The Hamiltonian describing the Hydrogen atom in external electric and magnetic fields

$$H_{ext} = H_0 + H_{fs} + \mu_B \frac{1}{\hbar} \vec{B} \cdot (\vec{L} + 2\vec{S}) + e\vec{E} \cdot \vec{R}$$

605.1. Constant, Uniform External Magnetic Field $\vec{B}$: The Zeeman Effect

The above Hamiltonian becomes

$$H = \frac{1}{2m}\vec{P}^2 - \frac{e^2}{R\pi\epsilon_0} + H_{kin} + H_{SO} + H_D + \mu_B \frac{1}{\hbar} \vec{B} \cdot (\vec{L} + 2\vec{S})$$

Choosing $\vec{B}$ to be in the z-direction $\vec{B} = B\hat{z}$, we have

$$H = H_0 + H_{fs} + \frac{\mu_B B}{\hbar}(L_z + 2S_z)$$

We can determine the energy level shifts simply in two limiting cases the weak field Zeeman effect and the strong field Zeeman effect (Paschen-Back effect). Weak & strong are relative words; in this case it is relative to the H_{so} term.

The weak B-field case:

Consider the magnetic field to be such that the energy shifts due to the magnetic moment interaction energies are much smaller than the spin-orbit energy shifts

$$\left|\frac{\mu_B B}{\hbar}(L_z + 2S_z)\right| \ll |H_{so}| .$$

Recalling that the matrix elements of H_{fs} in the $|n, l, s; J, M\rangle$ basis are diagonal, we can work in it and treat $H' = \frac{\mu_B B}{\hbar}(L_z + 2S_z)$ as a

perturbation. We found that these diagonal matrix elements of H_{fs} are independent of M; and hence are $(2J+1)$-fold degenerate. Applying degenerate perturbation theory we have that the first order energy shifts are given by (actually we consider this as non-degenerate R-S theory on the J's since different parity degenerate states cannot mix)

$$E_{nl_J}(M) = E_{nl_J} + \Delta E_{nl_J}(M)$$

where E_{nl_J} are the fine-structure energy levels we have already calculated (-942-)

same J, not J, J' as in the full case

$$E_{nl_J} = E_n^0 + \langle n, l, s=\tfrac{1}{2}, J, M | H_{fs} | n, l, s=\tfrac{1}{2}, J, M \rangle$$

and $\Delta E_{nl_J}(M)$ are the weak field Zeeman effect splittings we will find by diagonalizing the matrix elements of H' according to degenerate R-S perturbation theory (page -871-)

So we must consider $\Delta E_{nlJ}(M) =$

$$\langle n,l,s=\tfrac{1}{2};J,M'|H'|n,l,s=\tfrac{1}{2};J,M\rangle$$

$$= \frac{\mu_B B}{\hbar}\langle n,l,s=\tfrac{1}{2};J,M'|(L_z+2S_z)|n,l,s=\tfrac{1}{2};J,M\rangle$$

$$= \frac{\mu_B B}{\hbar}\langle n,l,s=\tfrac{1}{2};J,M'|(J_z+S_z)|n,l,s=\tfrac{1}{2};J,M\rangle$$

insert

since $J_z = L_z + S_z$. In order to evaluate the S_z matrix element we make use of the Wigner-Eckart Theorem (pages -818- and -819- to -821-). For a vector operator $\vec{V}$, its matrix elements are proportional to those of $\vec{J}$

$$\langle n;J,M'|\vec{V}|n;J,M\rangle = \frac{\langle n,J|\vec{J}\cdot\vec{V}|n,J\rangle}{\hbar^2 J(J+1)} \times$$

$$\times \langle n;J,M'|\vec{J}|n;J,M\rangle$$

(Recall our discussion of the Landé g-factor in the $\mathcal{H}(J)$ subspace $\vec{V} = c\vec{J}$. Thus $\langle \vec{J}\cdot\vec{V}\rangle = c\langle \vec{J}^2\rangle$, but in $\mathcal{H}(J)\langle \vec{J}^2\rangle = J(J+1)\hbar^2$, So $\vec{V} = \frac{\langle \vec{J}\cdot\vec{V}\rangle}{\hbar^2 J(J+1)}\vec{J}$)

Since $\vec{S}$ is a vector operator, we have

$$\langle n;J,M'|\vec{S}|n;J,M\rangle = \frac{\langle n,J|\vec{J}\cdot\vec{S}|n,J\rangle}{\hbar^2 J(J+1)} \times$$

$$\times \langle n;J,M'|\vec{J}|n;J,M\rangle$$

Then

$$\langle n,\ell,s=\tfrac{1}{2};J,M'|(L_z+2S_z)|n,\ell,s=\tfrac{1}{2};J,M\rangle$$

$$= \left[1 + \frac{\langle n,\ell,s=\frac{1}{2};J,M|\vec{J}\cdot\vec{S}|n,\ell,s=\frac{1}{2};J,M\rangle}{\hbar^2 J(J+1)}\right] M\hbar\,\delta_{MM'}$$

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

$$= \left[1 + \frac{J(J+1) - \ell(\ell+1) + \frac{3}{4}}{2J(J+1)}\right] M\hbar\,\delta_{MM'}$$

The H' matrix element is also diagonal according to R-S degenerate perturbation theory (page -8>(-1) These eigenvalues give the energy shifts

Then

$$\Delta E_{nl_J}(M) = \mu_B B M \left[1 + \frac{J(J+1) - l(l+1) + \frac{3}{4}}{2J(J+1)}\right]$$

The weak field Zeeman effect shift in the fine structure Hydrogen spectrum.

Now for $J = l \pm \frac{1}{2}$ this becomes after a little algebra

$$\Delta E_{nl_{J=l\pm\frac{1}{2}}}(M) = \mu_B B M \left[1 \pm \frac{1}{2l+1}\right]$$

Thus the energy of the $|n, l, s=\frac{1}{2}; J, M\rangle$ state including the fine structure and weak field Zeeman effects becomes in first order

$$E_{nl_{J=l\pm\frac{1}{2}}}(M) = E_n^0 + \langle n, l, s=\tfrac{1}{2}; J, M | H_{fs} | n, l, s=\tfrac{1}{2}; J, M\rangle + \mu_B B M \left[1 \pm \frac{1}{2l+1}\right]$$

with the Hfs matrix element discussed on pages -942- to -943-.

For the case of $n=2$; Recall that $l=0(=s), 1(=p)$ and $J=\frac{1}{2},\frac{3}{2}$ (pages -950- to -958-)

$$E_{2S_{1/2}}(M) = -\frac{mc^2\alpha^2}{8}\left[1+\frac{5}{16}\alpha^2\right] + 2M\mu_B B$$

$$E_{2P_{1/2}}(M) = -\frac{mc^2\alpha^2}{8}\left[1+\frac{5}{16}\alpha^2\right] + \frac{2}{3}M\mu_B B$$

$$E_{2P_{3/2}}(M) = -\frac{mc^2\alpha^2}{8}\left[1+\frac{1}{16}\alpha^2\right] + \frac{4}{3}M\mu_B B$$

The $2S_{1/2} - 2P_{1/2}$ degeneracy is Removed as well as the $(2J+1)$-fold degeneracy of each level.

We can easily find the energy shifts in the other limiting case. The strong field Zeeman also called the Paschen-Back effect:

The strong B-field case:

Now let the $\vec{B}$-field be such that the magnetic moment interaction energy is much greater than the spin-orbit energy shifts

$$\left| \frac{\mu_B B}{\hbar} (L_z + 2S_z) \right| >> |H_{so}| .$$

It now makes sense to use the basis states $|n, l, s=\frac{1}{2}; m, m_s\rangle$ since now H_0, H_{kin}, H_D and L_z, S_z are diagonal in this basis.

But $\vec{L}\cdot\vec{S}$ that is H_{so} is no longer diagonal,

$$\langle n, l, s=\tfrac{1}{2}; m', m_s' | H_{so} | n, l, s=\tfrac{1}{2}; m, m_s \rangle$$

$$= \frac{e^2}{2m^2c^2} \langle n, l, s=\tfrac{1}{2}; m', m_s' | \frac{1}{R^3} \vec{L}\cdot\vec{S} | n, l, s=\tfrac{1}{2}; m, m_s \rangle$$

but $\vec{L}\cdot\vec{S} = \frac{1}{2} L_+ S_- + \frac{1}{2} L_- S_+ + L_z S_z$, so

$$= \frac{e^2\hbar^2}{2m^2c^2} \langle n, l | \frac{1}{R^3} | n, l \rangle \Big[m m_s \delta_{mm'} \delta_{m_s m_s'}$$

$$+ \tfrac{1}{2}\sqrt{l(l+1) - m(m+1)}\, \delta_{m_s, \frac{1}{2}} \delta_{m_s', -\frac{1}{2}} \delta_{m', m+1}$$

$$+ \tfrac{1}{2}\sqrt{l(l+1) - m(m-1)}\, \delta_{m_s, -\frac{1}{2}} \delta_{m_s', \frac{1}{2}} \delta_{m', m-1} \Big]$$

Thus applying again R-S degenerate perturbation theory to $H = H_0 + H'$ with the energy shifts given by the eigenvalues of the H' matrix in the $|n,l,s=\frac{1}{2};m,m_s\rangle$ basis and

$$H' = H_{kin} + H_{so} + H_D + \frac{\mu_B B}{\hbar}(L_z + 2S_z).$$

$$\langle n,l,s=\tfrac{1}{2};m',m_s'|H'|n,l,s=\tfrac{1}{2};m,m_s\rangle$$

$$= \delta_{mm'}\delta_{m_s m_s'}\left[\langle n,l|H_{kin} + H_D + \frac{e^2\hbar^2}{2m^2c^2}\frac{m m_s}{R^3}|n,l\rangle + \mu_B B(m+2m_s)\right]$$

$$+\delta_{m',m+1}\delta_{m_s,\frac{1}{2}}\delta_{m_s',-\frac{1}{2}}\left[\tfrac{1}{2}\sqrt{l(l+1)-m(m+1)}\times \frac{e^2\hbar^2}{2m^2c^2}\langle n,l|\frac{1}{R^3}|n,l\rangle\right]$$

$$+\delta_{m',m-1}\delta_{m_s,-\frac{1}{2}}\delta_{m_s',\frac{1}{2}}\left[\tfrac{1}{2}\sqrt{l(l+1)-m(m-1)}\times \frac{e^2\hbar^2}{2m^2c^2}\langle n,l|\frac{1}{R^3}|n,l\rangle\right]$$

Thus we must find the eigenvalues of this matrix to find the first order energy level shifts in the Paschen-Back case.

To be specific we consider the $n=2$ $l=1(=p)$ states. Recall that

$$\langle 2p|H_{kin}|2p\rangle = -\frac{7}{384}mc^2\alpha^4 \qquad \text{(page-954-)}$$

$$\langle 2p|H_D|2p\rangle = 0 \qquad \text{(page-955-)}$$

$$\langle 2p|\frac{e^2\hbar^2}{2m^2c^2}\frac{1}{R^3}|2p\rangle = \frac{e^2\hbar^2}{2m^2c^2}\frac{1}{24a_0^3} \qquad \text{(page-946-)}$$

$$= \frac{1}{48}mc^2\alpha^4 \qquad \text{(page-923-)}$$

Thus the H' matrix is a 6×6 ($m=1,0,-1$, $m_s=\pm\frac{1}{2}$)

given by

$$\langle n=2, l=1, s=\tfrac{1}{2}; \underbrace{m', m_s'}_{\text{Rows}} | H' | n=2, l=1, s=\tfrac{1}{2}; \underbrace{m, m_s}_{\text{columns}}\rangle$$

$$\equiv (H')_{\underbrace{(m', m_s')}_{\text{Rows}}\ \underbrace{(m, m_s)}_{\text{columns}}}$$

$$\langle H' \rangle_{(m',m_s')(m,m_s)} =$$

$(m',m_s') \backslash (m,m_s)$	$(1,\frac{1}{2})$	$(1,-\frac{1}{2})$	$(0,\frac{1}{2})$	$(0,-\frac{1}{2})$	$(-1,\frac{1}{2})$	$(-1,-\frac{1}{2})$
$(1,\frac{1}{2})$	$(2\mu_B B - \frac{mc^2\alpha^4}{128})$	0	0	0	0	0
$(1,-\frac{1}{2})$	0	$-\frac{11}{384}mc^2\alpha^4$	$\frac{\sqrt{2}}{96}mc^2\alpha^4$	0	0	0
$(0,\frac{1}{2})$	0	$\frac{\sqrt{2}}{96}mc^2\alpha^4$	$(\mu_B B - \frac{7}{384}mc^2\alpha^4)$	0	0	0
$(0,-\frac{1}{2})$	0	0	0	$(-\mu_B B - \frac{7}{384}mc^2\alpha^4)$	$\frac{\sqrt{2}}{96}mc^2\alpha^4$	0
$(-1,\frac{1}{2})$	0	0	0	$\frac{\sqrt{2}}{96}mc^2\alpha^4$	$-\frac{11}{384}mc^2\alpha^4$	0
$(-1,-\frac{1}{2})$	0	0	0	0	0	$(-2\mu_B B - \frac{mc^2\alpha^4}{128})$

Thus the 6×6 is block diagonal

The first order energy shifts are the eigenvalues. For $(m=1, m_s=\frac{1}{2})$ and $(m=-1, m_s=-\frac{1}{2})$ we have

$$E_{2p}(m=+1, m_s=+\tfrac{1}{2}) = E_2^0 + 2\mu_B B - \frac{1}{128} mc^2\alpha^4$$

$$E_{2p}(m=-1, m_s=-\tfrac{1}{2}) = E_2^0 - 2\mu_B B - \frac{1}{128} mc^2\alpha^4$$

The remaining eigenvalues are found by diagonalizing the 2 (2×2) sub-matrices. We can do this to first order in $mc^2\alpha^4$ exploiting the fact that $\mu_B B >> mc^2\alpha^4$ here.

The 2×2 matrices have the form

$$\begin{bmatrix} A+a & b \\ b & c \end{bmatrix}$$ with $A >> a, b, c$ and $a \sim b \sim c \neq 0$.

We can diagonalize this to find

$$\begin{vmatrix} \lambda-(A+a) & b \\ b & \lambda-c \end{vmatrix} = 0 = \lambda^2 + (A+a)c - b^2 - (A+a+c)\lambda$$

$$\Rightarrow \lambda = \tfrac{1}{2}(A+a+c) \pm \tfrac{1}{2}\sqrt{(A+a+c)^2 - 4[(A+a)c - b^2]}$$

$$= \tfrac{1}{2}(A+a+c) \pm \tfrac{1}{2}\sqrt{(A+a-c)^2 + 4b^2}$$

$$= \tfrac{1}{2}(A+a+c) \pm \tfrac{1}{2}(A+a-c)\left(1 + 4\frac{b^2}{(A+a-c)^2}\right)^{1/2}$$

$$\approx \tfrac{1}{2}(A+a+c) \pm \tfrac{1}{2}(A+a-c)\left[1 + 2\frac{b^2}{(A+a-c)^2} + \cdots\right]$$

$$\lambda \approx \begin{cases} A+a + O\left(\frac{b^2}{A}\right) \\ c + O\left(\frac{b^2}{A}\right) \end{cases}$$

Thus the eigenvalues are just the diagonal matrix elements to first order in (a,b,c). Thus we can ignore the off-diagonal spin-orbit matrix elements to determine the energy shifts to first order; $mc^2\alpha^4$.

So

$$E_{2p}(m=1, m_s=-\tfrac{1}{2}) = E_2^0 - \frac{11}{384}mc^2\alpha^4$$

$$E_{2p}(m=0, m_s=\tfrac{1}{2}) = E_2^0 + \mu_B B - \frac{7}{384}mc^2\alpha^4$$

$$E_{2p}(m=0, m_s=-\tfrac{1}{2}) = E_2^0 - \mu_B B - \frac{7}{384}mc^2\alpha^4$$

$$E_{2p}(m=-1, m_s=\tfrac{1}{2}) = E_2^0 - \frac{11}{384}mc^2\alpha^4$$

Thus $E_{2p}(m=-1, m_s=\frac{1}{2}) = E_{2p}(m=1, m_s=-\frac{1}{2})$; to this order they are degenerate and independent of B.

Thus we can plot the Zeeman splitting of the 2p-energy levels in a Zeeman diagram. Recall that the C-G change of basis from $|m, m_s\rangle$ states to $|J, M\rangle$ states is unitary, so the eigenvalues of H' are independent of which basis we use to express H' matrix elements.

(Note: we could use C-G coefficients to find H' matrix in the $|J,M\rangle$ basis; no reason to since H' eigenvalues are independent of which basis we expand H'.

Recall

$$\left|J=\tfrac{3}{2}, M=\tfrac{1}{2}\right\rangle = \sqrt{\tfrac{2}{3}}\left|m=0, m_s=\tfrac{1}{2}\right\rangle + \tfrac{1}{\sqrt{3}}\left|m=1, m_s=-\tfrac{1}{2}\right\rangle$$

$$\left|J=\tfrac{1}{2}, M=\tfrac{1}{2}\right\rangle = \sqrt{\tfrac{2}{3}}\left|m=1, m_s=-\tfrac{1}{2}\right\rangle - \tfrac{1}{\sqrt{3}}\left|m=0, m_s=\tfrac{1}{2}\right\rangle$$

For instance; thus the H' submatrix becomes

$$\begin{array}{c|cc} (J,M') \backslash (J,M) & \left(\frac{3}{2},\frac{1}{2}\right) & \left(\frac{1}{2},\frac{1}{2}\right) \\ \left(\frac{3}{2},\frac{1}{2}\right) & \frac{2}{3}\mu_B B - \frac{mc^2\alpha^4}{128} & -\frac{\sqrt{2}}{3}\mu_B B \\ \left(\frac{1}{2},\frac{1}{2}\right) & -\frac{\sqrt{2}}{3}\mu_B B & \frac{1}{3}\mu_B B - \frac{5}{128}mc^2\alpha^4 \end{array}$$

i.e. $\left\langle \tfrac{3}{2},\tfrac{1}{2}\right| H' \left|\tfrac{3}{2},\tfrac{1}{2}\right\rangle = \left(\sqrt{\tfrac{2}{3}}\left\langle 0,\tfrac{1}{2}\right| + \tfrac{1}{\sqrt{3}}\left\langle 1,-\tfrac{1}{2}\right|\right) H' \left(\sqrt{\tfrac{2}{3}}\left|0,\tfrac{1}{2}\right\rangle + \tfrac{1}{\sqrt{3}}\left|1,-\tfrac{1}{2}\right\rangle\right)$

$$= \tfrac{2}{3}\mu_B B - \frac{mc^2\alpha^4}{128}.$$

The eigenvalues are the same as found in the $|m=1, m_s=-\tfrac{1}{2}\rangle$, $|m=0, m_s=\tfrac{1}{2}\rangle$ basis

$$\begin{vmatrix} \left(\lambda - \frac{2}{3}\mu_B B + \frac{mc^2\alpha^4}{128}\right) & \frac{\sqrt{2}}{3}\mu_B B \\ \frac{\sqrt{2}}{3}\mu_B B & \left(\lambda - \frac{1}{3}\mu_B B + \frac{5}{128}mc^2\alpha^4\right) \end{vmatrix} = 0$$

$$\Rightarrow \lambda^2 + \lambda\left(-\mu_B B + \frac{3}{64}mc^2\alpha^4\right) - \mu_B B\left(\frac{11}{384}mc^2\alpha^4\right) + \underbrace{\frac{5}{(128)^2}\left(mc^2\alpha^4\right)^2}_{\text{ignore as small}} = 0$$

$$\Rightarrow \lambda = \begin{cases} \mu_B B - \frac{7}{384}mc^2\alpha^4 \\ -\frac{11}{384}mc^2\alpha^4 \end{cases}$$

as found on page -984-.)

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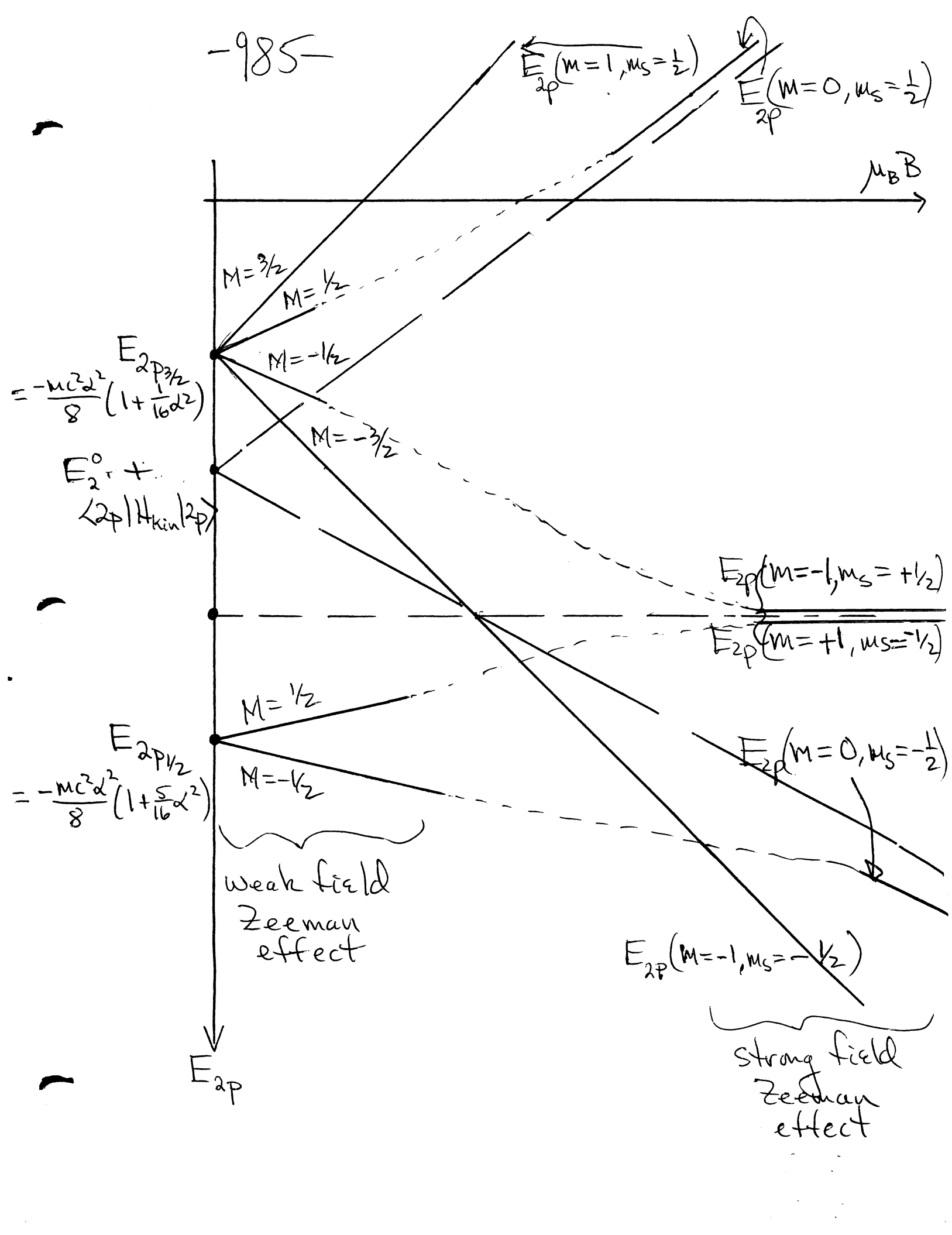
i.e. $H_{JM} = U^\dagger H_{LMS} U$ so the e.v. equation is

$$0 = \det|H_{JM} - \lambda\mathbb{1}| = \det|U^\dagger H_{LMS} U - \lambda \underbrace{U^\dagger U}_{\mathbb{1}}|$$

$$= \det U^\dagger \det U \det|H_{LMS} - \lambda\mathbb{1}|$$

$$= \underbrace{\frac{1}{\det U}}_{=1} \det U \det|H_{LMS} - \lambda\mathbb{1}|$$

$$= \det|H_{LMS} - \lambda\mathbb{1}|, \text{ the same e.v. } \lambda.$$


$E_{2p}(m=1, m_s=\frac{1}{2})$
$E_{2p}(m=0, m_s=\frac{1}{2})$
$\mu_B B$
$M=3/2$
$M=1/2$
$M=-1/2$
$M=-3/2$
$E_{2p_{3/2}} = -\frac{mc^2\alpha^2}{8}\left(1+\frac{1}{16}\alpha^2\right)$
$E_2^0 + \langle 2p|H_{kin}|2p\rangle$
$E_{2p}(m=-1, m_s=+1/2)$
$E_{2p}(m=+1, m_s=-1/2)$
$M=1/2$
$M=-1/2$
$E_{2p_{1/2}} = -\frac{mc^2\alpha^2}{8}\left(1+\frac{5}{16}\alpha^2\right)$
$E_{2p}(m=0, m_s=-\frac{1}{2})$
weak field Zeeman effect
$E_{2p}(m=-1, m_s=-1/2)$
strong field Zeeman effect
E_{2p}

In calculating these 2 limiting cases we ordered the perturbative effects due to H_{fs} and $H_{Zeeman} = \mu_B B \frac{1}{\hbar}(L_z + 2S_z)$. In the weak field case, we first diagonalized H_{at} + H_{fs} using degenerate R-S perturbation theory (i.e. $|n,l,s;J,M\rangle$ basis) and then we applied non-degenerate R-S perturbation theory to find the additional 1st order shift due to Hzeeman, i.e. we ignored off diagonal in J terms. In the strong field case, we proceeded oppositely, we first diagonalized H_{at} + H_{Zeeman} and then treated H_{fs} as a perturbation. In the general intermediate strength magnetic field case, we must consider both Hamiltonian simultaneously $H' = H_{fs} + H_{Zeeman}$ as the perturbation when applying degenerate R-S perturbation theory. Thus the first order energy shifts are found by diagonalizing this matrix in $|JLM\rangle$ space, i.e. diffrent non-diagonal in J but diagonal in M.