Magnetic Fields in Atoms

⑰ ~~[illegible]~~ : Spin-orbit Coupling.

<u>Hydrogen atom</u>: sol^n of TISE with pure Coulomb potential

$$E = \frac{-E_R}{(n_r + l + 1)^2}$$ with $n_r = 0, 1, 2, 3 \ldots$ radial quantum no.

$$= \frac{-E_R}{n^2}$$ with $n = 1, 2, 3 \ldots$

"accidental" degeneracies of combinations of n_r and l.

→ states with same n <u>degenerate</u>.

e.g. $n=2$ shell two groups of states · $n_r = 1$ $n > l$

$n_r = 2$ $l = 0$ 2s or $l = 1$ 2p

$m_l = 0$ $m_l = +1, 0 -1$ [8 elements in 2nd row of periodic table]

$m_s = \pm 1/2$ $m_s = \pm 1/2$ ↑

\# states = 2 $2 \times 3 = 6$ → 8 states in total

└ degenerate.

Relativistic effects cause small splittings removing the degeneracy of these states called "fine structure".

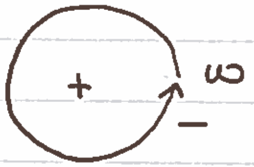
One effect is called spin-orbit coupling.

Sit on top of the electron

It sees the proton whizzing around it → current loop generating a magnetic field.

The electron energy then depends on which direction its magnetic moment points in.

~~At~~ Atom frame :



$\underline{L} = mr^2 \omega \, \hat{z}$

out of page

Electron frame :

proton +ve current $I = \frac{e\omega}{2\pi}$ out of page

$$\underline{B} = \frac{1}{2} \frac{\mu_0 I \hat{z}}{2r} = \frac{\mu_0 e \omega \hat{z}}{8\pi r} = \frac{\mu_0 e \underline{L}}{8\pi m r^3}$$

needs ↑

[except wrong ~~[illegible]~~ factor ×1/2

Thomas precession factor to do with

rotating ie accelerating frame].

approx factor 2

→ relativistic factor: calculating B in rotating frame of ref

Interaction : $E = -\underline{\mu} \cdot \underline{B}$

Transition to quantum mechanics $\hat{H}_{SO} = -\underline{\hat{\mu}} \cdot \underline{B}$ ← prop to $\underline{\hat{L}}$ ← prop to $\underline{\hat{S}}$ and q

$H_{SO} = f(r)\, \underline{\hat{L}} \cdot \underline{\hat{S}}$ ← bury all constants and radial dep in here!

Overall positive sign, lower energy if $\underline{S}$ and $\underline{L}$ are "anti parallell" — but caution in QM.

Magnetic effects small → treat as perturbation → need $\langle H_{SO} \rangle \propto \delta E = \langle \underline{L} \cdot \underline{S} \rangle$

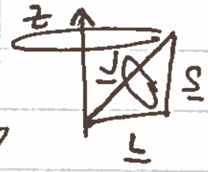
[if use ~~correct~~ combinations of the degenerate states ~~to avoid problems~~ that are not mixed by $\hat{\underline{L}} \cdot \hat{\underline{S}}$ to avoid trouble: ie. need [illegible] combinations that are eigenstates of $\underline{L} \cdot \underline{S}$]

The operator $\underline{\hat{L}} \cdot \underline{\hat{S}} =$ ~~$\hat{L}_x\hat{S}_x + \hat{L}_y\hat{S}_y + \hat{L}_z\hat{S}_z$~~ $= \sum_{i=x,y,z} \hat{L}_i \hat{S}_i$

so commutes with $\hat{L}^2$ and $\hat{S}^2$ → l and s remain good quantum n^os

but not with $\hat{L}_z$ and $\hat{S}_z$ → m_l and m_s won't be [final wavefunctions mixtures of their eigenfunctions]

Picture:



If consider $\underline{\hat{J}} = \underline{\hat{L}} + \underline{\hat{S}}$ ie. add orbital and spin

$j = |l+s| \ldots |l-s|$

$J \geq m_j \geq -J$

$\hat{J}^2 = \hat{L}^2 + \hat{S}^2 + 2\underline{\hat{L}} \cdot \underline{\hat{S}}$

$\rightarrow \underline{\hat{L}} \cdot \underline{\hat{S}} = \frac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2)$ so commutes with $\hat{J}^2$ and J_z

So choose to use mixtures of m_l and m_s eigenfunctions that are eigenstates of $\hat{J}^2$ and $\hat{J}_z$ → then avoid issues of degenerate states

eigenvalues $j(j+1)\hbar^2$ $m_j\hbar$

ang mom coupling use CG to construct wavefunctions.

write them as $\psi_{n\ell j m_j}$ as find you don't need to worry about their exact form.

So $\hat{L}.\hat{S}\,\psi_{n\ell j m_j} = \frac{\hbar^2}{2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]\psi_{n\ell j m_j}$

Using first-order perturbation theory:

$$\Delta E_j = \langle \hat{H}_{so} \rangle = \langle n\ell j m | f(r)\,\hat{L}.\hat{S} | n\ell j m \rangle$$

$$= \frac{\hbar^2}{2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right] \langle f(r) \rangle$$

Bury the details: $\varepsilon_{n\ell} = \langle f(r) \rangle \hbar^2$ (so within an $n\ell$ ~~[illegible]~~ group constant)

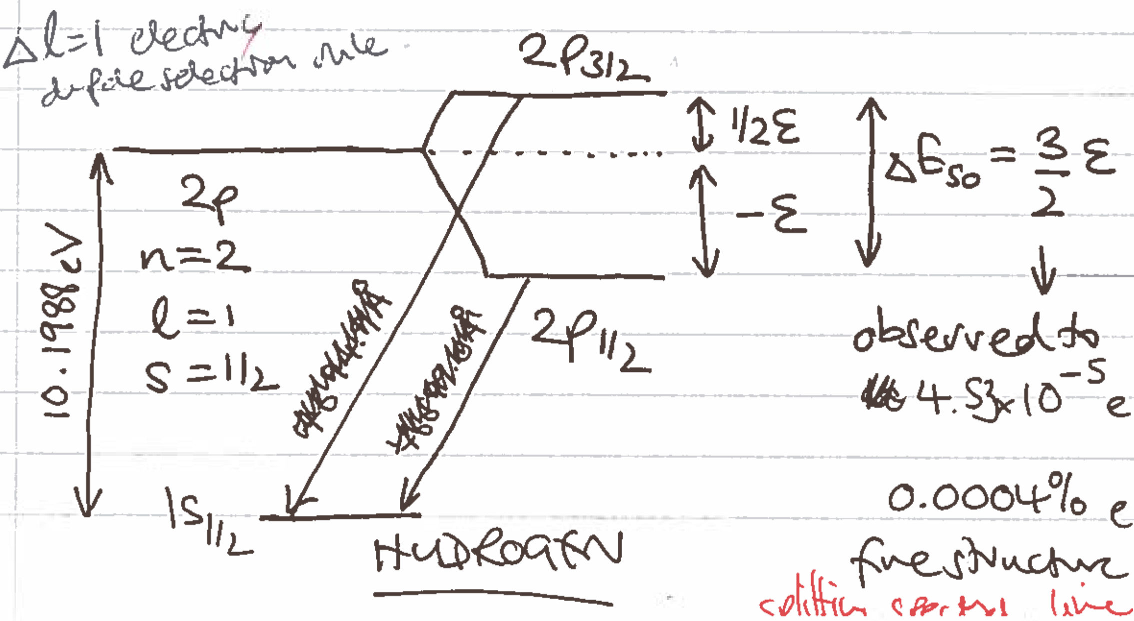
$$\Delta E_j = \frac{\varepsilon_{n\ell}}{2}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]$$

See this in action for the $n=2$, $\ell=1$ levels ($\ell=0$ 2s unaffected by ~~[illegible]~~ $j=s$)

$\ell = 1$, $j = 1 \otimes 1/2$
$s = 1/2$ $\quad = |\ell+s| \ldots\ldots |\ell - s| = 3/2, 1/2$

$j = 1/2 \qquad \Delta E_{1/2} = \varepsilon_{21} \cdot \frac{1}{2}\left[3/4 - 2 - 3/4\right] = -\varepsilon_{21}$

$= 3/2 \qquad \Delta E_{3/2} = \varepsilon_{21} \cdot \frac{1}{2}\left[\frac{15}{4} - 2 - 3/4\right] = \frac{1}{2}\varepsilon_{21}$



other relativistic effects put 2S really degenerate with $P_{1/2}$

$2S_{1/2}$

↓ observed to be 4.53×10^{-5} eV

no E1 transition

0.0004% effect.

fine structure.

splitting spectral line

Similar ideas extend to multi-electron atoms with a few valence ($\lesssim 3$) electrons:

Start with central field approx$^{\underline{n}}$ = potential for electron including shielding

small radii $\propto \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}$

large radii $\propto \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$

with few valence electrons → alkali metals / alkaline earths.

Poor job of e-e repulsion – need to add in a correction

(a) If e-e correction > spin-orbit int. ($\sum \underline{l}_i \cdot \underline{s}_i$ energy) → "LS coupling" usually low-Z atoms

Form $\hat{\underline{S}} = \sum \hat{\underline{S}}_i$ and $\hat{\underline{L}} = \sum \hat{\underline{L}}_i$ summing over all electrons

total electron spin q.# S and orbital L; couple to J and use in the eq$^{\underline{n}}$ above

(b) if spin orbit > e-e → "jj coupling" high-Z, ~~[illegible]~~ H$_{so}$ directly on individual electrons

each electron couple $\underline{j}_i = \underline{l}_i + \underline{s}_i$; $\underline{J} = \sum \underline{j}_i$

→ more complicated!

(c) many atoms s/o ~ e-e → even more complicate!

Atomic nuclei have magnetic moments, which can interact with electronic magnetic fields.

— changes in atomic levels ×10^3 smaller than fine structure

→ HYPERFINE STRUCTURE.

$\underline{I}$ nuclear couples with $\underline{J}$ electrons → $\underline{F}$ atomic spin.

→ internal interaction: might change l_1 & l_2 but not $\underline{L}$; doesn't depend on $\underline{S}$ } $\hat{H}_{e-e}$ must commute with $\underline{L}$ and $\underline{S}$

full shells couple to zero as all m_j occupied } $\underline{L}$ and $\underline{S}$ are effectively sum of valence electrons.

⑱ Atoms in Magnetic Fields : Zeeman Effect in LS coupled atoms

Recap : LS coupling: need to calc shifts in degenerate levels by $\hat{\underline{L}}\cdot\hat{\underline{S}}$

don't need in 2015

$[\hat{A},\hat{B}]=0$ know both quantities ; shared eigenfunctions .

$[\hat{A},\hat{C}]\neq 0$ can't know both ; different eigenfunctions .

ie . $\varphi_A = \sum a \varphi_C$ eigenfunctions of A are a mixture of C .

$\hat{\underline{L}}\cdot\hat{\underline{S}}$ commutes with $\hat{J}^2$ $\hat{J}_z$ $\hat{L}^2$ and $\hat{S}^2$ (but not $\hat{L}_z$ and $\hat{S}_z$)

So use eigenfncs of these since $\hat{\underline{L}}\cdot\hat{\underline{S}}$ won't mix them . (ie. mixtures of L_z and S_z)

Need this since pert^n theory for deg levels won't work if pert^n mixes eigenfncs .

Wrote $\hat{\underline{L}}\cdot\hat{\underline{S}}$ in terms of $\hat{J}^2$, $\hat{L}^2$ and $\hat{S}^2$

Found expect^n using chosen eigenfncs ; easy , can replace ops by eigenvalues .

$\hat{H} = \hat{H}_{\text{central field}} + \hat{H}_{so}$

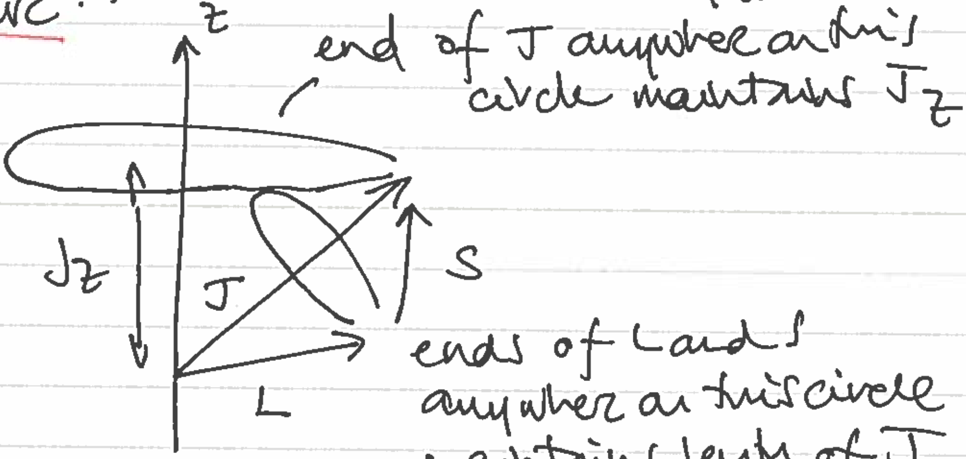
Vector picture of LS coupling .

Full shells of electrons → total ang mom = 0

$\underline{L} = \sum \underline{L}_i$ valence electrons

$\underline{S} = \sum \underline{S}_i$

Σ = ang mom coupling !



end of J anywhere on this circle maintains J_z

ends of L and S anywhere on this circle maintains length of J .

$\underline{L}$ $\underline{S}$ $\underline{J}$ definite lengths .

J_z definite ~~component~~ , not L_z nor S_z .

(fluctuate)

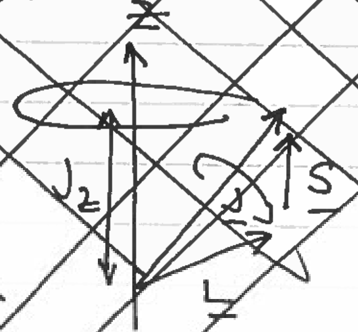
⑱ Atoms in Magnetic Fields : Zeeman Effect

Recap: calculated effect of $\hat{\underline{L}}.\hat{\underline{S}}$ perturbation.
$\hat{\underline{L}}.\hat{\underline{S}}$ commutes with $\hat{J}^2$, $\hat{J}_z$, $\hat{L}^2$ and $\hat{S}^2$ (not $\hat{L}_z$ and $\hat{S}_z$)
~~[illegible]~~
↓
Used eigenfunctions of these operators (ie. mixtures of $\hat{L}_z$ and $\hat{S}_z$)
~~[illegible]~~ to cope with deficiency of pert^{n} theory with degenerate levels.
↓
found LS in terms of $\hat{J}^2$, $\hat{L}^2$, $\hat{S}^2$
replaced ops with eigenvalues.

Vector picture
for $\underline{L}.\underline{S}$ coupling

— $\underline{L}$ and $\underline{S}$ definite length but not z comps.

— $\underline{J}$ definite length and z comp.



LS-coupled —— // ——

Now stick atom in weak magnetic field: $\hat{H} = \hat{H}_{central} + \hat{H}_{so} + \hat{H}_{mag}$
small | smaller.

$$\hat{H}_{mag} = \frac{e}{2m}(\hat{\underline{L}} + 2\hat{\underline{S}}).\underline{B}$$ ie. μ from spin and orbital
$g=2$

$$= \frac{eB}{2m}(\hat{L}_z + 2\hat{S}_z) \text{ if } \underline{B} \text{ defines z axis}.$$

$$= \frac{eB}{2m}(\hat{J}_z + \hat{S}_z) \text{ as } J_z = L_z + S_z$$
this needs to alter things is small.

If $\hat{H}_{mag}$ is small (less than $\hat{H}_{so}$) [add another perturbation smaller than H_{so}]
Perturbation theory says:

$$\Delta E_{mag} = \langle \hat{H}_{mag} \rangle = \frac{eB}{2m}\left[m_J \hbar + \langle \hat{S}_z \rangle \right]$$ as eigenstate of $\hat{J}_z$

Now need to find $\langle \hat{S}_z \rangle$ — appeal to vector model — QM tricky!

[More difficult since not in eigenstate of $\hat{S}_z$
in diagram $\underline{S}$ "~~precesses~~" with $\underline{L}$ around $\underline{J}$,
anywhere
$\underline{J}$ "~~precesses~~" anywhere around z].

Need to try write in terms of other ops.

uncertainty of $\underline{S}$ around $\underline{J}$ → only comp S_J along $\underline{J}$ non-zero

uncertainty of $\underline{J}$ around z → only the z-projection of S_J non-zero.

Uncertainty in direction of $\underline{S}$ around $\underline{J}$ implies only the comp of $\underline{S}$ ~~around~~along $\underline{J}$ will have non-zero expectation.
But, uncertainty of $\underline{J}$ around z, actually means only the z component of that!

~~Find component $\underline{S}$ in $\underline{J}$ direction~~

Decompose : $\underline{S} = (\underline{S}.\underline{n})\,\underline{n} + \underline{S}_{\perp}$

component of $\underline{S}$ along direction of unit vector $\underline{n}$

comp perpendicular to $\underline{n}$.

Want $\underline{n}$ in the $\underline{J}$ direction : $\underline{n} = \hat{\underline{J}} \big/ |\underline{J}| = \underline{J} \big/ \hbar\sqrt{J(J+1)}$

Hence $$\hat{\underline{S}} = \frac{(\hat{\underline{S}}.\hat{\underline{J}})}{J(J+1)\hbar^2}.\hat{\underline{J}} + \hat{\underline{S}}_{\perp}$$

Play scalar product trick : $\hat{\underline{L}}^2 = (\hat{\underline{J}} - \hat{\underline{S}})^2$ [illegible]

$$\longrightarrow \hat{\underline{S}}.\hat{\underline{J}} = \tfrac{1}{2}(\hat{\underline{J}}^2 + \hat{\underline{S}}^2 - \hat{\underline{L}}^2)$$

So
$$\hat{\underline{S}} = \frac{(\hat{J}^2 + \hat{S}^2 - \hat{L}^2)}{2J(J+1)\hbar^2}.\hat{\underline{J}} + \hat{\underline{S}}_{\perp}$$

~~Projecting z component~~

On average $\langle \hat{S}_{\perp} \rangle = 0$
and only z component of $\langle \hat{S} \rangle \neq 0$ } see diagram

$$\langle \hat{S}_z \rangle = \left[\frac{\langle \hat{J}^2 \rangle + \langle \hat{S}^2 \rangle - \langle \hat{L}^2 \rangle}{2J(J+1)\hbar^2} \right] \langle \hat{J}_z \rangle$$

$$= \frac{\hbar^2 (J(J+1) + S(S+1) - L(L+1))}{2J(J+1)\hbar^2} . m_J \hbar$$

since in eigenstate of ~~all~~ these operators, so replace with eigenvalues.

/ no need!

Hence $\left[\langle\hat{S}_z\rangle = \frac{\hbar}{2} m_J \left(\frac{J(J+1)+S(S+1)-L(L+1)}{J(J+1)} \right)\right]$

and

$$E_{mag} = \frac{e\hbar B}{2m} m_J \underbrace{\left[1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \right]}$$

$$= g_J \mu_B m_J . B$$

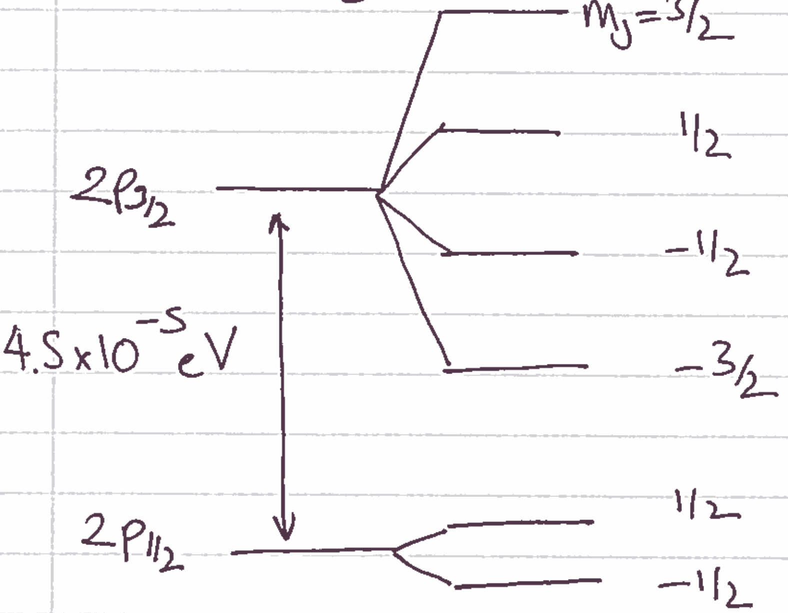
Landé g-factor.
[if you need this it is given]

ie. a level with q no. J will split into a ladder of states with different m_J values with separation $g_J \mu_B$.

Example: 2p levels in hydrogen $n=2$, $j=1/2, 3/2$
$l=1$ $S=1/2$.

$j=1/2$: $g_J = \left[1 + \frac{1/2 . 3/2 + 1/2 . 3/2 - 2}{2 \times 1/2 . 3/2} \right] = \frac{2}{3}$

$j=3/2$: $g_J = \left[1 + \qquad \right] = \frac{4}{3}$ splits twice as much since moments adding "in parallel"



instead of two spectroscopic lines to the $2S_{1/2}$ level now several.

selection rule $\Delta l = 1 \rightarrow \Delta m = 0, \pm 1$

Zeeman effect. ↓

work out possible transitions.

For perturbation theory to work: largest shift $\ll E_{so}$

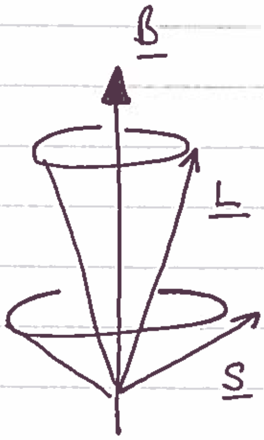
Largest shift: $g_{3/2} \cdot \mu_B \cdot \frac{3}{2} . B \ll 4.5 \times 10^{-5}$ eV

$$B \ll \frac{4.5 \times 10^{-5}}{\frac{4}{3} \times 5.8 \times 10^{-5} \times \frac{3}{2}} = 0.39\,T$$

ie. field of 0.04T or less as "weak"

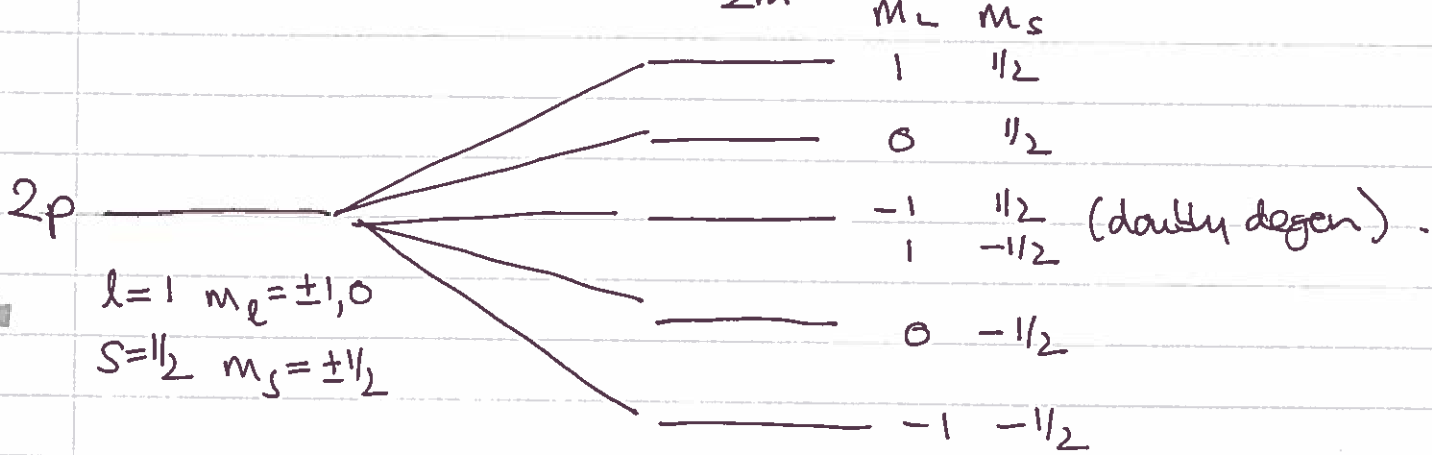
Now ramp up the field to much higher than this eg. 10T would need to switch around order of treating perturb^{n}s. ie. $\hat{H}_{mag}$ before $\hat{H}_{so}$

$\hat{H}_{mag} = \frac{eB}{2m}(\hat{L}_z + 2\hat{S}_z)$ — eigenstates of $\hat{L}_z$ and $\hat{S}_z$
m_L and m_s good quantum no's



"Paschen-Back effect"
unzips the coupling of $\underline{L}$ and $\underline{S}$ which now act independently.

$E_{mag} = \frac{eB\hbar}{2m}(m_L + 2m_s)$



P.S Zeeman effects at hyperfine level where $\underline{F} = \underline{I} + \underline{J}$ levels split in a weak field into m_F or strong fields decouple $\underline{I}$ and $\underline{J}$ in the Back Goudsmit effect.

[Eg. Precessing electron in B_z initially in α_x $\psi(t) = \frac{1}{\sqrt{2}}\begin{pmatrix} e^{-i\omega t} \\ e^{i\omega t} \end{pmatrix}$ ←

ie. manipulate α_x into other spinors
by turning on a field for certain lengths of time
evolves into α_y β_y β_x to within phase factor.]

(19) Quantum Information: Measurement and Entanglement

Mentioned that a 2-state system can act as a quantum bit of information, like a classical bit, spin up = 1 down = 0. But we can superpose qbits which in effect allows them to carry more information than a classical bit. Magnetic fields can process. One can exploit this quantum information for cryptography or computing if you rely on two features of QM: measurement and entanglement.

Measurement: QM has two different types of time dependence

(i) the evolution of the eigenstate encapsulated in the TDSE

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

⊏ preserves the normalisation
unitary matrices etc.

(ii) ~~the change~~ ~~[illegible]~~ brought about by measurement
if measure same observable with the result being a particular eigenvalue, the wavefunction immediately "collapses" into ~~an eigenstate~~ the corresponding ~~[illegible]~~. eigenstate.

eg. $\chi = c_1\alpha_z + c_2\beta_z$

Measure S_z and get result $+\frac{\hbar}{2}$

$$\chi \longrightarrow \alpha_z$$

The original information in χ is destroyed by the measurement.

[NB, can't tell what outcome is in single measurement
but if had many such states and made many
measurements prob of $+\hbar$ is $|c_1|^2$]

Entanglement:

Two things are entangled if the probabilities of outcomes of measurements on one are changed by measurements of the second.

For example:

A: $S=0$ spin-1/2 pair $\psi(1,2) = \frac{1}{\sqrt{2}}\left[\alpha_z(1)\beta_z(2) - \beta_z(1)\alpha_z(2)\right]$

Measure S_z of particle 1:

(i) if answer is $+\frac{\hbar}{2}$ $\psi(1,2) \longrightarrow \alpha_z(1)\beta_z(2)$

a measurement of particle 2 yields $-\frac{\hbar}{2}$ 100% prob.

(ii) if answer is $-\frac{\hbar}{2}$ $\psi(1,2) \rightarrow \beta_z(1)\alpha_z(2)$

measurement of particle 2 yields $\frac{\hbar}{2}$ 100% prob.

→ so entangled. [NB// on average with many such systems. get (i) and (ii) with 50% prob each]

B: $\psi(1,2) = \frac{1}{\sqrt{2}}\left[\alpha_z(1)\alpha_z(2) + \beta_z(1)\alpha_z(2)\right]$

Measure S_z of particle 1:

(i) if answer is $+\frac{\hbar}{2}$ $\psi(1,2) \rightarrow \alpha_z(1)\alpha_z(2)$

(ii) $-\frac{\hbar}{2}$ $\psi(1,2) \rightarrow \cancel{\alpha}\beta_z(1)\alpha_z(2)$

but in both cases 100% prob measuring particle 2 gives $\frac{\hbar}{2}$.

↓

so unentangled.

This state is a product:

$$\psi(1,2) = \frac{1}{\sqrt{2}}\left[\alpha_z(1) + \beta_z(1)\right]\alpha_z(2)$$

[Many ways to make entangled pairs
most popular now: "parametric down conversion" relies on non-linear optics: photon on a crystal converted elastically into two photons which are found to have perp polarisations.]

Going back to the entangled spin-0 pair

$$\psi(1,2) = \frac{1}{\sqrt{2}}\left[\alpha_z(1)\beta_z(2) - \beta_z(1)\alpha_z(2)\right]$$

if we were making measurements of S_x would want to use $\alpha_z = \frac{1}{\sqrt{2}}(\alpha_x + \beta_x)$ $\beta_z = \frac{1}{\sqrt{2}}(\alpha_x - \beta_x)$

subs and tidy you get

$$\psi(1,2) = \frac{1}{\sqrt{2}}\left[\beta_x(1)\alpha_x(2) - \alpha_x(1)\beta_x(2)\right]$$

so still entangled in this basis too! [Important for next lecture]

[Polarisation states of photons are two state systems that operate with similar AM. The two photons may travel apart ~~ab~~ before the measurements are made: a measurement of particle 1 at one location will tell you the outcome of a measurement at another location <u>before</u> you make it.

→ sounds weird - read about EPR paradox (like most paradoxes, it isn't one!)

[Entanglement arises naturally in systems with identical particles]

<u>Entanglement and identical particles:</u>

Two quantum mechanical particles of the same sort are absolutely identical!
[can't paint labels on electrons].

So the states $\psi(1,2)$ and $\psi(2,1)$ must have the same physical properties.
e.g. normalisation etc.
(otherwise probs change when particles switch]

So if $\hat{P}$ is an operator that exchanges particles

$\psi(2,1) = \hat{P}\,\psi(1,2) = p\,\psi(1,2)$ where p is some phase factor to ensure

$|\psi(2,1)|^2 = |\psi(1,2)|^2$

$\Downarrow$

$p^2 = 1$

$p = \pm 1$

~~[illegible] again~~ :

~~$\psi(1,2)$ [illegible] $\hat{P}\hat{P}\psi(1,2)$ [illegible]~~ $(1,2)$)

~~and [illegible]~~.

Either:

$p = +1$: wavefunction is symmetric under particle exchange
BOSONS. integer spin

$p = -1$: ~~[illegible]~~ is antisymmetric
FERMIONS. ½-integer spin.

spin-statistics theorem. consequence of ~~[illegible]~~ relativistic q. field theory ~~[illegible]~~ Pauli 1940

So if there are two particles in different states ϕ_n and ϕ_m:

needs relativistic approach to systems where relativistic effects otherwise negligible! ← but simple result should have simple explanation ???

boson pair : $\psi_{sym}(1,2) = \frac{1}{\sqrt{2}}\left[\phi_n(1)\phi_m(2) + \phi_m(1)\phi_n(2)\right]$

fermion pair : $\psi_{anti}(1,2) = \frac{1}{\sqrt{2}}\left[\phi_n(1)\phi_m(2) - \phi_m(1)\phi_n(2)\right]$

Swap particles : switch $m \Leftrightarrow n$: notice right signs.
Both are entangled states

If $m = n$ $\psi_{anti} = 0$ expression of Pauli exclusion.

~~Fermion [illegible] always entangled~~.

~~[illegible] entangled states~~.

→ and ψ_{sym} becomes unentangled!

~~[illegible] entangled~~.

Producing Entangled Systems.

(i) Positron annihilation ⇒ 2γ back to back with opp
$e^+ + e^-$ in S state; γ have spin polarisation.
which must be perp.

(ii) Low energy proton scat from hydrogen gas
incident/tgt protons move apart with $J=0, L=0$.

(iii) Parametric down conversion
nonlinear optical elastic conversion $\gamma \to 2\gamma$
perpendicular polarisations, although absolute
polarisation unknown.
beta barium borate

(iv) Splitting Cooper pairs in s/c
using single electron transistor.

(v) 500 ^{87}Rb atoms at μK.
put into a collective Rydberg state
ie. excite an electron in ensemble.
Stimulate emission of photon
entangled photon and "spin-wave" state
of ensemble.