C. Angular Momentum in Quantum Mechanics: A quick review

- A quantity (general symbol) $\vec{J}$ with components J_x, J_y, J_z; and magnitude squared J^2, for which their operators satisfying the commutation relations

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

(note cyclic pattern) (9)

$$[\hat{J}^2, \hat{J}_x] = 0 \,, \quad [\hat{J}^2, \hat{J}_y] = 0 \,, \quad [\hat{J}^2, \hat{J}_z] = 0$$

is an Angular Momentum in Quantum Mechanics

- AM is defined by the commutation relations (9) in QM
- Can find simultaneous eigenstates of $\hat{J}^2$ and one component (say $\hat{J}_z$)

one label: j another label: m_j

- It follows from (9) alone[+] that the eigenvalues of $\hat{J}^2$ and $\hat{J}_z$ must take on certain values

Let $|j, m_j\rangle$ be simultaneous eigenstates of $\hat{J}^2$ and $\hat{J}_z$

$$\hat{J}^2 |j, m_j\rangle = j(j+1)\hbar^2 \, |j, m_j\rangle$$

with j being — integers $(0, 1, 2, \ldots)$ OR half-integers $(1/2, 3/2, 5/2, \ldots)$ (10)

$$\hat{J}_z |j, m_j\rangle = m_j \hbar \, |j, m_j\rangle$$

with $m_j = \underbrace{j, j-1, \ldots, -j+1, -j}_{(2j+1) \text{ values}}$ for a given value of j

[+] See chapters in PHYS 3021 on Orbital AM, general AM, and Spin AM

- Why bother with General AM?
  - Nature makes use of AM cleverly $\Rightarrow$ Many angular momenta

e.g. simplest atom (Hydrogen atom)

electron has orbital AM ($Y_{\ell m_\ell}(\theta,\phi)$)

electron has spin AM ($|S| = \sqrt{\frac{3}{4}}\hbar$; $S_z = \frac{1}{2}\hbar, -\frac{1}{2}\hbar$)

electron has total AM ($\vec{J} = \vec{L} + \vec{S}$)

proton (nucleus) has spin AM

e.g. Many-electron atoms (all other atoms)

need to consider $\underbrace{\text{adding up spin AM}}_{\text{still an AM}}$ of electrons

$\overbrace{\text{adding up orbital AM}}^{\text{still an AM}}$ of electrons

(a) Orbital Angular Momentum $\vec{L}$

consistent with general result

$$\hat{L}^2 Y_{\ell m_\ell}(\theta,\phi) = \ell(\ell+1)\hbar^2 Y_{\ell m_\ell}(\theta,\phi)$$ with ℓ takes on integers ($\ell = 0, 1, 2, \cdots$)

$$\hat{L}_z Y_{\ell m_\ell}(\theta,\phi) = m_\ell \hbar \, Y_{\ell m_\ell}(\theta,\phi)$$

Reason: Addition B.C. on single-valued wave-function in the angular (θ,ϕ) variables

$$m_\ell = \underbrace{\ell, \cdots, -\ell}_{(2\ell+1) \text{ values}}$$

Physical Effect

$$\vec{\mu}_L = -\frac{e}{2m_e}\vec{L} \quad \text{OR} \quad \boxed{\vec{\mu}_L = -g_L \frac{\mu_B}{\hbar}\vec{L}}$$

$g_L = 1$

magnetic dipole moment due to $\vec{L}$

- $\vec{L}$ depends on the motion of electron

Recall: $\hat{L}_x, \hat{L}_y, \hat{L}_z, \hat{L}^2$ can be expressed explicitly as derivatives w.r.t. θ and ϕ

(b) Spin Angular Momentum $\vec{S}$ of electron

- $\underbrace{\text{Intrinsic}}$ property of electron

  Meaning: Same property for all electrons (anywhere, everywhere)

- S^2 of an electron⁺ is $\left(\frac{3}{4}\hbar^2\right)$ [a constant, true for all electrons]

  (c.f. all electrons have $\underbrace{\text{charge}}$ $(-e)$) another intrinsic property

- $\frac{3}{4}\hbar^2 = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2$

  $= s(s+1)\hbar^2$

$\therefore$ $\boxed{\text{Electron's spin angular momentum is characterized by } s = 1/2}$ (11)

"Electron is a spin-half particle"

$|S| = \sqrt{\frac{3}{4}}\,\hbar$ for all electrons (Magnitude of electron's spin AM)

⁺Recall: Stern - Gerlach experiment

- $S = 1/2 \Rightarrow$ any component (usually $\hat{S}_z$) can take on

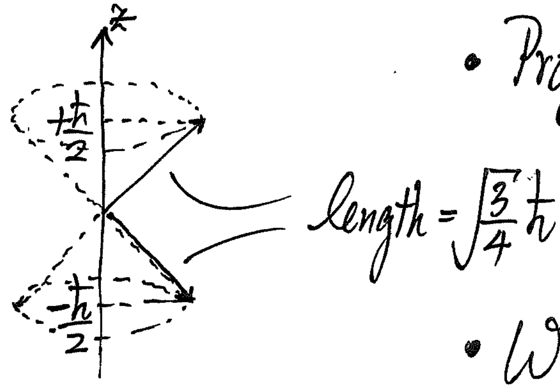
$$\text{either} \quad \underbrace{+\frac{\hbar}{2}}_{m_s = +1/2} \quad \text{OR} \quad \underbrace{-\frac{\hbar}{2}}_{m_s = -1/2} \quad \text{(2 values only)} \qquad (12)$$

$$\underbrace{|s, m_s\rangle}_{} \quad (\text{c.f. } |j, m_j\rangle)$$

$$|s = 1/2, m_s = +1/2\rangle = |1/2, 1/2\rangle \quad \text{"spin-up" OR } \alpha_z$$
$$|s = 1/2, m_s = -1/2\rangle = |1/2, -1/2\rangle \quad \text{"spin-down" OR } \beta_z \qquad (13)$$

Since $s = 1/2$ (always) for all electrons, a short-hand notation is to specify m_s only, i.e. $|m_s = +1/2\rangle$ OR $|m_s = -1/2\rangle$

Vector Model (just for illustrating key features, not to be taken seriously)



- Projection on $\hat{z}$-direction is either $+\frac{\hbar}{2}$ or $-\frac{\hbar}{2}$
- When S_z is certain, S_y and S_x are uncertain.

Mathematical Structure of spin-half particle

$$\hat{S}_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \frac{\hbar}{2}\sigma_x \; ; \quad \hat{S}_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \frac{\hbar}{2}\sigma_y \; ; \quad \hat{S}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \frac{\hbar}{2}\sigma_z \qquad (14)$$

Hence, $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

$\sigma_x, \sigma_y, \sigma_z$: Pauli Matrices

They satisfy the commutation relations.

α_z (spin-up of $\hat{S}_z$) $= \begin{pmatrix} 1 \\ 0 \end{pmatrix}$

β_z (spin-down of $\hat{S}_z$) $= \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

Electron Spin's Story

- Compton† (1921), Pauli† (1924), Goudsmit and Uhlenbeck (1925), Stern† and Gerlach (1922) experiment [† Nobel Laureates]

- In Schrödinger's QM, spin is an "add-on" quantity, i.e. Schrödinger's QM does not give electron spin naturally.

  "spin-up electron in Hydrogen 1s state" $\underbrace{\psi_{100}(r,\theta,\phi)}_{\text{from Schrödinger Eq.}} \cdot \overset{\text{spin up state}}{\alpha_z} \equiv \psi_{100,\underset{m_s}{+1/2}}$

- Dirac (1928) "The Quantum Theory of the Electron"

  gave a relativistic QM (Dirac) Equation, the solution of which for free electron automatically gave the electron its spin angular momentum.

- Spin is a <u>relativistic effect</u>!

D. Spin Magnetic Moment associated with Spin angular Momentum

- Very rough (don't take it seriously) picture
  - electron (charge $-e$) spinning $\Rightarrow$ Magnetic Moment
- From experiments (Stern-Gerlach type for example)

$$\boxed{\vec{\mu}_S = -\frac{e}{m_e}\vec{S}} \qquad (15) \qquad \text{c.f. } \vec{\mu}_L = \frac{-e}{2m_e}\vec{L}$$

Magnetic Moment due to electron's spin AM

charge $(-e)$

spin AM

- Generally, for a particle of spin $\vec{S}$, charge q, and mass m, write

$$\vec{\mu}_S = g_S \frac{q}{2m}\vec{S}$$

with g_S (often simply called the g-factor "g") determined experimentally

- For <u>electron</u>, g is known to great accuracy! $(q = -e,\ m = m_e)$

  $g(\text{electron}) = 2.002\,319\,304\,361\,82$ (NIST, USA)

  $\therefore\ g_s = 2$ is a good approximation

  Thus, $\boxed{\vec{\mu}_s = -\dfrac{e}{m_e}\vec{S} \quad \text{for electron spin}}$ (Take-home message)

- QED (Quantum Electrodynamics) gives highly accurate calculations of $g(\text{electron})$ (the most accurate theory ever!)
  - QED is a <u>Quantum Field Theory</u> (QFT)

QED?
- Dirac Eq. (relativistic QM) → <u>do QM again on Dirac Eq.</u> (Quantizing Dirac Field)
- Maxwell Eqs. (not QM) → <u>do QM on Maxwell's Eqs.</u> (Quantizing EM fields)
- Let the <u>two fields</u> (electrons interact via exchange of photons) <u>interact</u>

- Back to $\vec{\mu}_S = -\frac{e}{m_e}\vec{S}$, $|\vec{\mu}_S| = \frac{e}{m_e}|\vec{S}| = \frac{e}{m_e}\hbar\sqrt{\frac{3}{4}} = \sqrt{3}\,\frac{e\hbar}{2m_e} = \sqrt{3}\,\mu_B$

$\therefore$ $\underbrace{|\vec{\mu}_S|}$ $= \sqrt{3}\,\mu_B$ (<u>always</u>, one value[†] for all electrons' spin AM) (16)

$\boxed{\text{Magnetism in Solids come from electron's spin}}$

- $\mu_{S,z} = \frac{-e}{m_e} S_z$

$\mu_{S,z}$ takes on	
either $\frac{-e}{m_e}\cdot\left(\frac{\hbar}{2}\right)$	or $\frac{-e}{m_e}\left(-\frac{\hbar}{2}\right)$
$= -\mu_B$	$= +\mu_B$
(for $m_s = +\frac{1}{2}$)	(for $m_s = -\frac{1}{2}$)

(17)

- Expect $\vec{\mu}_S$ (like $\vec{\mu}_L$) to have some effects in the presence of $\vec{B}$
[related to Zeeman Effect? see later]

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† This point, looks trivial, is often ignored. But it is this point that makes some materials (e.g. Co, Fe, Ni) <u>magnetic</u>.

E. Total Angular Momentum $\vec{J} = \vec{L} + \vec{S}$

[Two ways of labelling single-particle states]

- Consider solutions to one-particle TISE (e.g. H-atom) for simplicity
- Including electron spin, a state is labelled by the quantum numbers

$$\Big(\underset{\substack{\text{principal}\\ \text{quantum \#}}}{n},\ \underbrace{\ell,\ m_\ell}_{\text{orbital AM}},\ \underbrace{\underset{\text{always } 1/2}{s},\ m_s}_{\text{spin AM}}\Big)$$

OR simply $(n, \ell, m_\ell, \quad m_s)$ $\quad$ ($s = 1/2$ is understood)

e.g. $\psi_{100+\frac{1}{2}}$ OR $\psi_{100\uparrow}$ (1s spin-up state) OR $\psi_{100}(r,\theta,\phi)\cdot\alpha_z$

$\uparrow m_s$

$\psi_{100-\frac{1}{2}}$ OR $\psi_{100\downarrow}$ (1s spin-down state) OR $\psi_{100}(r,\theta,\phi)\cdot\beta_z$

- An alternative and useful labelling scheme is to define the total angular momentum $\vec{J}$

$$\boxed{\vec{J} = \vec{L} + \vec{S}} \quad (18)$$

[an example of adding two angular momenta]

- $\vec{J}$ is an angular momentum

$\therefore$ Eigenvalues of $\hat{J}^2$ must be of the form $j(j+1)\hbar^2$

OR $|\vec{J}|$ (magnitude of $\vec{J}$) $= \sqrt{j(j+1)}\,\hbar$

[new quantum number j] j must be integer OR half-integer (positive)

$\hat{J}_z$ has eigenvalues $m_j\hbar$ OR $J_z = m_j\hbar$

where $m_j = \underbrace{j, j-1, \ldots, -j+1, -j}_{(2j+1)\text{ values}}$ (for given j)

[$\because$ $\vec{J}$ is an angular momentum in QM]

<u>Question:</u> $\vec{L}$ (quantum # ℓ), $\vec{S}$ (quantum # s ($s = \frac{1}{2}$ for electron))

$\vec{J}$ (quantum # j) $\boxed{\text{What are the values of } j\text{ ?}}$

- This is related to adding two AM in QM. It will be treated formally in more advanced QM course.
- Here, we simply state the results and apply them

(19) Rules of getting j values ($s = \frac{1}{2}$ case) — one electron as in H-atom

> Given ℓ, $s = \frac{1}{2}$
>
> j takes on the value(s)
>
> $j = \ell + \frac{1}{2}$ and $j = \ell - \frac{1}{2}$ for $\ell \neq 0$ (thus gives positive j)
>
> $j = \frac{1}{2}$ only for $\ell = 0$ ($\because j$ cannot be negative)

<u>Example</u> (a) p ($\ell=1$) states, $m_\ell = 1, 0, -1$ (3 states ignoring spin) $(2\ell+1)$

with $m_s = +\frac{1}{2}, -\frac{1}{2}$ (6 states including spin)

$(\uparrow)$ $(\downarrow)$

$$\underbrace{(2s+1)}_{2}\cdot\underbrace{(2\ell+1)}_{3} = 6$$

(b) Invoking j: $\ell = 1$, $s = \frac{1}{2}$

$j = \frac{3}{2}$ $\quad$ $j = \frac{1}{2}$

$m_j = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ $\quad$ $\frac{1}{2}, -\frac{1}{2}$

6 states $\displaystyle\sum_{j=\frac{3}{2},\frac{1}{2}} (2j+1) = 6$

(no more, no less)

(a) $(n, \ell=1, s=\frac{1}{2}, m_\ell, m_s)$ labels 6 states

(b) $(n, \ell=1, s=\frac{1}{2}, j, m_j)$ also labels 6 states

Simply different ways of labelling the states

Which way is better? Depending on situation under consideration.
[Do $\vec{L}$ and $\vec{S}$ couple strongly?]

Different labelling of states

(l, m_l, s, m_s)

$l=1 \begin{cases} m_l = 1 \\ m_l = 0 \\ m_l = -1 \end{cases}$

$s=\frac{1}{2}$, (always) $\begin{cases} m_s = +\frac{1}{2} \\ m_s = -\frac{1}{2} \end{cases}$

$\underbrace{(l=1, m_l, s=\frac{1}{2}, m_s)}$

$\Downarrow$

$2\cdot(2l+1)$

$= 6$ combinations

$\Downarrow$

6 p-states

(l, s, j, m_j)

$l=1, \quad s=\frac{1}{2}$

$\Rightarrow j = \overbrace{\frac{3}{2}}, \quad \overbrace{\frac{1}{2}}$

$m_j = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2} \quad \frac{1}{2} \quad -\frac{1}{2}$

$\underbrace{(l=1, s=\frac{1}{2}, j, m_j)}$

$\sum_{j=\frac{1}{2},\frac{3}{2}} (2j+1)$

$= 6$ combinations

[also 6 states]

Ex: How about $\underbrace{l=2 \text{ states}}_{\text{d-states}}$?

A way to "think" what the rule says

- largest $m_\ell = +1$, largest $m_s = +\frac{1}{2}$

  [when $\vec{L}$ tends to be more aligned with $\vec{S}$, the resultant $\vec{J}$ would be longer and thus would give largest J_z corresponding to largest m_j]

  largest $m_j = \left(1 + \frac{1}{2}\right) = +\frac{3}{2}$

  By QM AM properties, there must be $m_j = +\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$ (thus $j = 3/2$)

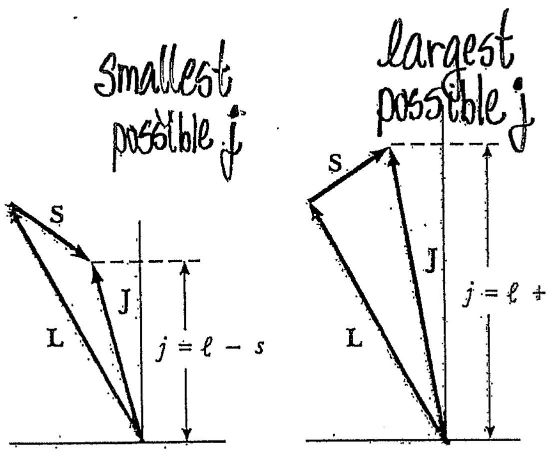
- But there are 6 (p) states. 2 not accounted for.

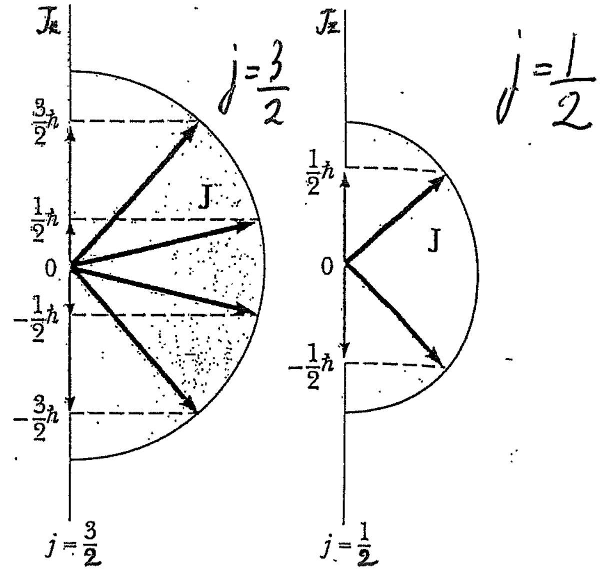
  To account for the 2 remaining states, must be $m_j = \underbrace{+1/2, -1/2}_{\text{2 states}}$,
  so must be $j = 1/2$ (thus $j = 1/2$)

[Ex: Repeat idea for $\ell = 2$ (d) states]

A picture in the Vector model

ℓ and $s = 1/2$





Technically (Optional)

- We are making linear combinations of 6 (p) states labelled by $(n, \ell=1, s=1/2, m_\ell, m_s)$ to form 6 other states, each labelled by $(n, \ell=1, s=1/2, j, m_j)$
  i.e. changing basis

How about Total Magnetic Moment?

$$\vec{L} \to \vec{\mu}_L \quad ; \quad \vec{S} \to \vec{\mu}_s$$

$$\boxed{\begin{aligned} \vec{\mu}_{total} = \vec{\mu}_L + \vec{\mu}_s &= \left(\frac{-e}{2m_e}\vec{L}\right) + \left(\frac{-e}{m_e}\vec{S}\right) \\ &= -\frac{e}{2m_e}\underbrace{(\vec{L} + 2\vec{S})}_{\text{this is NOT } \vec{J}\ (=\vec{L}+\vec{S})!} \qquad (20) \end{aligned}}$$

Key Point ⇓ More work to do!

- Could we take $\vec{\mu}_{total} \propto \vec{J}$, at least approximately[+]?

If so, j could be half-integer and there are $\underbrace{\text{even number of } m_j \text{ states}}_{}$,

Could lead to splitting in spectral line into even number of lines? [anomalous Zeeman effect] (seems OK!)

+ By now, (I hope) you are more comfortable in making approximations

Extensions: Adding Two Angular Momenta (Not necessarily $\vec{L}+\vec{S}$)

- What if adding up two spin-½ angular momenta?

[Why bother? Helium atom: 2 electrons (each spin-½)]

$$\vec{S}_1 = \underbrace{\text{Spin AM \#1}}_{s_1 = 1/2,\ m_{s_1} = \pm 1/2} \quad ; \quad \vec{S}_2 = \underbrace{\text{Spin AM \#2}}_{s_2 = 1/2,\ m_{s_2} = \pm 1/2} \quad [\text{c.f. } \vec{L}\ ;\ \vec{S}]$$

Total Spin Angular momentum $\vec{S} = \vec{S}_1 + \vec{S}_2$ [c.f. $\vec{J} = \vec{L} + \vec{S}$]

$\vec{S}$ is also an AM $\Rightarrow$ $\hat{S}^2$ has eigenvalues $S(S+1)\hbar^2$

$\hat{S}_z$ has eigenvalues $m_S\hbar$, $m_S = S, \cdots, -S$ for given S

$$S = \tfrac{1}{2} + \tfrac{1}{2}\ , \quad \tfrac{1}{2} - \tfrac{1}{2}$$
$$= \quad 1\ , \quad 0$$

[c.f. $\ell + \frac{1}{2}$, $\ell - \frac{1}{2}$, non-negative]

two values of S for adding two spin-½ AM

$S = 1$, $m_s = 1, 0, -1$ ($\therefore$ 3 spin-1 states, called "triplet states")

$S = 0$, $m_s = 0$ ($\therefore$ 1 spin-0 state, called "singlet state")

Total: 4 states

Two spin-½ AMs

$|\underbrace{\tfrac{1}{2}, \tfrac{1}{2}}_{\text{Spin \#1}}; \underbrace{\tfrac{1}{2}\ \tfrac{1}{2}}_{\text{Spin \#2}}\rangle$ (OR $|\uparrow, \uparrow\rangle$); $|\overset{s_1}{\tfrac{1}{2}}, \overset{m_{s_1}}{\tfrac{1}{2}}; \overset{s_2}{\tfrac{1}{2}}, \overset{m_{s_2}}{-\tfrac{1}{2}}\rangle$; $|\tfrac{1}{2} -\tfrac{1}{2}; \tfrac{1}{2}, \tfrac{1}{2}\rangle$; $|\tfrac{1}{2}, -\tfrac{1}{2}; \tfrac{1}{2}, -\tfrac{1}{2}\rangle$

$|\uparrow, \uparrow\rangle$; $|\uparrow, \downarrow\rangle$; $|\downarrow, \uparrow\rangle$; $|\downarrow, \downarrow\rangle$

(there are 4 states)

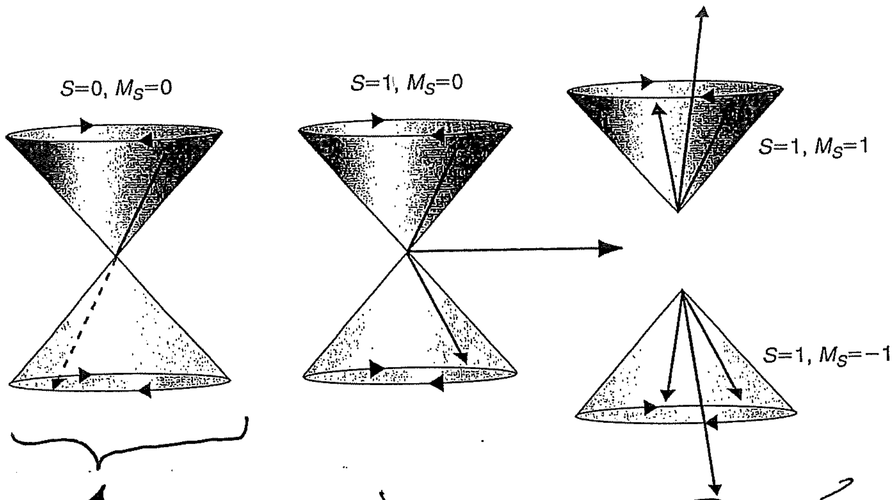
$\therefore$ Using $|s_1, m_{s_1}; s_2, m_{s_2}\rangle$, there are 4 states

Using $|\underset{\frac{1}{2}}{s_1}, \underset{\frac{1}{2}}{s_2}; S, m_s\rangle$, there are 4 states

(always)

no more, no less!

Vector Model



Vector model of the singlet and triplet states. The individual spin angular momentum vectors and their vector sum **S** (black arrow) are shown for the triplet states. For the singlet state (left image), $|\mathbf{S}| = 0$ and $M_S = 0$. The dashed arrow in the left image indicates that the vector on the yellow cone is on the opposite side of the cone from the vector on the blue cone.

Singlet state: Two spin angular momenta tend to be anti-parallel

triplet states: Two spin angular momenta tend to be aligned

- Whether two electrons prefer singlet or triplet state is dependent on the energy (thus Hamiltonian)
- important in understanding the microscopic origin of <u>Magnetism</u>
- important in treating multi-electron atoms

Remark:

- Electrons (fermions) obey Pauli Exclusion Principle
  - may rule out some states

Helium atom ground state:

"S=1, m_s=1" state

"1s" $\uparrow\uparrow$ (No!) $\Rightarrow$ triplet states are Out!

$\therefore$ Must be "S=0, m_s = 0" singlet state

Something like: 1s $\uparrow\downarrow$ (but which electron is up? which is down?)

Helium atom excited states:

2s	$\uparrow$	$\downarrow$	$\uparrow$	$\downarrow$
1s	$\uparrow$	$\uparrow$	$\downarrow$	$\downarrow$

all are legal.

$\Rightarrow$ Singlet (spin) state and Triplet (spin) states are both possible

[Which one has lower energy?]

Extension: What if adding three (more) angular momenta?

- Use the rule repeatedly [add two AMs, then use result and add in third one...]

Extension: $\vec{J} = \vec{L} + \vec{S}$, what if s is not $1/2$?

$\hat{J}^2$ has eigenvalues $j(j+1)\hbar^2$ ($\because \vec{J}$ is an angular momentum)

$$j = \underbrace{l+s}_{\text{maximum value}},\ l+s-1,\ \dots,\ |l-s|+1,\ \underbrace{|l-s|}_{\text{minimum value}}$$ (must be non-negative)

and for given value j, there are $(2j+1)$ values of m_j running through $+j, \dots, -j$

[Ex: Show that # states labelled by l and s is the same as labelled by j and m_j, no more and no less.]

What's next?

- Get back to hydrogen atom (simplest case)
  - an electron (one only) in some $R_{n\ell}(r)Y_{\ell m_\ell}(\theta,\phi)$ state (e.g. 2p, 3d, ...)
  - thus, there is $\vec{L}$
  - an electron has spin AM $\vec{S}$ (spin-1/2) $\Rightarrow \vec{\mu}_s \propto -\vec{S}$
  - $\vec{L} \Rightarrow$ orbital motion $\Rightarrow$ current loop $\Rightarrow$ magnetic field $\vec{B}$
  - thus $-\vec{\mu}_s \cdot \vec{B} \propto \underbrace{\vec{S}\cdot\vec{L}}_{\text{Spin AM - Orbital AM coupled!}}$

This will lead to fine structure (as observed exp'tally)