Physics 506 lecture 15

Stark effect + spin examples

Hydrogen atom in an external electric field

$$\hat{H}_0 = \frac{\hat{p}^2}{2\mu} - \frac{e^2}{r}$$

$$V_{\text{fine structure}} = -\frac{1}{8}\frac{\hat{p}^4}{\mu^3 c^2} + \frac{1}{2}\left(\frac{\hbar}{mc}\right)^2 \vec{L}\cdot\vec{S}\,\frac{e^2}{r^3}$$ (use Gottfried norm $\vec{L} = \frac{\vec{L}}{\hbar}$)

$$V_{\text{Stark}} = e\,\vec{\mathcal{E}}\cdot\vec{r} = e\,\mathcal{E}\,z = e\,\mathcal{E}\,r\cos\theta$$

(choose $\vec{\mathcal{E}}$ to lie along z axis)

What are good quantum numbers?

$\hat{H}_0$ — $\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z, \hat{J}^2, J_z$

$\hat{H}_0 + \hat{H}_{FS}$ — $\hat{L}^2, \hat{S}^2, \hat{J}^2, \hat{J}_z$

$\hat{H}_0 + \hat{H}_{FS} + \hat{H}_{\text{Stark}}$ — $\hat{S}^2, \hat{J}_z$

because z commutes with L_z, but not L_x or L_y.

$\Rightarrow$ does not commute with $\vec{L}^2$ or $\vec{J}^2$ but does for J_z.

$\hat{V}_{\text{Stark}}$ has odd parity, so connects only states with different parity (l odd with l even)

since ground state is an s-wave, no linear Stark shift

But for $n \geq 2$, different l are degenerate for $\hat{H}_0$

$\Rightarrow$ 1st order shift is possible.

Ground state $n=1$ $l=0$ $s=\frac{1}{2}$ $j=\frac{1}{2}$ degeneracy $m_j = \pm\frac{1}{2}$

but m_J is a good quantum number $\Rightarrow$ no first order shift.

so $E_{gs} = E_{FS} + \cancel{E^{(1)}_{stark}}^{\,0} + E^{(2)}_{stark}$

$$E^{(2)}_{stark} = \sum_{\substack{nj\ell \\ n\neq 1}}{}' \frac{|\langle n j m_J \ell | V_{stark} | n=1\ j=\tfrac{1}{2}\ m_J\ \ell=0\rangle|^2}{E_1^{(0)} - E_{nj\ell}^{(0)}}$$

smallest value of the denominator is $n=2$

denominator $\sim \frac{e^2}{a_0}$ and always negative

numerator $\sim e^2 \mathcal{E}^2 a_0^2$

$\Rightarrow$ shift $\sim \mathcal{E}^2 a_0^3$

$$|E^{(2)}| \leq \frac{e^2\mathcal{E}^2}{E_1^{(0)} - E_2^{(0)}} \sum_{nj\ell m'}{}' \langle 1 \tfrac{1}{2} m_J 0 | z | n j m' \ell\rangle\langle n j m' \ell | z | 1 \tfrac{1}{2} m_J 0\rangle$$

can sum over all n and m' since $n=0$ matrix element vanishes and $m' \neq m_J$ also vanishes

but $\sum_{njm'\ell} |njm'\ell\rangle\langle njm'\ell| = \mathbb{1}$

by completeness so

$$|E^{(2)}_{stark}| \leq \frac{e^2\mathcal{E}^2}{\underbrace{E_1^{(0)} - E_2^{(0)}}_{\frac{3}{8}\frac{e^2}{a_0}}} \underbrace{\langle 1 \tfrac{1}{2} m 0 | z^2 | 1 \tfrac{1}{2} m 0\rangle}_{a_0^2}$$

$$\leq \frac{8}{3} \mathcal{E}^2 a_0^3$$

This method is similar to the method of Dalgarno and Lewis (Shiff pg 266) which you may want to look at.

Strong field limit
neglect Fine structure

First non trivial case $n=2$

$J = 3/2,\ 1/2$ $\quad 2P_{3/2} \quad 2P_{1/2} \quad 2S_{1/2}$

$m_J = \pm 3/2$ terms have no linear shift (m_J good quantum #)

$m_J = \pm 1/2$ can mix p and s states turns out $m_J = \pm\frac{1}{2}$ are degenerate (called Kramer's doublets)

three states $|n j m \ell\rangle$

$|2\ \tfrac{3}{2}\ \tfrac{1}{2}\ 1\rangle \quad |2\ \tfrac{1}{2}\ \tfrac{1}{2}\ 1\rangle \quad |2\ \tfrac{1}{2}\ \tfrac{1}{2}\ 0\rangle$

In deg subspace we have

$$\begin{pmatrix} E_2^{(0)} & 0 & a \\ 0 & E_2^{(0)} & b \\ a^* & b^* & E_2^{(0)} \end{pmatrix} \qquad \begin{array}{l} a = e\mathcal{E}\langle 2\tfrac{3}{2}\tfrac{1}{2}1|z|2\tfrac{1}{2}\tfrac{1}{2}0\rangle = a^* \\ b = e\mathcal{E}\langle 2\tfrac{1}{2}\tfrac{1}{2}1|z|2\tfrac{1}{2}\tfrac{1}{2}0\rangle = b^* \end{array}$$

similar to HW problem.

Find $\quad a = -\sqrt{6}\, a_0 e\mathcal{E} \qquad b = -\sqrt{3}\, a_0 e\mathcal{E}$

(requires using wave functions and integrating)

$$\det\begin{pmatrix} E_2^0 - E & 0 & a \\ 0 & E_2^0 - E & \frac{1}{\sqrt{2}}a \\ a & \frac{1}{\sqrt{2}}a & E_2^0 - E \end{pmatrix} = (E_2^0 - E)^3 - (E_2^0 - E)\, a^2 \tfrac{3}{2} = 0$$

$$E = E_2^0, \qquad E = E_2^0 \pm a\sqrt{\tfrac{3}{2}}$$

$$= E_2^0 \pm 3 a_0 e\mathcal{E}$$

Weak field limit

normally take rel + SO first then add stark

but can do it all at once

$$\text{——} \quad 2P_{3/2} \qquad E_{3/2}$$

$$\text{——} \quad 2P_{1/2}\ 2S_{1/2} \qquad E_{1/2}$$

$$\begin{pmatrix} E_{3/2} & 0 & a \\ 0 & E_{1/2} & \frac{1}{\sqrt{2}}a \\ a & \frac{1}{\sqrt{2}}a & E_{1/2} \end{pmatrix}$$

$$\det\begin{pmatrix} E_{3/2}-E & 0 & a \\ 0 & E_{1/2}-E & \frac{1}{\sqrt{2}}a \\ a & \frac{1}{\sqrt{2}}a & E_{1/2}-E \end{pmatrix} = (E_{3/2}-E)(E_{1/2}-E)^2 - (E_{1/2}-E)|a|^2 - (E_{3/2}-E)\frac{|a|^2}{2} = 0$$

need to solve to get roots.

Algebra is straight forward but not too illuminating.

Spin example

3 spins on a triangle

$$H = A(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_2 \cdot \vec{S}_3 + \vec{S}_3 \cdot \vec{S}_1) + B S_1^z \qquad B \text{ small}$$

J_z is a good quantum number

eight states - organize via J, m_j

$j = 3/2$ — 4 states

$j = 1/2$ — 2 states

$j = 1/2$ — 2 states

Use $S_{tot}^- = S_1^- + S_2^- + S_3^-$ to get states

$$|j=3/2 \; m_j = 3/2\rangle = |\uparrow\uparrow\uparrow\rangle$$
$$|j=3/2 \; m_j = 1/2\rangle = \frac{1}{\sqrt{3}}\left[|\downarrow\uparrow\uparrow\rangle + |\uparrow\downarrow\uparrow\rangle + |\uparrow\uparrow\downarrow\rangle\right]$$
$$|j=3/2 \; m_j = -\tfrac{1}{2}\rangle = \frac{1}{\sqrt{3}}\left[|\downarrow\downarrow\uparrow\rangle + |\downarrow\uparrow\downarrow\rangle + |\uparrow\downarrow\downarrow\rangle\right]$$
$$|j=3/2 \; m_j = -\tfrac{3}{2}\rangle = |\downarrow\downarrow\downarrow\rangle$$

$$|j=\tfrac{1}{2} \; m_j = \tfrac{1}{2}\rangle = \frac{1}{\sqrt{2}}\left[|\downarrow\uparrow\uparrow\rangle - |\uparrow\downarrow\uparrow\rangle\right] \equiv |1\rangle$$
$$|j=\tfrac{1}{2} \; m_j = -\tfrac{1}{2}\rangle = \frac{1}{\sqrt{2}}\left[|\downarrow\uparrow\downarrow\rangle - |\uparrow\downarrow\downarrow\rangle\right]$$

$$|j=\tfrac{1}{2}, m_j = \tfrac{1}{2}\rangle' = \frac{1}{\sqrt{6}}\left[|\downarrow\uparrow\uparrow\rangle + |\uparrow\downarrow\uparrow\rangle - 2|\uparrow\uparrow\downarrow\rangle\right] \equiv |2\rangle$$
$$|j=\tfrac{1}{2} \; m_j = -\tfrac{1}{2}\rangle' = \frac{1}{\sqrt{6}}\left[|\downarrow\uparrow\downarrow\rangle + |\uparrow\downarrow\downarrow\rangle - 2|\downarrow\downarrow\uparrow\rangle\right]$$

Note $S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_1 = \frac{1}{2}\left[(S_1+S_2+S_3)^2 - S_1^2 - S_2^2 - S_3^2\right]$

useful trick

$$= \frac{1}{2}\begin{cases} \frac{3}{2}\cdot\frac{5}{2} - 3\cdot\frac{3}{4} = \frac{3}{4} & J = 3/2 \\ \frac{1}{2}\cdot\frac{3}{2} - 3\cdot\frac{3}{4} = -\frac{3}{4} & J = 1/2 \end{cases}$$

Consider $j = \frac{1}{2}$ $m_j = \frac{1}{2}$ state

$$E_0^0 = -\tfrac{3}{4}A \quad \text{two-fold degenerate}$$

$$\langle 1|S_1^z|1\rangle = 0$$

$$\langle 1|S_1^z|2\rangle = \frac{1}{\sqrt{2}}\left[\langle\downarrow\uparrow\uparrow| - \langle\uparrow\downarrow\uparrow|\right]\frac{1}{\sqrt{6}}\cdot\frac{1}{2}\left[-|\downarrow\uparrow\uparrow\rangle + |\uparrow\downarrow\uparrow\rangle - 2|\uparrow\uparrow\downarrow\rangle\right]$$

$$= \frac{1}{4\sqrt{3}}\cdot(-1-1) = \frac{-1}{2\sqrt{3}}$$

$$\langle 2|S_1^z|1\rangle = -\frac{1}{2\sqrt{3}}$$

$$\langle 2|S_1^z|2\rangle = \frac{1}{6}\cdot\frac{1}{2}\left[\langle\downarrow\uparrow\uparrow| + \langle\uparrow\downarrow\uparrow| - 2\langle\uparrow\uparrow\downarrow|\right]$$

$$\left[-|\downarrow\uparrow\uparrow\rangle + |\uparrow\downarrow\uparrow\rangle - 2|\uparrow\uparrow\downarrow\rangle\right]$$

$$= \frac{1}{12}\left[-1+1+4\right] = \frac{1}{3}$$

$$\det\begin{pmatrix} -\frac{3}{4}A - E & -B/2\sqrt{3} \\ -B/2\sqrt{3} & -\frac{3}{4}A + \frac{B}{3} - E \end{pmatrix} = 0$$

$$E^2 + E\left(-\tfrac{3}{2}A + \tfrac{B}{3}\right) + \tfrac{9}{16}A^2 - \tfrac{AB}{4} - \tfrac{B^2}{12} = 0$$

$$E = -\tfrac{3}{4}A + \tfrac{B}{6} \pm \tfrac{1}{2}\sqrt{\tfrac{9}{4}A^2 - AB + \tfrac{B^2}{9} - \tfrac{9}{4}A^2 + AB + \tfrac{B^2}{3}}$$

$$= -\tfrac{3}{4}A + \tfrac{B}{6} \pm \tfrac{1}{3}B = \begin{cases} -\tfrac{3}{4}A + \tfrac{1}{2}B \\ -\tfrac{3}{4}A - \tfrac{1}{6}B \end{cases}$$

to calculate 2nd order need MEs with $J = 3/2$

exact solution comes from cubic equation

$$\det\begin{pmatrix} -\frac{3A}{4}-E & -\frac{B}{2\sqrt{3}} & -\frac{B}{\sqrt{6}} \\ -\frac{B}{2\sqrt{3}} & -\frac{3}{4}A+\frac{1}{3}B-E & -\frac{B}{3\sqrt{2}} \\ -\frac{B}{\sqrt{6}} & -\frac{B}{3\sqrt{2}} & \frac{3}{4}A+\frac{1}{6}B-E \end{pmatrix} = 0$$

using mathematica gives

$E = -\frac{3}{4}A + \frac{1}{2}B$ $\checkmark$ exact to first order

$$E = -\frac{1}{4}\sqrt{9A^2+4AB+4B^2} \approx -\frac{3}{4}A - \frac{1}{6}B \quad \checkmark$$

$$E = \frac{1}{4}\sqrt{9A^2+4AB+4B^2} \approx \frac{3}{4}A + \frac{1}{6}B$$