1

Fine structure splitting: spin-orbit coupling

slide 1,3

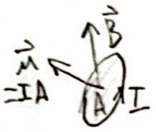
Interaction of electronic magnetic spin moment $\vec{\mu}_S$ with the orbital field given by:

$$H_{SO} = -\vec{\mu}_S \cdot \vec{B} \quad (1)$$

We have:

$$\vec{\mu}_L = -\frac{\overset{\approx 1}{g_L}\, e}{2m_e c}\vec{L} \quad (2) \qquad \vec{\mu}_S = -\frac{\overset{\approx 2}{g_e}\, e}{2m_e c}\vec{S} \quad (3)$$

orbital motion ≠ ~~the~~ magnetic moment



spin mag. mo.

Recall angular momentum coupling: $\vec{J} = \vec{L} + \vec{S}$ (4)

Hydrogen groundstate $1S_{1/2}$ fine structure

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Particle moving in an electric field $\vec{E}$ ~~produces~~ sees a magnetic field $\vec{B}$ in its reference frame due to special relativity:

$$\vec{B} = -\frac{1}{c^2}\vec{v} \times E + O\left(\frac{v^2}{c^2}\right) \quad (5)$$

- For hydrogen $Z=1$, $Ze=e$

Field; $\vec{E} = \frac{1}{e}\frac{\partial V(r)}{\partial r}\frac{\vec{r}}{r}$ (6), potential; $V(r) = \frac{-e^2}{4\pi\epsilon_0}\frac{1}{r}$ (7)

(1) becomes:

Sub. $(1) \rightarrow (8) \leftarrow (2) \leftarrow (3) \leftarrow (4)$

$$H_{so} = g_s \cdot \cancel{\frac{1}{2m_e} \cdot \frac{1}{m_e c^2}} \left(\frac{1}{r} \cdot \frac{\partial V(r)}{\partial r} \right) \vec{l} \cdot \vec{s} \qquad (8)$$

$$\frac{1}{2} g_s \frac{1}{2 m_e c^2}$$

$$\frac{\partial V(r)}{\partial r} = \frac{e^2}{4\pi \epsilon_0} \frac{1}{r^2} \qquad (9)$$

for hydrogen ($Z=1$).

Recall

- $g_s = 2$
- $\frac{1}{\epsilon_0} = \mu_0 c^2$

Sub. $(9) \rightarrow (8) \rightarrow (10)$

(8) becomes:

$$H_{so} = \left[\frac{1}{2 m_e^2 \cancel{c^2}} \frac{1}{r} \frac{e^2}{4\pi} \mu_0 \cancel{c^2} \frac{1}{r^2} \right] \vec{l} \cdot \vec{s}$$

$$= \left[\frac{\mu_0 e^2}{8\pi m_e^2} \frac{1}{r^3} \right] \vec{l} \cdot \vec{s} \qquad (10)$$

Recall from P.T. that perturbed Ham., H_{so}, acting on the unperturbed wave function $\psi^{(0)}$ gives interaction energy:

1st order

$$E_{so}^{(1)} = \langle \psi^{(0)} | H_{so} | \psi^{(0)} \rangle \qquad (11)$$

$$\overset{P.T.}{\Rightarrow} \frac{\mu_0 e^2}{8\pi m_e^2} \left\langle \frac{1}{r^3} \right\rangle \langle \vec{l} \cdot \vec{s} \rangle$$ ← expectation value of $\vec{l} \cdot \vec{s}$

- Evaluate $\langle \vec{l}\cdot\vec{s} \rangle$

Start with usual trick

$$\vec{j}^2 = \vec{l}^2 + \vec{s}^2 + 2\,\vec{l}\cdot\vec{s} \Rightarrow \vec{l}\cdot\vec{s} = \tfrac{1}{2}(\vec{j}^2 - \vec{l}^2 - \vec{s}^2)$$

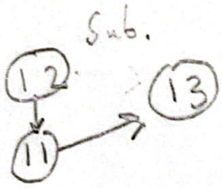
Recall

- $\langle j^2 \rangle = \hbar\, j(j+1)$

  $\langle l^2 \rangle = \hbar\, l(l+1)$

  $\langle s^2 \rangle = \hbar\, s(s+1)$

$$\therefore \quad \langle \vec{l}\cdot\vec{s} \rangle = \tfrac{1}{2}\hbar^2 [j(j+1) - l(l+1) - s(s+1)] \qquad (12)$$



giving expression for fine structure energy shift to 1st order of:

$$E^{(1)}_{SO} = \frac{\mu_0 e^2 \hbar^2}{8\pi m_e^2} \left\langle \frac{1}{r^3} \right\rangle \cdot \tfrac{1}{2}[j(j+1) - l(l+1) - s(s+1)]$$

for hydrogen

- general expression from P.T. for fine structure
- Analogous derivation for hyperfine splitting on top of the fine structure energy shift
- Now lets include the nuclear spin into the picture

Hyperfine splitting $\vec{F} = \vec{I} + \vec{J}$ (13)

- The coupling of $\vec{I} + \vec{J}$ to $\vec{F}$ gives additional 'hyperfine' states $F = I + J$ to ... $|I - J|$.

If $I < J \rightarrow 2I+1$ total states,

if $I > J \rightarrow 2J+1$ states

$\therefore$ knowledge of J + counting ~~number~~ # of states $\rightarrow$ nuclear spin, I

- Zero-field limit, energy splitting + atomic structure calculations gives us $\rightarrow$ nuclear moments $\mu, Q, \Omega, \ldots$

- Zeeman splitting

magnetic substates

$\rightarrow$ Weak field limit gives F ~~as a good number~~ # substates $m_f = -F, -F+1, \ldots, F-1, F$

$\rightarrow$ strong field limit, I, J decouple to individual projections $m_I, m_J \ldots$

lets define nuclear spin

$$\vec{I} = \sum_{i=1}^{A} (l_i + s_i)$$

you guys are in nuclear physics & will know all about shell structure of nuclei

$$= \vec{L} + \vec{S}$$

$$= \sum_{i=1}^{A} \vec{j}_i$$

- potentially very complicated, but nuclear ground state we only need to consider unpaired proton and/or unpaired neutron. Remaining nucleons ground state form spin ϕ pairs c.f. cooper pairs often referred to as the nuclear 'core'.

5/

Just as with the electron spin we have a nuclear magnetic dipole moment associated w/ treating the nucleus as a current loop.

$$\vec{\mu}_N = g_N \frac{\mu_N}{\hbar} \vec{I} \qquad (14)$$

Nuclear magneton $= \frac{e}{2 m_p} \hbar$ ← proton

n.b. $m_p \gg m_e$

nuclear g-factor ← some people consider g factor to be the actual nuclear structure part measured by the dipole moment. "everything we know"

$g_p \simeq 5.59$

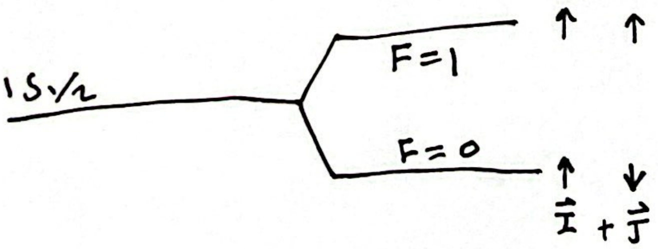
Similarly to FS, magnetic field produced at location of the nucleus by the orbital motion of its electron & $\vec{\mu}_s$ due to electron spin gives Ham:

$$H_{HF} = -\vec{\mu}_N \cdot \vec{B}_{int} \qquad (15)$$

Hyperfine structure of Hydrogen from p.t.

For hydrogen g.s. $1S_{1/2}$: $J = 1/2$, $I = 1/2$ (proton spin)

only two ways to couple : $F = 0, 1 \rightarrow 2$ levels



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classical magnetic dipole field from point charge / orbit / orbiting electron:

← Jackson E&M

$$\vec{B}_p = \frac{\mu_0}{4\pi r^3}\left[3(\vec{\mu}_p \cdot \hat{r})\hat{r} - \vec{\mu}_p\right] + \frac{2\mu_0}{3}\vec{\mu}_p\, \delta^3(\vec{r}) \qquad (16)$$

point not proton

6/ magnetic field at nucleus from electron orbital motion:

$$\vec{B}_L = \frac{2\mu_0}{r^3}\frac{\vec{L}}{\hbar} \qquad (17)$$

Just to make you aware this term exists for $L>0$

- $\vec{\mu}_p = \vec{\mu}_s$
- Hydrogen hand waving starts

$$\vec{B}_{int} = \cancel{-\frac{2\mu_0}{r^3}\frac{\vec{L}}{\hbar}} - \cancel{\frac{\mu_0}{4\pi r^3}\left[3(\vec{\mu}_p\cdot\hat{r})\hat{r} - \vec{\mu}_s\right]} - \frac{2\mu_0}{3}\vec{\mu}_s\,\delta^3(\vec{r}) \qquad (18)$$

For hydrogen g.s. ϕ for $1S_{1/2}$ — Averages to ϕ for s state (when we take expectation value later)

$$= -\frac{2\mu_0}{3}\vec{\mu}_s\,\delta^3(\vec{r}) \qquad \delta^3(\vec{r}) = \begin{cases} \phi & \text{if } \vec{r}>\phi \\ \infty & \text{if } \vec{r}=\phi \end{cases}$$

(at nucleus)

$(15) \rightarrow (19) \leftarrow (18)$

∴ (15) becomes

$$H_{HF} = -\frac{2\mu_0}{3}\vec{\mu}_p\cdot\vec{\mu}_s\,\delta^3(\vec{r}) \qquad (19)$$

1st order P.T. gives:

$$E^{(1)}_{HF} = \frac{\mu_0 g_p g_e e^2}{6 m_p m_e}\langle \vec{I}\cdot\vec{J}\rangle\,|\psi_{100}(0)|^2 \qquad (20)$$

nls — wave fn at origin

- recall $\vec{S}$ & $\vec{L}$ do not commute with H_{FS} ← fine structure Ham. but total $\vec{J}$ did. Similarly $\vec{I}$ & $\vec{J}$ don't commute but $\vec{F}$ does.

good op. — good op.

7/ using same trick as FS:

$$\vec{I}\cdot\vec{J} = \tfrac{1}{2}(F^2 - J^2 - I^2)$$

$$\langle \vec{I}\cdot\vec{J}\rangle = \frac{\hbar^2}{2}\left[F(F+1) - \overbrace{\underset{1/2}{J}(J+1) - \underset{1/2}{I}(I+1)}^{3/4}\right] \quad (21)$$

Hydrogenic wave function:

$$|\psi_{100}(0)| = \frac{1}{\pi a^3} \quad (22)$$

$n=1$

$F(F+1) = 0$ singlet ($F=0$)

or $= 2$ triplet ($F=1$)

$22 \rightarrow 20$

$21 \rightarrow 20 \rightarrow 23$

$\therefore$ (20) becomes

$$E^{(1)}_{HF} = \frac{\mu_0 g_p q_e e^2}{6 m_p m_e a^3 \pi}\frac{\hbar^2}{2}\begin{bmatrix} -\frac{3}{4} \text{ if } F=0 \\ +\frac{1}{4} \text{ if } F=1 \end{bmatrix}$$

$\Rightarrow \left[+\frac{1}{4}\right] \leftarrow$ triplet

$\Rightarrow \left[-\frac{3}{4}\right] \leftarrow$ singlet

$\uparrow$ number of m_F substates as we will see shortly w/ Zeeman splitting.

$$\Delta E^{(1)}_{HF} = E^{(1)}_{HF}(F=1) - E^{(1)}_{HF}(F=0)$$
$$= 5.88\times10^{-6}\,\text{eV}$$

$$\nu = \frac{\Delta E}{h} \approx 1420\ \text{MHz} \qquad \frac{c}{\nu} \approx 21\ \text{cm}$$

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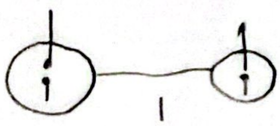

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In the absence of a magnetic field ... Slide 7

$$\Delta E_{HF} = \Delta E_M + \Delta E_Q + \Delta E_\Omega + \ldots$$

ΔE_M: GHz ~ MHz

ΔE_Q: nuclear electric quadrupole moment, MHz ~ kHz

ΔE_Ω: Nuclear magnetic octupole, > kHz

electric hexadecapole ... $\gtrsim$ Hz

$\Delta E_{HF}^{(2)}$ - 2nd order shift - close electronic states mix / make contribution. important for octupole extraction experimentally

In practice, general parameterization is used:

$$A = \frac{\mu_I B_e(0)}{\vec{I} \cdot \vec{J}} \quad (23)$$

(23) for different isotopes, same electronic state:

$$\frac{A_1}{A_2} \simeq \frac{(\mu_I/I)_1}{(\mu_I/I)_2}$$

$(\mu_I/I)_1$ - known moment

$(\mu_I/I)_2$ - unknown moment

Higher-order moments vanish for $l=0$ or $I = 0, \frac{1}{2}$.

Electric quadrupole moment H.F. shift:

$$\Delta E_Q^{(1)} = \underbrace{e Q \frac{\partial^2 V}{\partial z^2}}_{B} \frac{[3\langle \vec{I}\cdot\vec{J}\rangle \hbar^{-4} + \frac{3}{2}\langle \vec{I}\cdot\vec{J}\rangle \hbar^{-2} - I(I+1)J(J+1)]}{2I(2I-1)J(2J+1)}$$

Know

B ← hyperfine parameter B, nuclear electric quadrupole.

Again ratios work between isotopes, same electronic state:

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$$\frac{B_1}{B_2} \simeq \frac{Q_s^1}{Q_s^2}$$

9/ Zeeman effect from atom in external magnetic field $\vec{B}_{ext}$, interaction:

$$E = \frac{A\,\vec{I}\cdot\vec{J}}{\hbar} - \underbrace{\vec{\mu}_J\cdot\vec{B}_{ext} - \vec{\mu}_I\cdot\vec{B}_{ext}}_{\text{Both nuclear \& electronic magnetic moments interact with } \vec{B}_{ext}} \quad (24) \rightarrow \text{Slide 9}$$

Neglecting quadrupole effect.

Both nuclear & electronic magnetic moments interact with $\vec{B}_{ext}$

Weak-field Zeeman

If magnetic field is weak i.e. $\mu_J B_{ext} << A$, then it is appropriate to keep with notation of F states - as it has a constant projection along external field direction.

$\frac{A}{\hbar} \approx 100\,MHz \quad \mu_J \approx 1\mu_B$

$B_{ext} << \frac{A}{\mu_J} \sim 0.01\,T / 100\,G$

$F \rightarrow m_F = -F, -F+1, \ldots, F-1, F$

magnetic quantum number associated w/ F

We define $g_I' = g_I \frac{\mu_N}{\mu_B} \Rightarrow \mu_I = \frac{g_I \vec{I} \mu_N}{\hbar} = \frac{g_I' \vec{I} \mu_B}{\hbar}$

$$\mu_J = -\frac{g_J \vec{J} \mu_B}{\hbar}$$

$g_I' << g_J$

energy of an F state

(24) becomes $E = E_F + g_F \mu_B B_{ext} m_F$

where $$g_F = g_J \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} - g' \frac{F(F+1) - J(J+1) + I(I+1)}{2F(F+1)}$$

→ Slide 9

allows identification of sunspots from measurement of B

10/ Strong-field / Paschen-Bach

Slide 10

If $B_{ext} \gtrsim 0.01T/100G$, interaction of μ_J with B_{ext} becomes comparable with $A\vec{I}\cdot\vec{J}$, $\vec{I}\cdot\vec{J}$ coupling to $\vec{F}$ is no longer valid, instead I, m_I, J, m_J become appropriate.

i.e. the 'Paschen-Back effect' - independent precession around magnetic field.

↗

Important for astronomy for objects with high B, such as neutron stars & white dwarf stars

In general, increasing degeneracy splitting for:

- High nuclear spin I isomers
- Heavy / deformed nuclei
- complicated electronic structure → molecules: rotation, bending, vibration ...
- Intermediate field regions

→ Slides 11, 12

$$\text{Electronic structure} \xleftrightarrow{\text{Hyperfine structure}} \text{Nuclear structure}$$

→ slide 13

→ references: slide 14

→ transition / selection rules next