hbar]$ ✔

Claim: $\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z$

and $\boxed{\left[\hat{L}_i, \hat{L}_j\right] = i\hbar\hat{L}_k}$ (i, j, k cyclic:
x y z or
y z x or
z x y)

To prove, need two very useful identities: $[A+B,C]=[A,C]+[B,C]$
$[AB,C]=A[B,C]+[A,C]B$

Proof: $[L_x,L_y]=[yp_z-zp_y,zp_x-xp_z]=$

$$\underbrace{[yp_z,zp_x]}_{y\underbrace{[p_z,z]}_{-i\hbar}p_x}-\underbrace{[yp_z,xp_z]}_{0}-\underbrace{[zp_y,zp_x]}_{0}+\underbrace{[zp_y,xp_z]}_{x\underbrace{[z,p_z]}_{+i\hbar}p_y}=$$

all other terms like $[y, p_x] = 0$

$$=+i\hbar(xp_y-yp_x)=i\hbar L_z$$

(Have used $[x,p_x]=i\hbar$, $[x,y]=0$, $[x,p_y]=0$, $[p_x,p_y]=0$, etc.

I'm dropping the ˆ over operators when no danger of confusion.

Since $[L_x, L_y] \neq 0$, cannot have simultaneous eigenstates of $\hat{L}_x$ and $\hat{L}_y$.

$$\sigma_{L_x}^2\sigma_{L_x}^2 \geq \left(\frac{1}{2i}\underbrace{\left\langle[\hat{L}_x,\hat{L}_y]\right\rangle}_{i\hbar\langle\hat{L}_z\rangle}\right)^2=\left(\frac{\hbar}{2}\right)^2\langle L_z\rangle^2$$

However, $L^2=\vec{L}\cdot\vec{L}=L_x^2+L_y^2+L_z^2$ does commute with L_z.

Claim: $[L^2,L_z]=0$

$$\boxed{[L^2,L_i]=0}\quad, \text{i = x, y, or z}$$

Proof: $[L^2,L_z]=[L_x{}^2,L_z]+[L_y{}^2,L_z]+\underbrace{[L_z{}^2,L_z]}_{0}$

$$=L_x\underbrace{[L_x,L_z]}_{-i\hbar L_y}+\underbrace{[L_x,L_z]}_{-i\hbar L_y}L_x+L_y\underbrace{[L_y,L_z]}_{+i\hbar L_x}+\underbrace{[L_y,L_z]}_{+i\hbar L_x}L_y$$

= 0 (Note cancellations)

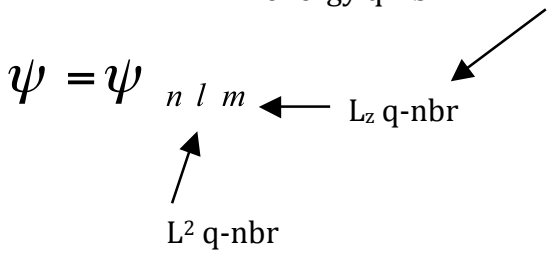
$[L^2, L_z] = 0$ => can have simultaneous eigenstates of $\hat{L}^2,\hat{L}_z$ (or $\hat{L}^2$, $\hat{L}_i$ any i)

Looking forward to H-atom:

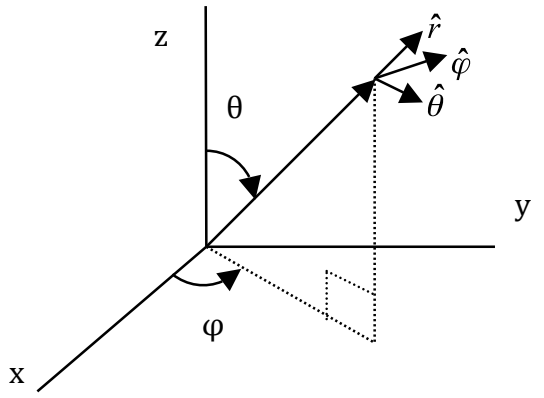
$$\hat{\mathcal{H}} = -\frac{\hbar}{2m}\nabla^2(\ ) + V(r)\cdot(\ )$$

We will show that $\left[\hat{\mathcal{H}}, \hat{L}^2\right] = 0$, $\left[\hat{\mathcal{H}}, \hat{L}_z\right] = 0$

=> simultaneous eigenstates of $\hat{\mathcal{H}}$, $\hat{L}^2$, $\hat{L}_z$



When we solve the TISE □ ψ = E ψ for the H-atom, the natural coordinates to use will be spherical coordinates: r, θ, φ (not x, y, z)



x = r sin θ cos φ
y = r sin θ sin φ
z = r cos θ

Just rewriting $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ in spherical coordinates is gawd-awful. But separation of variables will give special solutions, energy eigenstates, of form

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

The angular part of the solution Y (θ, φ) will turn out to be eigenstates of L^2, L_z and will have form completely independent of the potential V(r).

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Given only $[L^2, L_z] = 0$ and $\hat{L}^2$, $\hat{L}_z$ hermitean we know there must exist simultaneous eigenstates f (which will turn out to be the Y (θ, φ) mentioned above) such that

$$\hat{L}^2 f = \lambda \cdot f \quad , \quad \hat{L}_z f = \mu \cdot f$$

(λ will be related to *l*, and μ will be related to *m*)

We will show that *f* will depend on quantum-numbers *l, m*, so we write it as f_l^m, and that

★

$$\boxed{\begin{aligned} & L^2 f_l^m = \hbar^2 l(l+1) \cdot f_l^m \\ & L_z f_l^m = \hbar m \cdot f_l^m \\ & \text{where } l = 0, \tfrac{1}{2}, 1, \tfrac{3}{2}, \ldots \qquad m = -l, -l+1, \ldots l-1, l \end{aligned}}$$

$f_l^m = Y_l^m(\theta, \varphi)$ will be determined later.

Notice max eigenvalue of L_z (= $l\hbar$) is smaller than square root of eigenvalue of $L^2 = \hbar\sqrt{l(l+1)}$

So, in QM, $L_z < |L|$ Odd!

Also notice *l* = 0, *m* = 0 state has <u>zero</u> angular momentum ($L^2 = 0$, $L_z = 0$) so, unlike Bohr model, can have electron in state that is "just sitting there" rather than revolving about proton in H-atom.

Proof of boxed ★ formulae: (This proof takes 2 ½ pages!)

Define $L_+ = L_x + i L_y$ = "raising operator"

$L_- = L_x - i L_y$ = "lowering operator"

(Note $L_+^\dagger = L_-$, $L_-^\dagger = L_+$, $A^\dagger$ = hermitean adjoint of A)

Neither L_+ or L_- are hermitean (self-adjoint).

Note $\left[L^2, L_\pm\right] = 0$ $\left(\left[L^2, L_+\right] = \underbrace{\left[L^2, L_x\right]}_{0} + i \underbrace{\left[L^2, L_y\right]}_{0} = 0 \right)$

=> Consider *f*: $L^2 f = \lambda \cdot f \quad , \quad L_z f = \mu \cdot f$

Claim: $g = L_+ f$ is an eigenfunction of L_z with eigenvalue = $(\mu + \hbar)$. So L_+ operator raises eigenvalue of L_z by 1 $\hbar$.

Proof: $L^2 g = L^2(L_+ f) = L_+(L^2 f) = \lambda \cdot L_+ f = \lambda \cdot g$ ✓

To prove $L_z g = (\mu + \hbar)\, g$, need to show that $[L_z, L_+] = \hbar L_+$

$$\left[L_z, L_x + iL_y\right] = \underbrace{\left[L_z, L_x\right]}_{i\hbar L_y} + i\underbrace{\left[L_z, L_y\right]}_{-i\hbar L_x} = \hbar\underbrace{\left(L_x + iL_y\right)}_{L_+} \quad ✓$$

Now $L_z g = \underbrace{L_z(L_+ f)}_{L_+ L_z + \hbar L_+} = L_+ \underbrace{L_z f}_{\mu f} + \hbar L_+ f = \left(\mu + \hbar\right) L_+ f$

$$= \left(\mu + \hbar\right) g \quad ✓$$

So, operating on f with raising operator L_+ raises eigenvalues of L_Z by 1$\hbar$ but keeps eigenvalue of L^2 unchanged.

(Similarly, L_- lowers eigenvalue of L_z by 1$\hbar$.)

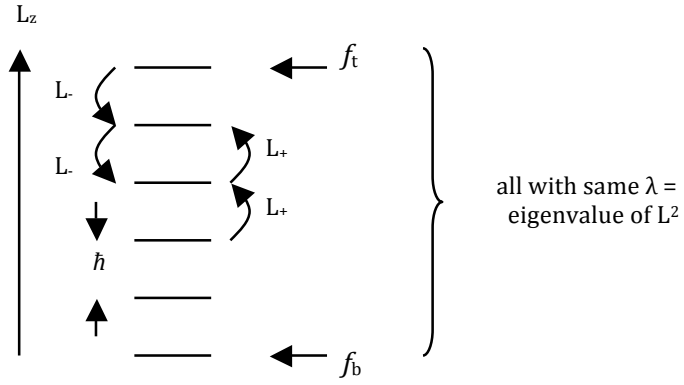
Operating repeatedly with L_+ raises eigenvalue of L_z by $\hbar$ each time: L_+ ($L_+ f$) has $(\mu + 2\hbar)$ etc.

But eigenvalue of L_z cannot increase without limit since $\langle L_z \rangle$ cannot exceed $\sqrt{\langle L^2 \rangle}$

$$\underbrace{\langle L^2 \rangle}_{\lambda} = \underbrace{\langle L_x^2 \rangle}_{\mu^2} + \underbrace{\langle L_y^2 \rangle}_{\geq 0} + \underbrace{\langle L_z^2 \rangle}_{\geq 0} \Rightarrow \lambda > \mu^2,$$

$$\lambda > |\mu|$$

There is only one way out. There must be for a given λ a "top state" f_t for which $L_+ f_t = 0$.
Likewise, there must be for a given λ a "bottom state" f_b for which $L_- f_b = 0$.



Write $L_z f = m\hbar \cdot f$, m changes by integers only

$L_z f_t = \ell \hbar \cdot f_t$, ℓ = max value of m

$L^2 f_t$ = ? Want to write L^2 in terms of L_+, L_z:

$$L_- L_+ = (L_x - iL_y)(L_x + iL_y) = \underbrace{L_x^2 + L_y^2}_{L^2 - L_z^2} + i\underbrace{[L_x, L_y]}_{i\hbar L_z}$$

$$\Rightarrow \quad L^2 = L_- L_+ + L_z^2 + \hbar L_z$$

(Also, $L^2 = L_+ L_- + L_z^2 - \hbar L_z$)

$$\Rightarrow \quad L^2 f_t = \underbrace{L_- L_+ f_t}_{0} + \underbrace{L_z^2 f_t}_{\hbar^2 \ell^2 f_t} + \underbrace{\hbar L_z f_t}_{\hbar^2 \ell f_t} = \hbar^2 \ell(\ell+1) f_t$$

So, $L^2 f = \underbrace{\hbar^2 \ell(\ell+1)}_{\lambda} f$ where ℓ = max m, same λ for all m's.

Repeat for f_b: $L_z f_b = \hbar \bar{\ell} f_b$, $\bar{\ell}$ = min value of m.

$$L^2 f_b = \underbrace{L_+ L_- f_b}_{0} + \underbrace{L_z^2 f_b}_{\hbar^2 \bar{\ell}^2 f_b} + \underbrace{\hbar L_z f_b}_{-\hbar^2 \bar{\ell} f_b} = \underbrace{\hbar^2 \bar{\ell}(\bar{\ell}-1)}_{\lambda} f_b$$

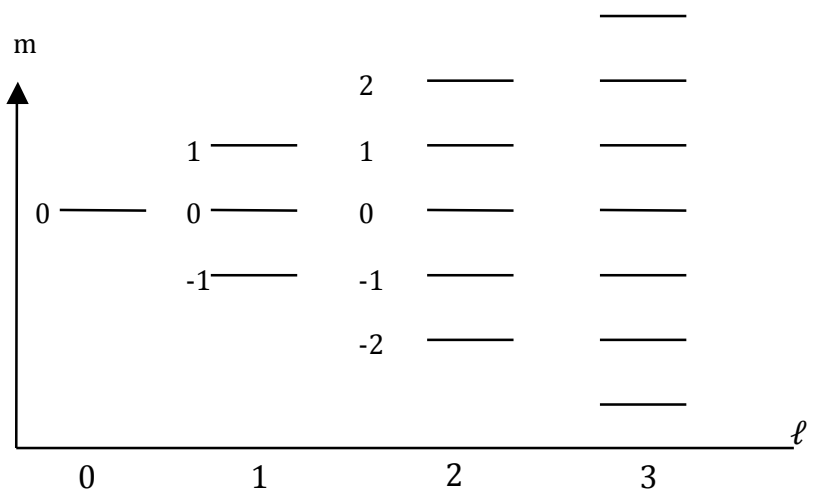
$\lambda = \lambda \Rightarrow \ell(\ell+1) = \bar{\ell}(\bar{\ell}-1) \Rightarrow \bar{\ell} = -\ell$ (try it!)

So $m_{min} = - m_{max}$ and m changes only in units of 1.

$$\Rightarrow m = \underbrace{-\ell, -\ell+1, \ldots \ell-2, \ell-1, \ell}_{\text{N integer steps}}$$

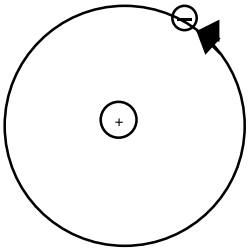
=> $2\ell = N$, $\ell = N / 2$ => $\ell = 0, 1/2, 1, 3/2, 2, 5/2, \ldots$

End of proof of ★



We'll see later that there are 2 flavors of angular momentum:

1. Orbital
Ang. Mom.
(integer ℓ only)

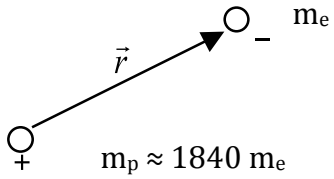


2. Spin
Ang. Mom.
(integer or ½ integer OK)

The H- atom

$m_p >> m_e$ =>

proton (nearly) <u>stationary</u>



Hamiltonian of electron $= \hat{\mathcal{H}} = \frac{\hat{\vec{p}}^2}{2m} + V(r)$

$V(r) = \frac{-ke^2}{r}$, $k = 1/4\pi\varepsilon_0$ (or $V(r) = \frac{-kZe^2}{r}$)

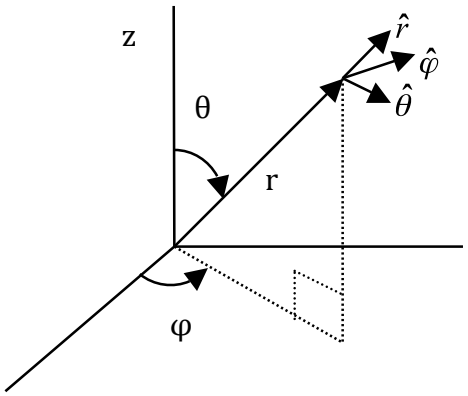
$\frac{\hat{\vec{p}}^2}{2m} = \frac{\hat{\vec{p}}^2 \cdot \hat{\vec{p}}^2}{2m} = \frac{-\hbar^2}{2m}\nabla^2(\ )$

TISE: $\hat{\mathcal{H}}\psi_n = E_n\psi_n \Rightarrow$ <u>special</u> solutions (stationary states).

$\psi_n(x) = \psi_n(x,t) = \psi_n(x)e^{-iE_nt/\hbar}$

General Solution to TDSE: $\Psi(x,t) = \sum_n c_n e^{-iE_nt/\hbar}\psi_n(x)$

Spherical Coordinate System:



z = r cos θ
x = r sin θ cos φ
y = r sin θ sin φ

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

Normalization: $\int dV|\psi|^2 = 1$ (volume)

$$\int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\varphi\, r^2 \sin\theta |\psi|^2 = 1$$

Need ∇^2 in spherical coordinates

Hard Way: $\nabla^2 f = \nabla\cdot\nabla f = \frac{\partial^2 f}{\partial x^2} + \ldots$

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial r}\frac{\partial r}{\partial x} + \frac{\partial f}{\partial \theta}\frac{\partial \theta}{\partial x} + \frac{\partial f}{\partial \varphi}\frac{\partial \varphi}{\partial x} = g$$

$$\frac{\partial^2 f}{\partial x^2} = \frac{\partial g}{\partial x} = \frac{\partial g}{\partial r}\frac{\partial r}{\partial x} + \ldots \text{ (nightmare!)}$$

Also need 9 derivatives: $\frac{\partial r}{\partial x}$, $\frac{\partial r}{\partial y}$ … $\frac{\partial \theta}{\partial x}$…

Easier Way: Curvilinear coordinates (See Boas)

path element:

$$d\vec{s} = \hat{x}dx + \hat{y}dy + \hat{z}dz$$

$$= \hat{r}dr + \hat{\theta}\, r\, d\theta + \hat{\varphi}\, r \sin\theta\, d\varphi$$

$$= \hat{e}_1 h_1\, dx_1 + \hat{e}_2\, h_2\, dx_2 + \hat{e}_3 h_3\, dx_3$$

$$= \sum_{i=1}^{3} \hat{e}_i h_i\, dx_i \quad (\mathrm{h_i} = \text{"scale factor"})$$

$$\nabla f = \sum_{i=1} \hat{e}_i \frac{1}{h_i}\frac{\partial f}{\partial x_i}$$

$$\nabla^2 f = \frac{1}{h_1 h_2 h_3}\left[\frac{\partial}{\partial x_1}\left(\frac{h_2 h_3}{h_1}\frac{\partial f}{\partial x_1}\right) + \frac{\partial}{\partial x_2}\left(\frac{h_1 h_3}{h_2}\frac{\partial f}{\partial x_2}\right) + \ldots\right]$$

Spherical coordinates: $\{x_i\} = \{r,\ \theta,\ \varphi\}$
$\{h_i\} = \{1,\ r,\ r\sin\theta\}$

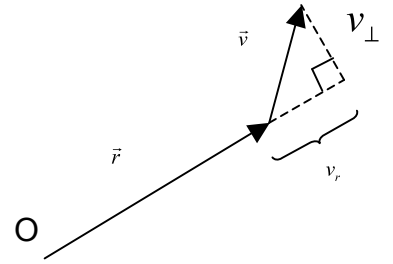
$$\Rightarrow \nabla^2 f =$$

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

$$= \text{(radial)} + \frac{1}{r^2}\text{(angular)}$$

In Classical Mechanics (CM), KE = $p^2/2m$ = KE = (radial motion KE) + (angular, axial motion KE)

$$\left|\hat{L}\right| = \left|\vec{r} \times m\vec{v}\right| = mrv_\perp \quad (\Rightarrow v_\perp = L/mr)$$



$$\mathrm{KE} = \frac{1}{2}mv^2 = \frac{m}{2}(v_r^2 + v_\perp^2) = \underbrace{\frac{p_r^2}{2m}}_{\text{radial}} + \underbrace{\frac{L^2}{2mr^2}}_{\frac{1}{r^2}\times \text{angular}}$$

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Same splitting in QM:

$$\hat{L}^2 = \left(\frac{\hbar}{i}\vec{r}\times\nabla\right)^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

(Notice $\hat{L}^2$ depends only on θ, φ and not r.)

$$\hat{\mathcal{H}}\psi = \frac{-\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\cdot\psi$$

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

Separation of Variables! (as usual)
Seek special solution of form:

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

Normalization: $\int dV\,|\psi|^2 =$

$$\underbrace{\int_0^\infty dr\,r^2|R|^2}_{1}\cdot\underbrace{\int_0^\pi d\theta\int_0^{2\pi}d\varphi\,\sin\theta\,|Y|^2}_{1} = 1$$

(Convention: normalize radial, angular parts individually)

Plug $\psi = R\cdot Y$ into TISE =>

$$\frac{-\hbar^2}{2m}\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{R}{2mr^2}\hat{L}^2Y + V\cdot R\cdot Y = E\cdot R\cdot Y$$

Multiply thru by $\frac{-2mr^2}{\hbar^2}\frac{1}{R\cdot Y}$:

$$\underbrace{\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}(V-E)\right\}}_{f(r)} = \underbrace{\frac{1}{\hbar^2 Y}\hat{L}^2Y}_{g(\theta,\varphi)}$$

=> $f(r) = g(\theta,\varphi)$ = constant C = $\ell(\ell+1)$

$$\hat{L}^2Y = \hbar^2\,C\cdot Y = \hbar^2\ell(\ell+1)Y$$ (Page H-5)

Have separated TISE into radial part $f(r) = \ell(\ell+1)$, involving V(r), and angular part $g(\theta, \varphi) = \ell(\ell+1)$ which is independent of V(r).
=> All problems with spherically symmetric potential (V = V(r)) have exactly same angular part of solution: Y = Y(θ, φ) called "spherical harmonics".

We'll look at angular part later. Now, let's examine

Radial SE: $\left(\times -\frac{\hbar^2}{2mr} \cdot R \right)$

$$\frac{-\hbar^2}{2mr}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + r\cdot R(V-E) = \frac{-\hbar^2\cdot rR}{2mr^2}\ell(\ell+1)$$

Change of variable: u (r) = r · R(r)

$$\left(\int_0^\infty dr\,|u|^2 = 1\right)$$

Can show that $\frac{1}{r}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) = \frac{d^2u}{dr^2}$:

$$\frac{du}{dr} = R + r\frac{dR}{dr}, \qquad \frac{d^2u}{dr^2} = \frac{dR}{dr} + \frac{dR}{dr} + r\frac{d^2R}{dr^2}$$

same!

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

$$\boxed{\frac{-\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu}$$

Notice: identical to 1D TISE:

$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dr^2} + V\cdot\psi = E\psi$ <u>except</u>

r: 0 -> ∞ instead of x: - ∞ -> + ∞ and

V(x) replaced with $\boxed{V_{eff} = V(r) + \frac{\hbar^2}{2mr^2}\ell(\ell+1)}$

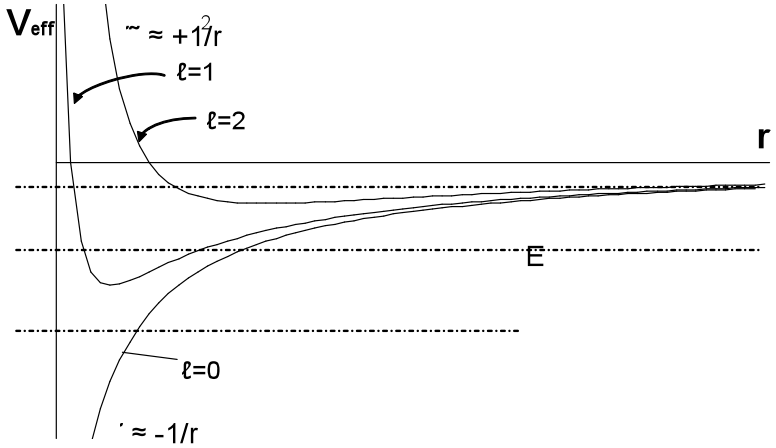
V_{eff} = "effective potential"

Boundary conditions:

u (r = ∞) = 0 from normalization $\int dr\, |u|^2 = 1$

u (r = 0) = 0, otherwise $R = \frac{u}{r}$ blows up at r=0 (subtle!)

$$V(r) = -\frac{A}{r},\ V_{eff} = -\frac{A}{r} + \frac{B}{r^2}$$



Notice that energy eigenvalues given by solution to radial equation alone.

Seek bound state solutions E < 0

E > 0 solutions are unbound states, scattering solutions

Full solution of radial SE is very messy, even though it is effectively a 1D problem (different problem for each ℓ)

Power series solution (see text for details). Solutions depend on 2 quantum numbers: n and ℓ (for each effective potential ℓ = 0, 1, 2, … have a set of solutions labeled by index n.)

Solutions: n = 1, 2, 3, …
ℓ = 0, 1, … (n - 1) } for given n ℓ_{max} = (n – 1)

n = "principal quantum number"

energy eigenvalues depend on n only (it turns out)

$$E_n = \frac{E_1}{n^2}\ ,\ E_1 = -\frac{m(ke^2)^2}{2\hbar^2}$$ (independent of ℓ)

- same as Bohr model, agrees with experiment!

First few solutions: $R_{n\ell}(r)$

normalization "Bohr radius"

$$R_{10} = A_{10}e^{-r/a_0}, \quad a_0 = \hbar^2/\kappa m e^2 = 4\pi\varepsilon_0\hbar^2/me^2$$

$$R_{20} = A_{20}\left(1 - \frac{r}{2a_0}\right)e^{-r/2a_0}$$

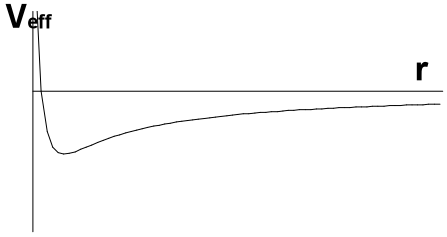
$$R_{21} = A_{21}\left(\frac{r}{a_0}\right)e^{-r/2a_0}$$

NOTE:

- for $\ell = 0$ (s states), R (r = 0) ≠ 0 => wavefunction ψ "touches" nucleus.
- for $\ell \neq 0$, R (r = 0) = 0 => ψ does not touch nucleus.

$\ell \neq 0$ => electron has angular momentum. Same as classical behavior, particle with non-zero L cannot pass thru origin $(\vec{L} = \vec{r} \times \vec{p} : r = 0 \Rightarrow p = \infty)$

Can also see this in QM: for $\ell \neq 0$, V_{eff} has infinite barrier at origin = > u(r) must decay to zero at r=0 exponentially.



=> exponential decay in $R(r) = \frac{u(r)}{r}$ as well.

Back to angular equation: $\hat{L}^2 Y_l^m = \hbar^2 \ell(\ell+1) Y_\ell^m$ Want to solve for the Y_ℓ^m's - "spherical harmonics". Before, started with commutation relations,

$$\left[\hat{L}_i, \hat{L}_j\right] = i\hbar \hat{L}_k \ , \ \left[L^2, L_i\right] = 0$$

and, using operator algebra, solved for the eigenvalues of L^2, L_z. We found

$$\left.\begin{aligned} L^2 Y_\ell^m &= \hbar^2 \ell(\ell+1) Y_\ell^m \\ L_z Y_\ell^m &= m\hbar Y_\ell^m \end{aligned}\right\} \quad \text{where } \ell = 0, \tfrac{1}{2}, 1, 3/2, \ldots \quad m = -\ell, -\ell+1 \ldots +\ell$$

In the process, we defined raising and lowering operators:

$$\hat{L}_\pm = \hat{L}_x \pm \hat{L}_y$$

$$\hat{L}_+ Y_\ell^m = c_m Y_\ell^{m+1} \qquad (\text{for } m < m_{max} = \ell)$$

$$\hat{L}_- Y_\ell^m = c_m Y_\ell^{m-1} \qquad (\text{for } m > m_{min} = \ell)$$

(c_m is some constant)

$$\hat{L}_+ f_{top} = \hat{L}_+ Y_\ell^\ell = 0 \text{ and } \hat{L}_- Y_\ell^{-\ell} = 0$$

So, if we can find (for a given ℓ) a single eigenstate Y_ℓ^m , then we can generate all the others (other m's) by repeated application of $\hat{L}_+$ or $\hat{L}_-$.

$Y_\ell^m = Y_\ell^m(\theta, \varphi)$.

It's easy to find the φ-dependence; don't need the $\hat{L}_\pm$ business yet.

$\hat{L}_z = \dfrac{\hbar}{i}\dfrac{\partial}{\partial\varphi}$ (showed in HW)

$\hat{L}_z Y = \dfrac{\hbar}{i}\dfrac{\partial Y}{\partial\varphi} = \hbar m Y$ (and you can cancel the $\hbar$)

Assume $Y(\theta, \varphi) = \Theta(\theta)\ \Phi(\varphi) \ \Rightarrow$

$$\frac{d\Phi}{d\varphi} = im\ \Phi \quad \Rightarrow \quad \boxed{\Phi(\varphi) = e^{+im\varphi}}$$

If we assume (postulate) that ψ is single-valued than

$$\Phi(\varphi + 2m) = \Phi(\varphi) \Rightarrow e^{im2\pi} = 1$$

=> m = 0, ± 1, ± 2, ... But m = - ℓ, ... + ℓ

So for orbital angular momentum, ℓ must be integer only: ℓ = 0, 1, 2, ... (throw out ½ integer values)

*

(algebra!)

$$L_+ = L_x + iL_y \quad = \quad \hbar e^{i\varphi}\left(\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right)$$

$$L_- = L_x - iL_y \quad = \quad \hbar e^{-i\varphi}\left(-\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\varphi}\right)$$

($L_- = L_+^\dagger$ ← adjoint $\left\langle f\middle|A^\dagger g\right\rangle = \left\langle Af\middle|g\right\rangle$)

Can deduce Y_ℓ^m from $\hat{L}_+ Y_\ell^\ell = 0$

=> $$\frac{\partial Y_\ell^\ell}{\partial\theta} + i\cot\theta\frac{\partial Y_\ell^\ell}{\partial\varphi} = 0$$

$$\boxed{Y_\ell^\ell(\theta,\varphi) = (\sin\theta)^\ell\ e^{i\ell\varphi}}$$ Solution: (un-normalized)

Checks: Plug back in.

$$\ell(\sin\theta)^{\ell-1}\cos\theta\, e^{i\ell\varphi} + i\cot\theta(\sin\theta)^\ell(i\ell)e^{i\ell\varphi} = 0$$

$$\ell(\sin\theta)^\ell\underbrace{\frac{\cos\theta}{\sin\theta}}_{\cot\theta} - \cot\theta(\sin\theta)^\ell\cdot\ell = 0 \quad ✓$$

Now, can get other Y_ℓ^m's by repeated application of $\hat{L}_-$. Somewhat messy (HW!)

Normalization from $\int d\theta\int d\varphi\sin\theta\ \left|Y_\ell^m\right|^2$

Notice case $\ell = 0$ $\boxed{Y_0^0 = \text{const} = 1/\sqrt{4\pi}}$:

(since $\int_0^\pi d\theta\int_0^{2\pi} d\varphi\sin\theta = \int d\Omega = 4\pi$)

Example:

$$Y_1^1 = -\sqrt{\frac{3}{8\pi}}\sin\theta e^{+i\varphi}$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_1^{-1} = +\sqrt{\frac{3}{8\pi}}\sin\theta e^{-i\varphi}$$

Convention on ± sign: $Y_\ell^{-m} = (-1)^m\left(Y_\ell^m\right)^*$

The spherical harmonics form a complete, orthonormal set (since eigenfunctions of hermitean operators)

$$\int d\Omega \; (Y_\ell^m)^* \, Y_{\ell'}^{m'} \;=\; \delta_{\ell\ell'} \, \delta_{mm'}$$

Any function of angles $f = f(\theta, \varphi)$ can be written as linear combo of Y_ℓ^m's :

$$f(\theta,\varphi) \;=\; \sum_{\ell=0}^{\infty} \; \sum_{m=-\ell}^{+\ell} Y_\ell^m$$

Likewise: $\int_0^\infty dr\, r^2 (R_{n\ell})^* \, R_{n'\ell'} = \delta_{nn'} \delta_{\ell\ell'}$

=> H-atom <u>energy</u> <u>eigenstates</u> are

$$\psi_{n\ell m}(r,\theta,\varphi) \;=\; R_{n\ell}(r) Y_\ell^m(\theta,\varphi) \;=\; R_{n\ell} \Theta_{\ell m} e^{im\varphi}$$

n = 1, 2, … ; ℓ = 0, 1 … (n-1) ; m = -ℓ … + ℓ

Arbitrary (bound) state is

$$\psi \;=\; \sum_{n,\ell,m} c_{n\ell m} \cdot \psi_{n\ell m} \qquad \text{(c's are any complex constants)}$$

energy of state (n, ℓ, m) depends only on n.

E_n = - constant/n^2 (states ℓ, m with same n are <u>degenerate</u>)

		ℓ = 0	1	2	3
n=	4	4 (1)	4p (3)	4d (5)	4f (7)
	3	3	3p	3d	
	2	2	2p		
	1	1			

Degeneracy of n^{th} level is n^2
($2 \bullet n^2$ if you include spin)

Radial Probability Density

$$\int dV|\psi|^2 = 1$$

Prob (find particle in dV about $\vec{r}$) = $|\psi(\vec{r})|^2 dV$

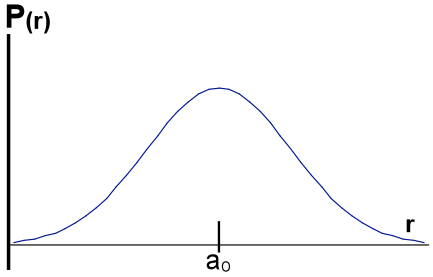
If $\ell = 0$, $\psi = \psi(r)$ then $\int dV|\psi|^2 = \int dr 4\pi r^2 |\psi(r)|^2$

Prob (find in r → r + dr) = $\boxed{P(r)dr = 4\pi r^2 |\psi(r)|^2 dr}$

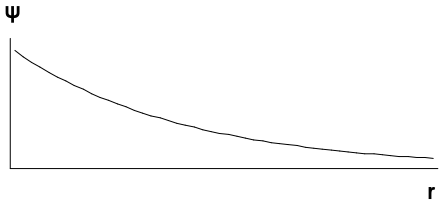
P(r) = radial probability density

Ground state: $\psi_{100} = Ae^{-r/a_0}$

$P(r) = |A|^2 4\pi r^2 e^{-2r/a_0}$



Notice P(r) very different from ψ(r):



If $\ell \neq 0$, $\psi = \psi(r, \theta, \varphi) = R(r)\, Y(\theta, \varphi)$, then

$$\int dV|\psi|^2 = \underbrace{\int dr\, r^2 |R|^2}_{1} \quad \underbrace{\int d\Omega |Y|^2}_{1} = 1$$

"solid angle"

Prob (find in r → r + dr) = $r^2 |R|^2 dr$

$\boxed{P(r) = r^2 |R|^2}$ even if $\ell \neq 0$

Note: $\psi = \psi(r) = R \cdot Y = R \cdot \frac{1}{\sqrt{4\pi}} \Rightarrow |R|^2 = 4\pi|\psi|^2$ if

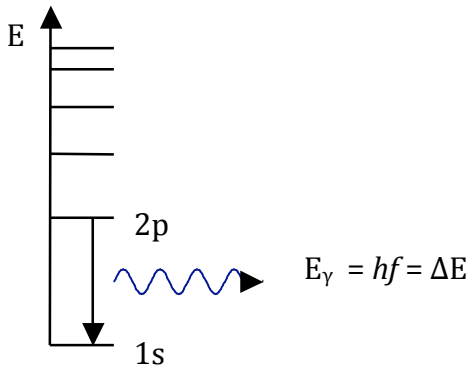
so $P(r) = r^2|R|^2 = 4\pi\, r^2|\psi|^2$

H-atom and emission/absorption of radiation:

If H-atom is in excited state (n = 2, ℓ = 1, m = 0) then it is in energy eigenstate = <u>stationary</u> state. If atom is <u>isolated</u>, then atom should remain in state ψ_{210} <u>forever</u>, since stationary state has simple time dependence:

$$\Psi(\vec{r},t) = \psi_{210}(r) \cdot e^{-eE_2 t/\hbar}$$

But, experimentally, we find that H-atom emits photon and de-excites: ψ_{210} -> ψ_{100} in ≈ 10^{-7} s -> 10^{-9} s



The reason that the atom does not remain in stationary state is that it is not truly isolated. The atom feels a fluctuating EM field due to "vacuum fluctuations". Quantum Electrodynamics is a relativistic theory of the QM interaction of matter and light. It predicts that the "vacuum" is not "empty" or "nothing" as previously supposed, but is instead a seething foam of virtual photons and other particles. These vacuum fluctuations interact with the electron in the H-atom and slightly alter the potential V(r). So eigenstates of the coulomb potential are not eigenstates of the actual potential: $V_{coulomb} + V_{vacuum}$

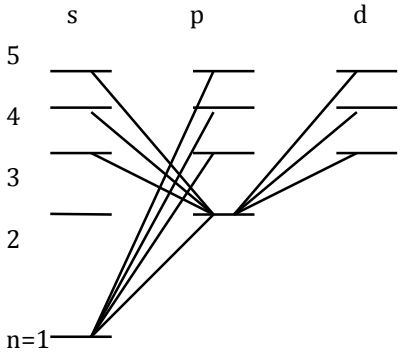
Photons possess an intrinsic angular momentum (spin) of 1 $\hbar$, meaning

$$\ell = 1 \Rightarrow \left|\vec{L}\right| = \hbar\sqrt{\ell(\ell+1)} = \sqrt{2}\hbar$$

$$\text{and } L_{z_{max}} = \hbar$$

So when an atom absorbs or emits a single photon, its angular momentum must change by 1 $\hbar$, by Conservation of Angular Momentum, so the orbital angular momentum quantum number ℓ must change by 1.

"Selection Rule": $\Delta\ell = \pm 1$ in any process involving emission or absorption of 1 photon => allowed transitions are:



If an H-atom is in state 2s (n = 2, $\ell = 0$) then it cannot de-excite to ground state by emission of a photon. (since this would violate the selection rule). It can only lose its energy (de-excite) by collision with another atom or via a rare 2-photon process.

Matrix Formulation of QM

complete orthonormal set

$$|\psi\rangle = \sum_n c_n |n\rangle \quad , \qquad |\psi\rangle \to \{c_n\} = \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \\ c_n \\ \vdots \end{pmatrix}$$

$$|u_1\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix} \quad |u_2\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix}$$

$$|\psi\rangle = \sum_n c_n |u_n\rangle \to \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{pmatrix} = c_1 \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix} + c_2 \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix} + \cdots$$

If ket's are represented by column vectors, then bra's are represented by the transpose conjugate of column = row, complex conjugate.

$$|\psi\rangle = \sum_n c_n |u_n\rangle \to \langle\psi| = \sum_n c_n^* \langle u_n|$$

$$\langle\psi| = \begin{pmatrix} c_1^* & c_2^* & c_3^* & \ldots \end{pmatrix}$$

$$\langle\psi|\psi\rangle = \begin{pmatrix} c_1^* & c_2^* & c_3^* & \ldots \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ \vdots \end{pmatrix} = |c_1|^2 + |c_2|^2 + \ldots = \sum_n |c_n|^2$$

Operators can be represented by matrices:

no hat on matrix element

$$\hat{A} \to \{A_{mn}\} = \left\{ \langle m | \hat{A} n \rangle \right\} = \begin{pmatrix} A_{11} & A_{12} & \cdots \\ A_{21} & A_{22} & \\ \vdots & & \end{pmatrix}$$

where {| n >} is some complete orthonormal set.

Why is that? Where does that matrix come from?

Consider the operator $\hat{A}$ and 2 state vectors $|\psi\rangle, |\varphi\rangle$ related by

$$|\varphi\rangle = \hat{A}\,|\psi\rangle \qquad (\ \star\ )$$

In basis {| n >} ,

$$|\psi\rangle = \sum_n c_n |n\rangle \;=\; \sum_n |n\rangle \underbrace{\langle n|\psi\rangle}_{c_n}$$

$$|\varphi\rangle = \sum_n d_n |n\rangle \;=\; \sum_n |n\rangle \underbrace{\langle n|\varphi\rangle}_{d_n}$$

Now project equation ☆ onto | m > by acting with bra:

$$\langle m|\varphi\rangle \;=\; \langle m|\hat{A}|\psi\rangle \;=\; \sum_n c_n \langle m|\hat{A}|n\rangle$$

$$d_n = \sum_n A_{mn}\, c_n$$

But, this is simply the rule for multiplication of matrix × column.

$$\begin{pmatrix} d_1 \\ d_2 \\ d_3 \\ \vdots \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} & \cdots \\ A_{21} & A_{22} & \\ & & \\ \vdots & & \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \\ \vdots \end{pmatrix}$$

So there you have it, that's why the operator is defined as this matrix, in this basis!

Now, suppose $\hat{A} = \hat{\mathcal{H}}$ and $\{|\mathrm{n}\rangle\}$ are energy eigenstates, then

$$\hat{\mathcal{H}}|n\rangle \;=\; E_n|n\rangle, \qquad \hat{\mathcal{H}}_{mn} = \langle m|\hat{\mathcal{H}}|n\rangle = E_n \delta_{mn}$$

$$\hat{\mathcal{H}}|2\rangle \;=\; E_2|2\rangle \Rightarrow \begin{pmatrix} E_1 & & & 0 \\ & E_2 & & \\ & & E_3 & \\ 0 & & & \ddots \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix} \;=\; E_2 \begin{pmatrix} 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix}$$

A matrix operator $\langle m|\hat{A}|n\rangle$ is <u>diagonal</u> when represented in the basis of its own eigenstates, and the diagonal elements are the eigenvalues.

Notice that in general operators don't commute $\hat{A}\hat{B} \neq \hat{B}\hat{A}$. Same goes for Matrix Multiplication: $\mathbb{A}\ \mathbb{B} \neq \mathbb{B}\ \mathbb{A}$

Claim: The matrix of a hermitian operator is equal to its transpose conjugate:

$$\boxed{\hat{A} \text{ hermitian} \Leftrightarrow \; A_{mn} = A^*_{nm}}$$

Proof:

$$\langle m|\hat{A}n\rangle = \langle \hat{A}m|n\rangle = \langle n|\hat{A}m\rangle^*$$

$$\Rightarrow A_{mn} = A^*_{nm}$$

Similarly, adjoint (or "Hermitian conjugate") $\hat{A}^\dagger$: $A^\dagger_{mn} = A^*_{nm}$

Proof:

$$\langle \hat{A}m|n\rangle = \langle m|\hat{A}^\dagger n\rangle = \langle n|\hat{A}m\rangle^*$$

Of course, it's difficult to do calculations if the matrices and columns are infinite dimensional. But there are Hilbert subspaces that are finite dimensional. For instance, in the H-atom, the full space of bound states is spanned by the full set {n, ℓ, m} (= | nℓm>). The sub-set {n=2, ℓ=1, m = +1, 0, -1} forms a vector space called a subspace.

Subspace? In ordinary Euclidean space, any plane is a subspace of the full volume. If we consider just the xy components of a vector $\vec{R}_{xy} = \hat{x}R_x + \hat{y}R_y$, then we have a perfectly valid 2D vector space, even though the "true" vector is 3D.

Likewise, in Hilbert space, we can restrict our attention to a subspace spanned by a small number of basis states.

Example: H-atom subspace {n=2, ℓ=1, m = +1, 0, -1}

Basis states are $\{|m\rangle\} = |+1\rangle,\ |0\rangle,\ |-1\rangle$ (can drop n=2, ℓ=1 in label since they are fixed.)

$$\hat{L}_z|m\rangle = \hbar\, m|m\rangle$$

$$\hat{L}^2|m\rangle = \hbar^2 \ell(\ell+1)|m\rangle \quad (\ell = 1) \quad = \quad 2\hbar^2|m\rangle \text{ (for all m)}$$

$$\Rightarrow (L_z)_{mn} = \langle m|\hat{L}_z|n\rangle = \hbar \begin{pmatrix} +1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$L^2_{mn} = \langle m|\hat{L}^2|n\rangle = 2\hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

(What about L_x? L_y?)

Before seeing what all this matrix stuff is good for, let's examine spin because it's very important physically and because it will lead to 2D Hilbert space with simple 2 x 2 matrices.

Review of Dirac Bra - Ket Notation

bracket or inner-product:

$$\langle f|g\rangle = \int dx f^*(x) g(x) \text{ or } \int dV f^*(\vec{r}) g(\vec{r}) \text{ or } d\Omega\ (\theta, \varphi) \ldots$$

Which integral you do depends on the configuration space of problem.

Key defining properties of bracket:

- $\langle f | g \rangle^* = \langle g | f \rangle$ c = constant
- $\langle f | c \bullet g \rangle = c \langle f | g \rangle$, $\langle c \bullet f | g \rangle = c^* \langle f | g \rangle$
- $\langle \alpha | (b | \beta \rangle + c | \gamma \rangle) = b \langle \alpha | \beta \rangle + c \langle \alpha | \gamma \rangle$

Dirac proclaims: $\langle g | f \rangle$ = $\langle g |$ next to $| f \rangle$
bracket = "bra" and "ket"

Ket $| f \rangle$ represents vector in H-space (Hilbert Space)

"ket" "wavefunction"
$|\psi\rangle$ is to $\psi(x)$ as $\vec{R}$ is to (R_x, R_y, R_z)

Both ψ and ψ(x) describe same state, but $|\psi\rangle$ is more general:

$$\psi(x_0) = \langle x_0 | \psi \rangle \qquad g_{x_0} = \delta(x - x_0)$$

$$\Phi(p) = \langle p | \psi \rangle \qquad f_p = \frac{1}{\sqrt{}} e^{ipx/\hbar}$$

$$\{c_n\} = \{ \langle u_n | \psi \rangle \} \qquad \hat{H} u_n = E_n u_n$$

Different "representations" of same H=space vector $|\psi\rangle$

 position-representation, momentum-rep, energy-rep.

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What is a "bra"? < g | is a new kind of mathematical object, called a "functional".

$$\langle g| \_ = \int dx\, g^*(x)\, \_$$

Insert state function here

	input	output
function:	number	number
operator:	function	function
functional:	function	numbe

< g | wants to bind with | f > to produce inner product < g | f >

For every ket | f > there is a corresponding bra < f |. Like the kets, the bra's form a vector space.

- | c f > ⟷ < c f | = c^* < f |
- | α f + β g > ⟷ < α f + β g | = α^* < f | + β^* < g | (?)
- < α f + β g | h > = α^* < f | h > + β^* < g | h > ✓

Complex number × bra = another bra
any linear combo of bra's = another bra
} => bra's form vector space

The vector space of bras is called a "dual space". It's the dual of the ket vector space.

$\hat{A}|f\rangle = |\hat{A}f\rangle$ is a ket. What is the corresponding bra? $|\hat{A}f\rangle \to \langle \hat{A}f| = \langle f|A^\dagger$ ← Def'n of $A^\dagger$

Definition: hermitean conjugate or adjoint $A^\dagger$ of operator $\hat{A}$ ($\hat{A}^\dagger$ = "A - dagger")
$\langle \hat{A}f|g\rangle \equiv \langle f|A^\dagger g\rangle$ for all *f, g*.
(If $\hat{A} = A^\dagger$, then $\hat{A}$ is hermitean or self-adjoint.)
Some properties:

- $(\hat{A}\hat{B})^\dagger = \hat{B}^\dagger \hat{A}^\dagger$
- $(\hat{A}^\dagger)^\dagger = \hat{A}$

$$\left[\text{Proof}: \langle f|(\hat{A}^\dagger)^\dagger g\rangle = \langle \hat{A}^\dagger f|g\rangle = \right.$$
$$\left. \langle g|\hat{A}^\dagger f\rangle^* = \langle \hat{A}g|f\rangle^* = \langle f|\hat{A}f\rangle \right]$$

✓

The adjoint of an operator is analogous to complex conjugate of a complex number:

$c^{**} = c$, $\hat{A}^{\dagger\dagger} = \hat{A}$

$c^{*} = c \Rightarrow c$ real, $\hat{A}^{\dagger} = \hat{A} \Rightarrow \hat{A}$ hermitean.

The "ket-bra" | f > < g | is an operator. It turns a ket (function) into another ket (function):

$$\left(|f\rangle\langle g| \right) |h\rangle = |f\rangle \langle g|h\rangle$$

Projection Operators

$$\hat{\mathcal{H}}\, u_n(x) = E_n u_n(x) \rightarrow \hat{\mathcal{H}}|n\rangle = E_n|n\rangle$$

$$\psi(x) = \sum_n c_n u_n(x) = \sum_n \langle u_n|\psi\rangle\, u_n(x) \rightarrow$$

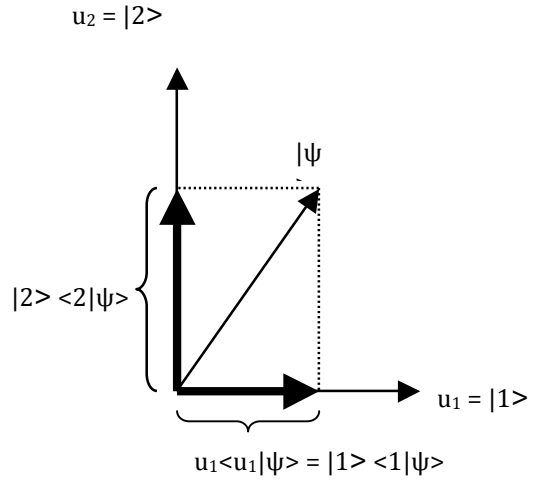
$$|\psi\rangle = \sum_n c_n|n\rangle = \sum_n \langle n|\psi\rangle\, |n\rangle = \sum_n |n\rangle \langle n|\psi\rangle$$

$\boxed{\sum_n |n\rangle\langle n| = \hat{1}}$ => "Completeness relation" (discrete spectrum case)

$\boxed{\hat{P}_n = |n\rangle\langle n|}$ = "projection operator"

$\hat{P}_n$ picks out portion of vector | ψ > that lies along | n >

$$\hat{P}_n\, |\psi\rangle = |n\rangle\, \langle n|\psi\rangle = c_n|n\rangle$$



$|n\rangle\langle n|$ is like $\hat{x}\,(\hat{x}\cdot\_)$

$\hat{x}\left(\hat{x}\cdot\vec{R}\right) = \hat{x}R_x$

$|\psi\rangle = \sum_n |n\rangle\langle n|\psi\rangle$ like $\vec{R} = \hat{x}\left(\vec{x}\cdot\vec{R}\right) + \hat{y}\left(\hat{y}\cdot\vec{R}\right)$

$\hat{\mathbf{1}} = \sum_n |n\rangle\langle n|$ like $\mathbf{1} = \hat{x}(\vec{x}\cdot\_\,) + \hat{y}(\hat{y}\cdot\_\,)$

Anywhere there is a vertical bar in the bracket, or a ket or a bra, we can replace the bar with $1 = \sum_n |n\rangle\langle n|$

Example: $\langle\psi|\psi\rangle = 1$

=> $\sum_n \langle\psi|n\rangle\langle n|\psi\rangle = 1 \Rightarrow \sum_n c_n^* c_n = \sum_n |c_n|^2 = 1$

If eigenvalue spectrum is continuous (as for $\hat{x}$ or $\hat{p}$) then must use integral, rather than sum, over states.

$\boxed{\int \mathrm{dx}\,|x\rangle\langle x| = \hat{\mathbf{1}}}$ Completeness Relation (continuous spectrum)

Example: $\Phi(p) = \langle f_p|\psi\rangle = \int dx \langle f_p|x\rangle\langle x|\psi\rangle = \frac{1}{2\pi\hbar}\int dx\, e^{-ipx/\hbar}\psi(x)$

The Measurement Postulates 3 and 4 can be restated in terms of the projection operator:

Starting with state $|\psi\rangle = \sum_n c_n|n\rangle = \sum_n |n\rangle\langle n|\psi\rangle$,

where sum {n} is over any complete set of states, if we measure observable associated with n, then we will find value n_0 with probability

$P(n_0) = |c_n|^2 = \langle\psi|n_0\rangle\langle n_0|\psi\rangle = \langle\psi|\hat{P}_{n_0}|\psi\rangle$

$\boxed{P(n_0) = \langle\hat{P}_{n_0}\rangle = \langle\psi|\hat{P}_{n_0}|\psi\rangle}$

Probability of finding eigenvalue n0 = expectation value of projection operator $\hat{P}_{n_0}$.

And as result of measurement state | ψ > collapses to state $|n_0\rangle = \hat{P}_{n_0}|\psi\rangle$.

(apart from normalization)

We can now generalize to case of states described by more than one eigenvalue, such as H-atom.

$$\Psi = \sum_{n\ell m} c_{n\ell m}\psi_{n\ell m} \rightarrow |\psi\rangle = \sum_{n\ell m} |n\ell m\rangle\langle n\ell m|\psi\rangle$$

If we measure energy (but not also $|\vec{L}|, L_z$), find n_0, then we are projecting onto subspace spanned by $\{\ell, m\}$ with some n_0.

$$\hat{P}_{n_0} = \sum_{\ell m} |n_0\ell m\rangle\langle n_0\ell m|$$

$$P(n_0) = \langle\psi|\hat{P}_{n_0}|\psi\rangle = \sum_{\ell m} |c_{n_0\ell m}|^2$$

$$\ell = 0, 1 \ldots (n_0 - 1)$$

$$m = -\ell \ldots +\ell$$

State collapses to $\hat{P}_{n_0}|\psi\rangle = \sum_{\ell m} |n_0\ell m\rangle\langle n_0\ell m|\psi\rangle$

must renormalize

Spin ½

Recall that in the H-atom solution, we showed that the fact that the wavefunction $\Psi(r)$ is single-valued requires that the angular momentum quantum # be integer: ℓ = 0, 1, 2.. However, *operator* algebra allowed solutions ℓ = 0, 1/2, 1, 3/2, 2…

Experiment shows that the electron possesses an intrinsic angular momentum called *spin* with ℓ = ½. By convention, we use the letter s instead of ℓ for the spin angular momentum quantum number : s = ½.

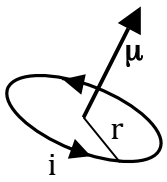
The existence of spin is not derivable from non-relativistic QM. It is not a form of orbital angular momentum; it cannot be derived from $\vec{L} = \vec{r} \times \vec{p}$.

(The electron is a point particle with radius r = 0.)

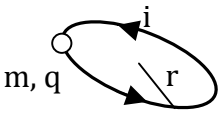
Electrons, protons, neutrons, and quarks all possess spin s = ½. Electrons and quarks are elementary point particles (as far as we can tell) and have no internal structure. However, protons and neutrons are made of 3 quarks each. The 3 half-spins of the quarks add to produce a total spin of ½ for the composite particle (in a sense, ↑↑↓ makes a single ↑). Photons have spin 1, mesons have spin 0, the delta-particle has spin 3/2. The graviton has spin 2. (Gravitons have not been detected experimentally, so this last statement is a theoretical prediction.)

Spin and Magnetic Moment

We can detect and measure spin experimentally because the spin of a charged particle is always associated with a magnetic moment.



Classically, a magnetic moment is defined as a vector $\boldsymbol{\mu}$ associated with a loop of current. The direction of $\boldsymbol{\mu}$ is perpendicular to the plane of the current loop (right-hand-rule), and the magnitude is $\mu = iA = i\pi r^2$.



The connection between orbital angular momentum (not spin) and magnetic moment can be seen in the following classical model: Consider a particle with mass m, charge q in circular orbit of radius r, speed v, period T.

$$i = \frac{q}{T}, \qquad v = \frac{2\pi r}{T} \quad \Rightarrow \quad i = \frac{qv}{2\pi r} \qquad \mu = iA = \left(\frac{qv}{2\pi r}\right)\left(\pi r^2\right) = \frac{qvr}{2}$$

| angular momentum | = $L = p\,r = m\,v\,r$, so $v\,r = L/m$, and $\mu = \frac{qvr}{2} = \frac{q}{2m}L$.

So for a classical system, the magnetic moment is proportional to the orbital angular momentum: $\boxed{\vec{\mu} = \frac{q}{2m}\vec{L} \quad \text{(orbital)}}$.

The same relation holds in a quantum system.

In a magnetic field B, the energy of a magnetic moment is given by

$E = -\vec{\mu}\cdot\vec{B} = -\mu_z B$ (assuming $\vec{B} = B\hat{z}$). In QM, $L_z = \hbar m$.

Writing electron mass as m_e (to avoid confusion with the magnetic quantum number m) and q = –e we have $\mu_z = -\frac{e\hbar}{2m_e}m$, where m = – ⁄.. +⁄ The quantity

$\mu_B \equiv \dfrac{e\hbar}{2m_e}$ is called the Bohr magneton. The possible energies of the magnetic moment in $\vec{B} = B\hat{z}$ is given by $E_{orb} = -\mu_z B = -\mu_B B m$.

For *spin* angular momentum, it is found experimentally that the associated magnetic moment is twice as big as for the orbital case: $\boxed{\vec{\mu} = \dfrac{q}{m}\vec{S} \quad \text{(spin)}}$

(We use S instead of L when referring to spin angular momentum.)

This can be written $\mu_z = -\dfrac{e\hbar}{m_e} m = -2\mu_B m$.

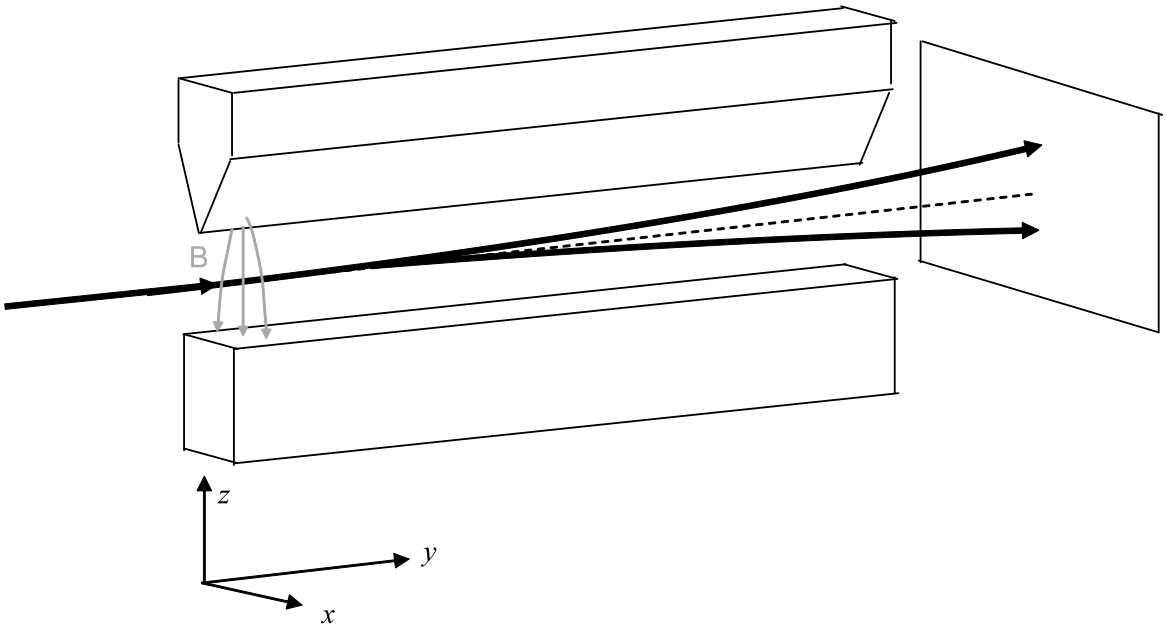
The energy of a spin in a field is $E_{spin} = -2\mu_B B m$ $(m = \pm 1/2)$ a fact which has been verified experimentally.

The existence of spin (s = ½) and the strange factor of 2 in the gyromagnetic ratio (ratio of $\vec{\mu}$ to $\vec{S}$) was first deduced from spectrographic evidence by Goudsmit and Uhlenbeck in 1925.

Another, even more direct way to experimentally determine spin is with a Stern-Gerlach device, next page

(This page from QM notes of Prof. Roger Tobin, Physics Dept, Tufts U.)

Stern-Gerlach Experiment (W. Gerlach & O. Stern, Z. Physik **9**, 349-252 (1922).



$\vec{F} = \vec{\nabla}\left(\vec{\mu} \bullet \vec{B}\right) = (\vec{\mu} \bullet \vec{\nabla})\vec{B}$ (in current free regions), or here, $\vec{F} = \hat{z}(\mu_z \frac{\partial B_z}{\partial z})$ (this is a little crude - see Griffiths Example 4.4 for a better treatment, but this gives the main idea)

Deflection of atoms in z-direction is proportional to z-component of magnetic moment μ_z, which in turn is proportional to L_z. The fact that there are two beams is proof that ℓ = s = ½. The two beams correspond to m = +1/2 and m = –1/2. If ℓ = 1, then there would be three beams, corresponding to m = –1, 0, 1. The separation of the beams is a direct measure of μ_z, which provides proof that $\mu_z = -2\mu_B m$

The extra factor of 2 in the expression for the magnetic moment of the electron is often called the "g-factor" and the magnetic moment is often written as $\mu_z = -g\mu_B m$. As mentioned before, this cannot be deduced from non-relativistic QM; it is known from experiment and is inserted "by hand" into the theory.

However, a relativistic version of QM due to Dirac (1928, the "Dirac Equation") predicts the existence of spin (s = ½) and furthermore the theory predicts the value g = 2. A later, better version of relativistic QM, called Quantum Electrodynamics (QED) predicts that g is a little larger than 2. The g-factor has been carefully measured with fantastic precision and the latest experiments give g = 2.0023193043718(±76 in the last two places). Computing g in QED requires computation of ab infinite series of terms that involve progressively more messy integrals, that can only be solved with approximate numerical methods. The computed value of g is not known quite as precisely as experiment, nevertheless the agreement is good to about 12 places. QED is one of our most well-verified theories.

Spin Math

Recall that the angular momentum commutation relations

$[L^2, L_z] = 0$, $[L_i , L_j] = i\hbar L_k$ (i j k cyclic)

were derived from the definition of the orbital angular momentum operator:

$\vec{L} = \vec{r} \times \vec{p}$.

The spin operator $\vec{S}$ does not exist in Euclidean space (it doesn't have a position or momentum vector associated with it), so we cannot derive its commutation relations in a similar way. Instead we boldly ***postulate*** that the same commutation relations hold for spin angular momentum:

$[S^2, S_z] = 0$, $[S_i , S_j] = i\hbar S_k$. From these, we derive, just a before, that

$$S^2 \left| s\, m_s \right\rangle = \hbar^2 s(s+1) \left| s\, m_s \right\rangle = \frac{3}{4}\hbar^2 \left| s\, m_s \right\rangle \qquad (\text{since } s = ½)$$

$$S_z \left| s\, m_s \right\rangle = \hbar m_s \left| s\, m_s \right\rangle = \pm\frac{1}{2}\hbar \left| s\, m_s \right\rangle \qquad (\text{since } m_s = -s, +s = -1/2, +1/2)$$

Notation: since s = ½ always, we can drop this quantum number, and specify the eigenstates of L^2 , L_z by giving only the m_s quantum number. There are various ways to write this: $\left| s\, m_s \right\rangle = \left| m_s \right\rangle = \begin{matrix} \left| +\tfrac{1}{2} \right\rangle, \left| -\tfrac{1}{2} \right\rangle \\ \left| + \right\rangle, \left| - \right\rangle \\ \left| \uparrow \right\rangle, \left| \downarrow \right\rangle \end{matrix}$

These states exist in a 2D subset of the full Hilbert Space called *spin space*. Since these two states are eigenstates of a hermitian operator, they form a complete orthonormal set (within their part of Hilbert space) and any, arbitrary state in spin space can always be written as $\left| \chi \right\rangle = a \left| \uparrow \right\rangle + b \left| \downarrow \right\rangle = \begin{pmatrix} a \\ b \end{pmatrix}$ (Griffiths' notation is $\chi = a\chi_+ + b\chi_-$)

Matrix notation: $\left| \uparrow \right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $\left| \downarrow \right\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$. Note that $\left\langle \uparrow \middle| \uparrow \right\rangle = \left\langle \downarrow \middle| \downarrow \right\rangle = 1$, $\left\langle \uparrow \middle| \downarrow \right\rangle = 0$

If we were working in the full Hilbert Space of, say, the H-atom problem, then our basis states would be $\left| n\ \ell\ m_\ell\ m_s \right\rangle$. Spin is another degree of freedom, so that the full specification of a basis state requires 4 quantum numbers. (More on the connection between spin and space parts of the state later.)

[Note on language: throughout this section I will use the symbol S_z (and S_x , etc) to refer to both the observable ("the measured value of S_z is $+\hbar/2$ ") and its associated operator ("the eigenvalue of S_z is $+\hbar/2$ ").]

The matrix form of S^2 and S_z in the $\left|m^{(z)}\right\rangle$ basis can be worked out element by element. (Recall that for any operator $\hat{A}$, $A_{mn} = \langle m|\hat{A}|n\rangle$.)

$$\langle\uparrow|S^2|\uparrow\rangle = \frac{3}{4}\hbar^2, \quad \langle\uparrow|S^2|\downarrow\rangle = 0, \text{ etc.} \quad \langle\uparrow|S_z|\uparrow\rangle = +\frac{1}{2}\hbar, \quad \langle\uparrow|S_z|\downarrow\rangle = 0, \text{ etc.}$$

$$\boxed{S^2 = \frac{3}{4}\hbar^2\begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} \qquad S_z = \frac{1}{2}\hbar\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}}$$

Operator equations can be written in matrix form, for instance,

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

We are going ask what happens when we make measurements of S_z, as well as S_x and S_y, (using a Stern-Gerlach apparatus). Will need to know: What are the matrices for the operators S_x and S_y? These are derived from the raising and lowering operators:

$$\begin{aligned} S_+ &= S_x + iS_y \\ S_- &= S_x - iS_y \end{aligned} \quad \Rightarrow \quad \begin{aligned} S_x &= \tfrac{1}{2}(S_+ + S_-) \\ S_y &= \tfrac{1}{2i}(S_+ - S_-) \end{aligned}$$

To get the matrix forms of S_+, S_-, we need a result from the homework:

$$\begin{aligned} S_+|s, m_s\rangle &= \hbar\sqrt{s(s+1) - m(m+1)}\ |s, m_s + 1\rangle \\ S_-|s, m_s\rangle &= \hbar\sqrt{s(s+1) - m(m-1)}\ |s, m_s - 1\rangle \end{aligned}$$

For the case s = ½, the square root factors are always 1 or 0. For instance, s = ½, m = −1/2 gives $s(s+1) - m(m+1) = \tfrac{1}{2}\left(\tfrac{3}{2}\right) - \left(-\tfrac{1}{2}\right)\left(\tfrac{1}{2}\right) = 1$. Consequently,

$S_+|\downarrow\rangle = \hbar|\uparrow\rangle$, $S_+|\uparrow\rangle = 0$ and $S_-|\uparrow\rangle = \hbar|\downarrow\rangle$, $S_-|\downarrow\rangle = 0$, leading to

$\langle\uparrow|S_+|\uparrow\rangle = 0$, $\langle\uparrow|S_+|\downarrow\rangle = \hbar$, etc. and

$$S_+ = \hbar\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix} \qquad S_- = \hbar\begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}$$

Notice that S_+ , S_- are not hermitian.

Using $S_x = \frac{1}{2}(S_+ + S_-)$ and $S_y = \frac{1}{2i}(S_+ - S_-)$ yields

$$S_x = \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \qquad S_y = \frac{\hbar}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}$$

These are hermitian, of course.

Often written: $\vec{S} = \frac{\hbar}{2}\vec{\sigma}$, where $\sigma_x = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}$, $\sigma_y = \begin{pmatrix}0 & i\\ -i & 0\end{pmatrix}$, $\sigma_z = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$ are called the *Pauli spin matrices*.

Now let's make some measurements on the state $|\chi\rangle = a|\uparrow\rangle + b|\downarrow\rangle = \begin{pmatrix}a\\ b\end{pmatrix}$.

Normalization: $\langle\chi|\chi\rangle = 1 \;\Rightarrow\; |a|^2 + |b|^2 = 1$.

Suppose we measure S_z on a system in some state $|\chi\rangle = \begin{pmatrix}a\\ b\end{pmatrix}$.

Postulate 2 says that the possible results of this measurement are one of the S_z eigenvalues: $+\hbar/2$ or $-\hbar/2$. Postulate 3 says the probability of finding, say $-\hbar/2$, is Prob(find $-\hbar/2$) $= \left|\langle\downarrow|\chi\rangle\right|^2 = \left|\begin{pmatrix}0 & 1\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix}\right|^2 = |b|^2$.

Postulate 4 says that, as a result of this measurement, which found $-\hbar/2$, the initial state $|\chi\rangle$ collapses to $|\downarrow\rangle$.

But suppose we measure S_x ? (Which we can do by rotating the SG apparatus.) What will we find? Answer: one of the eigenvalues of S_x, which we show below are the same as the eigenvalues of S_z : $+\hbar/2$ or $-\hbar/2$. (Not surprising, since there is

nothing special about the z-axis.) What is the probability that we find, say, S_x = $+\hbar/2$? To answer this we need to know the eigenstates of the S_x operator. Let's call these (so far unknown) eigenstates $\left|\uparrow^{(x)}\right\rangle$ and $\left|\downarrow^{(x)}\right\rangle$ (Griffiths calls them $\left|\chi_{+}^{(x)}\right\rangle$ and $\left|\chi_{-}^{(x)}\right\rangle$). How do we find these? We must solve the eigenvalue equation: $S_x|\chi\rangle = \lambda|\chi\rangle$, where λ are the unknown eigenvalues. In matrix form this is,

$\begin{pmatrix} 0 & \hbar/2 \\ \hbar/2 & 0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \lambda\begin{pmatrix} a \\ b \end{pmatrix}$ which can be rewritten $\begin{pmatrix} -\lambda & \hbar/2 \\ \hbar/2 & -\lambda \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = 0$. In linear algebra, this last equation is called the characteristic equation.

This system of linear equations only has a solution if

$$\mathrm{Det}\begin{pmatrix} -\lambda & \hbar/2 \\ \hbar/2 & -\lambda \end{pmatrix} = \begin{vmatrix} -\lambda & \hbar/2 \\ \hbar/2 & -\lambda \end{vmatrix} = 0. \quad \text{So } \lambda^2 - (\hbar/2)^2 = 0 \quad \Rightarrow \quad \lambda = \pm\hbar/2$$

As expected, the eigenvalues of S_x are the same as those of S_z (or S_y).

Now we can plug in each eigenvalue and solve for the eigenstates:

$$\frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \frac{\hbar}{2}\begin{pmatrix} a \\ b \end{pmatrix} \Rightarrow a = b \; ; \quad \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = -\frac{\hbar}{2}\begin{pmatrix} a \\ b \end{pmatrix} \Rightarrow a = -b.$$

So we have $\left|\uparrow^{(x)}\right\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ and $\left|\downarrow^{(x)}\right\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$

Now back to our question: Suppose the system in the state $\left|\uparrow^{(z)}\right\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, and we measure S_x. What is the probability that we find, say, $S_x = +\hbar/2$? Postulate 3 gives

the recipe for the answer:

$$\text{Prob}(\text{find } S_x = +\hbar/2) = \left| \left\langle \uparrow^{(x)} | \uparrow^{(z)} \right\rangle \right|^2 = \left| \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right|^2 = \left| \frac{1}{\sqrt{2}} \right|^2 = 1/2$$

Question for the student: Suppose the initial state is an arbitrary state $|\chi\rangle = \begin{pmatrix} a \\ b \end{pmatrix}$

and we measure S_x. What are the probabilities that we find $S_x = +\hbar/2$ and $-\hbar/2$?

Let's review the strangeness of Quantum Mechanics.

Suppose an electron is in the $S_x = +\hbar/2$ eigenstate $\left|\uparrow^{(x)}\right\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$. If we ask: What is the value of S_x? Then there is a definite answer: $+\hbar/2$. But if we ask: What is the value of S_z , then this is no answer. The system *does not possess* a value of S_z. If we measure S_z, then the act of measurement will produce a definite result and will force the state of the system to collapse into an eigenstate of S_z, but that very act of measurement will destroy the definiteness of the value of S_x. The system can be in an eigenstate of either S_x or S_z, but not both.