Perturbing Hydrogen Atom by Magnetic field (Zeeman Effect)

In the presence of a magnetic field, the Hamiltonian for a hydrogen atom is :

$$H = \frac{1}{2m}\left(\vec{p} + \frac{e\vec{A}}{c}\right)^2 - \frac{Ze^2}{r} + g_e \mu_B \vec{\sigma} \cdot \vec{B} + H_{fs}$$

where H_{fs} is the Hamiltonian that aceonts for the fine structure, $\mu_B = \frac{e}{2m_e c}$ is the Bohr magneton and $g_e \approx 2$.

Choosing the gauge $\vec{A} = \frac{1}{2}(\vec{B} \times \vec{r})$, the kinetic energy term is

$$\frac{1}{2m}\left[\vec{p} + \frac{e}{2c}\vec{B} \times \vec{r}\right]^2$$

$$= \frac{\vec{p}^{\,2}}{2m} + \frac{e}{2m_e c}\vec{B} \cdot \vec{L} + O(B^2).$$

$$= \frac{\vec{p}^{\,2}}{2m} + \mu_B \vec{B} \cdot \vec{L} + O(B^2).$$

where $\vec{L} = \vec{r} \times \vec{p}$ is the orbital angular momentum. We will only consider the case when $|\vec{B}|$ is small enough so that $O(B^2)$ term can be neglected. Therefore, if we keep terms to only linear order in $\vec{B}$,

$$H = \underbrace{\frac{p^2}{2m} - \frac{Ze^2}{r} + H_{fs}}_{H_0} + \underbrace{\mu_B \vec{B} \cdot (\vec{L} + 2\vec{\sigma})}_{H_1}$$

$$= H_0 + H_1$$

Assuming $|\vec{B}|$ is small, we will treat H_1 perturbatively. As discussed earlier, the eigenspectrum of H_0 is

$$H_0 = \sum_{n,j,m,l} E_0(n,j) \, |n\, l\, j\, m_J\rangle\langle n\, l\, j\, m_J|$$

where $\vec{J} = \vec{L} + \vec{\sigma}$ is the total angular mom.

$\vec{J}^2 |n l j m_j\rangle = j(j+1)|n l j m_j\rangle$, $\vec{L}^2 |n l j m_j\rangle = l(l+1)|n l j m_j\rangle$

and $J_z|n\ell j m_j\rangle = m_J|n\ell j m_J\rangle$.

while $E_0(n,j) = \mathcal{E}_n\left[1 + \frac{(Z\alpha)^2}{n^2}\left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right]\right]$

with $\mathcal{E}_n = -\frac{Z^2}{n^2}\, 13.6\ \text{eV}$

The above expression for $E(n,j)$ is a bit complex, the main thing to notice is that only depends on 'n' and 'j' (and not ℓ).

Since we assume that $\mu_B B$ is much smaller than $\mathcal{E}_{n+1} - \mathcal{E}_n$, we can neglect the mixing between different 'n' values due to H_1.

$\boxed{n=1}$:

When $n=1$, the only levels are

$|n=1, \ell=0, j=\frac{1}{2}, m_J = \pm\frac{1}{2}\rangle$.

i.e. $\vec{J} = \vec{\sigma}$ (since $\vec{L}=0$).

Choosing $\vec{B}$ along the z-direction, the magnetic-field term in this case is simply $2\mu_B B\, m_J$ and therefore is already diagonal in the H_0 eigenbasis. Therefore, $\vec{B}$ simply lifts the degeneracy between the $m_J = \pm\frac{1}{2}$ states.

$\boxed{n=2}$:

$n=2$ case is more interesting. The eigenspectrum of H_0 has the following states:

$$|n=2, l=0, j=\tfrac{1}{2}, m_J = \pm\tfrac{1}{2}\rangle,$$

$$|n=2, l=1, j=\tfrac{1}{2}, m_J = \pm\tfrac{1}{2}\rangle,$$

$$|n=2, l=1, j=\tfrac{3}{2}, m_J = -\tfrac{3}{2}, -\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{3}{2}\rangle.$$

There are a total of eight states ($= 2n^2$ as expected).

Since we are interested in only linear order in B, only needs to diagonalize $H_0 + H_1$ within this eight-dimensional subspace. Choosing the basis as the eigenstates of H_0 i.e. $|n l j m\rangle$, then one needs to find the matrix elements.

$$\langle n=2, l, j, m_J | L_z + 2\sigma_z | n=2, l', j', m_J' \rangle$$

$$= \langle n=2, l, j, m_J | J_z + \sigma_z | n=2, l', j', m_J' \rangle$$

$$= m_J + \langle n=2, l, j, m_J | \sigma_z | n=2, l', j', m_J' \rangle$$

where we have used $L_z + \sigma_z = J_z$ and

$$J_z | n, l, j, m_J \rangle = m_J | n, l, j, m_J \rangle .$$

Since $[\sigma_z, J_z] = 0$, only the matrix elements with $m_J = m'_J$ can be non-zero. Furthermore, σ_z is the z-component of a vector operator, and is even under parity. The parity eigenvalue of angular momentum l is $(-)^l$. Therefore, $|l - l'|$ must be even [Proof: let's call $\hat{P}$ the unitary operator that measures parity. Then

$$\langle l | \sigma_z | l' \rangle = \langle l | P^\dagger \sigma_z P | l' \rangle$$

$$= (-)^{l'-l} \langle l | \sigma_z | l' \rangle \Rightarrow \langle l | \sigma_z | l' \rangle$$

vanishes unless $l' - l$ = even].

σ_z being a vector operator implies that $|j - j'| = 0$ or 1.

The parity constraint ("selection rule") implies that $|n=2,\ l=0,\ j=\frac{1}{2},\ m_J=\pm\frac{1}{2}\rangle$ states do not mix with any $l=1$ states. (i.e. the corresponding matrix elements vanish). The effect of B on $l=0$ states is then similar to the case $n=1$ discussed above i.e. the energy shifts by an amount $2\langle S_z\rangle B$ $= 2\langle j_z\rangle B = 2Bm_J$ for $m_J=\pm\frac{1}{2}$.

Similarly, $m_J=m'_J$ constraint implies that $|n=2,\ l=1,\ j=\frac{3}{2},\ m_J=\pm\frac{3}{2}\rangle$ states also don't mix with any other states. Based on above discussion, the energy shift is

$\Delta E \ (m_J = \pm 3/2) =$

$B\, m_J + \langle n=2, l=1, j=\frac{3}{2}, m_J | \sigma_z | n=2, l=1, j=\frac{3}{2}, m_J \rangle$

To find the above matrix element, we insert a complete set of states $|l, \sigma, l_z, \sigma_z\rangle$ and use C-G coefficients $\langle l=1, \sigma=\frac{1}{2}, j=\frac{3}{2}, m_J | l=1, \sigma=\frac{1}{2}, l_z, \sigma_z\rangle$.

This is given by (see Gottfried Eq. 183, or pset 5, prob. 1),

$$\langle l, \sigma=\frac{1}{2}, j=\frac{3}{2}, m_J | l, \sigma=\frac{1}{2}, l_z, \sigma_z = \frac{1}{2}\rangle$$

$l_z = m_J - \frac{1}{2}$ here

$$= \frac{\sqrt{l + m_J + \frac{1}{2}}}{\sqrt{2l+1}},$$

and

$$\langle l, \sigma=\frac{1}{2}, j=\frac{3}{2}, m_J | l, \sigma=\frac{1}{2}, l_z, \sigma_z = -\frac{1}{2}\rangle$$

$l_z = m_J + \frac{1}{2}$ here

$$= \frac{\sqrt{l - m_J + \frac{1}{2}}}{\sqrt{2l+1}}$$

Therefore,

$$\langle n=2, l=1, j=\tfrac{3}{2}, m_J | \sigma_z | n=2, l=1, j=\tfrac{3}{2}, m_J \rangle$$

$$= \sum_{\sigma_z = \pm 1/2} \langle l=1, \sigma=\tfrac{1}{2}, j=\tfrac{3}{2}, m_J | l=1, \sigma=\tfrac{1}{2}, l_z = m_J - \sigma_z, \sigma_z \rangle$$

$$\cdot \sigma_z \cdot \langle l=1, \sigma=\tfrac{1}{2}, l_z = m_J - \sigma_z, \sigma_z | l=1, \sigma=\tfrac{1}{2}, j=\tfrac{3}{2}, m_J \rangle$$

$$= \frac{1}{2} \times \left[\frac{l + m_J + \frac{1}{2}}{2l+1} - \frac{\left(l - m_J + \frac{1}{2}\right)}{2l+1} \right]$$

with $l = 1$ here.

$$= \frac{m_J}{3}$$

$$\Rightarrow \Delta E \quad (m_J = \pm 3/2)$$

$$= B \left[m_J + \frac{m_J}{3} \right] = \frac{4 B m_J}{3}.$$

Having discussed the effect of magnetic field (to the linear order) on

$|n=2, l=0, j=\frac{1}{2}, m_J=\pm\frac{1}{2}\rangle$,

and

$|n=2, l=1, j=\frac{3}{2}, m_J=\pm\frac{3}{2}\rangle$,

we are now left with four states:

$|n=2, l=1, j=\frac{1}{2}, m_J=\pm\frac{1}{2}\rangle$

and

$|n=2, l=1, j=\frac{3}{2}, m_J=\pm\frac{1}{2}\rangle$.

Again, off-diagonal matrix elements will be non-zero between states that satisfy $\Delta m_J = 0$. There are no constraint prohibiting mixing of

$|n=2, l=1, j=\frac{1}{2}, m_J\rangle$

$|n=2, l=1, j=3/2, m_J\rangle$ for $m_J = 1/2$

or $m_J = -\frac{1}{2}$. Therefore, we only need to diagonalize the 2×2 matrix

$$\begin{bmatrix} B\langle l=1, j=\tfrac{1}{2}, m_J|\sigma_z|l=1, j=\tfrac{1}{2}, m_J\rangle + E_0(n=2, j=1) + Bm_J & B\langle l=1, j=\tfrac{3}{2}, m_J|\sigma_z|l=1, j=\tfrac{1}{2}, m_J\rangle \\ B\langle l=1, j=\tfrac{1}{2}, m_J|\sigma_z|l=1, j=\tfrac{1}{2}, m_J\rangle & B\langle l=1, j=\tfrac{3}{2}, m_J|\sigma_z|l=1, j=\tfrac{3}{2}, m_J\rangle + E_0(n=2, j=\tfrac{3}{2}) + Bm_J \end{bmatrix}$$

where $m_J = \frac{1}{2}$ or $-\frac{1}{2}$.

Note that on the diagonal, we have added the fine-structure eigenvalues $E_0(n,j)$ since $j=\frac{1}{2}$ and $j=\frac{3}{2}$ have different $E_0(n,j)$.

Let's calculate all matrix elements that appear above using C-G coefficients.

(i) $\langle l=1, j=\frac{1}{2}, m_J|\hat{\sigma}_z|l=1, j=\frac{1}{2}, m_J\rangle$

$$= \sum_{\sigma_z} \langle l=1, j=\tfrac{1}{2}, m_J | l=1, \sigma=\tfrac{1}{2}, l_z=m_J-\sigma_z, \sigma_z\rangle \cdot \sigma_z \cdot$$

$$= \pm\frac{1}{2} \langle l=1, \sigma=\tfrac{1}{2}, l_z=m_J-\sigma_z, \sigma_z | l=1, j=\tfrac{1}{2}, m_J\rangle$$

$$= \frac{1}{2}\left[\frac{l - m_J + \frac{1}{2}}{2l+1} - \frac{l + m_J + \frac{1}{2}}{2l+1}\right]$$

$$= \frac{-m_J}{2l+1} \quad \text{with} \quad l = 1$$

$$= \frac{-m_J}{3}$$

(ii) $\langle l=1, j=\frac{3}{2}, m_J | \hat{\sigma}_z | l=1, j=\frac{3}{2}, m_J \rangle$

$$= \sum_{\sigma_z = \pm 1/2} \langle l=1, \sigma=\tfrac{1}{2}, j=\tfrac{3}{2}, m_J | l=1, \sigma=\tfrac{1}{2}, l_z = m_J - \sigma_z, \sigma_z \rangle$$

$$\cdot \sigma_z \cdot \langle l=1, \sigma=\tfrac{1}{2}, l_z = m_J - \sigma_z, \sigma_z | l=1, \sigma=\tfrac{1}{2}, j=\tfrac{3}{2}, m_J \rangle$$

$$= \frac{1}{2} \times \left[\frac{l + m_J + \frac{1}{2}}{2l+1} - \frac{(l - m_J + \frac{1}{2})}{2l+1}\right]$$

with $l = 1$ here.

$$= \frac{m_J}{3}$$

(iii) $\langle l=1, j=\frac{3}{2}, m_J | \hat{\sigma}_z | l=1, j=\frac{1}{2}, m_J \rangle$

$$= \sum_{\sigma_z=\pm\frac{1}{2}} \langle l=1, j=\frac{3}{2}, m_J | l=1, \sigma=\frac{1}{2}, l_z = m_J - \sigma_z \rangle \cdot \sigma_z \cdot \langle l=\frac{1}{2}, \sigma=\frac{1}{2}, l_z = m_J - \sigma_z | l=1, j=\frac{1}{2}, m_J \rangle$$

$$= \frac{1}{2}\left[-\frac{\sqrt{l+m_J+\frac{1}{2}}}{\sqrt{2l+1}} \frac{\sqrt{l-m_J+\frac{1}{2}}}{\sqrt{2l+1}} - \frac{\sqrt{l-m_J+\frac{1}{2}}}{\sqrt{2l+1}} \frac{\sqrt{l+m_J+\frac{1}{2}}}{\sqrt{2l+1}} \right]$$

with $l=1$

$$= \frac{1}{2} \frac{\sqrt{\left(\frac{3}{2}\right)^2 - m_J^2}}{3} \times -2$$

$$= -\frac{1}{3}\sqrt{\frac{9}{4} - m_J^2} = -\frac{\sqrt{2}}{3}$$

Since $m_J = \pm\frac{1}{2}$ for our problem.

Putting everything together, the effective Hamiltonian is,

$$\begin{array}{cc} |n=2, l=1, j=\tfrac{1}{2}\rangle & |n=2, l=1, j=\tfrac{3}{2}\rangle \\ \end{array}$$

$$\begin{bmatrix} E_0(n=2, j=\frac{1}{2}) + \frac{2}{3} B m_J & -\frac{1}{3} B\sqrt{2} \\ -\frac{1}{3} B\sqrt{2} & E_0(n=2, j=\frac{3}{2}) + \frac{4}{3} B m_J \end{bmatrix}$$

Denoting $E_0(n=2, j=\frac{3}{2}) - E_0(n=2, j=\frac{1}{2}) = \Delta$, the eigenvalues of this 2×2 matrix are

$$E^{\pm}_{m_J} = \frac{\Delta}{2} + B m_J \pm \frac{1}{2}\sqrt{\Delta^2 + \frac{4}{3} B \Delta m_J + B^2}$$
$$+ E_0(n=2, j=\tfrac{1}{2}).$$

See Fig. 5.2 in Gottfried-Yan for a plot of these eigenvalues.

The above result can be probed in two different limit: (i) $B \ll \Delta$: in this case B does not mix $j=\frac{1}{2}$ and $j=\frac{3}{2}$ states and therefore, one may neglect the off-diagonal elements above. The two eigenvalues are then just

$$E_0(n=2, j=\tfrac{1}{2}) + \frac{2}{3} B m_J \quad \text{and} \quad E_0(n=2, j=\tfrac{3}{2}) + \frac{4}{3} B m_J.$$

(ii) $B \gg \Delta$: In this case, one may treat fine-structure as a perturbation over the magnetic field. That is, the unperturbed Hamiltonian is

$$H_0 = -\frac{Ze^2}{r} + \frac{p^2}{2m} + \mu_B B (L_z + 2\sigma_z)$$

and the perturbation is H_{fs}. The eigenvalues can then be understood as the expectation value of H_{fs} w.r.t. to the states $|n, l, l_z, \sigma_z\rangle$.

For example, consider the state $|n=2, l=1, l_z=0, \sigma_z=\frac{1}{2}\rangle$.

It's unperturbed energy is

$$E(n=2) + \mu_B B\,(l_z + 2\sigma_z)$$

$$= E(n=2) + \mu_B B$$

where $E(n=2) = -\dfrac{Z^2\, 13.6\,eV}{n^2}$ is the hydrogenic spectra <u>without</u> fine-structure.

The leading-order shift due to fine-structure is

$$\langle n=2, l=1, l_z=0, \sigma_z=\tfrac{1}{2} | H_{fs} | n=2, l=1, l_z=0, \sigma_z=\tfrac{1}{2}\rangle$$

as one may verify (see Gottfried-Yan for details).