Problem Set 4

Due: Friday 5pm, Mar 4, via Canvas upload or in envelope outside 26-255
TA: Yu-Kun Lu
Email: yukunlu@mit.edu
Office hours TBA, in 26-214 (CUA seminar room)

1 Sum rule for fine structure (6 pts.)

In class I mentioned that the "center of mass" of the fine structure shifts is zero. This is an example of a sum rule. The sum over all energy levels of the Hamiltonian $\vec{L}\cdot\vec{S}$, weighted by the degeneracy of each level, is zero. In a way this is obvious, since $\vec{L}\cdot\vec{S}$ is a scalar, and averaged over all possible rotations of the vectors (which is averaging over all possible states) I better get zero, as no direction in space is special. But let's investigate the statement formally. We will do this for general L and S in one sweep, not just $S = 1/2$.

a) Classical argument: Taking $\vec{L}$ and $\vec{S}$ to be classical vectors show that the average of $\vec{L}\cdot\vec{S}$ over all possible orientations is zero. Yes, this one is easy.

Because $\vec{L}$ and $\vec{S}$ are uncorrelated, after averaging over all orientations:

$$\langle\vec{L}\cdot\vec{S}\rangle = \langle\vec{L}\rangle\cdot\langle\vec{S}\rangle = 0. \tag{1}$$

b) Quantum mechanically, the statement is

$$\sum_{J,m_J}\left\langle J,m_J|\vec{L}\cdot\vec{S}|J,m_J\right\rangle = 0 \tag{2}$$

To see the statement in a form in which it is not obvious, replace $\vec{L}\cdot\vec{S}$ as in class by an expression involving J, L, S, and perform the sum over m_J. You should obtain a statement that a certain sum over J (from what to what value?) is zero. To prove the statement this way is tedious, and you can do it this way but you don't have to. Instead, let's do this differently.

Because $\vec{L}\cdot\vec{S} = (J^2 - L^2 - S^2)/2$, so we have:

$$\sum_{J,m_J}\left\langle J,m_J|\vec{L}\cdot\vec{S}|J,m_J\right\rangle = \sum_{J,m_J}(J(J+1) - L(L+1) - S(S+1))/2. \tag{3}$$

After summing over m_J, the expression reduces to:

$$\sum_{J,m_J}\left\langle J,m_J|\vec{L}\cdot\vec{S}|J,m_J\right\rangle = \sum_{J=|L-S|}^{J=|L+S|}(2J+1)(J(J+1) - L(L+1) - S(S+1))/2. \tag{4}$$

We can perform this summation by using $\sum_{k=1}^{k=n} k^3 = n^2(n+1)^2/4$, $\sum_{k=1}^{k=n} k^2 = n(n+1)(2n+1)/6$ and $\sum_{k=1}^{k=n} k = n(n+1)/2$. In the end we get:

$$\begin{aligned}&\sum_{J=|L-S|}^{J=|L+S|}(2J+1)(J(J+1)-L(L+1)-S(S+1))\\ =&(L(L+1)+S(S+1))(2S+1)(2L+1)-(2S+1)(2L+1)(L(L+1)+S(S+1))\\ =&0.\end{aligned} \tag{5}$$

Thus the sum rule is proven.

c) The statement can be written as $\mathrm{Tr}(\vec{L}\cdot\vec{S}) = 0$, where Tr is the trace over the eigenstates. A trace is invariant under a basis change, so it can be evaluated in any basis. Evaluate the trace in the basis where $\vec{L}$ and $\vec{S}$ are uncoupled, i.e. $|Lm_L Sm_S\rangle$. You should find zero, thereby proving the sum rule.

We can rewrite the dot product as:

$$\vec{L}\cdot\vec{S} = L_z S_z + \frac{1}{2}(L^+S^- + L^-S^+) \tag{6}$$

In the uncoupled basis, the second term which involves the raising and lowering operators does not contribute to the expectation value (becuse the m_L and m_S will not be matched). Thus, the expression simplifies to:

$$\mathrm{Tr}(\vec{L}\cdot\vec{S}) = \mathrm{Tr}(L_z S_z) = \mathrm{Tr}(L_z)\mathrm{Tr}(S_z) = 0. \tag{7}$$

Thus the sum rule is proven.

In fact, the choice of basis is not even needed: we can calculate the trace of $\vec{L}\cdot\vec{S}$ at the operator level:

$$\mathrm{Tr}(\vec{L}\cdot\vec{S}) = \sum_{i=x,y,z}\mathrm{Tr}(L_i S_i) = \sum_{i=x,y,z}\mathrm{Tr}(L_i)\mathrm{Tr}(S_i) = 0. \tag{8}$$

Note that the trace of tensor products of operators is equal to the product of their traces. In the last equality we have used the fact that the angular momentum operators are always traceless. This method is in direct analogy with what we have done in part (a).

2 Atoms with two valence electrons: From LS-coupling to jj coupling

Atoms with two valence electrons are of great importance for the most precise optical atomic clocks to date as well as optical tweezer experiments. Clocks operate on the highly

forbidden ${}^3P_0 - {}^1S_0$ transition (see e.g. this paper by Jun Ye's group). We will here understand how spin-orbit coupling gives rise to the ${}^3P_{J=0,1,2}$ states, and what occurs to these states when spin-orbit coupling becomes strong.

Consider an atom with two valence electrons, with spins $\vec{s}_1$ and $\vec{s}_2$ and angular momenta $\vec{l}_1$ and $\vec{l}_2$. We have seen in the case of excited states of Helium (such as $1s2p$) how the exchange interaction (part of the Coulomb interaction between electrons) forces electrons to be either in a spin singlet ($S = 0$) or spin triplet ($S = 1$). We recall that we can write this interaction effectively as an interaction

$$H_{\text{exch}} = \alpha \vec{s}_1 \cdot \vec{s}_2$$

(apart from a constant). The interaction makes $\vec{s}_1$ and $\vec{s}_2$ precess about their sum $\vec{S} = \vec{s}_1 + \vec{s}_2$, which is conserved and S and M_S are good quantum numbers. The spin-orbit interaction

$$H_{SO} = \beta_1 \vec{l}_1 \cdot \vec{s}_1 + \beta_2 \vec{l}_2 \cdot \vec{s}_2$$

is, for low-Z atoms, only a small perturbation on top of this, which can be written (by projecting the individual angular momenta onto the conserved $\vec{S}$ and $\vec{L}$) as $\beta_{LS} \vec{L} \cdot \vec{S}$. So in this case, first we couple the individual spins to form $\vec{S}$ and the individual orbital angular momenta to form $\vec{L} = \vec{l}_1 + \vec{l}_2$, then we couple $\vec{S}$ and $\vec{L}$ as a perturbation. This is the LS-coupling scheme.

However, if the spin-orbit coupling is much stronger than the exchange interaction, as in high-Z atoms, then the spin-orbit terms $\beta_1 \vec{l}_1 \cdot \vec{s}_1$ etc. first make $\vec{l}_1$ and $\vec{s}_1$ precess about their sum $\vec{j}_1 = \vec{l}_1 + \vec{s}_1$, and $\vec{s}_2$ and $\vec{l}_2$ precess about $\vec{j}_2 = \vec{l}_2 + \vec{s}_2$. So $\vec{j}_1$ and $\vec{j}_2$ are conserved, and j_1, m_{j1} and j_2, m_{j2} are good quantum numbers. The exchange interaction is then only a small perturbation, which we can write (by projecting the individual spins onto the $\vec{j}$'s) as an effective $\vec{j}_1 \cdot \vec{j}_2$ coupling.

Let's investigate this crossover for the $nsn'p$ example (with $n \neq n'$ so that the Pauli principle is automatically satisfied). So we have $l_1 = 0$, $l_2 = 1$, $s_1 = s_2 = 1/2$. The Hamiltonian is, in units of the exchange interaction,

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

First let's consider the extreme cases:

a) Give the suitable eigenbasis and find the eigenvalues for the case $\beta = 0$ (no spin-orbit coupling). Check that the corresponding sum rule holds.

The term $\vec{s}_1 \cdot \vec{s}_2$ makes the two individual spins precess in sync about their sum $\vec{S} = \vec{s}_1 + \vec{s}_2$. The good basis has s_1, s_2, S, m_s as good quantum numbers. $\vec{l}_2 \equiv \vec{L}$ is a bystander in this case, so L and m_L are good, too. We can write the eigenbasis in a way that keeps track of what is coupled to what by writing $|L, m_L, (s_1, s_2)S, m_S\rangle$. Often, one just writes this as $|L, m_L, S, m_S\rangle$ without the given s_1 and s_2. Or just

$|Lm_LSm_S\rangle$ (no commas). Given $\vec{S} = \vec{s}_1 + \vec{s}_2$ we can have $S = 0$, $m_S = 0$ or $S = 1$ with $m_S = \pm 1, 0$. We have

$$H = \frac{1}{2}\left(\vec{S}^{\,2} - \vec{s}_1^{\,2} - \vec{s}_2^{\,2}\right)$$

So in our basis this is diagonal and we find for the diagonal elements

$$\begin{aligned} E_S &= \langle Lm_LSm_S|H|Lm_LSm_S\rangle \\ &= \frac{1}{2}(S(S+1) - s_1(s_1+1) - s_2(s_2+1)) = \frac{1}{2}S(S+1) - \frac{3}{4} \end{aligned}$$

which only depend on S. One thus gets for

$$\begin{aligned} S = 0 \quad &\rightarrow \quad E_{S=0} = -\frac{3}{4} \\ S = 1 \quad &\rightarrow \quad E_{S=1} = \frac{1}{4} \end{aligned}$$

We have three $S = 1$ states and only one $S = 0$ state, so $3 \times \frac{1}{4} + 1 \times (-\frac{3}{4}) = 0$ and the sum rule holds.

b) Give the suitable eigenbasis and find the eigenvalues for the case $\beta \gg 1$ (spin-orbit coupling dominating, neglect exchange completely). Check again that the corresponding sum rule holds.

Now we have $\vec{l}_2$ and $\vec{s}_2$ precess in sync about their sum $\vec{j}_2 = \vec{l}_2 + \vec{s}_2$. $\vec{j}_1 = \vec{s}_1$ is a bystander. The good quantum numbers are $s_1 = j_1$, $m_{s_1} = m_{j_1}$, $l_2 = L$, s_2, j_2 and m_{j_2}. We write the basis $|j_1, m_{j_1}, (l_2, s_2)j_2, m_{j_2}\rangle$ or just $|j_1 m_{j_1} j_2 m_{j_2}\rangle$, remembering that l_2 and s_2 are given. As $l_2 = 1$ and $s_2 = 1/2$, we can have $j_2 = \frac{1}{2}$ and $j_2 = \frac{3}{2}$. Expressed in terms of $\vec{j}_2$, the Hamiltonian is (neglecting exchange completely):

$$H = \frac{\beta}{2}\left(\vec{j}_2^{\,2} - \vec{l}_2^{\,2} - \vec{s}_2^{\,2}\right)$$

This is diagonal in the basis above, with diagonal elements

$$\begin{aligned} E_{j_2} &= \langle j_1 m_{j_1} j_2 m_{j_2}|H|j_1 m_{j_1} j_2 m_{j_2}\rangle \\ &= \frac{\beta}{2}\left(j_2(j_2+1) - l_2(l_2+1) - s_2(s_2+1)\right) = \beta\left(\frac{1}{2}j_2(j_2+1) - \frac{11}{8}\right) \end{aligned}$$

which only depend on j_2. We thus get for

$$\begin{aligned} j_2 = \frac{1}{2} \quad &\rightarrow \quad E_{j_2} = \beta\left(\frac{1}{2}\frac{1}{2}\frac{3}{2} - \frac{11}{8}\right) = -\beta \\ j_2 = \frac{3}{2} \quad &\rightarrow \quad E_{j_1} = \beta\left(\frac{1}{2}\frac{3}{2}\frac{5}{2} - \frac{11}{8}\right) = \frac{1}{2}\beta \end{aligned}$$

We have 2 magnetic sub-states with $j_2 = 1/2$, and 4 substates with $j_2 = 3/2$, so $2 \times (-1) + 4 \times (1/2) = 0$ and the sum rule holds.

c) Now let's work at weak spin-orbit coupling, so $\beta \ll 1$ but non-zero. It will cause splitting of some or all energy levels you found in a). Calculate the eigenenergies to first order in β due to the $\vec{l}_2 \cdot \vec{s}_2$ term. Make a sketch, labelling the unperturbed state with its term ^{2S+1}L and the perturbed states with $^{2S+1}L_J$, and mark the shifts you found. Check that the new energy levels again obey the sum rule.
Hints: $\vec{l}_2$ is still "sharp", i.e. the basis in a) is also an eigenbasis of $\vec{l}_2^2$ and l_{2z}, since here $\vec{L} = \vec{l}_2$. The spin $\vec{s}_2$ is however precessing about $\vec{S}$, so only it's projection $\frac{\langle \vec{s}_2 \cdot \vec{S} \rangle}{\langle \vec{S} \cdot \vec{S} \rangle} \vec{S}$ on $\vec{S}$ is "sharp". So replace $\vec{l}_2 \cdot \vec{s}_2 \to \frac{\langle \vec{s}_2 \cdot \vec{S} \rangle}{\langle \vec{S} \cdot \vec{S} \rangle} \vec{L} \cdot \vec{S}$ and proceed from there, using a new basis in which $\vec{L} \cdot \vec{S}$ is diagonal.

For $\beta \ll 1$ the exchange term dominates, so S and m_S are good quantum numbers. $\vec{s}_2$ precesses about $\vec{S}$, so only it's projection $\frac{\langle \vec{s}_2 \cdot \vec{S} \rangle}{\langle \vec{S} \cdot \vec{S} \rangle} \vec{S}$ on $\vec{S}$ is "sharp". We thus replace $\vec{l}_2 \cdot \vec{s}_2 \to \frac{\langle \vec{s}_2 \cdot \vec{S} \rangle}{\langle \vec{S} \cdot \vec{S} \rangle} \vec{L} \cdot \vec{S}$, thereby neglecting terms that can change S. The operator $\vec{L} \cdot \vec{S}$ is diagonal in a basis of given J and m_J, where $\vec{J} = \vec{L} + \vec{S}$ is the total angular momentum, orbital and spin, of the two electrons. This basis can be written $|((s_1, s_2)S, L)J, m_J\rangle$, which again makes clear the order of couplings: First, $\vec{s}_1$ and $\vec{s}_2$ were coupled to $\vec{S}$, useful for the exchange term, then, the resultant $\vec{S}$ was coupled to $\vec{L}$ to give $\vec{J}$, useful to handle the perturbation (and not spoiling the diagonal form of the exchange term, which only depends on S and not on m_S). Often, one writes this $|SLJm_J\rangle$ hiding the given values of s_1 and s_2. What remains is to figure out the projection in this basis. The symbol $\langle \dots \rangle$ really denotes the expectation value in one of the basis states of given S, L, J, m_J.

$$\left\langle \vec{s}_2 \cdot \vec{S} \right\rangle = \langle \vec{s}_2^{\,2} + \vec{s}_1 \cdot \vec{s}_2 \rangle \tag{9}$$

$$= \left\langle \vec{s}_2^{\,2} + \frac{1}{2}\left(\vec{S}^{\,2} - \vec{s}_1^{\,2} - \vec{s}_2^{\,2}\right) \right\rangle \tag{10}$$

$$= \left\langle \frac{1}{2}\left(\vec{S}^{\,2} - \vec{s}_1^{\,2} + \vec{s}_2^{\,2}\right) \right\rangle \tag{11}$$

$$= \frac{1}{2} S(S+1) \tag{12}$$

So $\frac{\langle \vec{s}_2 \cdot \vec{S} \rangle}{\langle \vec{S} \cdot \vec{S} \rangle} = \frac{1}{2}$. Of course we could have obtained this result by simply picturing the addition of two vectors of equal length to a total vector $\vec{S}$. The expression $\vec{s}_2 \cdot \frac{\vec{S}}{|\vec{S}|}$ is the projection of one of the vectors onto $\vec{S}$, which must be half the vector itself. The

final expression for the energy correction due to the spin-orbit coupling term is

$$\begin{aligned}\Delta E_{SJ} &= \frac{\beta}{2}\frac{1}{2}\left(J(J+1)-S(S+1)-l_2(l_2+1)\right)\\ &= \frac{\beta}{4}\left(J(J+1)-S(S+1)-2\right)\end{aligned}$$

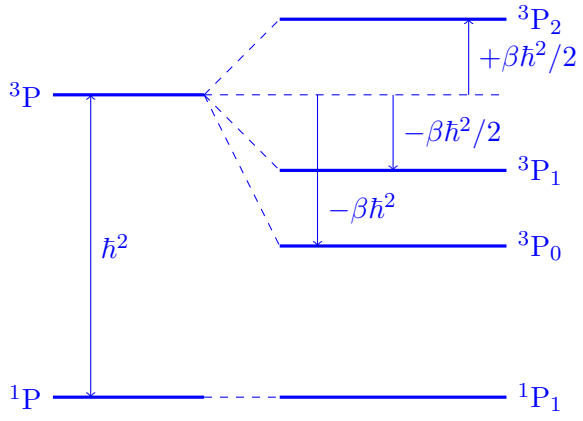
it depends on S and J. Now $\vec{J}=\vec{L}+\vec{S}$ gives eigenvalues $J=|L-S|,\dots|L+S|$, so given $L=1$ we have, for $S=1$, the values $J=0,1,2$ and for $S=0$ we have $J=1$. We thus have

$$\begin{aligned}S=0, J=1 &\rightarrow \Delta E_{01}=\frac{\beta}{4}(2-2)=0\\ S=1, J=0 &\rightarrow \Delta E_{10}=\frac{\beta}{4}(-4)=-\beta\\ S=1, J=1 &\rightarrow \Delta E_{11}=\frac{\beta}{4}(-2)=-\frac{1}{2}\beta\\ S=1, J=2 &\rightarrow \Delta E_{12}=\frac{\beta}{4}(6-2-2)=\frac{1}{2}\beta\end{aligned}$$

The result for $S=0$ is obvious - where there is no spin, there is no spin-orbit coupling. Note for the triplet states $S=1$ the interval rule: The difference between adjacent states J and $J-1$ grows as J. So $J=2$ is twice as far away from $J=1$ as $J=1$ is from $J=0$ (see figure).

We have $(2J+1)$ states for each J level, so let's check the sum rule: We have $5\times\frac{1}{2}\beta+3\times(-\frac{1}{2}\beta)+1\times(-\beta)=0$ for the triplet states. The $S=0$ state stays put anyways.

The energy level diagram looks like (not to scale):



d) In the opposite limit of large spin-orbit coupling, $\beta\gg 1$, the exchange interaction $\vec{s}_1\cdot\vec{s}_2$ is the perturbation. Calculate the corresponding corrections to the eigenenergies

you found in the $\beta \to \infty$ limit in b). Again make a sketch, labelling the various states by their J-quantum number.
Hint: It's useful that $\vec{j}_1 = \vec{s}_1$, so $\vec{s}_1$ is "sharp" already in this limit. But $\vec{s}_2$ precesses about $\vec{j}_2$, so only it's component along $\vec{j}_2$ is "sharp", namely $\frac{\langle \vec{s}_2 \cdot \vec{j}_2 \rangle}{\langle \vec{j}_2 \cdot \vec{j}_2 \rangle} \vec{j}_2$. So we should replace $\vec{s}_1 \cdot \vec{s}_2 \to \frac{\langle \vec{s}_2 \cdot \vec{j}_2 \rangle}{\langle \vec{j}_2 \cdot \vec{j}_2 \rangle} \vec{j}_1 \cdot \vec{j}_2$ and work in a new basis where $\vec{j}_1 \cdot \vec{j}_2$ is diagonal.

We have $\vec{j}_1 = \vec{s}_1$, so $\vec{s}_1$ is "sharp" already in this limit. But $\vec{s}_2$ precesses about $\vec{j}_2$, so only it's component along $\vec{j}_2$ is "sharp", namely $\frac{\langle \vec{s}_2 \cdot \vec{j}_2 \rangle}{\langle \vec{j}_2 \cdot \vec{j}_2 \rangle} \vec{j}_2$. So we replace $\vec{s}_1 \cdot \vec{s}_2 \to \frac{\langle \vec{s}_2 \cdot \vec{j}_2 \rangle}{\langle \vec{j}_2 \cdot \vec{j}_2 \rangle} \vec{j}_1 \cdot \vec{j}_2$ and work in a new basis where $\vec{j}_1 \cdot \vec{j}_2$ is diagonal.

This basis can be written $|(j_1, (s_2, l_2) j_2) J, m_J\rangle$, again denoting that $\vec{s}_2$ and $\vec{L} = \vec{l}_2$ are first coupled to $\vec{j}_2$, and then $\vec{j}_1$ and $\vec{j}_2$ are coupled to $\vec{J} = \vec{j}_1 + \vec{j}_2$. An abbreviation would be to write $|j_1 j_2 J m_J\rangle$, remembering what s_2 and l_2 are.

The projection $\vec{s}_2 \cdot \vec{j}_2 = \vec{s}_2^{\,2} + \vec{s}_2 \cdot \vec{l}_2 = \frac{1}{2}\left(\vec{j}_2^{\,2} + \vec{s}_2^{\,2} - \vec{l}_2^{\,2}\right)$ evaluated in this basis is $\left\langle \vec{s}_2 \cdot \vec{j}_2 \right\rangle = \frac{1}{2}\left(j_2(j_2+1) + \frac{3}{4} - 2\right) = \frac{1}{2}\left(j_2(j_2+1) - \frac{5}{4}\right)$ and so $\frac{\langle \vec{s}_2 \cdot \vec{j}_2 \rangle}{\langle \vec{j}_2 \cdot \vec{j}_2 \rangle} = \frac{1}{2} - \frac{5}{8}\frac{1}{j_2(j_2+1)}$. Finally, the energy correction due to the exchange interaction in the limit $\beta \gg 1$ is

$$\Delta E_{j_2 J} = \left(\frac{1}{2} - \frac{5}{8}\frac{1}{j_2(j_2+1)}\right)\frac{1}{2}\left(J(J+1) - j_1(j_1+1) - j_2(j_2+1)\right) \quad (13)$$

$$= \left(\frac{1}{2} - \frac{5}{8}\frac{1}{j_2(j_2+1)}\right)\frac{1}{2}\left(J(J+1) - j_2(j_2+1) - \frac{3}{4}\right) \quad (14)$$

We have for $j_2 = \frac{1}{2}$

$$\Delta E_{\frac{1}{2} J} = \left(\frac{1}{2} - \frac{5}{8}\frac{4}{3}\right)\frac{1}{2}\left(J(J+1) - \frac{3}{2}\right) \quad (15)$$

$$= -\frac{1}{6}\left(J(J+1) - \frac{3}{2}\right) \quad (16)$$

Combining $\vec{J} = \vec{j}_1 + \vec{j}_2$ with $j_1 = j_2 = \frac{1}{2}$ gives $J = 0$ or $J = 1$. We have

$$\Delta E_{\frac{1}{2} 0} = \frac{1}{6}\frac{3}{2} = \frac{1}{4} \quad (17)$$

$$\Delta E_{\frac{1}{2} 1} = -\frac{1}{6}\left(2 - \frac{3}{2}\right) = -\frac{1}{12} \quad (18)$$

There are 3 states with $J = 1$, and 1 state with $J = 0$, so $3 \times (-\frac{1}{12}) + 1 \times \frac{1}{4} = 0$, the sum rule holds.

For $j_2 = \frac{3}{2}$ we have

$$\Delta E_{\frac{3}{2}J} = \left(\frac{1}{2} - \frac{5}{8}\frac{4}{15}\right)\frac{1}{2}\left(J(J+1) - \frac{15}{4} - \frac{3}{4}\right) \tag{19}$$

$$= \frac{1}{6}\left(J(J+1) - \frac{9}{2}\right) \tag{20}$$

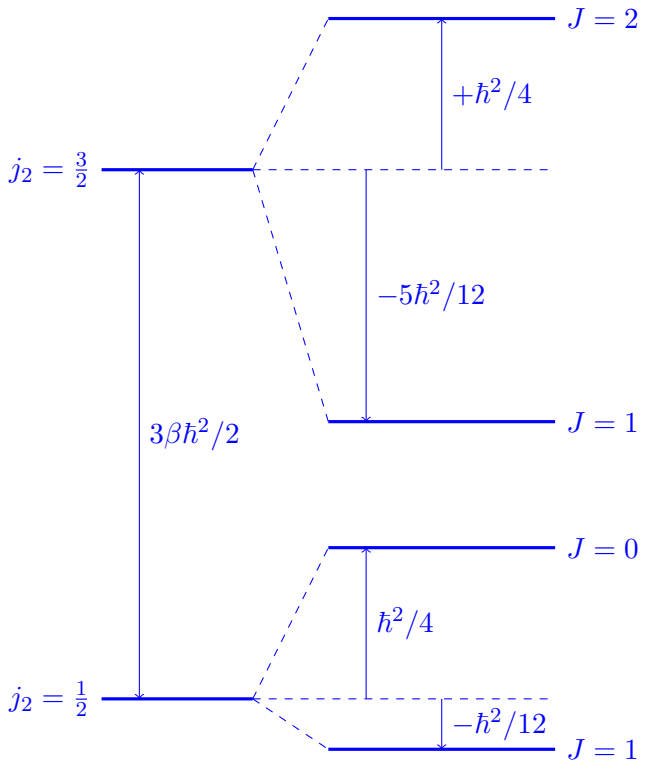
For $j_2 = \frac{3}{2}$ the two values of J are $J = 1$ and $J = 2$. We have

$$\Delta E_{\frac{3}{2}1} = \frac{1}{6}\left(2 - \frac{9}{2}\right) = -\frac{5}{12} \tag{21}$$

$$\Delta E_{\frac{3}{2}2} = \frac{1}{6}\left(2 \times 3 - \frac{9}{2}\right) = \frac{1}{4} \tag{22}$$

We have 5 states with $J = 2$ and 3 states with $J = 1$, so $5 \times \frac{1}{4} + 3 \times (-\frac{5}{12}) = 0$, the sum rule holds.

The energy-level diagram looks like (not to scale):



e) We can quite easily solve for the eigenvalues for any β. One way is to use the uncoupled basis $|LM_L\, s_1 m_{s1}\, s_2 m_{s2}\rangle$. For the first term $\vec{s}_1 \cdot \vec{s}_2$ the $|LM_L\rangle$ states are

"bystanders", so we only need to evaluate it in the reduced basis $|s_1 m_{s1}\, s_2 m_{s2}\rangle$. For the second term $\vec{s}_2 \cdot \vec{l}_2 = \vec{s}_2 \cdot \vec{L}$ it is the states $|s_1 m_{s1}\rangle$ that are irrelevant, so we can evaluate this in the reduced basis $|L M_L\, s_2 m_{s2}\rangle$. You will need the usual tricks such as $\vec{L} \cdot \vec{s}_2 = L_z s_{2z} + \frac{1}{2}(L_+ s_{2-} + L_- s_{2+})$ and know that $L_- |L = 1, M_L = 1\rangle = \sqrt{2}\,|L = 1, M_L = 0\rangle$ etc. Enter the total matrix in e.g. Mathematica and have it diagonalize it for you (yes, it's 12×12, but very sparse). Plot the eigenvalues and compare to your approximations above. This is usually a good way to check your result.

There is a more elegant method, but you do not need to go that route: The Hamiltonian commutes with the total angular momentum $\vec{J}^2$ and J_z. So only states with the same J and M_J value can ever couple. Now there is only one state with $J = 2$ (times five equivalent orientations M_J), the stretched state with $L = 1$ and $S = 1$, and also $j_1 = 1/2$ and $j_2 = 3/2$. This is automatically an eigenstate at all β, and your "perturbation" result is actually valid at any coupling strength. The same is true for $J = 0$, which must be the unique $L = 1$, $M_L = 0$, $S = 1$, $M_S = 0$ state, equal to the singlet superposition of the $j_1 = 1/2$ and $j_2 = 1/2$ spins. The only states that actually couple are the two $J = 1$ states one can form from $L = 1$ with $S = 1$ or $S = 0$, which are linearly related to the two $J = 1$ states one can produce from $j_1 = 1/2$ with $j_2 = 1/2$ and from $j_1 = 1/2$ with $j_2 = 3/2$. We therefore see that the problem is actually reduced to a 2×2 matrix.

Elegant solution:

The system always has full rotational symmetry and also the symmetry under rotation along z axis. Therefore, the good quantum numbers in this problem are J^2 and m_J.

When we couple two $s = 1/2$ spins with $l = 1$ orbital angular momentum, we get $J = 2$, $J = 1$ (twice) and $J = 0$ states. From the symmetries, we know that only the states with the same J and m_J can couple. Thus, we should expect the Hamiltonian to take a block diagonal form with three 2×2 blocks (for the $J = 1$ states with $m_J = 1, 0, -1$) and six 1×1 blocks (for the 5 $J = 2$ states and 1 $J = 0$ state).

For the 1×1 blocks, the eigenvalues can be obtained directly (as we did in part c): $E = 1/4 + \beta/2$ for the $J = 2$ states and $E = 1/4 - \beta$ for the $J = 0$ state.

For the 2×2 blocks, since different choices of m_J are related by a rotation, their eigenvalues shoud be the same. Thus, we can just calculate the $m_J = 1$ case. By using the Clebsch–Gordan coefficients, we can get the two states in the $|J = 1, m_J = 1\rangle$ subspace. In practice, we can choose to couple the two spins first, then couple it to the orbital angular momentum. We choose our basis in the subspace such that one of the state is in the spin singlet configuration, while the other one is in triplet.

For the state with $S = 0$, the state has to be $|L = 1, m_l = 1, S = 0, m_S = 0\rangle$. Remember the singlet state is $|S = 0, m_S = 0\rangle = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/2$. Thus, this state reads $(|1, 1/2, -1/2\rangle - |1, -1/2, 1/2\rangle)/\sqrt{2}$. Here the states are labeled by $|m_{l_2}, m_{s_1}, m_{s_2}\rangle$.

For the state with $S = 1$, it can be written as $(|L = 1, m_l = 1, S = 1, m_S = 0\rangle - |L = 1, m_l = 0, S = 1, m_S = 1\rangle)/\sqrt{2}$. By using $|S = 1, m_S = 0\rangle = (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/2$ and $|S = 1, m_S = 1\rangle = |\uparrow\uparrow\rangle$, we get the state: $(|1, 1/2, -1/2\rangle + |1, -1/2, 1/2\rangle - \sqrt{2}|0, 1/2, 1/2\rangle)/2$.

Finally by taking the matrix elements of the Hamiltonian, we get the 2×2 matrix in the subspace:

$$H_{2\times 2} = \begin{pmatrix} -3/4 & -\beta/\sqrt{2} \\ -\beta/\sqrt{2} & 1/4 - \beta/2 \end{pmatrix}. \tag{23}$$

The eigenvalues of this matrix can be calculated as $E_\pm = (-1-\beta\pm\sqrt{4 - 4\beta + 9\beta^2})/4$.

In summary, the eigenvalues are: $1/4 + \beta/2$ ($J = 2$, 5 folds degeneracy), $1/4 - \beta$ ($J = 0$, no degeneracy) and $(-1 - \beta \pm \sqrt{4 - 4\beta + 9\beta^2})/4$ ($J = 1$, 3 folds degeneracy each).

Brute-force solution:

Alternatively, we can also write down the 12×12 matrix directly and then diagonalize it.

The matrix can be obtained by taking the tensor product of the individual angular momentum operators, as long as we know the matrix representation of them (Pauli matrices for spin $1/2$, 3×3 matrices for spin 1). The tensor product is just concatenation of the matrices, so no extra calculations are needed.

Attached is the Mathematica code for analytic calculation and numerical plot:

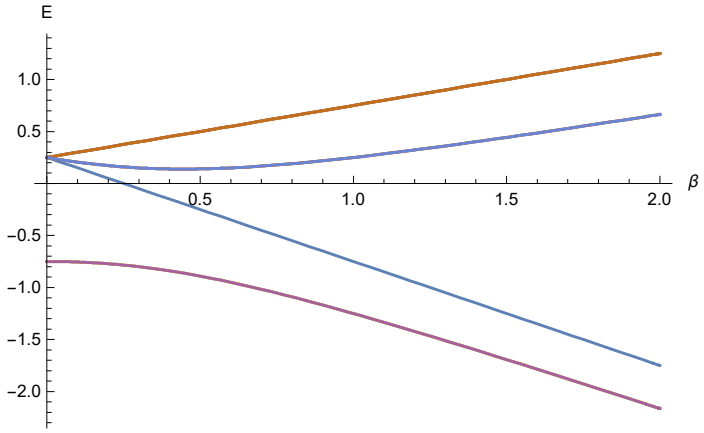
In[208]:=
```
(*The state is labeled as |ml2, ms1, ms2>*)
Clear["Global`*"]
Sx = PauliMatrix[1] / 2;
Sy = PauliMatrix[2] / 2;
Sz = PauliMatrix[3] / 2;
Lz = {{1, 0, 0}, {0, 0, 0}, {0, 0, -1}};
Lx = {{0, 1, 0}, {1, 0, 1}, {0, 1, 0}} / Sqrt[2];
Ly = {{0, -I, 0}, {I, 0, -I}, {0, I, 0}} / Sqrt[2];
H = KroneckerProduct[IdentityMatrix[3], Sz, Sz] + KroneckerProduct[
    IdentityMatrix[3], Sy, Sy] + KroneckerProduct[IdentityMatrix[3], Sx, Sx] +
   β * (KroneckerProduct[Lz, IdentityMatrix[2], Sz] + KroneckerProduct[Ly,
       IdentityMatrix[2], Sy] + KroneckerProduct[Lx, IdentityMatrix[2], Sx]);
H // MatrixForm
Eig = FullSimplify[Eigenvalues[H]];
Eig
Plot[Eig, {β, 0, 2}, AxesLabel → {"β", "E"}]
```

Out[216]//MatrixForm=

$$\begin{pmatrix}
\frac{1}{4}+\frac{\beta}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -\frac{1}{4}-\frac{\beta}{2} & \frac{1}{2} & 0 & \frac{\beta}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{1}{2} & -\frac{1}{4}+\frac{\beta}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{1}{4}-\frac{\beta}{2} & 0 & 0 & \frac{\beta}{\sqrt{2}} & 0 & 0 & 0 & 0 & 0 \\
0 & \frac{\beta}{\sqrt{2}} & 0 & 0 & \frac{1}{4} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -\frac{1}{4} & \frac{1}{2} & 0 & \frac{\beta}{\sqrt{2}} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{\beta}{\sqrt{2}} & 0 & \frac{1}{2} & -\frac{1}{4} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{4} & 0 & 0 & \frac{\beta}{\sqrt{2}} & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{\beta}{\sqrt{2}} & 0 & 0 & \frac{1}{4}-\frac{\beta}{2} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\frac{1}{4}+\frac{\beta}{2} & \frac{1}{2} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\beta}{\sqrt{2}} & 0 & \frac{1}{2} & -\frac{1}{4}-\frac{\beta}{2} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{4}+\frac{\beta}{2}
\end{pmatrix}$$

Out[218]=
$$\left\{\frac{1}{4}-\beta,\ \frac{1}{4}(1+2\beta),\ \frac{1}{4}(1+2\beta),\ \frac{1}{4}(1+2\beta),\ \frac{1}{4}(1+2\beta),\ \frac{1}{4}(1+2\beta),\right.$$
$$\frac{1}{4}\left(-1-\beta-\sqrt{4+\beta(-4+9\beta)}\right),\ \frac{1}{4}\left(-1-\beta-\sqrt{4+\beta(-4+9\beta)}\right),\ \frac{1}{4}\left(-1-\beta-\sqrt{4+\beta(-4+9\beta)}\right),$$
$$\left.\frac{1}{4}\left(-1-\beta+\sqrt{4+\beta(-4+9\beta)}\right),\ \frac{1}{4}\left(-1-\beta+\sqrt{4+\beta(-4+9\beta)}\right),\ \frac{1}{4}\left(-1-\beta+\sqrt{4+\beta(-4+9\beta)}\right)\right\}$$

Out[219]=



In[204]:=
```
(*Expansion for large β*)
Series[(-1 - β - Sqrt[4 + β * (9 * β - 4)])/4, {β, Infinity, 0}]
```

Out[204]=
$$-\beta-\frac{1}{12}+0\left[\frac{1}{\beta}\right]^1$$

In[205]:=
```
(*Expansion for small β*)
Series[(-1 - β - Sqrt[4 + β * (9 * β - 4)])/4, {β, 0, 1}]
```

Out[205]=
$$-\frac{3}{4}+0[\beta]^2$$

In[206]:=
```
(*Expansion for large β*)
Series[(-1 - β + Sqrt[4 + β * (9 * β - 4)])/4, {β, Infinity, 0}]
```

Out[206]=
$$\frac{\beta}{2}-\frac{5}{12}+0\left[\frac{1}{\beta}\right]^1$$

In[207]:=
```
(*Expansion for small β*)
Series[(-1 - β + Sqrt[4 + β * (9 * β - 4)])/4, {β, 0, 1}]
```

Out[207]=
$$\frac{1}{4}-\frac{\beta}{2}+0[\beta]^2$$