Phys 506 lecture 19: Degenerate Perturbation Theory IV: Stark effect & spin examples

1 Hydrogen atom in an electric field

Consider a hydrogen atom in an external electric field:

$$\hat{H}_0 = \frac{\hat{p}^2}{2\mu} - \frac{e^2}{\hat{r}}, \text{ and } \hat{V}_{FS} = -\frac{1}{8}\frac{\hat{p}^4}{\mu^3 c^2} + \frac{1}{2}\left(\frac{\hbar}{mc}\right)^2 \hat{\mathbf{L}}\cdot\hat{\mathbf{S}}\frac{e^2}{\hat{r}^3}$$

and if we choose the electric field to be in the z-direction, we have that

$$\hat{V}_{Stark} = e\varepsilon\cdot\hat{\mathbf{r}} = e\varepsilon z = e\varepsilon r\cos\theta.$$

What are good quantum numbers? For $\hat{H}_0$:

$$\hat{L}^2, \hat{L}_z, \hat{S}^2, \hat{S}_z, \hat{J}^2, \hat{J}_z$$

For $\hat{H}_0 + \hat{H}_{FS}$:

$$\hat{L}^2, \hat{S}^2, \hat{J}^2, \hat{J}_z$$

and for $\hat{H}_0 + \hat{H}_{FS} + \hat{H}_{Stark}$:

$$\hat{S}^2, \hat{J}_z.$$

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

Since the ground state is an s-wave, there is no linear Stark shift. But, for $n \geq 2$ different l are degenerate for $\hat{H}_0$ so a first order shift is possible.

The ground state has $n = 1, l = 0, s = \frac{1}{2}$, and $j = \frac{1}{2}$ with degeneracy coming from the fact that $m_j = \pm\frac{1}{2}$. But m_j is a good quantum number so there is no first order shift. So,

$$E_{gs} = E_{FS} + E^{(2)}_{Stark}$$

since $E^{(1)}_{Stark} = 0$. Then,

$$E^{(2)}_{Stark} = \sum_{njl, n\neq 1} \frac{|\left\langle njm_s l\middle|\hat{V}_{Stark}\middle|n{=}1, j{=}\tfrac{1}{2}, m_j, l{=}0\right\rangle|^2}{E^{(0)}_1 - E^{(0)}_{njl}}$$

The smallest value of the denominator is for $n = 2$. The denominator goes like $\sim \frac{e^2}{a_0}$ and the numerator goes like $e^2\varepsilon^2 a_0^2$ so the shift is on the order of $\varepsilon^2 a_0^3$.

$$|E^{(2)}| \leq \frac{e^2\varepsilon^2}{E^{(0)}_1 - E^{(0)}_2} \sum_{njlm'} \left\langle \frac{1}{2}\ 1\ m_j\ 0\middle|z\middle|njm'l\right\rangle \left\langle njm'l\middle|z\middle|\frac{1}{2}\ 1\ m_j\ 0\right\rangle$$

But, by completeness

$$\sum_{njlm'} |njm'l\rangle \langle njm'l| = \mathbb{I}$$

so,

$$|E^{(2)}| \leq \frac{e^2\varepsilon^2}{E_1^{(0)} - E_2^{(0)}} \left\langle 1\ \frac{1}{2}\ m\ 0 \middle| z^2 \middle| 1\ \frac{1}{2}\ m\ 0 \right\rangle$$

Therefore,

$$|E^{(2)}| \leq \frac{8}{3}\varepsilon^2 a_0^3.$$

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

2 Strong field limit

Here, we can neglect fine structure. The first nontrivial case is $n = 2$. This gives us $j = \frac{3}{2}, \frac{1}{2}$, $m_j = \pm\frac{3}{2}$ (which have no linear shift) and $m_j = \pm\frac{1}{2}$ (which can mix states). It turns out that $m_j = \pm\frac{1}{2}$ are degenerate and called *Kramer's doublets*. This gives us three states $|njml\rangle$:

$$\left|2\ \frac{3}{2}\ \frac{1}{2}\ 1\right\rangle, \left|2\ \frac{1}{2}\ \frac{1}{2}\ 1\right\rangle, \left|2\ \frac{1}{2}\ \frac{1}{2}\ 0\right\rangle$$

In the degenerate subspace we have

$$\begin{pmatrix} E_2^{(0)} & 0 & a \\ 0 & E_2^{(0)} & b \\ a^* & b^* & E_2^{(0)} \end{pmatrix}$$

which is similar to a HW problem. Note that

$$a = e\varepsilon \left\langle 2\ \frac{3}{2}\ \frac{1}{2}\ 1 \middle| z \middle| 2\ \frac{1}{2}\ \frac{1}{2}\ 0 \right\rangle = a^*$$
$$b = e\varepsilon \left\langle 2\ \frac{1}{2}\ \frac{1}{2}\ 1 \middle| z \middle| 2\ \frac{1}{2}\ \frac{1}{2}\ 0 \right\rangle = b^*$$

After converting to wavefunctions and integrating, one can find

$$a = -\sqrt{6}a_0 e\varepsilon$$
$$b = -\sqrt{3}a_0 e\varepsilon$$

Now, we find the eigenvalues,

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

$$\implies E = E_2^0, E = E_2^0 \pm 3a_0 e\varepsilon$$

3 Weak field limit

We normally take relativistic effects and spin orbit coupling first then add the Stark effect but we can do it all at once. The $2p_{3/2}$ level has energy $E_{3/2}$ and the $2p_{1/2}2s_{1/2}$ level has energy $E_{1/2}$.

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

which we solve to get the roots. The algebra is straightforward but not too illuminating.

4 Spin example

Consider 3 spins on a triangle:

$$\hat{H} = A(\hat{\mathbf{S}_1}\cdot\hat{\mathbf{S}_2} + \hat{\mathbf{S}_2}\cdot\hat{\mathbf{S}_3} + \hat{\mathbf{S}_3}\cdot\hat{\mathbf{S}_1}) + BS_1^z$$

for a small B-field. Here J_z is a good quantum number. Here there are $2^3 = 8$ states labeled with J, m_j. $j = \frac{3}{2}$ has 4 states, $j = \frac{1}{2}$ has 2 states, and $j = \frac{1}{2}$ has 2 states. Use $S_{tot}^- = S_1^- + S_2^- + S_3^-$ to get all of the states.

$$\left|j=\frac{3}{2}, m_j = \frac{3}{2}\right\rangle = |\uparrow\uparrow\uparrow\rangle$$
$$\left|j=\frac{3}{2}, m_j = \frac{1}{2}\right\rangle = \frac{1}{\sqrt{3}}(|\downarrow\uparrow\uparrow\rangle + |\uparrow\downarrow\uparrow\rangle + |\uparrow\uparrow\downarrow\rangle)$$
$$\left|j=\frac{3}{2}, m_j = -\frac{1}{2}\right\rangle = \frac{1}{\sqrt{3}}(|\downarrow\downarrow\uparrow\rangle + |\downarrow\uparrow\downarrow\rangle + |\uparrow\downarrow\downarrow\rangle)$$
$$\left|j=\frac{3}{2}, m_j = -\frac{3}{2}\right\rangle = |\downarrow\downarrow\downarrow\rangle$$

Then,

$$\left|j=\frac{1}{2}, m_j = \frac{1}{2}\right\rangle = \frac{1}{\sqrt{2}}(|\downarrow\uparrow\uparrow\rangle - |\uparrow\downarrow\uparrow\rangle) \equiv |1\rangle$$
$$\left|j=\frac{1}{2}, m_j = -\frac{1}{2}\right\rangle = \frac{1}{\sqrt{2}}(|\downarrow\uparrow\downarrow\rangle - |\uparrow\downarrow\downarrow\rangle)$$

and

$$\left|j=\frac{1}{2}, m_j = \frac{1}{2}\right\rangle' = \frac{1}{\sqrt{6}}(|\downarrow\uparrow\uparrow\rangle + |\uparrow\downarrow\uparrow\rangle - 2\,|\uparrow\uparrow\downarrow\rangle) \equiv |2\rangle$$
$$\left|j=\frac{1}{2}, m_j = -\frac{1}{2}\right\rangle' = \frac{1}{\sqrt{6}}(|\downarrow\uparrow\downarrow\rangle + |\uparrow\downarrow\downarrow\rangle - 2\,|\downarrow\downarrow\uparrow\rangle)$$

Note $S_1\cdot S_2 + S_2\cdot S_3 + S_3\cdot S_1 = \frac{1}{2}((S_1+S_2+S_3)^2 - S_1^2 - S_2^2 - S_3^2)$. Now, consider the $j=\frac{1}{2}, m_j = \frac{1}{2}$ state.

$$E_0^0 = -\frac{3}{4}A$$

which is two-fold degenerate. Then,

$$\begin{aligned}
\langle 1|S_1^z|1\rangle &= 0\\
\langle 1|S_1^z|2\rangle &= \frac{1}{\sqrt{2}}(\langle\downarrow\uparrow\uparrow| - \langle\uparrow\downarrow\uparrow|)\frac{1}{\sqrt{6}}\cdot\frac{1}{2}(|\downarrow\uparrow\uparrow\rangle + |\uparrow\downarrow\uparrow\rangle - 2\,|\uparrow\uparrow\downarrow\rangle)\\
&= -\frac{1}{2\sqrt{3}}\\
\langle 2|S_1^z|1\rangle &= -\frac{1}{2\sqrt{3}}\\
\langle 2|S_1^z|2\rangle &= \frac{1}{6}\cdot\frac{1}{2}(\langle\downarrow\uparrow\uparrow| + \langle\uparrow\downarrow\uparrow| - 2\,\langle\uparrow\uparrow\downarrow|)(|\downarrow\uparrow\uparrow\rangle + |\uparrow\downarrow\uparrow\rangle - 2\,|\uparrow\uparrow\downarrow\rangle)\\
&= \frac{1}{3}
\end{aligned}$$

Then, we find the eigenvalues

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

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

Hence,

$$E = -\frac{3}{4}A + \frac{B}{6} \pm \frac{1}{3}B$$

Compare with the exact solution which comes from a cubic equation.

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

Using Mathematica gives

$$\begin{aligned}
E &= -\frac{3}{4}A + \frac{1}{2}B \checkmark\\
E &= -\frac{1}{4}\sqrt{9A^2 + 4AB + 4B^2} = -\frac{3}{4}A - \frac{1}{6}B + \cdots \checkmark\\
E &= \frac{1}{4}\sqrt{9A^2 + 4AB + 4B^2} = \frac{3}{4}A + \frac{1}{6}B + \cdots
\end{aligned}$$