**One-electron atom in a Magnetic Field**

When the atom is in a magnetic field $\vec{B}$ the magnetic moment of the electron due to its orbital motion and its spin interacts with the field and the Schrodinger Hamiltonian is

$$\hat{H} = \frac{1}{2m}\left(\hat{\vec{P}} + e\vec{A}\right)^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} - \hat{\vec{\mu}}_S \bullet \vec{B} + W(r)\hat{\vec{L}} \bullet \hat{\vec{S}}$$

where $\vec{A}$ is the vector potential, $e$ is the proton charge and $\hat{\vec{\mu}}_S = -g_e\mu_B\hat{\vec{S}}$ the magnetic moment of the electron. We have also included the spin-orbit term since it splits the levels with non-zero orbital angular momentum. Lets first consider the vector potential term $\frac{1}{2m}\left(\hat{\vec{P}} + e\vec{A}\right)^2$. Expanding the square and keeping in mind that the momentum is a differential operator, $\hat{\vec{P}} = \frac{\hbar}{i}\nabla$, we have

$$\frac{1}{2m}\left(\hat{\vec{P}}^2 + e^2\vec{A}^2 + e\hat{\vec{P}} \bullet \vec{A} + e\vec{A} \bullet \hat{\vec{P}}\right).$$

The question is does $\hat{\vec{P}}$ commute with $\vec{A}$? Let $g$ be an arbitrary function and note that

$$\hat{\vec{P}} \bullet \vec{A}g = \frac{\hbar}{i}\nabla_\alpha A_\alpha g = \frac{\hbar}{i}\left(A_\alpha \nabla_\alpha g + g\nabla_\alpha A_\alpha\right) = \vec{A} \bullet \hat{\vec{P}}g + \frac{\hbar}{i}g\nabla \bullet \vec{A}$$

and so

$$\hat{\vec{P}} \bullet \vec{A} - \vec{A} \bullet \hat{\vec{P}} = \frac{\hbar}{i}\nabla \bullet \vec{A}$$

And so if we use the Coulomb gauge where $\nabla \bullet \vec{A} = 0$, $\hat{\vec{P}}$ and $\vec{A}$ do commute and we can write the Hamiltonian as

$$\hat{H} = \frac{1}{2m}\hat{\vec{P}}^2 - \frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{e}{m}\vec{A} \bullet \hat{\vec{P}} + \frac{e^2}{2m}\vec{A}^2 + W(r)\hat{\vec{L}} \bullet \hat{\vec{S}}$$

or

$$\hat{H} = \hat{H}^0 + \frac{e}{m}\vec{A} \bullet \hat{\vec{P}} + \frac{e^2}{2m}\vec{A}^2 + W(r)\hat{\vec{L}} \bullet \hat{\vec{S}}$$

Let's first consider the term linear in $\vec{A}$. Since a constant magnetic induction $\vec{B}$ is derivable from the vector potential $\vec{A} = -\frac{1}{2}\left(\vec{r} \times \vec{B}\right)$ we can write

$$\vec{A} \bullet \hat{\vec{P}} = -\frac{1}{2}\vec{r} \times \vec{B} \bullet \hat{\vec{P}} = -\frac{1}{2}\varepsilon_{\alpha\beta\gamma} r_\beta B_\gamma \hat{P}_\alpha = \frac{1}{2}\varepsilon_{\gamma\beta\alpha} B_\gamma r_\beta \hat{P}_\alpha = \frac{1}{2}\vec{B} \bullet \vec{r} \times \hat{\vec{P}}$$

and since the orbital angular momentum $\hat{\vec{L}} = \vec{r} \times \hat{\vec{P}}$ we have

$$\frac{e}{m}\vec{A} \bullet \hat{\vec{P}} = \frac{e\hbar}{2m}\vec{B} \bullet \hat{\vec{L}}$$

where we measure the angular momentum in multiples of $\hbar$. As noted previously the quantity $\frac{e\hbar}{2m}$ is called the Bohr magneton, $\mu_B$ and equals $9.27413 \times 10^{-24}\ \frac{J}{T}$ $\left(\frac{J}{T} \equiv \frac{Joule}{Tesla}\right)$. The orbital magnetic moment operator can be written as $\hat{\vec{\mu}}_L = -\mu_B \hat{\vec{L}}$ and so the contribution to the Hamiltonian due to terms linear in the vector potential takes the familiar form $-\hat{\vec{\mu}}_L \bullet \vec{B}$, often called the Zeeman term.

Lets now consider the term $\frac{e^2}{2m}\vec{A}^2$. We can write

$\vec{A} \bullet \vec{A} = A_\alpha A_\alpha = \frac{1}{4}\varepsilon_{\alpha\beta\gamma} r_\beta B_\gamma \varepsilon_{\alpha\lambda\rho} r_\lambda B_\rho = \frac{1}{4}\left(\delta_{\beta\gamma}\delta_{\gamma\rho} - \delta_{\beta\rho}\delta_{\gamma\lambda}\right) r_\beta B_\gamma r_\lambda B_\rho = \frac{1}{4}\left(r^2 B^2 - \left(\vec{r} \bullet \vec{B}\right)^2\right)$. If the magnetic field defines the $z$ axis this becomes $\frac{1}{4} r^2 B^2 \sin^2\theta$ and the contribution to the Hamiltonian is $\frac{e^2 B^2}{8m} r^2 \sin^2\theta$. Note that the dimensions of $\frac{eB}{m}$ are $\frac{C \bullet kg}{kg \bullet S\ C} = S^{-1}$ and it's a frequency. One defines the Larmor frequency $\omega_L$ as $\frac{eB}{2m}$ and so the diamagnetic contribution to the Hamiltonian is sometimes written $\frac{1}{2} m\omega_L^2 r^2 \sin^2\theta$. The total Hamiltonian can be written

$$\hat{H} = H^0 + \mu_B\left(\hat{\vec{L}} + g_e \hat{\vec{S}}\right) \bullet \vec{B} + \frac{e^2 B^2}{8m} r^2 \sin^2\theta + W(r)\hat{\vec{L}} \bullet \hat{\vec{S}}$$

The term linear in *B* is approximately $0.47B\frac{cm^{-1}}{T}$ while the quadratic term is approximately $\frac{e^2a_0^2B^2}{8m}=5.0\times10^{-7}B^2\frac{cm^{-1}}{T^2}$, the ratio being $\sim10^{-6}B$. So even in a fairly large field of 10T the term quadratic in *B* is negligible compared with the term linear in *B* so we will consider the Hamiltonian

$$\hat{H}=\hat{H}^0+W(r)\hat{\vec{L}}\bullet\hat{\vec{S}}+\hat{H}_{Zeeman}$$

with $\hat{H}_{Zeeman}=\mu_B\left(\hat{\vec{L}}+2\hat{\vec{S}}\right)\bullet\vec{B}=\mu_B\left(\hat{L}_Z+2\hat{S}_Z\right)B$ and with B in the z direction. Note that the spin-orbit term is intrinsic to the atom while the Zeeman term depends on B and can have any value.

Let's now consider the effect of a magnetic field when the spin-orbit splitting is much larger then the Zeeman interaction. In this case we can perturb the fine structure terms independently. Since each spin-orbit level is $2j+1$ fold degenerate we need to see if degenerate perturbation theory is needed. Accordingly we form the matrix of the perturbation for the $2j+1$ degenerate states for a given $j$ and we need $\left\langle\Phi_{jm_j'l1/2}\left|\left(\hat{L}_z+2\hat{S}_z\right)\right|\Phi_{jm_jl1/2}\right\rangle$. We can write $\hat{L}_z+2\hat{S}_z=\hat{J}_z+\hat{S}_z$ and so

$$\left\langle\Phi_{jm'l1/2}\left|\left(\hat{L}_z+2\hat{S}_z\right)\right|\Phi_{jml1/2}\right\rangle=m\delta_{m'm}+\left\langle\Phi_{jm'l1/2}\left|\hat{S}_z\right|\Phi_{jml1/2}\right\rangle.$$

Using the explicit form for the angular functions we have

$$\left\langle\Phi_{jm'l1/2}\left|\hat{S}_z\right|\Phi_{jml1/2}\right\rangle=\frac{\pm m}{2l+1}\delta_{m'm}$$

and so the perturbation matrix is diagonal and each degenerate state shifts according to $E^{(1)}_{jml}\left(Zeeman\right)=\mu_BBm_j\left(1\pm\frac{1}{2l+1}\right)$ where one uses the upper sign when $j=\ell+1/2$ and the lower when $j=\ell-1/2$. Note that we can define an effective *g* factor for each *l* value $g_{jl}=1\pm\frac{1}{2l+1}$ and write the energy shift as

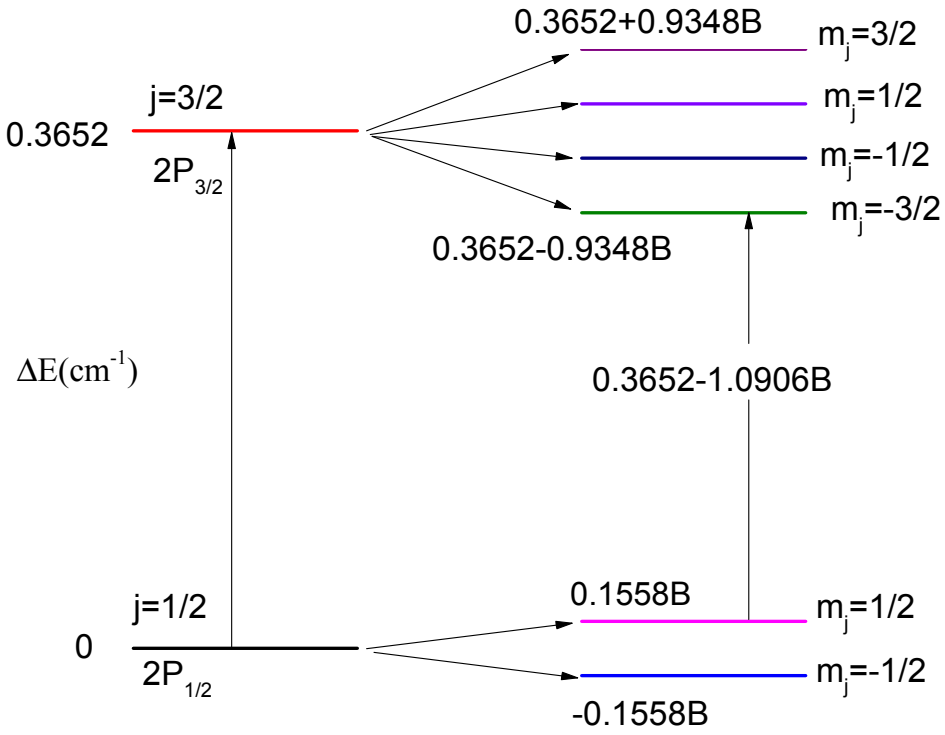
$E^{(1)}_{jm_j l}\left(Zeeman\right) = g_{j\ell} m_j \mu_B B = 0.4674 g_{j\ell} m_j B\ cm^{-1}$. Note further that for the $ns_{1/2}$, with $\ell = 0$ only the plus sign is relevant and so $g = 2$.

With the Zeeman term the total energy is

$$E(njm_j\ell) = E_n + \frac{\alpha^2 R_\infty Z^4}{2} \frac{\left(j(j+1) - \ell(\ell+1) - 3/4\right)}{n^3 \ell\left(\ell + 1/2\right)\left(\ell+1\right)} + g_{jl} m_j \mu_B B$$

Note that the Zeeman term is independent of the principal quantum number $n$. Let's first look at the splitting in the $ns_{1/2}$ level where the spin-orbit interaction is zero. Since $g_{ij} = 2$ each state is shifted by $0.9348 m_j B\ cm^{-1}$ and they are split by $0.9348\ B\ cm^{-1}$. This energy separation can be measured via ESR spectroscopy. A transition between the two $m_j = \pm\frac{1}{2}$ levels, $\pm.4674 B cm^{-1}$ can be induced by applying an oscillating electromagnetic field at right angles to $\vec{B}$. If the frequency of the radiation is $\nu$ in Hertz we have the equality $h\nu = 2(0.4674) B cm^{-1}$. Using $h = 3.335885 \times 10^{-11} cm^{-1}\,\text{sec}$ and expressing $B$ in Gauss we have $B = \frac{\nu}{2.8023 \times 10^6} G$. Many ESR spectrometers have a fixed frequency (X-band) around $9.3 \times 10^9 Hz$ so the resonance magnetic field for H is approximately 3320 G.

Now consider the $\ell \neq 0$ case and in particular the $2P_{1/2}$ & $2P_{3/2}$ levels. These are split by the magnetic field into 2 and 4 states respectively with the energies $E(2P_{1/2}) = 0.3116 m_j B\ cm^{-1}$ and $E(2P_{3/2}) = 0.6232 m_j B\ cm^{-1}$. These energies are shown schematically the figure below.




The question is what is the strength of a weak field for the perturbation of the individual fine structure levels to be valid? Taking the energy of the $2P_{1/2}$ level as zero places the unperturbed $2P_{3/2}$ level at 0.3652 $cm^{-1}$ (the fine structure separation), the lowest state $m_j = -3/2$ at $0.3652 - 0.9348B\ cm^{-1}$ and the highest $2P_{1/2}$ state at $0.1558B\ cm^{-1}$, the resulting separation being $0.3652 - 1.0906B\ cm^{-1}$. Clearly the closer these two states, the less reliable is perturbation theory. When this separation is zero the field is 0.335T or 3350G so something considerably smaller than this, perhaps 0.10T would seem reasonable. Note that no such limit is imposed on the $ns_{1/2}$ states because there is no spin-orbit coupling and a field of 0.355T is perfectly acceptable!

If we relax the condition that the field is week enough that it doesn't mix the spin orbit states of the $2P_{1/2}$ & $2P_{3/2}$ then we must treat the perturbation as

$$W(r)\hat{\vec{L}} \bullet \hat{\vec{S}} + \hat{H}_{Zeeman}$$

and the unperturbed states as the three 2p levels each with an $\alpha$ or $\beta$ *spin*.

Alternatively we may take the $2P_{1/2}$ & $2P_{3/2}$ wavefunctions as the unperturbed states since they are also eigenfunctions of $\hat{H}^0$ and that's what we will do since we already have all 6 of the diagonal elements of the perturbation matrix in this basis and these are in general

$$\left\langle R_{n\ell}\Phi_{jm_j\ell}\left|W(r)\hat{\vec{L}}\bullet\hat{\vec{S}}+\hat{H}_{Zeeman}\right|R_{n\ell}\Phi_{jm_j\ell}\right\rangle=\frac{\alpha^2R_\infty Z^4}{2}\frac{\left(j(j+1)-\ell(\ell+1)-3/4\right)}{n^3\ell\left(\ell+1/2\right)\left(\ell+1\right)}+g_{jl}m_j\mu_BB$$

We then need to see how the Zeeman operator couples the $2P_{1/2}$ & $2P_{3/2}$ states. We can do this in general by evaluating

$$\left\langle j=\ell-1/2,m_j,\ell,1/2\left|\mu_BB\left(\hat{L}_z+2\hat{S}_z\right)\right|j=\ell+1/2,m_j,\ell,1/2\right\rangle$$

and using the explicit form of the eigenfunctions we find this is diagonal in $m_j$ and equals

$\frac{-\mu_BB}{2\ell+1}\sqrt{\ell+m_j+1/2}\sqrt{\ell-m_j+1/2}$ which for $\ell=1$ equals $-\frac{\mu_BB}{3}\sqrt{3/2+m_j}\sqrt{3/2-m_j}$

so only the $m_j=\pm1/2$ states are coupled, the matrix element being $-\frac{\sqrt{2}}{3}\mu_BB$. If we order the unperturbed functions $2P_{1/2}$ & $2P_{3/2}$ as

$$\left|1/2,1/2\right\rangle,\left|3/2,1/2\right\rangle,\left|1/2,-1/2\right\rangle,\left|3/2,-1/2\right\rangle,\left|3/2,3/2\right\rangle\&\left|3/2,-3/2\right\rangle$$

the perturbation matrix is block diagonal with two 2x2 blocks and two 1x1 blocks.

If we let $A=\frac{\alpha^2R_\infty}{48}$ & $C=\frac{\mu_BB}{3}$ the 2x2 blocks are

$$A\begin{pmatrix}-2&0\\0&+1\end{pmatrix}+C\begin{pmatrix}1&-\sqrt{2}\\-\sqrt{2}&2\end{pmatrix}$$

with eigenvalues

and

$$A\begin{pmatrix} -2 & 0 \\ 0 & +1 \end{pmatrix} + C\begin{pmatrix} -1 & -\sqrt{2} \\ -\sqrt{2} & -2 \end{pmatrix}$$

with eigenvalues

and the uncoupled $m_{\pm 3/2}$ energies,.

We plot these 6 eigenvalues as well as the two $2s_{1/2}$ states (energies $-5A \pm 3C$) as a function of B.