D. 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

$$\big(\overbrace{\underbrace{n}_{\text{principal quantum \#}},\ \underbrace{\ell,\ m_\ell}_{\text{orbital AM}}}^{\text{spatial}},\ \overbrace{\underbrace{\underbrace{s}_{\text{always } 1/2},\ m_s}_{\text{spin AM}}}^{\text{spin}}\big)$$

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

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

($+\frac{1}{2}$ is 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 <u>define</u> the <u>total angular momentum</u> $\vec{J}$

$$\boxed{\vec{J} = \vec{L} + \vec{S}} \qquad (11)$$

[an example of <u>adding two angular momenta</u>]

- $\vec{J}$ is an <u>angular momentum</u>

$\therefore$ 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 (<u>positive</u>)

$\hat{J}_z$ 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 ($s = 1/2$ 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

(12) Rules of getting j values ($s = 1/2$ case) — one electron as in H-atom

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

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

with $m_s = +1/2, -1/2$ (6 states including spin)

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

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

(b) Invoking j: $l = 1$, $s = 1/2$

[From (12)] → $j = 3/2$ $j = 1/2$

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

6 states (no more, no less) $\sum_{j=3/2,1/2} (2j+1) = 6$

(a) (n, $l=1$, $s=1/2$, m_l, m_s) labels 6 states

(b) (n, $l=1$, $s=1/2$, j, m_j) also labels 6 states

$\boxed{\text{Simply different ways of labelling the states}}$

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)

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

$$s=\tfrac{1}{2}, \quad \begin{cases} m_s = +\tfrac{1}{2} \\ m_s = -\tfrac{1}{2} \end{cases}$$

(always)

$$\underbrace{\left(l=1, m_l, s=\tfrac{1}{2}, m_s\right)}$$

$\Downarrow$

$$2\cdot(2l+1)$$

$= 6$ combinations

$\Downarrow$

6 p-states

(l, s, j, m_j)

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

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

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

$$\underbrace{\left(l=1, s=\tfrac{1}{2}, j, m_j\right)}$$

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

$= 6$ 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 $j = 3/2$)

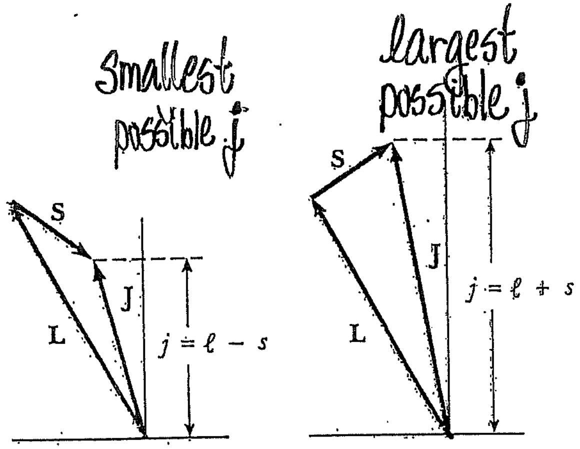
- But there are 6 (p) states. 2 not accounted for.

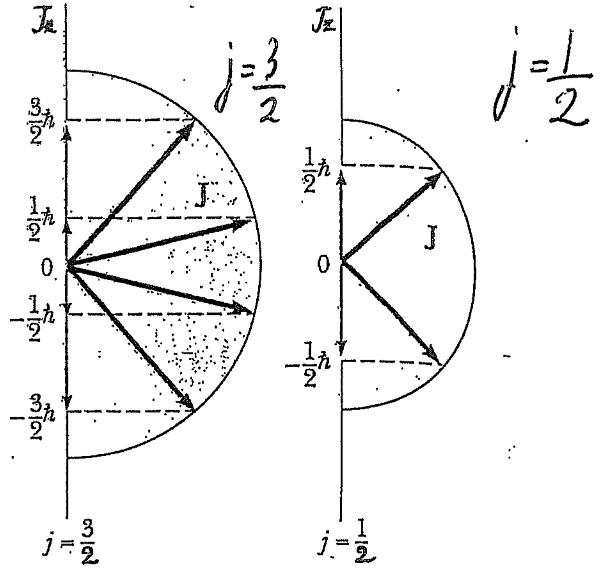
  To account for the 2 remaining states, must be $m_j = \underbrace{+1/2, -1/2}_{2 \text{ states}}$,
  so must be $j = 1/2$ (thus $j = 1/2$)

[Ex: Repeat idea for $l = 2$ (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 $(n, l=1, s=1/2, m_l, m_s)$ to form 6 other states, each labelled by $(n, l=1, s=1/2, j, m_j)$

  i.e. changing basis

  [They are degenerate w.r.t. $\hat{H}_{atom}$ with energy E_{n1}.]

How about Total Magnetic Moment?

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

$$\boxed{\begin{aligned}\vec{\mu}_{total} &= \vec{\mu}_L + \vec{\mu}_S = \left(\frac{-e}{2m_e}\vec{L}\right) + \left(\frac{-e}{m_e}\vec{S}\right) \\ &= -\frac{e}{2m_e}\underbrace{\left(\vec{L} + 2\vec{S}\right)}_{\text{this is NOT } \vec{J}\ (=\vec{L}+\vec{S})\,!} \qquad (13)\end{aligned}}$$

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 even number of m_j states,

$\underbrace{\qquad}_{}$ 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

$$S = \tfrac{1}{2} + \tfrac{1}{2}\ , \quad \tfrac{1}{2} - \tfrac{1}{2} \qquad [\text{c.f. } \ell + \tfrac{1}{2},\ \ell - \tfrac{1}{2},\ \underline{\text{non-negative}}]$$

$$= \quad 1 \quad , \quad 0$$

↑ two values of S when adding up two spin-half angular momenta

$S = 1$, $m_s = 1, 0, -1$ ($\therefore$ 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

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

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

(there are 4 states)

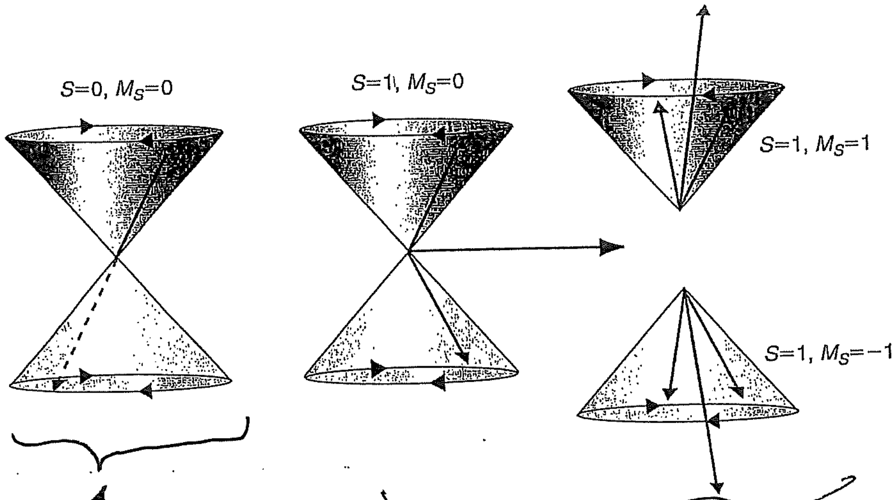
$\therefore$ Using $|s_1, m_{s_1} ; s_2, m_{s_2}\rangle$, there are 4 states

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 Magnetism
- important in treating multi-electron atoms

Remarks:

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

Helium atom ground state:

"1s" $\uparrow\uparrow$ (No!) $\quad$ "$S=1$, $m_s=1$" state $\Downarrow$ 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?]

- When we have <u>Two</u> (or more) electron spins, we have the possibility of quantum entanglement

$$|\uparrow\uparrow\rangle,\ |\downarrow\downarrow\rangle,\ \underbrace{|\uparrow\downarrow\rangle,\ |\downarrow\uparrow\rangle}$$

$$\left.\begin{matrix} |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \\ |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \end{matrix}\right\}\ \text{entangled states}$$

(second quantum revolution)

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 $\frac{1}{2}$?

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

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

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

[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-½) $\Rightarrow \vec{\mu}_S \propto -\vec{S}$
  - $\vec{L} \Rightarrow$ 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)