

Lecture 13: Spin

- Recall that found angular momentum algebra (commutation relations)

$$[J_i, J_j] = i\hbar \epsilon_{ijk} J_k$$

allow $j = \frac{1}{2}n$, $0, \frac{1}{2}, 1, \frac{3}{2}, 2, \dots$

So far only looked at $j \in \mathbb{Z}$, implemented via scalar group of fnc's that transform only through their coord. argument.

$$\Psi(\hat{n}) \xrightarrow{R_{\vec{\theta}}} e^{-\frac{i}{\hbar} \vec{\theta} \cdot \vec{L}} \Psi(\hat{n}) = \Psi(R_{\vec{\theta}} \hat{n})$$

$\approx (1 - \frac{i}{\hbar} \vec{\theta} \cdot \vec{L}) \Psi(\hat{n})$ implemented via a differential operator acting on single fnc $\Psi(\hat{n})$

$$\vec{\theta} = \epsilon \hat{z} \quad = (1 - \frac{i}{\hbar} \epsilon \partial_{\phi}) \Psi(\theta, \phi)$$

- How do we realize states with half integer j ? Cannot do it with single-valued fnc of coordinate; recall $e^{im\phi} \xrightarrow{2\pi} e^{im(\phi+2\pi)} = (e^{im2\pi}) e^{im\phi}$

Answer: introduce many-component state: $m \in \mathbb{Z}$.

$$\Psi_{\sigma}(\theta, \phi), \quad \sigma = 1, 2, 3, \dots, n$$

$$\Psi(\theta, \varphi) \rightarrow \Psi_\sigma(\theta, \varphi) = \begin{pmatrix} \Psi_1(\theta, \varphi) \\ \Psi_2(\theta, \varphi) \\ \vdots \\ \Psi_n(\theta, \varphi) \end{pmatrix}$$

↑
Spinor

- has continuous coordinates θ, φ & discrete coordinate $\sigma = 1, 2, \dots, n$.

- Generalized unitary operator on $\Psi_\sigma(\theta, \varphi)$

$$\Psi_\sigma(\theta, \varphi) \xrightarrow{R_{\vec{\varepsilon}}} \sum_{\sigma'} U_{\sigma\sigma'}^s \Psi_{\sigma'}(R_{\vec{\varepsilon}} \hat{n}) = e^{-\frac{i}{\hbar} \vec{\varepsilon} \cdot \vec{L}} \sum_{\sigma'} U_{\sigma\sigma'}^s \Psi_{\sigma'}(\theta, \varphi)$$

$\vec{L}$ only acts on θ, φ coord.

$U_{\sigma\sigma'}^s$ only acts on σ spin coord.

$$U_{\sigma\sigma'} = \underbrace{U^L}_{\text{direct product acting on spinor space}} \otimes U_{\sigma\sigma'}^s = e^{-\frac{i}{\hbar} \vec{\varepsilon} \cdot \vec{L}} e^{-\frac{i}{\hbar} \vec{\varepsilon} \cdot \vec{S}_{\sigma\sigma'}} \uparrow \quad \uparrow$$

act on different spaces & so commute.

$$\Psi_\sigma(\theta, \varphi) \in V_e = V_o \otimes V_s \quad \xrightarrow{J}$$

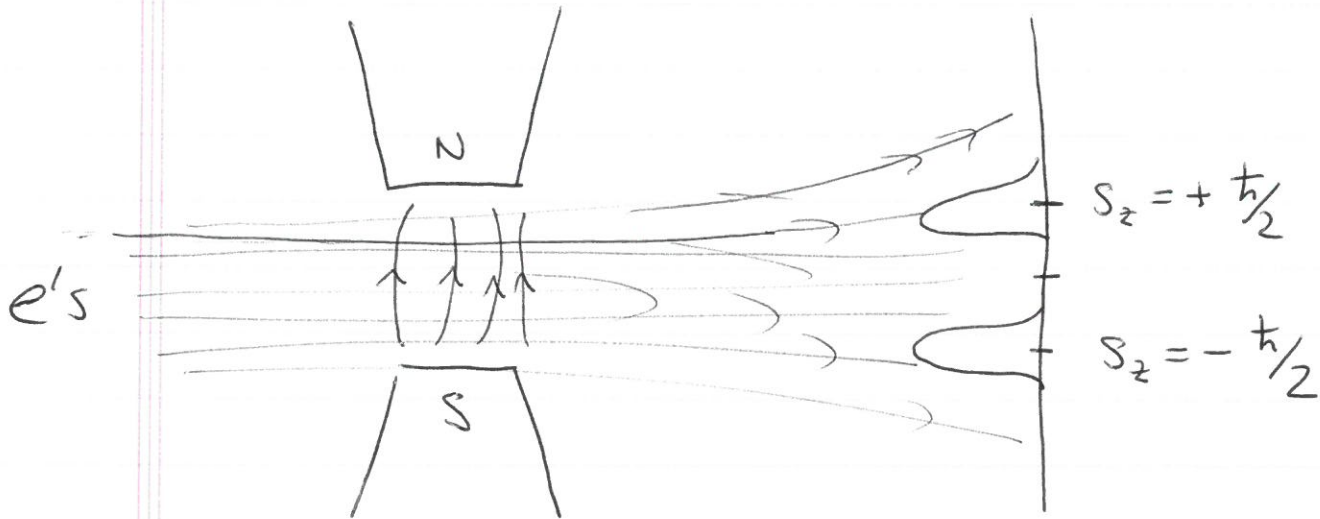
$$U_{\sigma\sigma'} \simeq 1 - \frac{i}{\hbar} \vec{\varepsilon} \cdot (\vec{L} \delta_{\sigma\sigma'} + \vec{S}_{\sigma\sigma'})$$

- Recall for $j = 1/2$, $m_j = \pm 1/2 \rightarrow$ just two states
 $\Rightarrow \vec{S}_{\sigma\sigma'}$ are 2×2 matrices

$$([J_i, J_j] = i\hbar \epsilon_{ijk} J_k; [L_i, L_j] = i\hbar \epsilon_{ijk} L_k; [S_i, S_j] = i\hbar \epsilon_{ijk} S_k)$$

• Why?

A: Stern-Gerlach (and other) experiment demands it! That is electron (and more generally fermions) has $s = \frac{1}{2}$!



$$E = -\gamma \vec{B} \cdot \vec{S} = -\gamma B S_z$$

$$\vec{F} = -\vec{\nabla} E = -\gamma S_z \vec{\nabla} B$$

two spots $\Rightarrow S_z$ takes on only 2 values

$$\Rightarrow S_z = \pm \frac{\hbar}{2}.$$

- Recall j^{th} representation is implementable via $(2j+1) \times (2j+1)$ matrix

$\Rightarrow$ for $j = s = \frac{1}{2} \Rightarrow 2 \times 2$ matrix

simple computation (see hw 7) gives:

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

with $\Psi_a(x, y, z) = \begin{pmatrix} \Psi_+(\vec{r}) \\ \Psi_-(\vec{r}) \end{pmatrix} = \Psi_+(r) \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \Psi_-(r) \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

$$\mathbb{1} \vec{L} |\Psi\rangle = \begin{bmatrix} \vec{L} & 0 \\ 0 & \vec{L} \end{bmatrix} \begin{pmatrix} \Psi_+(\vec{r}) \\ \Psi_-(\vec{r}) \end{pmatrix}$$

$\uparrow$
eigenstates
of $\hat{S}_z$ with
 $S_z = \pm \hbar/2$

- basis for $\forall e$: $|\vec{r}, s_z\rangle = |\vec{r}\rangle \otimes |s = \frac{1}{2}, s_z\rangle$

If $H = H_0 + H_s$

$$\Rightarrow |\Psi(t)\rangle = |\Psi_0(t)\rangle \otimes |\chi_s(t)\rangle$$

where $H_0 |\Psi_0\rangle = E_0 |\Psi_0\rangle$ $\leftarrow$ diff. spin components have independent evolution.
 $H_s |\chi_s\rangle = E_s |\chi_s\rangle$

$$E = E_0 + E_s.$$

• Focus on spinor part for now

$$\rightarrow |s, m\rangle = |1/2, 1/2\rangle \xrightarrow{\text{in } S_z \text{ basis}} \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

$$|s, m\rangle = |1/2, -1/2\rangle \rightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\Rightarrow |\chi\rangle = \alpha |1/2, 1/2\rangle + \beta |1/2, -1/2\rangle \xrightarrow{S_z \text{ basis}} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

$$\langle \chi | \chi \rangle = 1 = |\alpha|^2 + |\beta|^2$$

$$\rightarrow \langle \frac{1}{2} \pm \frac{1}{2} | \vec{S} | \frac{1}{2}, \pm \frac{1}{2} \rangle = \pm \frac{\hbar}{2} \hat{z}$$

more generally eigenstates of

$$(\hat{n} \cdot \vec{S}) | \hat{n}, \pm \rangle = \pm \frac{\hbar}{2} | \hat{n}, \pm \rangle$$

$$| \hat{n}, \pm \rangle = \text{in } \hat{n} \text{ basis} \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$= \text{in } \hat{z} \text{ basis} \begin{pmatrix} \cos \theta/2 \\ e^{+i\varphi} \sin \theta/2 \end{pmatrix}, \begin{pmatrix} \sin \theta/2 \\ -e^{+i\varphi} \cos \theta/2 \end{pmatrix}$$

orthogonal $\psi_{\uparrow}, \psi_{\downarrow}$

$$\langle \hat{n}, + | \hat{n}, - \rangle = 0 \quad \checkmark$$

$$\langle \hat{n} \pm | \vec{S} | \hat{n} \pm \rangle = \pm \frac{\hbar}{2} \hat{n}$$

2 d.o.f. θ, φ .

$$|\chi\rangle = \alpha |1/2, 1/2\rangle + \beta |1/2, -1/2\rangle$$

$$\alpha, \beta \rightarrow 2 \text{ d.o.f. } (2 \text{ complex} \cdot 2 - 1 \text{ (norm)} - 1 \text{ overall phase})$$

$$\Rightarrow \hat{n} \text{ can label a spinor } (s=1/2) \text{ as } | \hat{n}, \pm \rangle.$$

Hence for every spinor $|x\rangle$ (characterized by α, β)

can equivalently characterize

by $\hat{n}$ s.t. $(\hat{n} \cdot \vec{S})|x\rangle = \frac{\hbar}{2}|x\rangle$
 (not so for $j > \frac{1}{2}$)

• Props of $\vec{S} = \frac{\hbar}{2} \vec{\sigma}$

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

$$\sigma_i = (\sigma_x, \sigma_y, \sigma_z); \quad \sigma_\alpha = (\sigma_x, \sigma_y, \sigma_z, \mathbb{1})$$

props of σ 's:

→ traceless, Hermitian

$$\rightarrow [\sigma_i, \sigma_j] = i 2 \epsilon_{ijk} \sigma_k$$

$$\rightarrow [\sigma_i, \sigma_j]_+ = 2 \delta_{ij} \mathbb{1}$$

$$\rightarrow \sigma_i \sigma_j = i \epsilon_{ijk} \sigma_k + \delta_{ij} \mathbb{1} \Rightarrow (\text{Tr } \sigma_\alpha \sigma_\beta = 2 \delta_{\alpha\beta})$$

$$\rightarrow \text{Tr } \sigma_i = 0$$

$$\rightarrow (\vec{a} \cdot \vec{\sigma})(\vec{b} \cdot \vec{\sigma}) = \vec{a} \cdot \vec{b} \mathbb{1} + i(\vec{a} \times \vec{b}) \cdot \vec{\sigma}$$

$$\Rightarrow (\hat{n} \cdot \vec{\sigma})^2 = \mathbb{1}$$

Note: σ_α is a complete set, i.e. any 2×2

matrix $M = \sum_{\alpha=0}^3 C_\alpha \sigma_\alpha$

proof? find C_α : $\text{Tr}(M \sigma_\beta) = \sum_{\alpha} C_\alpha \underbrace{\text{Tr}(\sigma_\alpha \sigma_\beta)}_{2 \delta_{\alpha\beta}}$

$$\Rightarrow \underline{C_\alpha = \frac{1}{2} \text{Tr}(M \sigma_\alpha)}$$



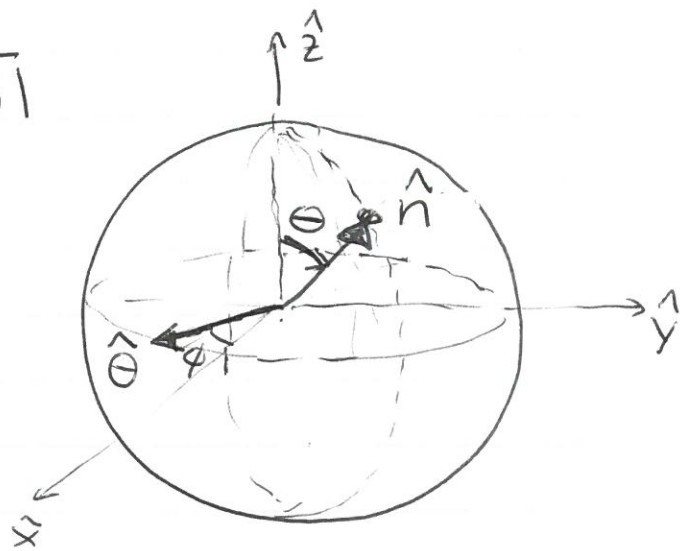
Using props of σ 's can show (see Shankar)

$$U_{R\vec{\theta}} = e^{-\frac{i}{\hbar} \vec{\theta} \cdot \vec{S}} = (\cos \frac{\theta}{2}) \mathbb{1} - i (\sin \frac{\theta}{2}) \hat{\theta} \cdot \vec{\sigma}$$

How does one construct $|\hat{n}, \pm\rangle$?

via $U_{R\vec{\theta}}$ applied to $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$

with $\vec{\theta} = \theta \frac{\hat{z} \times \hat{n}}{|\hat{z} \times \hat{n}|}$



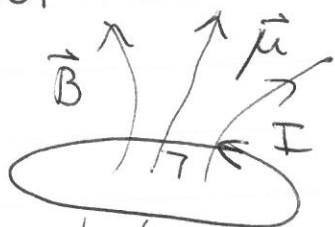
- Spm dynamics: precession

$$\vec{\tau} = \vec{\mu} \times \vec{B} \leftarrow \text{torque of moment } \vec{\mu}$$

$$\Rightarrow H = -\vec{\mu} \cdot \vec{B}$$



→ classically think about current loop



$$\vec{\mu} = \hat{n} I A / c$$

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

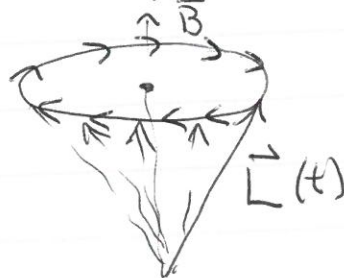
is just the magnetostatic interaction of $\vec{B}$ with current (that itself generates B via Ampere's law) I in the loop.

Note: $I = \frac{qV}{2\pi r} \Rightarrow \mu = \frac{qV}{2\pi r} \frac{\pi r^2}{c} = \frac{qVr}{2c} = \left(\frac{q}{2mc}\right) mvr$

$$\Rightarrow \vec{\mu} = \left(\frac{q}{2mc}\right) \vec{L}$$

$\Rightarrow$ precession: $\frac{d\vec{L}}{dt} = \vec{\tau} = \vec{\mu} \times \vec{B} = \left(\frac{q}{2mc}\right) \vec{L} \times \vec{B}$

$$\boxed{\vec{\omega}_0 = \frac{q}{2mc} \vec{B}}$$



→ quantum mechanically:

$$i\hbar \partial_t \hat{\vec{J}} = [\hat{\vec{J}}, H]$$

$$i\hbar \partial_t \hat{J}_i = [\hat{J}_i, -\gamma \hat{\vec{J}} \cdot \vec{B}]$$

$$= -\gamma B_j \epsilon_{ijk} i\hbar \hat{J}_k$$

$$\Rightarrow \underline{\partial_t \hat{\vec{J}} = \gamma \hat{\vec{J}} \times \vec{B}} \leftarrow \underline{\text{precession of operators}}$$

▲ Orbital Zeeman energy:

$$H = \frac{(\vec{p} - q\vec{A}/c)^2}{2m} = \frac{p^2}{2m} - \frac{q}{2mc} (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}) + \frac{q^2}{2mc^2} A^2$$

$$\vec{B} \text{ const} \Rightarrow \vec{A} = -\frac{1}{2} \vec{r} \times \vec{B}, \Rightarrow \vec{\nabla} \cdot \vec{A} = 0$$

$$H = \frac{p^2}{2m} - \frac{q}{mc} \underbrace{\vec{A} \cdot \vec{p}} + \frac{q^2 B^2}{8mc^2} r_{\perp}^2$$

$$-\frac{1}{2} \epsilon_{ijk} r_i B_j p_k = \frac{1}{2} \underbrace{(\vec{r} \times \vec{p}) \cdot \vec{B}}_{\vec{L} \cdot \vec{B}}$$

$$\Rightarrow H = \frac{p^2}{2m} - \frac{q}{2mc} \underbrace{\vec{L} \cdot \vec{B}}_{\text{Zeeman effect}} + \frac{m}{2} \underbrace{\left(\frac{qB}{2mc}\right)^2}_{\text{oscillator potential}} r_{\perp}^2$$

Zeeman effect

oscillator potential
with $\omega_0 = \frac{qB}{2mc}$
tiny magnetic
environment: diamagn.
see hw 7 term.

$$H_{\text{Zeeman}} = - \frac{q}{2mc} \vec{L} \cdot \vec{B} \equiv - \vec{\mu} \cdot \vec{B}$$

$$\vec{\mu} = \frac{q}{2mc} \vec{L}, \text{ as in classical case.}$$

$\equiv \gamma$ - gyromagnetic ratio

$$\mu_z = \left(\frac{qh}{2mc} \right) m, \quad m = 0, \pm 1, \pm 2, \dots$$

$\frac{qh}{2mc}$ - Bohr magneton of particle with charge q , mass m .
electrons Bohr magneton:

$$\mu_B = \frac{eh}{2mc} \approx 0.6 \times 10^{-8} \text{ eV/G}$$

$$\mu_{\text{nucleon}} = \frac{1}{2000} \mu_B, \text{ since } M_p \approx 2000 m_e.$$

$$H_{\text{Zeeman}} = - \vec{\mu} \cdot \vec{B} = - \mu_B B m$$

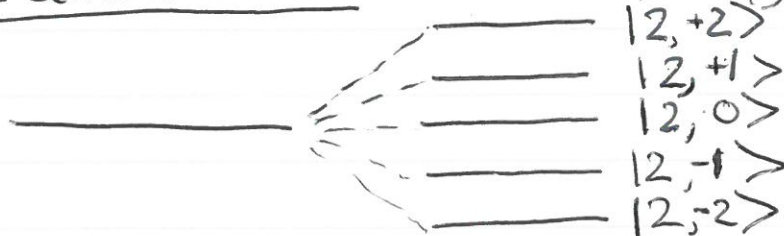
$\vec{B}$ breaks rot. symm.

$\Rightarrow$ splits l levels into $2l+1$ equally spaced ones.

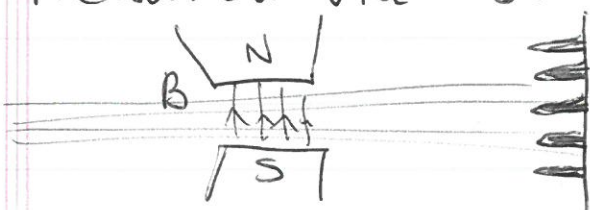
(1896 Zeeman)

Zeeman effect

$l=2$
 m



Measured via Stern-Gerlach exp



need inhomogeneous B field
such that $\vec{F} = -\nabla(\vec{\mu} \cdot \vec{B})$

▲ Spin magnetic moment → Anomalous Zeeman effect

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

comes from Dirac eqn for spin $\frac{1}{2}$ (on S) charged particle in a $\vec{B}$ field

$$H_{\text{Dirac}} = c(\vec{p} - \frac{q\vec{A}}{c}) \cdot \vec{\alpha} + mc^2 \beta$$

$\uparrow$ matrices $\uparrow$

$$\boxed{1} H_{\text{Klein Gordon}} = H_{\text{Dirac}}^2$$

in 2D: $\vec{\alpha} = (\sigma_x, \sigma_y)$

$$H_{\text{Schrod.}} = \sqrt{H_{\text{KG}}^2 - mc^2}$$

Taylor expanded
in $\frac{p}{mc}$

$\beta = \sigma_z$

in 3D: $\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}_{4 \times 4}$

$$\beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}_{4 \times 4}$$

see hw 7 & QM-II

$$\Rightarrow H_{\text{sch}} = \frac{(\vec{p} - \frac{q\vec{A}}{c})^2}{2m} - \frac{2\left(\frac{q}{2mc}\right) \vec{S} \cdot \vec{B}}{\hbar}$$

twice as big as orbital effect

$$g = 2 \left[1 + \frac{\alpha}{2n} + \dots \right]$$

For electron: $\vec{\mu} = g \left(\frac{-e}{2mc} \right) \vec{S}$

$$= -g \mu_B S_z$$

QED theory agrees with exp to $\mathcal{O}(\alpha^3)$ 10 signif. digits.

much worse for p, n since here $\alpha_s \approx 15!$

→ Spin precession revisited:

(a) via Heisenberg eqn & angular momentum algebra

$$\Rightarrow \partial_t \hat{\vec{S}} = \gamma \hat{\vec{S}} \times \vec{B}$$

(b) via evolution operator

$$U(t) = e^{-iHt/\hbar} = e^{i\gamma t(\vec{S} \cdot \vec{B})/\hbar}$$

$$\begin{aligned} \Rightarrow |\chi(t)\rangle &= U(t) |\chi(0)\rangle \\ &= e^{\underbrace{-\frac{i}{\hbar}(-\gamma t \vec{B}) \cdot \vec{S}}_{\equiv \vec{\Theta}(t)}} |\chi(0)\rangle \end{aligned}$$

$$\vec{\Theta}(t) = -\gamma \vec{B} t$$

t-dependent rotation operator!

$$\underline{\vec{\omega}_0 = -\gamma \vec{B}}$$

More explicitly $\vec{B} = B \hat{z} \Rightarrow U(t) = \begin{pmatrix} e^{i\omega_0 t/2} & 0 \\ 0 & e^{-i\omega_0 t/2} \end{pmatrix}$

take $|\chi(0)\rangle = |\hat{n}, +\rangle = \begin{pmatrix} \cos \theta/2 e^{-i\phi/2} \\ \sin \theta/2 e^{i\phi/2} \end{pmatrix}$

$$\Rightarrow |\chi(t)\rangle = \begin{pmatrix} \cos \theta/2 e^{-\frac{1}{2}i(\phi - \omega_0 t)} \\ \sin \theta/2 e^{\frac{1}{2}i(\phi - \omega_0 t)} \end{pmatrix}$$

$$\Rightarrow \phi(t) = \phi_0 - \omega_0 t \Rightarrow \dot{\phi} = -\omega_0$$

▲ Applications: Paramagnetic Resonance

Combination of dc + ac B fields, causes transitions between j_z states.
(see Shankar ch. 14)

▲ Hydrogen atom with spin in $\vec{B}$ field.

$$H = H_0 + H_s = \frac{(\vec{p} + \frac{e}{c}\vec{A})^2}{2m} - \frac{e^2}{r} + 2\frac{e}{2mc}\vec{S} \cdot \vec{B}$$

$$\text{since } [\hat{\vec{S}} \cdot \vec{B}, H_0] = 0$$

$$\Rightarrow |\psi\rangle = |\psi_0\rangle \otimes |\chi_s\rangle$$

$$\uparrow \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \alpha \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \beta \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$m_s = +1/2 \quad m_s = -1/2$

$$\Rightarrow |\psi\rangle = |n\ell m; m_s\rangle$$

$$\Rightarrow \psi_{n\ell m}(r, \theta, \varphi) \chi_{\alpha}^{m_s}, \quad m_s = \pm 1/2$$

$$\Rightarrow H |n\ell m; m_s\rangle = \left[-\frac{E_R}{n^2} + \frac{eB\hbar}{2mc}(m + 2m_s) \right] |n\ell m; m_s\rangle$$

splits the degeneracy

$$\Rightarrow \text{g.s.} \begin{cases} \uparrow m_s = +1/2 \\ \downarrow m_s = -1/2 \end{cases}$$

$n=1, \ell=0$

▲ Spm-orbit interaction

relativistic effect $\rightarrow$ Dirac eqn,
from which spm arises, links spm.
& orbital spaces $\Rightarrow$ leads to terms
like $\vec{L} \cdot \vec{S}$

"Hand-waving": in proton's reference
frame just $\vec{E}_{\text{Coulomb}}$ field. In e's (moving)
ref. frame there is also a $\vec{B}_{\text{Coul}}$ field

$$\vec{B}_{\text{Coul}} \approx -\frac{\vec{v}}{c} \times \vec{E}_{\text{Coul}} = -\frac{\vec{v}}{c} \times (-\vec{\nabla} V_{\text{Coul}})$$

$$\Rightarrow H_{\text{Zeeman}}^{S-O} = -2\left(\frac{e}{2mc}\right) \vec{S} \cdot \vec{B}_{\text{Coul}} \approx \frac{1}{2}$$

$$= \frac{+e}{2m^2c^2} \vec{p} \times \vec{\nabla} V_{\text{Coul}} \cdot \vec{S}$$

$\uparrow$
Thomas
precession

$$H^{S-O} = \frac{-e^2}{2m^2c^2 r^3} (\underbrace{\vec{p} \times \vec{r}}_{-\vec{L}}) \cdot \vec{S} \quad e \vec{\nabla} \frac{1}{r} = -\frac{e}{r^2} \hat{r}$$

$$H^{S-O} = \left(\frac{e^2}{2m^2c^2 r^3}\right) \vec{L} \cdot \vec{S} \rightarrow \text{minimize (need to include Thomas precession)}$$

$\vec{J}$, since $\vec{L} \& \vec{S}$ anti parallel.

$\Rightarrow$ now $|\psi\rangle \neq |\psi_0\rangle \otimes |\chi\rangle$ since must diagonalize

$$\vec{L} \cdot \vec{S} = \frac{1}{2}(\vec{L} + \vec{S})^2 - \frac{1}{2}L^2 - \frac{1}{2}S^2$$

very important in spectra of atoms

$$(\text{In 3D } \vec{p} \cdot \vec{\alpha} + \beta mc^2 + \bar{V} = H_{\text{Dirac}})$$

$$\beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}, \quad \vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}; \text{ note: no } \beta \text{ on } \bar{V} \text{ since } \bar{V} \text{ is heavy}$$

& this is $\bar{\psi} \rightarrow (\bar{E} - V)\psi$

- $H = H_0 + H_1$

$\nwarrow$ matrix
 $\nearrow$ e.g. $-\vec{B} \cdot \vec{S}$

$\nwarrow$ e.g. $\frac{p^2}{2m} + V(r)$

$$H|E\rangle = E|E\rangle$$

$$\Rightarrow H_{\sigma\sigma'} \psi_E^{\sigma'}(r) = E \psi_E^{\sigma}(r)$$

$\uparrow$
 2×2 matrix but if separable $\Rightarrow$

$$\Rightarrow |E\rangle = |nlm\rangle \otimes |m_s\rangle$$

$$\Leftrightarrow \begin{pmatrix} \psi_E^{\uparrow}(r) \\ \psi_E^{\downarrow}(r) \end{pmatrix} = \psi_{nlm}(r) \begin{pmatrix} \chi_{\uparrow} \\ \chi_{\downarrow} \end{pmatrix}_{m_s}$$

- In most realistic situations spin-orbit coupling, i.e. terms like

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

$\rightarrow$ origin of SO coupling: Dirac eqn, heuristics.

$\rightarrow$ could solve by solving from "scratch" two coupled Sch. Egn. for $\begin{pmatrix} \psi_E^{\uparrow}(r) \\ \psi_E^{\downarrow}(r) \end{pmatrix}$

$\rightarrow$ short cut?

addition of angular momenta

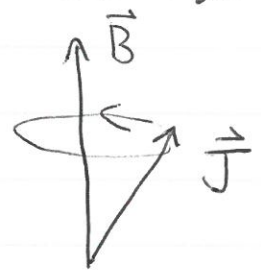
$\vec{J}_1 \cdot \vec{J}_2$ diagonalization

trick $[\vec{J}_1 \cdot \vec{J}_2, (\vec{J}_1 + \vec{J}_2)^2] = 0 = [\vec{J}_1 \cdot \vec{J}_2, (\vec{J}_1 + \vec{J}_2)_z]$!

$\Rightarrow \vec{J}_1 \cdot \vec{J}_2$ diagonalized by eigenstates of J^2, J_z, J_1^2, J_2^2

Lecture Summary

- $H_J = -\gamma \vec{J} \cdot \vec{B}$
simplest Hamiltonian
→ precession about $\vec{B}$

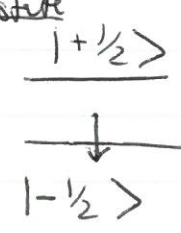


$[J_z, H_J] = 0 \Rightarrow J_z = m - \text{fixed.}$

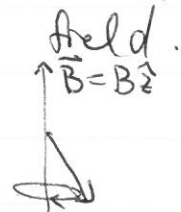
How to make $\vec{J}$ undergo transitions between m 's?

Apply $\vec{B}$ field in different direction → transverse so as to make $|1, m_J\rangle$ not an eigenstate

For $\vec{J} = \vec{S} \Rightarrow g = 1/2$
 $H_S = -\gamma \vec{B} \cdot \vec{S} = -\gamma B_z S_z - \gamma B_x S_x$

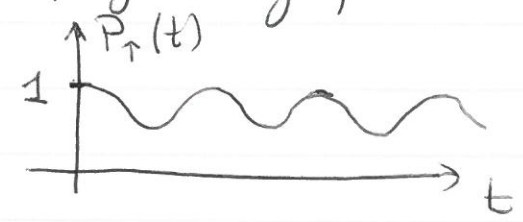
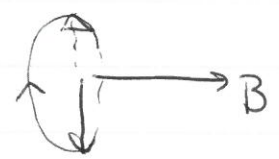


$\Leftrightarrow$



$\Rightarrow |\hat{z}, -1/2\rangle$ not eigenstate of $H_S \rightarrow$ will evolve in time, oscillating between $|\hat{z}, -1/2\rangle$ & $|\hat{z}, +1/2\rangle$

→ physically precesses around new $\vec{B}$



Rabi oscillations

- So far considered only $H = H_0 + H_S$
→ in general spm-orbit $\Rightarrow \psi_a(t) = \psi(r) \chi_a$
coupling $H_{so} = \alpha \vec{S} \cdot \vec{L}$
 - ▲ derive
 - ▲ $[H_{so}, S_z] \neq 0, [H_{so}, L_z] \neq 0$
 - but $[H_{so}, J_z] = 0, [H_{so}, J^2] = 0$
 - $\Rightarrow$ Look at eigenstates of $\vec{J} = \vec{S} + \vec{L}$ (J^2, J_z)
 $|1, m_J; l, s\rangle$ instead of $|1, m_S\rangle \otimes |l, m_L\rangle$
 - $\Rightarrow$ Addition of angular momenta problem.

Summary on Spin:

- $\Psi(\vec{r}) \Rightarrow \Psi_a(\vec{r}) \leftarrow \text{spinor}$

$$|\Psi_r\rangle \xrightarrow{R} e^{-\frac{i}{\hbar} \vec{\Theta} \cdot (\vec{L} + \vec{S})} |\Psi_a\rangle$$

- $S = 1/2 \Rightarrow \vec{S} = \frac{\hbar}{2} \vec{\sigma}, \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \dots$

$$\rightarrow \hat{S}^2 |\frac{1}{2}, s_z\rangle = \hbar^2 \frac{3}{4} |\frac{1}{2}, s_z\rangle, \quad S_z |\frac{1}{2}, \pm \frac{1}{2}\rangle = \pm \frac{\hbar}{2} |\frac{1}{2}, \pm \frac{1}{2}\rangle$$

$$\rightarrow |\frac{1}{2} \pm \frac{1}{2}\rangle \rightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\rightarrow \text{quant. axes along } \hat{n}: \hat{n} \cdot \vec{S} |\hat{n}, \pm \frac{1}{2}\rangle = \pm \frac{\hbar}{2} |\hat{n}, \pm \frac{1}{2}\rangle$$

$$|\hat{n}, \pm \frac{1}{2}\rangle \rightarrow \begin{pmatrix} \cos \theta/2 \\ e^{i\phi} \sin \theta/2 \end{pmatrix}, \begin{pmatrix} \sin \theta/2 \\ -e^{i\phi} \cos \theta/2 \end{pmatrix}, \text{ by diagonalizing } \hat{n} \cdot \vec{S} \text{ or by rotating } \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\rightarrow e^{-\frac{i}{\hbar} \vec{\Theta} \cdot \vec{S}} = \cos \theta/2 + i \hat{\Theta} \cdot \vec{\sigma} \sin \theta/2 = \begin{pmatrix} \cos \theta/2 & i \sin \theta/2 \\ i \sin \theta/2 & \cos \theta/2 \end{pmatrix}$$

$$\hat{\Theta} = \frac{\hat{z} \times \hat{n}}{|\hat{z} \times \hat{n}|}$$

$$\rightarrow \text{props of } \vec{\sigma}'s: [\sigma_i, \sigma_j] = i \epsilon_{ijk} \sigma_k, \quad \text{Tr } \sigma_i = 0, \quad \sigma_i^\dagger = \sigma_i, \quad \sigma_i \sigma_j = \dots$$

- physical consequences of spin: huge!

- chemistry $\rightarrow$ life
- materials/metals, insulators, magnetism, etc.
 $\rightarrow$ mainly stemming from 2x as many states for each orbital states for fermions.

$\rightarrow$ Zeeman effect (1896)

▲ orbital $\rightarrow$ splitting of atomic spectra

▲ spin $\rightarrow$ anomalous Z. effect.

$\rightarrow$ no classical intuition

$\rightarrow$ origin of spin: Dirac eqn. in B field.

$$-\vec{\mu} = \frac{q}{2mc} \vec{L}, \quad E = -\vec{\mu} \cdot \vec{B}$$

$$\vec{\mu} = 2 \left(\frac{q}{2mc} \right) \vec{S}, \quad g = 2 + \dots$$

$\rightarrow \vec{J}$ precession $\Rightarrow$ paramagnetic resonance: flipping spin with B_1

- Spin-orbit interaction:

$\rightarrow$ L-S coupling origin:

▲ Dirac eqn.

▲ semiclassical via Lorentz transf./or Bloch-Savart B at e deep.

$\rightarrow L_z, S_z$ not good q.#'s

$$\vec{J}^2 = (\vec{L} + \vec{S})^2, \quad \& \quad J_z$$

- Addition of J's.

Lecture 14: Addition of Angular Momenta

Hilbert space of 2 spins spanned by

$$|s_1, m_1\rangle \otimes |s_2, m_2\rangle \equiv |s_1, m_1, s_2, m_2\rangle$$

4 states — eigenstates of S_1^2, S_{1z}

... but often convenient to work with eigenstates of total $\vec{S} = \vec{S}_1 + \vec{S}_2$ i.e.

$$S^2, S_z$$

$$S_z |++\rangle = \hbar |++\rangle$$

$$S_z |+-\rangle = 0 |+-\rangle \quad \left. \begin{array}{l} S_z |-+\rangle = 0 |-+\rangle \\ S_z |--\rangle = -\hbar |--\rangle \end{array} \right\} \text{two-fold degenerate}$$

$$S_z |-+\rangle = 0 |-+\rangle$$

$$S_z |--\rangle = -\hbar |--\rangle$$

but $|m_1, m_2\rangle$ not eigenstates of S^2
since

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

$$\Rightarrow [S^2, S_{1z}] = [S^2, S_{2z}] \neq 0 \text{ because of } \leftarrow$$

$$S^2 = \hbar^2 \begin{matrix} & ++ & +- & -+ & -- \\ \begin{matrix} ++ \\ +- \\ -+ \\ -- \end{matrix} & \begin{bmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{bmatrix} \end{matrix}$$

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

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

Diagonalize S^2 by

$$\begin{aligned} \text{triplet (symmetric)} \quad & \begin{cases} |S=1, m=1, S_1=\frac{1}{2}, S_2=\frac{1}{2}\rangle = |++\rangle \\ |S=1, m=0, S_1=\frac{1}{2}, S_2=\frac{1}{2}\rangle = \frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle) \\ |S=1, m=-1, S_1=\frac{1}{2}, S_2=\frac{1}{2}\rangle = |--\rangle \end{cases} \end{aligned}$$

$$\begin{aligned} \text{singlet (antisymmetric)} \quad & |S=0, m=0; S_1=\frac{1}{2}, S_2=\frac{1}{2}\rangle = \frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle) \\ & \underbrace{\hspace{10em}}_{\text{singlet (antisymmetric)}} \end{aligned}$$

Addition of L 's :

$$\begin{aligned} \text{change basis from } (S_1^2, S_2^2, S_{1z}, S_{2z}) &\longrightarrow \\ &\longrightarrow (S^2, S_z, S_1^2, S_2^2) \end{aligned}$$

$$\frac{1}{2} \otimes \frac{1}{2} = 1 \oplus 0$$

$$\underbrace{2 \times 2 = 4 \text{ states}}_{\text{2} \times \text{2} = 4 \text{ states}} = 3 \text{ states} + 1 \text{ state} \quad \checkmark$$

Group theory jargon:

$|S_{1z}\rangle \otimes |S_{2z}\rangle$ is a reducible representation

break it down to two irreducible representations

$$|S=1, S_z\rangle \oplus |S=0, 0\rangle$$

Fermion total ψ must be antisymmetric
 $\Rightarrow |\psi\rangle = |O_A\rangle \otimes |S=1, S_z\rangle$
 or $|\psi\rangle = |O_S\rangle \otimes |S=0, 0\rangle$

Ex. He atom 2 e's

both e's are in $|n=1, l=0, m=0\rangle$

$$|\psi_{\text{He}}^{\text{ground}}\rangle = |\psi_0\rangle \otimes |\chi_S\rangle$$

$\uparrow$ $\quad \quad \quad \nwarrow$
 $|100\rangle \otimes |100\rangle$
 $\underbrace{\hspace{1.5cm}}_{l=0, \text{symmetric}} \quad \quad \quad \text{singlet } S=0 \text{ (antisymmetric)}$

Which basis ($|m_1, m_2\rangle$ vs $|S, m\rangle$) to use depends on H .

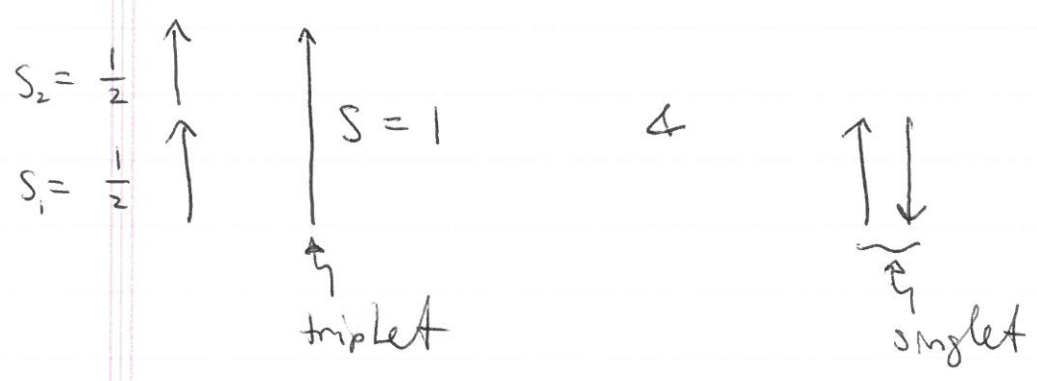
$$H = -(\gamma_1 S_1 + \gamma_2 S_2) \cdot \vec{B} \rightarrow \text{best } |m_1, m_2\rangle$$

on the other hand

$$H = A S_1 \cdot S_2 = \frac{A}{2} (S^2 - S_1^2 - S_2^2)$$

total S basis diagonalizes H .

Graphical addition:



$$|1, 1\rangle, |1, 0\rangle, |1, -1\rangle \quad |0, 0\rangle$$

General problem of addition $\vec{J}_1, \vec{J}_2$

$(2j_1 + 1)(2j_2 + 1)$ - dimensional reducible tensor product space

$$|j_1, m_1\rangle \otimes |j_2, m_2\rangle = |j_1, m_1; j_2, m_2\rangle$$

$$\vec{J} = \vec{J}_1 + \vec{J}_2$$

J_z is diagonal in product basis but J^2 is not degen.

$\uparrow$ highly degenerate, except for $|j_1 \pm j_1; j_2 \pm j_2\rangle$

e.g. $m = j_1 + j_2 - 2$ is a linear combination of

$$|m_1 = j_1, m_2 = j_2 - 2\rangle; |m_1 = j_1 - 1, m_2 = j_2 - 1\rangle, |j_1 - 2, j_2\rangle$$

Graphically: $j_1 + j_2$

$$\begin{array}{c} \uparrow j_2 \\ \uparrow j_1 \end{array} = \uparrow j_1 + j_2 \quad ; \quad \begin{array}{c} \nearrow \\ \uparrow j_1 \end{array} = \uparrow j_1 + j_2 - 1$$

$$\begin{array}{c} \rightarrow \\ \uparrow \end{array} = \uparrow j_1 + j_2 - j_2 = j_1, \dots \quad \begin{array}{c} \uparrow \\ \downarrow \end{array} = \uparrow j_1 - j_2$$

$$j_1 \otimes j_2 = (j_1 + j_2) \oplus (j_1 + j_2 - 1) \oplus \dots \oplus (j_1 - j_2)$$

$$(2j_1 + 1)(2j_2 + 1)$$

check dimensionality: $D = \sum_{j=j_1-j_2}^{j_1+j_2} (2j+1) = \sum_{j=0}^{j_1+j_2} (2j+1) -$

$$- \sum_{j=0}^{j_1-j_2-1} (2j+1) = \left[\cancel{2(j_1+j_2)(j_1+j_2+1)} + j_1+j_2+1 \right] - \left[(j_1-j_2-1)(j_1-j_2) + j_1-j_2 \right]$$

$$= 4j_1 j_2 + 2j_1 + 2j_2 + 1 = (2j_1 + 1)(2j_2 + 1) \quad \checkmark$$

Example with $j_1 = \frac{1}{2}, j_2 = \frac{1}{2}$

$$|\frac{1}{2}, \frac{1}{2}\rangle \otimes |\frac{1}{2}, \frac{1}{2}\rangle = |1, 1\rangle \quad \text{nondegenerate}$$

$$\text{with } S^2 |1, 1\rangle = \hbar^2 2 |1, 1\rangle, S_z |1, 1\rangle = \hbar |1, 1\rangle$$

$$|1, 1\rangle = |\frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle$$

$$\begin{aligned} \text{check: } (S_1^2 + S_2^2 + 2S_{1z}S_{2z} + S_{1+}S_{2-} + S_{1-}S_{2+})|\frac{1}{2}\frac{1}{2}; \frac{1}{2}\frac{1}{2}\rangle \\ = \hbar^2(3/4 + 3/4 + 2 \cdot \frac{1}{2} \cdot \frac{1}{2} + 0 + 0)|\frac{1}{2}\frac{1}{2}; \frac{1}{2}\frac{1}{2}\rangle \end{aligned}$$

$$\boxed{S^2 |\frac{1}{2}\frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle = \hbar^2 2 |\frac{1}{2}\frac{1}{2}; \frac{1}{2}\frac{1}{2}\rangle} \quad \checkmark$$

$$|1, 0\rangle = ? \quad \text{expect linear combination of} \\ |\underbrace{\frac{1}{2} - \frac{1}{2}}_{m=0}; \underbrace{\frac{1}{2} + \frac{1}{2}}_{m=0}\rangle \triangleq |\underbrace{\frac{1}{2}\frac{1}{2}}_{m=0}; \underbrace{\frac{1}{2} - \frac{1}{2}}_{m=0}\rangle$$

$$S_- |1, 1\rangle = \hbar \sqrt{2} |1, 0\rangle$$

$$= (S_{1-} + S_{2-}) |\frac{1}{2}\frac{1}{2}; \frac{1}{2}\frac{1}{2}\rangle = \hbar |\frac{1}{2} - \frac{1}{2}; \frac{1}{2}\frac{1}{2}\rangle + \hbar |\frac{1}{2}\frac{1}{2}; \frac{1}{2} - \frac{1}{2}\rangle$$

$$\Rightarrow |1, 0\rangle = \frac{1}{\sqrt{2}} (|-\frac{1}{2}, \frac{1}{2}\rangle + |\frac{1}{2} - \frac{1}{2}\rangle)$$

$$|1, -1\rangle = |-\frac{1}{2}, -\frac{1}{2}\rangle$$

$j=1$ states

$$|11\rangle = |++\rangle$$

$$|10\rangle = \frac{1}{\sqrt{2}}(|+-\rangle + |-+\rangle)$$

$$|1-1\rangle = |--\rangle$$

$j=0$ state $\rightarrow$ require to be orthogonal to $|10\rangle$

$$\Rightarrow |00\rangle = \frac{1}{\sqrt{2}}(|+-\rangle - |-+\rangle)$$

Convention choice: coeff +1 of the $|m_1=j_1\rangle$

General j_1, j_2

$$|j_1+j_2, j_1+j_2\rangle = |j_1 j_1; j_2 j_2\rangle$$

$$J_- |j_1+j_2, j_1+j_2\rangle = \hbar \sqrt{2(j_1+j_2)} |j_1+j_2, j_1+j_2-1\rangle$$

$$\begin{aligned} \Rightarrow |j_1+j_2, j_1+j_2-1\rangle &= \frac{1}{\hbar \sqrt{2(j_1+j_2)}} (J_- + J_{2-}) |j_1 j_1; j_2 j_2\rangle \\ &= \frac{1}{\sqrt{2(j_1+j_2)}} \left(\sqrt{2j_1} |j_1 j_1-1; j_2 j_2\rangle + \sqrt{2j_2} |j_1 j_1; j_2 j_2-1\rangle \right) \end{aligned}$$

$$|j_1+j_2, j_1+j_2-1\rangle = \sqrt{\frac{j_1}{j_1+j_2}} |j_1 j_1-1; j_2 j_2\rangle + \sqrt{\frac{j_2}{j_1+j_2}} |j_1 j_1; j_2 j_2-1\rangle$$

continue until $|j_1+j_2, -(j_1+j_2)\rangle$

$$\text{Now look at } |j_1+j_2-1, j_1+j_2-1\rangle = \alpha |j_1 j_1-1; j_2 j_2\rangle + \beta |j_1 j_1; j_2 j_2-1\rangle$$

pick α, β s.t. $|\alpha|^2 + |\beta|^2 = 1$ & orthogonal to $|j_1+j_2, j_1+j_2-1\rangle$

$$|j_1+j_2-1; j_1+j_2-1\rangle = \sqrt{\frac{j_1}{j_1+j_2}} |j_1 j_1, j_2 j_2-1\rangle - \sqrt{\frac{j_2}{j_1+j_2}} |j_1 j_1-1, j_2 j_2\rangle$$

want this coeff be > 0
(convention)

Clebsch-Gordan Coefficients

$$|j m, j_1 j_2\rangle = \sum_{m_1} \sum_{m_2} |j_1 m_1, j_2 m_2\rangle \underbrace{\langle j_1 m_1, j_2 m_2 | j m, j_1 j_2 \rangle}_{\text{C-G coeff}}$$

C-G coeff

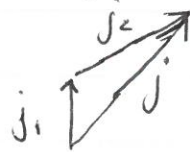
for expansion
of $(J_1+J_2)^2$ eigenstates
in terms of J_{1z}, J_{2z}
eigenstates

Props of C-G coeff:

(1) $\langle j_1 m_1, j_2 m_2 | j m \rangle \neq 0$

only if $|j_1 - j_2| \leq j < j_1 + j_2$

(triangle inequality)



(2) $\langle j_1 m_1, j_2 m_2 | j m \rangle \neq 0$ only if $m_1 + m_2 = m$

(3) C-G coeff are real (by convention)

(4) $\langle j_1 j_1, j_2 (j-j_1) | j j \rangle$ is positive (by convention)

(5) $\langle j_1 m_1, j_2 m_2 | j m \rangle = (-1)^{j_1+j_2-1} \langle j_1 (-m_1), j_2 (-m_2) | j (-m) \rangle$

Find CG coeff for (a) $\frac{1}{2} \otimes 1 = \frac{3}{2} \oplus \frac{1}{2}$

(b) $1 \otimes 1 = 2 \oplus 1 \oplus 0$

(6) $\langle j, m | j_1, m_1, j_2, m_2 \rangle = \langle j_1, m_1, j_2, m_2 | j, m \rangle$
 orthogonal matrix, since real CG coeff.

Ex $\frac{1}{2} \otimes \frac{1}{2}$ prob.

$$\begin{pmatrix} |j, m\rangle \\ |1, 1\rangle \\ |1, 0\rangle \\ |1, -1\rangle \\ |0, 0\rangle \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \end{pmatrix} \begin{pmatrix} |m, m_2\rangle \\ |++\rangle \\ |+-\rangle \\ |-+\rangle \\ |--\rangle \end{pmatrix}$$

can invert the relation.

Application: strong L.S coupling in atoms $\Rightarrow$ eigenstates are better approximated by total $\vec{J} = \vec{L} + \vec{S}$ eigenstates

$$|j = l + \frac{1}{2}, m_j\rangle = \alpha |l, m_j - \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle + \beta |l, m_j + \frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\rangle$$

$$|j = l - \frac{1}{2}, m_j\rangle = \alpha' |l, m_j - \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle + \beta' |l, m_j + \frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\rangle$$

orthonormality $\Rightarrow \alpha^2 + \beta^2 = \alpha'^2 + \beta'^2 = 1$
 $\alpha\alpha' + \beta\beta' = 0$

AND: $J^2 |j = l + \frac{1}{2}, m_j\rangle = \hbar^2 (l + \frac{1}{2})(l + \frac{3}{2}) |j = l + \frac{1}{2}, m_j\rangle$

$$\Rightarrow |j = l \pm \frac{1}{2}, m_j\rangle = \frac{1}{(2l+1)^{1/2}} \left[\pm (l + \frac{1}{2} \pm m_j)^{1/2} |l, m_j - \frac{1}{2}; \frac{1}{2}, \frac{1}{2}\rangle + (l + \frac{1}{2} \mp m_j)^{1/2} |l, m_j + \frac{1}{2}; \frac{1}{2}, -\frac{1}{2}\rangle \right]$$

Note: In adding j_1 & j_2 , state of total $\vec{J}$ is labelled by $j = 2j_1, 2j_1 - 1, 2j_1 - 2, \dots, 0$

$\uparrow$ $\uparrow$ $\uparrow$
 symm antisymm symm.

Lowering operator $J_- = J_{1-} + J_{2-}$ does not change symmetry

Ex. $\frac{1}{2} \otimes \frac{1}{2} = 1 + 0$

$\uparrow$ $\uparrow$
 symm antisymm.

Ex. $1 \otimes 1 = 2 \oplus 1 \oplus 0$

$\uparrow$ $\uparrow$ $\uparrow$
 symm antisymm symm.

Notation: in atomic physics.

In absence of spin we used $s, p, d, f, \dots$ to denote l .

With spin new spectroscopic notation:

$2S+1$
 $\uparrow$
total
spin

$\uparrow$
 Capital letter
 denoting orbital L , i.e. $S, P, D, \dots$
total

$\Rightarrow$ j value

$2P_{3/2}$ denotes: $L=1, S=1/2$
 $J=3/2$

Multi-electron atoms

$$\vec{L}_1, \vec{L}_2, \vec{L}_3, \dots; \vec{S}_1, \vec{S}_2, \vec{S}_3, \dots$$

$$\vec{J}_1 = \vec{L}_1 + \vec{S}_1, \vec{J}_2 = \vec{L}_2 + \vec{S}_2, \dots$$

$$\vec{L} = \vec{L}_1 + \vec{L}_2 + \vec{L}_3 + \dots; \vec{S} = \vec{S}_1 + \vec{S}_2 + \vec{S}_3 + \dots$$

Two competing effects:

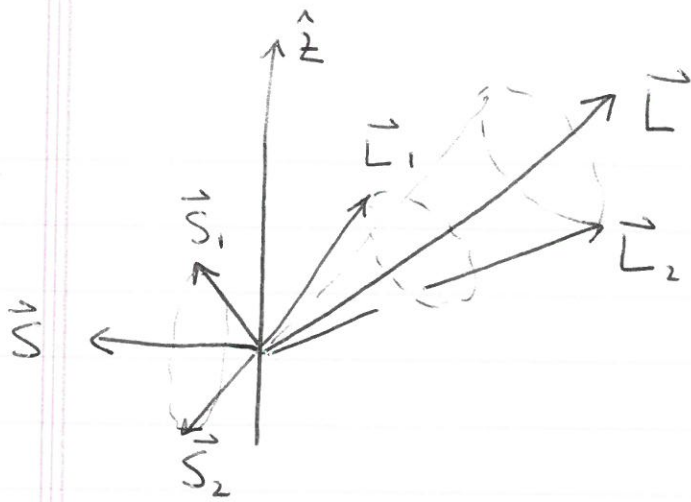
1. (Exchange) Coulomb interaction (beyond Hartree)
2. Spin-orbit.

- Exchange Coulomb couples S_i 's & L_i 's into $\vec{S}$ & $\vec{L}$ with max. value having lowest energy; this is due to the fact that in largest $\vec{S}$ & $\vec{L}$, e's stay away from each other thereby lowering Coulomb repulsion.

$\Rightarrow S_{iz}, L_{iz}$ is not conserved, but S^2, S_z & L^2, L_z are

- Spin orbit leads to $\vec{J}_i = \vec{S}_i + \vec{L}_i$, with $\vec{S}_i$ & $\vec{L}_i$ precessing about total $\vec{J}_i$.

In most atoms (except for largest Z) Exchange dominates $\Rightarrow \vec{L}_i \rightarrow \vec{L}; \vec{S}_i \rightarrow \vec{S}$ weakly coupled by $\vec{L} \cdot \vec{S}$. This is LS coupling (Russell-Saunders) (JJ coupling for large Z : $\vec{S}_i, \vec{L}_i \rightarrow \vec{J}_i$ & then $\vec{J}_i \rightarrow \vec{J}$)



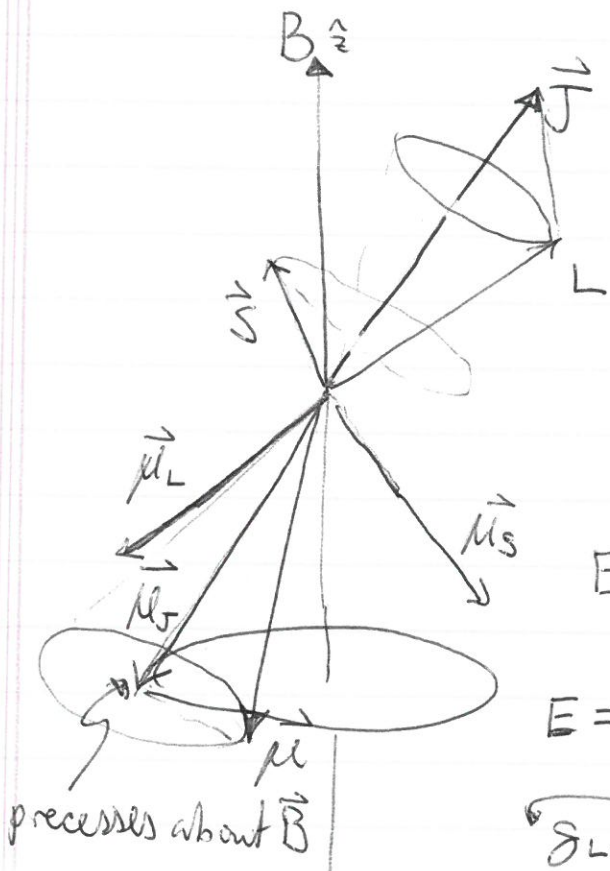
Implications for Zeeman effect: (see Eisenberg & Resnick)

$$\vec{\mu} = -\frac{\mu_B}{\hbar} \vec{L}_1 - \frac{\mu_B}{\hbar} \vec{L}_2 - \dots$$

$$-g \frac{\mu_B}{\hbar} \vec{S}_1 - g \frac{\mu_B}{\hbar} \vec{S}_2 - \dots$$

$$\vec{\mu} = -\frac{\mu_B}{\hbar} (\vec{L} + 2\vec{S}) = -\frac{\mu_B}{\hbar} (\vec{J} + \vec{S})$$

$\Rightarrow \vec{\mu}$ not anti parallel to $\vec{J}$!



$$\mu_J = \mu \frac{\vec{\mu} \cdot \vec{J}}{\mu_J}$$

$$= -\frac{\mu_B}{\hbar} \frac{(\vec{L} + 2\vec{S}) \cdot (\vec{L} + \vec{S})}{J}$$

$$E = -\vec{\mu} \cdot \vec{B} = -\mu_J B \cos \theta$$

$$= +B \frac{\mu_B}{\hbar} \frac{(\vec{L} + 2\vec{S}) \cdot (\vec{L} + \vec{S})}{J} \left(\frac{J_z}{J} \right)$$

$$E = \frac{\mu_B}{\hbar} B \frac{(L^2 + 2S^2 + 3\vec{L} \cdot \vec{S})}{J^2} J_z$$

$$E = \frac{\mu_B}{\hbar} \frac{(3J^2 + S^2 - L^2)}{2J^2} J_z B$$

$$g_{Lande} = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}$$