Problem Set 4

Due: Friday 5pm, Mar 4, via Canvas upload or in envelope outside 26-255
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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.

b) Quantum mechanically, the statement is

$$\sum_{J,m_J} \left\langle J, m_J|\vec{L}\cdot\vec{S}|J, m_J\right\rangle = 0 \tag{1}$$

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.

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. $|Lm_LSm_S\rangle$. You should find zero, thereby proving the sum rule.

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.

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.

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.

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.

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 $|LM_L\, s_2 m_{s2}\rangle$. 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 $L = 1$, $M_L = 0$, $S = 0$, $M_S = 0$ 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.