electrodynamics (QED). One finds that the $2s_{1/2}$ level is raised wrt the $2p_{1/2}$ level by the "Lamb shift"

$$\begin{array}{l} 2s_{1/2} \ \underline{\qquad\qquad} \\ \qquad\qquad\quad \updownarrow \ \sim 4.4\times 10^{-6}\,\mathrm{eV} \ (\sim 1057\ \mathrm{MHz}) \\ 2p_{1/2} \ \underline{\qquad\qquad} \end{array}$$

6.5. The Hydrogen Atom In Electric and Magnetic Fields

In addition to the fine structure relativistic corrections to the Coulomb Hydrogen spectrum, we can also consider the effects of external, constant uniform electric and magnetic fields on the spectrum. The electric field $\vec{E}$ and magnetic field $\vec{B}$ are given in terms of the scalar ϕ and vector $\vec{A}$ potentials

$$\vec{B} = \vec{\nabla} \times \vec{A}$$

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial}{\partial t}\vec{A} \ .$$

Recall that the physical values of the electric & magnetic fields $\vec{B}, \vec{E}$ are given by an equivalence class of potentials ϕ and $\vec{A}$. That is given $\phi, \vec{A}$ we have a unique $\vec{E}$ & $\vec{B}$ given above, but given $\vec{E}$ and $\vec{B}$ we do not determine $\phi, \vec{A}$ uniquely only up to a <u>gauge transformation</u>.

If $\vec{A}' \equiv \vec{A} + \vec{\nabla}\Lambda$ and $\phi' \equiv \phi - \frac{\partial}{\partial t}\Lambda$

where $\Lambda = \Lambda(\vec{r}, t)$ is an arbitrary function,

then
$$\vec{E}' = -\vec{\nabla}\phi' - \frac{\partial}{\partial t}\vec{A}'$$
$$= -\vec{\nabla}\phi + \vec{\nabla}\frac{\partial}{\partial t}\Lambda - \frac{\partial}{\partial t}\vec{A} - \frac{\partial}{\partial t}\vec{\nabla}\Lambda$$
$$= \vec{E} - \left[\frac{\partial}{\partial t}, \vec{\nabla}\right]\Lambda$$
$$= \vec{E} \qquad \text{for smooth enough } \Lambda,$$

and likewise
$$\vec{B}' = \vec{\nabla}\times\vec{A}'$$
$$= \vec{\nabla}\times\vec{A} + \vec{\nabla}\times\vec{\nabla}\Lambda$$
$$= \vec{\nabla}\times\vec{A} = \vec{B}.$$

$\vec{E}$ & $\vec{B}$ are invariant under gauge transformation

Then when a charged particle interacts with an electric and magnetic field it must do it in a manner that is also gauge invariant, that is that depends only on the gauge equivalence class of potentials $\phi, \vec{A}$, not the particular choice within an equivalence class.

Since the potential energy of a charged q particle in the scalar potential ϕ is simply $q\phi$ a gauge transformation of $\phi \to \phi' = \phi - \frac{\partial}{\partial t}\Lambda$ will change the Hamiltonian $H \to H - q\frac{\partial}{\partial t}\Lambda$. Then

for Schrödinger's equation to be unchanged we must make a gauge transformation of the wavefunction by a phase that depends on time and space

$$\psi'(\vec{r},t) \equiv e^{+\frac{iq}{\hbar}\Lambda(\vec{r},t)}\,\psi(\vec{r},t)$$

Then

$$i\hbar\frac{\partial}{\partial t}\psi' = -q\frac{\partial}{\partial t}\Lambda\,\psi' + e^{+\frac{iq}{\hbar}\Lambda}\,i\hbar\frac{\partial}{\partial t}\psi$$

will give rise to a $-q\frac{\partial}{\partial t}\Lambda$ term exactly cancelling the $-q\frac{\partial}{\partial t}\Lambda$ term from the Hamiltonian. But now the wavefunction ψ' depends on a Λ-phase then since the momentum in the $\{|\vec{r}\rangle\}$ basis is just the gradient we have that

$$\vec{p}\,\psi' = -i\hbar\vec{\nabla}\psi'$$

$$= +q\vec{\nabla}\Lambda\,\psi' + e^{+\frac{iq\Lambda}{\hbar}}(-i\hbar\vec{\nabla}\psi).$$

Hence we pick up an extra term that depends on the gauge Λ. Then if ψ interacts with $\vec{A}$ in such a way that whenever we have a momentum factor we also have a $-q\vec{A}$ factor: under a gauge transformation this will result in

$$(\vec{p} - q\vec{A})\psi \longrightarrow (\vec{p} - q\vec{A}')\psi'$$

$$= (-i\hbar\vec{\nabla} - q\vec{A} - q\vec{\nabla}\Lambda)e^{+\frac{iq}{\hbar}\Lambda}\psi$$

$$= (-q\cancel{\vec{\nabla}\Lambda} + q\cancel{\vec{\nabla}\Lambda})\psi'$$

$$+ e^{+\frac{iq}{\hbar}\Lambda}(-i\hbar\vec{\nabla} - q\vec{A})\psi$$

$$= e^{+\frac{iq}{\hbar}\Lambda}(\vec{p} - q\vec{A})\psi$$

The unwanted gauge phase Λ cancels! Thus we have the means of determining the form of interaction of a charged particle with electric and magnetic fields in a gauge invariant manner.

<u>The gauge Principle</u>: If a (spinless) charged particle evolves in time according to the Hamiltonian $H(\vec{P}, \vec{R})$ in the absence of electric and magnetic fields; then in their presence the charged particle evolves in time according to the Hamiltonian

$$H_{E\text{-}M} = H(\vec{P} - q\vec{A}, \vec{R}) + q\phi(\vec{R}, t) .$$

The replacement of $\vec{P} \rightarrow \vec{P} - q\vec{A}$ is called the principle of minimal substitution.

To summarize then: The simultaneous transformation of the state $|\psi\rangle \to |\psi'\rangle$ and the electromagnetic potentials $\phi \to \phi'$; $\vec{A} \to \vec{A}'$ by a gauge transformation

$$\phi' = \phi - \frac{\partial}{\partial t}\Lambda$$

$$\vec{A}' = \vec{A} + \vec{\nabla}\Lambda$$

$$|\psi'\rangle = e^{+\frac{iq}{\hbar}\Lambda}|\psi\rangle$$

leaves the Schrödinger equation unchanged (i.e. the dynamics) is given for the above equivalence class)

$$i\hbar\frac{\partial}{\partial t}|\psi'\rangle = H_{E\text{-}m}(\vec{P}-q\vec{A}', q\phi', \vec{R})|\psi'\rangle$$

$$\Leftrightarrow i\hbar\frac{\partial}{\partial t}|\psi\rangle = H_{e\text{-}m}(\vec{P}-q\vec{A}, q\phi, \vec{R})|\psi\rangle.$$

Since $|\psi'\rangle = U(\Lambda)|\psi\rangle$ is a unitary transformation,
(OK) ~~all matrix elements are left invariant,~~
so all physical observables are the same,
Thus for a free particle with charge

which is described by the Hamiltonian

$$H_0 = \frac{1}{2m}\vec{P}^2$$

we have that the Hamiltonian describing the particle's interaction with the external electromagnetic fields is simply

$$H_{em} = \frac{1}{2m}(\vec{P} - q\vec{A})^2 + q\phi$$

$$= \frac{1}{2m}\vec{P}^2 - \frac{q}{2m}(\vec{P}\cdot\vec{A} + \vec{A}\cdot\vec{P}) + \frac{q^2}{2m}\vec{A}^2 + q\phi$$

as we already know.

For constant, uniform external electric and magnetic fields we can choose a gauge so that

$$\vec{A} = \frac{1}{2}\vec{B}\times\vec{R}$$

$$\phi = -\vec{E}\cdot\vec{R} \quad .$$

Thus we can check that $\vec{E} = -\vec{\nabla}\phi - \cancel{\frac{\partial}{\partial t}\vec{A}}^{\,0}$
$= +\vec{\nabla}(\vec{E}\cdot\vec{R}) = \vec{E}$ ✓

$$\vec{B} = \vec{\nabla}\times\vec{A} \Rightarrow B_i = \epsilon_{ijk}\frac{\partial}{\partial x_j}A_k$$

$$= \epsilon_{ijk}\frac{\partial}{\partial x_j}\left(\frac{1}{2}\epsilon_{klm}B_l x_m\right)$$

$$= \frac{1}{2}\underbrace{\epsilon_{ijk}\epsilon_{klm}}_{=(\delta_{il}\delta_{jm}-\delta_{im}\delta_{jl})} B_l \underbrace{\frac{\partial}{\partial x_j}x_m}_{=\delta_{jm}}$$

$$= \tfrac{1}{2}(\delta_{i\ell}\delta_{jm} - \delta_{im}\delta_{j\ell}) B_\ell \delta_{jm}$$
$$= \tfrac{1}{2}(\delta_{i\ell}\delta_{jj} - \delta_{ij}\delta_{j\ell}) B_\ell = \tfrac{1}{2}(3B_i - B_i)$$
$$= B_i \checkmark .$$

Thus

$$H_{em} = \frac{1}{2m}\vec{P}^2 - \frac{q}{2m}\left[\vec{P}\cdot\tfrac{1}{2}(\vec{B}\times\vec{R}) + \tfrac{1}{2}(\vec{B}\times\vec{R})\cdot\vec{P}\right]$$
$$+ \frac{q^2}{2m}\,\frac{1}{4}(\vec{B}\times\vec{R})^2 - q\vec{E}\cdot\vec{R}$$

As usual

$$\vec{P}\cdot\tfrac{1}{2}(\vec{B}\times\vec{R}) + \tfrac{1}{2}(\vec{B}\times\vec{R})\cdot\vec{P}$$
$$= \tfrac{1}{2}P_i\,\epsilon_{ijk}B_jX_k + \tfrac{1}{2}\epsilon_{ijk}B_jX_kP_i$$
$$= \tfrac{1}{2}\epsilon_{ijk}B_j\left[X_kP_i + \underbrace{[P_i, X_k]}_{=-i\hbar\delta_{ik}} + X_kP_i\right]$$
$$= \epsilon_{ijk}B_jX_kP_i - \frac{i\hbar}{2}\underbrace{\epsilon_{iji}}_{0}B_j$$
$$= \vec{B}\cdot(\vec{R}\times\vec{P})$$
$$= \vec{B}\cdot\vec{L} = \vec{L}\cdot\vec{B} .$$

And
$$\vec{A}^2 = \frac{1}{4}(\vec{B}\times\vec{R})^2$$
$$= \frac{1}{4}\epsilon_{ijk}\epsilon_{ilm} B_j X_k B_l X_m$$
$$= \frac{1}{4}(\delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl}) B_j B_l X_k X_m$$
$$= \frac{1}{4}\left(\vec{B}^2\vec{R}^2 - (\vec{B}\cdot\vec{R})^2\right) .$$

Thus
$$\boxed{H_{em} = \frac{1}{2m}\vec{P}^2 - \frac{q}{2m}\vec{B}\cdot\vec{L} + \frac{q^2}{8m}[\vec{B}^2\vec{R}^2 - (\vec{B}\cdot\vec{R})^2] - q\vec{E}\cdot\vec{R} .}$$

If in addition the particle has spin it will have a magnetic moment and hence an interaction with the magnetic field

$$H_{mag} = -\vec{\mu}\cdot\vec{B}$$

with $\vec{\mu} = g\frac{q}{2M}\vec{S}$

anomalous magnetic moment

So $\boxed{H_{mag} = -g\frac{q}{2m}\vec{B}\cdot\vec{S}}$

For a spin $\frac{1}{2}$ electron we have that

$g \simeq 2$; $q = -e$ so this becomes

$$H_{mag} = \frac{e}{m}\vec{B}\cdot\vec{S}$$

$$= 2\mu_B \frac{1}{\hbar}\vec{B}\cdot\vec{S}$$

where the Bohr magneton $\mu_B = \frac{e\hbar}{2m}$.

For a Hydrogen atom subjected to external constant uniform electric and magnetic fields we proceed similarly. Recall the Hamiltonian in the absence of the external fields

$$H = H_0 + H_{fs} \quad \text{with}$$

$$H_0 = \frac{1}{2m}\vec{P}^2 - \frac{e^2}{R4\pi\epsilon_0}$$

$$H_{fs} = H_{kin} + H_{so} + H_D \quad \text{where}$$

$$H_{Kin} = -\frac{1}{8m^3c^2}\vec{P}^4 = mc^2\alpha^4\left(\frac{-a_0^4}{8\hbar^4}\vec{P}^4\right)$$

$$H_{SO} = +\frac{e^2/4\pi\epsilon_0}{2m^2c^2}\frac{1}{R^3}\vec{L}\cdot\vec{S} = mc^2\alpha^4\left(\frac{a_0^3}{2\hbar^2}\frac{1}{R^3}\vec{L}\cdot\vec{S}\right)$$

$$H_D = \frac{\pi e^2\hbar^2}{4\pi\epsilon_0 2m^2c^2}\delta^3(\vec{R}) = mc^2\alpha^4\left(\frac{\pi}{2}a_0^3\delta^3(\vec{R})\right).$$

Thus in the presence of additional external electric and magnetic fields the Hydrogen Hamiltonian is

$$H_{ext} = \frac{1}{2m}(\vec{P}+e\vec{A})^2 - \frac{1}{8m^3c^2}(\vec{P}+e\vec{A})^4$$

$$+\frac{e^2}{4\pi\epsilon_0}\frac{1}{2m^2c^2}\frac{1}{R^3}\vec{L}\cdot\vec{S} + \frac{\pi e^2\hbar^2}{4\pi\epsilon_0 2m^2c^2}\delta^3(\vec{R})$$

$$+ 2\mu_B\frac{1}{\hbar}\vec{B}\cdot\vec{S} - \frac{e^2}{R4\pi\epsilon_0} + e\vec{E}\cdot\vec{R}$$

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

$$+\frac{e^2}{8m}\left[\vec{B}^2\vec{R}^2 - (\vec{B}\cdot\vec{R})^2\right] + e\vec{E}\cdot\vec{R}$$

$$-\frac{1}{8m^3c^2}\left[(\vec{P}+e\vec{A})^4 - \vec{P}^4\right]$$

having used Hem from before.

Note that this is just the Hamiltonian we would find if we 1) couple the orbital and spin magnetic moments to the $\vec{B}$-field and 2) we make a non-relativistic expansion of the relativistic kinetic energy formula

$$T = \sqrt{(\vec{p}+e\vec{A})^2c^2 + m^2c^4} - mc^2$$

$$\simeq \frac{1}{2m}(\vec{P}+e\vec{A})^2 - \frac{1}{8m^3c^2}(\vec{P}+e\vec{A})^4$$

3) include electrostatic energy $q\phi$, in addition to the spin-orbit and Darwin fine structure terms of before.

In general the external field energy is quite small compared to mc^2 and so we will only keep terms through the order of $\left(\frac{\text{kinetic energy}}{mc^2}\right)^2$ and ignore terms the order of $\left(\frac{\text{kinetic energy} \times \text{field energy}}{m^2c^4}\right)$. Thus we drop the $\frac{[(\vec{P}+e\vec{A})^4 - \vec{P}^4]}{m^3c^2}$ term.

In addition the $\vec{B}^2$ and $(\vec{B}\circ\vec{R})^2$ terms are dropped. Thus we have

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

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

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

The above Hamiltonian becomes

$$H = \frac{1}{2m}\vec{P}^2 - \frac{e^2}{R 4\pi\epsilon_0} + H_{kin} + H_{SO} + H_D$$
$$+ \mu_B \frac{1}{\hbar} \vec{B} \cdot (\vec{L} + 2\vec{S})$$

Choosing $\vec{B}$ to be in the z-direction

$\vec{B} = B\hat{z}$; we have

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

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.

<u>The weak B-field case</u>:

Consider the magnetic field to be such that the energy shifts due to the magnetic moment interaction energy 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, since different parity degenerate states cannot mix)

$$E_{n\ell_J}(M) = E_{n\ell_J} + \Delta E_{n\ell_J}(M)$$

where $E_{n\ell_J}$ are the fine-structure energy levels we have already calculated (- -)

Same J but J, J as in the full case

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

and $\Delta E_{n\ell_J}(M)$ 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 - -)

So consider

$$\Delta E_{n l_J}(M)$$

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

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

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

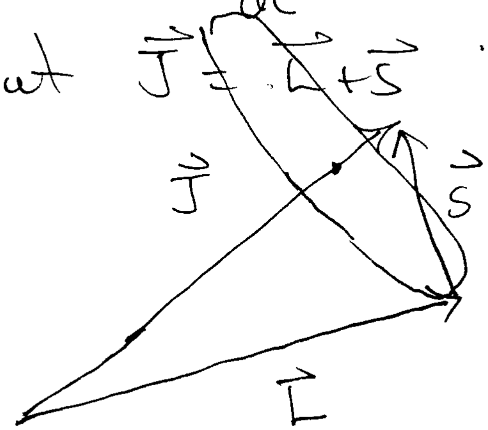
Since

$$J_z = L_z + S_z .$$

Now the total angular momentum commutes with H, and so is a constant

$$\frac{d}{dt}\langle\vec{J}\rangle = \frac{i}{\hbar}\langle[H,\vec{J}]\rangle = 0$$ Ehrenfest's Theorem

But $\vec{J} = \vec{L} + \vec{S}$ So



$\vec{L}$ & $\vec{S}$ precess rapidly about $\vec{J}$ (Classically)

But the time average of $\vec{S}$ is just its projection onto $\vec{J}$

$$\vec{S}_{average} = \frac{\vec{S}\cdot\vec{J}}{\vec{J}^2}\vec{J}$$

Now $\vec{S}\cdot\vec{J} = \frac{1}{2}[\vec{J}^2 + \vec{S}^2 - \vec{L}^2]$ Hence

$(\vec{J} = \vec{L} + \vec{S})$

$$\langle n,l,s=\tfrac{1}{2};J,M'|\,(\vec{L}+2\vec{S})\,|n,l,s=\tfrac{1}{2},J,M\rangle$$

$$= \langle n,l,s=\tfrac{1}{2},J,M'|\left(1+\frac{\vec{S}\cdot\vec{J}}{\vec{J}^2}\right)\vec{J}\,|n,l,s=\tfrac{1}{2},J,M\rangle$$

$$= \langle n,l,s=\tfrac{1}{2},J,M'|\left[1+\frac{1}{2}\frac{J(J+1)+s(s+1)-l(l+1)}{J(J+1)}\right]\vec{J}\,|n,l,s=\tfrac{1}{2},J,M\rangle$$

$$= \left[1+\frac{J(J+1)+\frac{3}{4}-l(l+1)}{2J(J+1)}\right]\langle n,l,s=\tfrac{1}{2},J,M'|\vec{J}|n,l,s=\tfrac{1}{2},J,M\rangle$$

Now since $\vec{B} = B\hat{k}$ we have

$$\boxed{\langle n, l, s=\tfrac{1}{2}; J, M' | L_z + 2S_z | n, l, s=\tfrac{1}{2}, J, M \rangle = \left[1 + \frac{J(J+1) - l(l+1) + \frac{3}{4}}{2J(J+1)}\right] \hbar M \delta_{MM'}}$$

Bohr magneton $\mu_B = \frac{e\hbar}{2m} = 5.788 \times 10^{-5}\ eV/T$

So

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

$$\equiv \mu_B g_J M B$$

where $g_J = \left[1 + \frac{J(J+1) - l(l+1) + \frac{3}{4}}{2J(J+1)}\right]$

g_J is the Landé g-factor.

Now for $J = l \pm \frac{1}{2}$ this becomes

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

(Just to repeat

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

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

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

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

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

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

Then back to the energy shift

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

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

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

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

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

with the H_{fs} matrix element discussed on pages - to - .

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

$$\boxed{\begin{aligned} E_{2s_{1/2}}(M) &= -\frac{mc^2\alpha^2}{8}\left[1+\frac{5}{16}\alpha^2\right] + 2M\mu_B B \\ E_{2p_{1/2}}(M) &= -\frac{mc^2\alpha^2}{8}\left[1+\frac{5}{16}\alpha^2\right] + \frac{2}{3}M\mu_B B \\ E_{2p_{3/2}}(M) &= -\frac{mc^2\alpha^2}{8}\left[1+\frac{1}{16}\alpha^2\right] + \frac{4}{3}M\mu_B B \end{aligned}}$$

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 <u>strong field Zeeman</u> also called the <u>Paschen-Back effect</u>:

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,

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

$$= \frac{\frac{e^2}{4\pi\epsilon_0}}{2m^2c^2}\langle n,l,s=\tfrac{1}{2}; m', m_s'|\frac{1}{R^3}\vec{L}\cdot\vec{S}|n,l,s=\tfrac{1}{2}; m, m_s\rangle$$

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

$$= \frac{e^2\hbar^2}{4\pi\epsilon_0 2m^2c^2}\langle n,l|\frac{1}{R^3}|n,l\rangle\Big[m m_s \delta_{mm'}\delta_{m_s m_s'}$$

Gr. prob. 4.19 (4.121) (4.136)

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

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

Thus applying again R-S degenerate perturbation theory to $H = H_0 + H'$ will 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

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

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

$$= \delta_{mm'}\delta_{m_s m_s'}\Big[\langle n,l|H_{Kin} + H_D + \frac{e^2\hbar^2}{4\pi\epsilon_0\, 2m^2c^2}\frac{m\, m_s}{R^3}|n,l\rangle + \mu_B B(m+2m_s)\Big]$$

$$+\delta_{m',m+1}\delta_{m_s,\frac{1}{2}}\delta_{m_s',-\frac{1}{2}}\Big[\tfrac{1}{2}\sqrt{l(l+1)-m(m+1)} \times \frac{e^2\hbar^2}{4\pi\epsilon_0\, 2m^2c^2}\langle n,l|\tfrac{1}{R^3}|n,l\rangle\Big]$$

$$+\delta_{m',m-1}\delta_{m_s,-\frac{1}{2}}\delta_{m_s',\frac{1}{2}}\Big[\tfrac{1}{2}\sqrt{l(l+1)-m(m-1)} \times \frac{e^2\hbar^2}{4\pi\epsilon_0\, 2m^2c^2}\langle n,l|\tfrac{1}{R^3}|n,l\rangle\Big]$$

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

$$\langle 2p | H_{Kin} | 2p \rangle = -\frac{7}{384} mc^2 \alpha^4 \qquad \text{(page -200-)}$$

$$\langle 2p | H_D | 2p \rangle = 0 \qquad \text{(page -201-)}$$

$$\langle 2p | \frac{e^2\hbar^2}{2m^2c^2} \frac{1}{R^3} | 2p \rangle = \frac{e^2\hbar^2}{4\pi\epsilon_0 2m^2c^2} \frac{1}{24 a_0^3} \qquad \text{(page -192-)}$$

$$= \frac{1}{48} mc^2 \alpha^4 \qquad \text{(page -169-)}$$

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

given by

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

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

$$
(H')_{(m',m_s')(m,m_s)} =
$$

$$
\begin{array}{c|c}
 (m',m_s') \backslash (m,m_s) & \begin{array}{cccccc} \quad(1,\tfrac{1}{2})\quad & \quad(1,-\tfrac{1}{2})\quad & \quad(0,\tfrac{1}{2})\quad & \quad(0,-\tfrac{1}{2})\quad & \quad(-1,\tfrac{1}{2})\quad & (-1,-\tfrac{1}{2}) \end{array} \\
 \begin{array}{c} (1,\tfrac{1}{2}) \\ (1,-\tfrac{1}{2}) \\ (0,\tfrac{1}{2}) \\ (0,-\tfrac{1}{2}) \\ (-1,\tfrac{1}{2}) \\ (-1,-\tfrac{1}{2}) \end{array} &
 \begin{bmatrix}
 \left(2\mu_B B - \frac{mc^2\alpha^4}{128}\right) & 0 & 0 & 0 & 0 & 0 \\
 0 & -\frac{11}{384}mc^2\alpha^4 & \frac{\sqrt{2}}{96}mc^2\alpha^4 & 0 & 0 & 0 \\
 0 & \frac{\sqrt{2}}{96}mc^2\alpha^4 & \left(\mu_B B - \frac{7}{384}mc^2\alpha^4\right) & 0 & 0 & 0 \\
 0 & 0 & 0 & \left(-\mu_B B - \frac{7}{384}mc^2\alpha^4\right) & \frac{\sqrt{2}}{96}mc^2\alpha^4 & 0 \\
 0 & 0 & 0 & \frac{\sqrt{2}}{96}mc^2\alpha^4 & -\frac{11}{384}mc^2\alpha^4 & 0 \\
 0 & 0 & 0 & 0 & 0 & \left(-2\mu_B B - \frac{mc^2\alpha^4}{128}\right)
 \end{bmatrix}
\end{array}
$$

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

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

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

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

We can diagonalize this to find

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

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

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

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

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

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

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

$$\boxed{\begin{aligned} E_{2p}(m=1, m_s=-\tfrac{1}{2}) &= E_2^0 - \tfrac{11}{384} mc^2\alpha^4 \\ E_{2p}(m=0, m_s=\tfrac{1}{2}) &= E_2^0 + \mu_B B - \tfrac{7}{384} mc^2\alpha^4 \\ E_{2p}(m=0, m_s=-\tfrac{1}{2}) &= E_2^0 - \mu_B B - \tfrac{7}{384} mc^2\alpha^4 \\ E_{2p}(m=-1, m_s=\tfrac{1}{2}) &= E_2^0 - \tfrac{11}{384} mc^2\alpha^4 \end{aligned}}$$

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

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

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

for instance; thus the H′ submatrix becomes

$$\begin{array}{c|c} {}_{(J,M')}\backslash^{(J,M)} & \begin{array}{cc} \quad(\tfrac{3}{2},\tfrac{1}{2}) \qquad\qquad & \qquad (\tfrac{1}{2},\tfrac{1}{2}) \end{array} \\ \begin{array}{c} (\tfrac{3}{2},\tfrac{1}{2}) \\[3em] (\tfrac{1}{2},\tfrac{1}{2}) \end{array} & \begin{pmatrix} \tfrac{2}{3}\mu_B B - \tfrac{mc^2\alpha^4}{128} & -\tfrac{\sqrt{2}}{3}\mu_B B \\[2em] -\tfrac{\sqrt{2}}{3}\mu_B B & \tfrac{1}{3}\mu_B B - \tfrac{5}{128}mc^2\alpha^4 \end{pmatrix} \end{array}$$

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

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

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

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

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

$\Rightarrow$

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

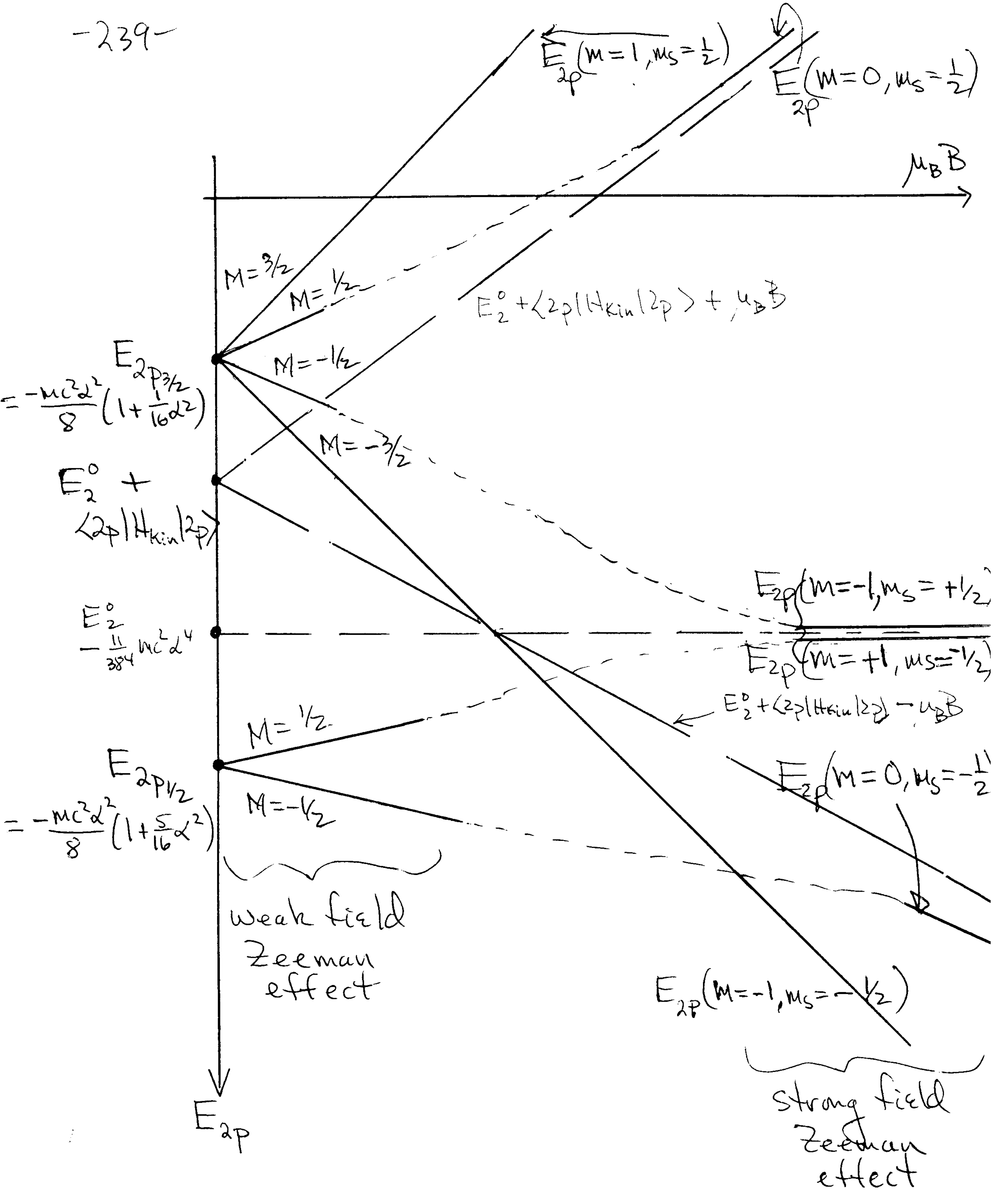
as found on page .)

<u>i.e</u> $H_{JM} = U^\dagger H_{lm_s} U$ so the e.v. equation is

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

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

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


$E_{2p}(m=1, m_s=\frac{1}{2})$
$E_{2p}(m=0, m_s=\frac{1}{2})$
$\mu_B B$
$M=3/2$
$M=1/2$
$E_2^0 + \langle 2p|H_{kin}|2p\rangle + \mu_B B$
$E_{2p_{3/2}} = -\frac{mc^2\alpha^2}{8}\left(1+\frac{1}{16}\alpha^2\right)$
$M=-1/2$
$M=-3/2$
$E_2^0 + \langle 2p|H_{kin}|2p\rangle$
$E_{2p}(m=-1, m_s=+1/2)$
$E_2^0 - \frac{11}{384}mc^2\alpha^4$
$E_{2p}(m=+1, m_s=-1/2)$
$E_2^0 + \langle 2p|H_{kin}|2p\rangle - \mu_B B$
$M=1/2$
$E_{2p_{1/2}} = -\frac{mc^2\alpha^2}{8}\left(1+\frac{5}{16}\alpha^2\right)$
$M=-1/2$
$E_{2p}(m=0, m_s=-\frac{1}{2})$
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 $H_0 + H_{fs}$ 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 H_{Zeeman}, i.e. we ignored off diagonal in J terms. In the strong field case, we proceeded oppositely, we first diagonalized $H_0 + H_{Zeeman}$ 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 $|JM\rangle$ - space, i.e. different non-diagonal in J but diagonal in M.