Atoms in a magnetic Field (Zeeman Effect)

Recall: for the orbital motion

\[ \vec{\mu}_L = - \frac{m_e}{\hbar} \vec{L} \quad \mu_B = \frac{e}{2m} \text{ g-factor is 1} \]

\[ \vec{\mu}_S = - \frac{m_B}{\hbar} \vec{S} \]

here the extra factor of 2 comes from the fact that here the g-factor is 2

We also know that \[ \vec{J} = \vec{L} + \vec{S} \]

Since the total magnetic moment is \[ \vec{M} = \vec{M}_L + \vec{M}_S \]

\[ \vec{M} = - \frac{m_B}{\hbar} \left( \vec{L} + 2\vec{S} \right) \]

But \( \vec{L} + 2\vec{S} \neq \vec{J} \)

So, what is the g factor of an atom?

We see that the above expression is a weird average of atom L and S operators. We want instead something like

\[ \vec{M}_{\text{atom}} = - \frac{g}{h} \mu_B \vec{J} \]

But we have \[ \vec{M}_{\text{atom}} = - \frac{m_B}{\hbar} \left( \vec{L} + 2\vec{S} \right) \]

ok, so let's try to set them equal
\[ g \tilde{J}^a = (\tilde{L} + 2\tilde{S}) \]

Standard trick, write

\[ g \tilde{J} = \tilde{L} + 2\tilde{S} = \frac{3}{2}(\tilde{L} + \tilde{S}) - \frac{1}{2}(\tilde{L} - \tilde{S}) \]

This is just \( \tilde{J} \)

This we can deal with.. see

Let's try to multiply both sides by \( \tilde{F} \)

\[ g \tilde{J}^2 = \frac{3}{2} \tilde{J}^2 - \frac{1}{2} (\tilde{L} - \tilde{S}) (\tilde{L} + \tilde{S}) \]

\[ = \frac{3}{2} \tilde{J}^2 - \frac{1}{2} (\tilde{L}^2 - \tilde{S}^2) \]

This is an operator diagonal in the total angular momentum basis \(|J,M,L,S\rangle\)

\[ \tilde{J}^2 |J,M\rangle = \hbar^2 \, \tilde{J}(\tilde{J}+1) |J,M\rangle \]

\[ \tilde{J}^2 |J,M, (L,S)\rangle = \hbar^2 \, \tilde{J}(\tilde{J}+1) |J,M, (L,S)\rangle \]

\[ \tilde{L}^2 |J,M, (L,S)\rangle = \hbar^2 \, \tilde{L}(\tilde{L}+1) |J,M, (L,S)\rangle \]

\[ \tilde{S}^2 |J,M, (L,S)\rangle = \hbar^2 \, \tilde{S}(\tilde{S}+1) |J,M, (L,S)\rangle \]

In this basis operators go to numbers

\[ g \hbar^2 \, \tilde{J}(\tilde{J}+1) = \frac{3}{2} \hbar^2 \, \tilde{J}(\tilde{J}+1) - \frac{1}{2} \hbar^2 \left[ \tilde{L}(\tilde{L}+1) - \tilde{S}(\tilde{S}+1) \right] \]
So \( g \) is found to be

\[
g = \frac{3/2 \cdot J(J+1) - \frac{1}{2} \cdot L(L+1)}{J(J+1)} + \frac{3/2}{2 \cdot J(J+1)}
\]

This number is called Lande g-factor

Note: It is not 1 or 2 but a function of \( L \) and \( J \)

Example: For the \( P_{1/2} \) state of hydrogen

\[
J = \frac{1}{2} \quad g = 1 + \left( \frac{\frac{3}{2}}{\frac{3}{2} - 2} \right) = \frac{2}{3}
\]

For the \( P_{3/2} \) state \( \ell = 1, J = 3/2 \)

\[
g = \frac{4}{3}
\]

What happens in the presence of a magnetic field?

If \( B_{\text{ext}} \ll B_{\text{int}} \), fine structure dominates and the good quantum numbers are \( n, J, L \) and \( M_J \). Under this approximation we can use the expression for the Lande factor we just derived and get a Hamiltonian of the form
The $P_{3/2}$ has a larger magnetic moment than the $P_{1/2}$.

But what happens when these levels meet?
We have to be careful since we mentioned that our previous analysis was only valid for weak fields.

Consider this

\[ H = H_{0} + H_{\text{field}} \]

When the field is big compared with the fine structure then the fine structure is the perturbation. This is the strong field limit

\[ H_{\text{field}} = -\mu_{a} \omega \cdot \vec{B} = \frac{\mu_{0}}{\hbar} \left( \vec{L} + 2\vec{S} \right) \cdot \vec{B} \]

If as before \( \vec{B} = B_{0} \hat{z} \) then

\[ H = \frac{\mu_{0} B_{0}}{\hbar} \left( L_{z} + 2S_{z} \right) \]

In this case the Hamiltonian is not diagonal in the coupled basis but instead it is diagonal in the uncoupled basis \( |L,m_{l}\rangle \mid S_{m_{s}}\rangle \)

\[ |L,m_{l}\rangle \mid S_{m_{s}}\rangle = \mu_{0} B_{0} \left( m_{l} + 2m_{s} \right) \]

And the energy shift it is not proportional to \( M_{J} \)
Consider the 2P states as an example

<table>
<thead>
<tr>
<th>( m_L )</th>
<th>( m_S )</th>
<th>( m_{L+2m_S} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/2</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>-1/2</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>1/2</td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>-1/2</td>
<td>-1</td>
</tr>
<tr>
<td>-1</td>
<td>1/2</td>
<td>0</td>
</tr>
<tr>
<td>-1</td>
<td>-1/2</td>
<td>-2</td>
</tr>
</tbody>
</table>

So at high magnetic field you get

Remarks:
1) At low field the coupled basis \(| J, M's, (L,S) \rangle\) are the good eigenstates and the shift is proportional to \( M_J \).
2) At high fields the uncoupled basis $|L_m, S_m\rangle$
Is the good eigenstates

3) In the intermediate regime any of these
two basis sets are good. we have to
learn how to deal with it

In the Intermediate field regime neither the fine structure
or the field Hamiltonian dominate and both have to
be treated on equal footing.
Let's do an example $n = 2$ where $L=0$ or $L=1$

$$\text{Coupled basis } |I,J,M\rangle \quad \text{Uncoupled basis } |L,m_L\rangle \quad |S, m_S\rangle$$

$$\begin{cases}
|\psi_0\rangle = |\frac{1}{2}, \frac{1}{2}\rangle = |00\rangle |\frac{1}{2}, \frac{1}{2}\rangle \\
|\psi_1\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle = |00\rangle |\frac{1}{2}, -\frac{1}{2}\rangle
\end{cases}$$

$$\begin{cases}
|\psi_3\rangle = |\frac{1}{2}, \frac{1}{2}\rangle = \frac{1}{\sqrt{3}} |11\rangle |\frac{1}{2}, \frac{1}{2}\rangle + \frac{1}{\sqrt{3}} |\frac{1}{2}, \frac{1}{2}\rangle + \frac{1}{\sqrt{3}} |\frac{1}{2}, -\frac{1}{2}\rangle \\
|\psi_5\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle = -\frac{1}{\sqrt{3}} |11\rangle |\frac{1}{2}, \frac{1}{2}\rangle + \frac{1}{\sqrt{3}} |\frac{1}{2}, \frac{1}{2}\rangle + \frac{1}{\sqrt{3}} |\frac{1}{2}, -\frac{1}{2}\rangle \\
|\psi_6\rangle = |\frac{1}{2}, \frac{1}{2}\rangle = -\frac{1}{\sqrt{3}} |11\rangle |\frac{1}{2}, \frac{1}{2}\rangle - \frac{1}{\sqrt{3}} |\frac{1}{2}, \frac{1}{2}\rangle + \frac{1}{\sqrt{3}} |\frac{1}{2}, -\frac{1}{2}\rangle \\
|\psi_8\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle = -\frac{1}{\sqrt{3}} |11\rangle |\frac{1}{2}, \frac{1}{2}\rangle + \frac{1}{\sqrt{3}} |\frac{1}{2}, \frac{1}{2}\rangle - \frac{1}{\sqrt{3}} |\frac{1}{2}, -\frac{1}{2}\rangle
\end{cases}$$

Now our field Hamiltonian is

$$\hat{H} = \frac{u_0}{\hbar} \mathbf{B} \cdot (\hat{L}_z + 2 \hat{S}_z)$$

The atom Hamiltonian is the fine structure one which depends on $n$ and $J$
Since $|\psi_1\rangle >$ to $|\psi_4\rangle >$ are single product states, these states are not coupled by the total Hamiltonian.

\[
\begin{align*}
\langle \psi_1 | H | \psi_1 \rangle &= \psi_0 B_0 \\
\langle \psi_1 | H | \psi_2 \rangle &= -\psi_0 B_0 \\
\langle \psi_3 | H | \psi_3 \rangle &= 2\psi_0 B_0 \\
\langle \psi_4 | H | \psi_4 \rangle &= -2\psi_0 B_0
\end{align*}
\]

\[
\begin{align*}
\langle \psi_5 | H_{\text{int}} | \psi_5 \rangle &= \langle \psi_6 | H_{\text{int}} | \psi_6 \rangle = \langle \psi_7 | H_{\text{int}} | \psi_7 \rangle = \langle \psi_8 | H_{\text{int}} | \psi_8 \rangle \\
&= -\frac{\psi}{3} \left( \frac{\psi}{3} \right)^2 \cdot 3.6 \text{ eV} \\
\langle \psi_5 | H_{\text{int}} | \psi_3 \rangle &= \langle \psi_5 | H_{\text{int}} | \psi_3 \rangle = \langle \psi_7 | H_{\text{int}} | \psi_7 \rangle = \langle \psi_8 | H_{\text{int}} | \psi_8 \rangle \\
&= \left( \frac{\psi}{3} \right)^2 \cdot 13.6 \text{ eV}
\end{align*}
\]

We also see that $|\psi_5\rangle >$ can only be coupled to $|\psi_6\rangle >$ and that $|\psi_7\rangle >$ can only be coupled to $|\psi_8\rangle >$ so we have a block diagonal matrix:

\[
H = \begin{bmatrix}
\begin{array}{ccc}
\text{diagonal} \\
\text{a x a}
\end{array}
\end{bmatrix}
\begin{bmatrix}
2 \times 2 \\
2 \times 2
\end{bmatrix}
\]

After diagonalizing we obtain the following energy levels
Hyperfine Hamiltonian

So far we have ignored the fact that the protons and neutrons also have spin. Therefore the nucleus has also a net magnetic moment

\[ \mu_N = \frac{g_N e}{2 m_p} \sim \text{proton mass} \]
\[ g_N: \text{nuclear magneton} \]

\( (g_N=5.59 \text{ t for the protons}. \) It is larger than the electron g factor since the proton is made of quarks

Consider a hydrogen atom. For an \( L=0 \) state, the interaction between the proton spins and the electron spin is

\[ \mathbf{H}_{HF} = \mu_B \left( \frac{m_e}{m_p} \right) \left( \mathbf{s_e} \cdot \mathbf{I} \right) \sim 10^{-3} \text{ times smaller than fine structure} \]

\( S_e=1/2 \text{and l=1/2 for a proton} \)

\[ \mathbf{s_e} \cdot \mathbf{I} = \left( \frac{F^2 - S_e^2 - I^2}{2} \right) \]
\[ F = \mathbf{s_e} + \mathbf{I} \]

Consequently for \( F=1 \) (triplet) or \( F=0 \) (Singlet) the energy is going to be different. This energy shift falls in the microwave. The frequency of a photon emitted from the singlet to triplet transition is an important form of radiation in the universe.