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Course: **8.421 - AMO I**
Problem set: **#4**
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1. Sum rule for fine structure

(a) For classical $\vec{L}, \vec{S}$, we simply have

$$\langle \vec{L} \cdot \vec{S} \rangle = LS \langle \cos\theta \rangle_\theta = \frac{LS}{2\pi} \int_0^{2\pi} \cos\theta \, d\theta = 0$$

as expected.

(b) It turns out that the same thing happens in quantum mechanics, but there are subtleties. $\vec{L}$ and $\vec{S}$ are now operators, and we have

$$\vec{L} \cdot \vec{S} = \frac{1}{2}\left[(\vec{J} + \vec{S})^2 - \vec{L}^2 - \vec{S}^2\right] = \frac{1}{2}(J^2 - L^2 - S^2)$$

where

$$\vec{J} = \vec{L} + \vec{S}.$$

Note that a more explicit notation for the kets would be $\left|L, S, J, m_J\right\rangle$ which has all of the good quantum numbers and suggests that we are working in the $\{J, m_J\}$ basis. From here is it clear that $\left|J, m_J\right\rangle$'s are eigenstates of J^2, L^2, S^2. In any case, we have

$$\begin{aligned}
\sum_{J,m_J} \left\langle J, m_J \right| \vec{L} \cdot \vec{S} \left| J, m_J \right\rangle &= \frac{1}{2} \sum_{J,m_J} \left\langle J, m_J \right| J^2 - L^2 - S^2 \left| J, m_J \right\rangle \\
&= \frac{1}{2} \sum_{J,m_J} [J(J+1) - L(L+1) - S(S+1)] \\
&= \frac{1}{2} \sum_{J} \underbrace{\sum_{m_J=-J}^{J}}_{2J+1 \text{ terms}} [J(J+1) - L(L+1) - S(S+1)] \\
&= \frac{1}{2} \sum_{J=|L-S|}^{|L+S|} (2J+1)[J(J+1) - L(L+1) - S(S+1)].
\end{aligned}$$

Just for fun, let us prove this statement directly. Assume without loss of generality that $L \geq S$, so we could drop the absolute value sign to write

$$\sum_{J,m_J} \left\langle J, m_J \right| \vec{L} \cdot \vec{S} \left| J, m_J \right\rangle = \frac{1}{2} \sum_{J=L-S}^{L+S} (2J+1)[J(J+1) - L(L+1) - S(S+1)].$$

To simplify, let's introduce $J' = J - L$, so that we can write

$$\sum_{J,m_J} \left\langle J, m_J \right| \vec{L} \cdot \vec{S} \left| J, m_J \right\rangle = \frac{1}{2} \sum_{J'=-S}^{S} (2(J'+L)+1)[(J'+L)((J'+L)+1) - L(L+1) - S(S+1)]$$

Now we take $S = n/2$ where $n \in \mathbb{N}$. We will show that the sum above vanishes by induction on S (not n! This is a subtle point). For $S = 0$, the sum is trivially zero (which makes sense since there is no $\vec{S}$ to couple with $\vec{L}$). Now assume that the sum is zero for $S = N/2$ for some $N \in \mathbb{N}$. We will show that the sum is also zero for $S' = N/2 + 1$. To this end, we simply calculate:

$$
\begin{aligned}
\sum_{J,m_J} \left\langle J, m_J \middle| \vec{L} \cdot \vec{S}' \middle| J, m_J \right\rangle &= \frac{1}{2} \sum_{J'=-S'}^{S'} (2(J'+L)+1)[(J'+L)((J'+L)+1) - L(L+1) - S'(S'+1)] \\
&= \frac{1}{2} \sum_{J'=-N/2-1}^{N/2+1} (2(J'+L)+1) \left[(J'+L)((J'+L)+1) - L(L+1) - \left(\frac{N}{2}+1\right)\left(\frac{N}{2}+1+1\right) \right] \\
&= \frac{1}{2} \sum_{J'=-N/2-1}^{N/2+1} (2(J'+L)+1) \left[(J'+L)((J'+L)+1) - L(L+1) - \frac{N}{2}\left(\frac{N}{2}+1\right) - 2\left(\frac{N}{2}+1\right) \right] \\
\text{(inductive hypothesis)} \quad &= \frac{2(-N/2-1+L)+1}{2} [(-N/2-1+L)((-N/2-1+L)+1) - L(L+1) - N/2\,(N/2+1)] \\
&\quad + \frac{2(N/2+1+L)+1}{2} [(N/2+1+L)((N/2+1+L)+1) - L(L+1) - N/2\,(N/2+1)] \\
&\quad + \frac{1}{2} \sum_{J'=-N/2-1}^{N/2+1} (2(J'+L)+1) \left[-2\left(\frac{N}{2}+1\right) \right] + 0 \\
&= -L(-1+2L-N)(2+N) + (1+L)(2+N)(3+2L+N) - ((1+2L)(2+N)(3+N)) \\
&= 0.
\end{aligned}
$$

Therefore, by the principle of induction we have shown that

$$
\sum_{J,m_J} \left\langle J, m_J \middle| \vec{L} \cdot \vec{S} \middle| J, m_J \right\rangle = 0.
$$

Notice that by picking N to be odd and even we can cover all cases. The proof for the case where S is fixed and L varies is similar. As a result, the sum rule is proved.

(c) That was tedious! An elegant way to prove the statement above is to notice that

$$
\sum_{J,m_J} \left\langle J, m_J \middle| \vec{L} \cdot \vec{S} \middle| J, m_J \right\rangle = \mathrm{Tr}\left(\vec{L} \cdot \vec{S}\right).
$$

Since the trace of an operator is invariant under a basis change, we may move to the $|L m_L S m_S\rangle$ basis:

$$
\begin{aligned}
\sum_{J,m_J} \left\langle J, m_J \middle| \vec{L} \cdot \vec{S} \middle| J, m_J \right\rangle &= \mathrm{Tr}\left(\vec{L} \cdot \vec{S}\right) \\
&= \sum_{m_L, m_S} \langle m_L m_S | \, \vec{L} \cdot \vec{S} \, | m_L m_S \rangle \\
&= \sum_{m_L, m_S} \langle m_L m_S | \, L_x S_x + L_y S_y + L_z S_z \, | m_L m_S \rangle \\
&= \sum_{m_L, m_S} \langle m_L m_S | \, \frac{1}{2}(L_+ S_- + L_- S_+) + L_z S_z \, | m_L m_S \rangle \\
&= \sum_{m_L, m_S} \langle m_L m_S | \, L_z S_z \, | m_L m_S \rangle \\
&= \sum_{m_L=-L}^{L} \sum_{m_S=-S}^{S} m_L m_S \\
&= 0,
\end{aligned}
$$

where we have expressed L_x, L_y, S_x, S_y in terms of the associated lowering and raising operators:

$$\begin{aligned} L_x &= \frac{1}{2}(L_+ + L_-) \\ L_y &= \frac{1}{2i}(L_+ - L_-) \\ S_x &= \frac{1}{2}(S_+ + S_-) \\ S_y &= \frac{1}{2i}(S_+ - S_-). \end{aligned}$$

And we're done with the proof of the sum rule.

2. Atoms with two valance electrons: From LS-coupling to jj-coupling. We have two atoms with spins $\vec{s}_1, \vec{s}_2$ and angular momenta $\vec{l}_1, \vec{l}_2$. There is the exchange interaction $\vec{s}_1 \cdot \vec{s}_2$ which makes $\vec{s}_1, \vec{s}_2$ precess about their sum $\vec{S}$ which makes S, m_S good quantum numbers. There is also the spin-orbit interaction with contributions from both atoms, so the term in the Hamiltonian looks like $\beta_1 \vec{l}_1 \cdot \vec{s}_1 + \beta_2 \vec{l}_2 \cdot \vec{s}_2$. When this is only a small perturbation, we couple the individual spins and individual angular momenta and rewrite the Hamiltonian as $\vec{L} \cdot \vec{S}$. This is the LS-coupling. However, if the spin-orbit coupling is strong than the exchange interaction, then $\vec{l}_i, \vec{s}_i$ precess about their sum $\vec{j}_i$'s which are now conserved. In this regime, we have $\vec{j}_1 \cdot \vec{j}_2$ coupling.

We want to work out the details across all regimes. This requires exact solutions. We will look at the $nsn'p$ example ($n' \neq n$ so that the Pauli exclusion principle is satisfied). Here, we have $l_1 = 0, l_2 = 1, s_1 = s_2 = 1/2$. The Hamiltonian for this problem is

$$\mathcal{H} = \vec{s}_1 \cdot \vec{s}_2 + \beta \vec{l}_1 \cdot \vec{s}_2.$$

We will work through the extreme cases first, then go to the intermediate regimes.

(a) Suppose $\beta = 0$, then we only have

$$\mathcal{H}_{\beta=0} = \vec{s}_1 \cdot \vec{s}_2.$$

In this case, there is no spin-orbit coupling. As discussed, the spins precess about their sum $\vec{S} = \vec{s}_1 + \vec{s}_2$ which is conserved. As a result, S, m_S are good quantum numbers. The suitable eigenbasis is therefore $|s_1, s_2, S, m_S\rangle$. In this basis, the Hamiltonian is diagonal, with matrix elements along the diagonal:

$$\begin{aligned} \langle s_1, s_2, S, m_S | \vec{s}_1 \cdot \vec{s}_2 | s_1, s_2, S, m_S\rangle &= \frac{1}{2} \langle s_1, s_2, S, m_S | S^2 - s_1^2 - s_2^2 | s_1, s_2, S, m_S\rangle \\ &= \frac{1}{2}[S(S+1) - s_1(s_1+1) - s_2(s_2+1)] \\ &= \frac{1}{2}\left[S(S+1) - \frac{3}{4} - \frac{3}{4}\right] \\ &= \frac{1}{2}\left[S(S+1) - \frac{3}{2}\right]. \end{aligned}$$

Since we have $S = 0$ and $S = 1$, the eigenvalues are $-3/4$ (singlet, $m_S = 0$) and $1/4$ (triplet, $m_S = -1, 0, 1$) respectively.

The sum rule holds:

$$\begin{aligned}
\sum_{S,m_S} \langle S, m_S | \vec{s}_1 \cdot \vec{s}_2 | S, m_S \rangle &= \frac{1}{2} \sum_{S,m_S} \left[S(S+1) - \frac{3}{2} \right] \\
&= \sum_{S=0}^{1} \frac{(2S+1)}{2} \left[S(S+1) - \frac{3}{2} \right] \\
&= -\frac{1}{2}\frac{3}{2} + \frac{3}{2}\left(2 - \frac{3}{2}\right) \\
&= 0,
\end{aligned}$$

as desired.

(b) Now we go to the other extreme where $\beta \gg 1$. Here we ignore the exchange interaction completely. As discuss, $\vec{l}_2, \vec{s}_2$ precess about their sum $\vec{j}_2$ which is conserved. So, the good quantum numbers are j_2, m_{j_2}. We note that $j_1 = m_{j_1} = 0$ trivially. In this basis, the Hamiltonian is diagonal, with matrix elements along the diagonal:

$$\begin{aligned}
\left\langle j_2, m_{j_2} \right| \vec{l}_2 \cdot \vec{s}_2 \left| j_2, m_{j_2} \right\rangle &= \frac{1}{2} \left\langle j_2, m_{j_2} \right| j_2^2 - l_2^2 - s_2^2 \left| j_2, m_{j_2} \right\rangle \\
&= \frac{1}{2}[j_2(j_2+1) - l_2(l_2+1) - s_2(s_2+1)] \\
&= \frac{1}{2}\left[j_2(j_2+1) - 1(1+1) - \frac{1}{2}\left(\frac{1}{2}+1\right) \right] \\
&= \frac{1}{2}\left[j_2(j_2+1) - \frac{11}{4} \right].
\end{aligned}$$

Since we have $j_2 = 1/2$ and $j_2 = 3/2$, the eigenvalues are -1 and $1/2$ respectively.

The sum rule holds:

$$\begin{aligned}
\sum_{j_2,m_{j_2}} \left\langle j_2, m_{j_2} \right| \vec{l}_2 \cdot \vec{s}_2 \left| j_2, m_{j_2} \right\rangle &= \frac{1}{2} \sum_{j_2,m_{j_2}} \left[j_2(j_2+1) - \frac{11}{4} \right] \\
&= \sum_{j_2=1/2}^{3/2} \frac{(2j_2+1)}{2} \left[j_2(j_2+1) - \frac{11}{4} \right] \\
&= \frac{(2(1/2)+1)}{2} \left[(1/2)(1/2+1) - \frac{11}{4} \right] + \frac{(3+1)}{2} \left[(3/2)(3/2+1) - \frac{11}{4} \right] \\
&= 0,
\end{aligned}$$

as desired.

(c) Now we will work in the regime where the spin-orbit coupling is a perturbation. We wish to calculate the energy shifts due to $\beta \ll 1$. To this end, we use perturbation theory to find the eigenenergies to first order in β. But which basis do we use? We shall follow the hint and make a replacement using

$$\vec{l}_2 \cdot \vec{s}_2 = \frac{\langle \vec{s}_2 \cdot \vec{S} \rangle}{\langle \vec{S} \cdot \vec{S} \rangle} \vec{L} \cdot \vec{S}$$

where

$$\begin{aligned}
\vec{L} &= \vec{l}_1 + \vec{l}_2 = \vec{l}_2 \\
\vec{S} &= \vec{s}_1 + \vec{s}_2.
\end{aligned}$$

We may choose a basis in which $\vec{L} \cdot \vec{S}$ is diagonal. Let us call this basis $\left| J m_J \right\rangle$, where $\vec{J} = \vec{L} + \vec{S}$.

(d)

(e)