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Quantum Mechanics

Lecture 12

Hyperfine structure;
Singlet and triplet states;
Addition of angular momentum;
Clebsch-Gordan coefficients.

A quick recap

The spin and orbital AM of an electron couple to give **fine structure**.

$$H_{SO} \propto \mathbf{S} \cdot \mathbf{L} \qquad [\mathbf{S}, \mathbf{L}] = 0$$

Some of old quantum numbers become "bad" and must be replaced:

$$[H_{SO}, S_z] \neq 0\,,\ [H_{SO}, L_z] \neq 0$$

We defined a new total AM operator: $\mathbf{J} = \mathbf{S} + \mathbf{L}\,,\quad [S^2, J_z] = [L^2, J_z] = 0$

The symmetries of H_{SO} are now:

$$[H_{SO}, S^2] = [H_{SO}, L^2] = [H_{SO}, J^2] = [H_{SO}, J_z] = 0$$

$$\underset{\text{old quantum numbers}}{(l, m_l, s, m_s)} \rightarrow \underset{\text{new quantum numbers}}{(l, s, j, m_j)}$$

(n is still good, too)

A quick recap

The new quantum numbers j, m_j are expressions of conservation of AM:

$$m_j = m_l + \frac{1}{2}\,,\; j = l \pm \frac{1}{2}$$

The new states that diagonalize H_{SO} are linear combinations of the old ones:

$$|\chi_1\rangle = |\,l, m_j - \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\rangle\,, \quad |\chi_2\rangle = |\,l, m_j + \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}\rangle$$

$$|\,l \pm \frac{1}{2}, m_j\rangle = \alpha_\pm |\chi_1\rangle \pm \beta_\pm |\chi_2\rangle$$

(Just some coefficients… we can look them up.)

The corrections to the energy are found by taking expected values.

$$E_{SO}^{(1)} = \langle n, j, m_j \,|\, H_{SO} \,|\, n, j, m_j \rangle$$

Hyperfine structure

We can follow this recipe again to understand the **hyperfine structure**, i.e. the splitting in energies due to spin-spin coupling between the electron and proton.

For simplicity, we restrict our discussion to the hydrogen ground state $n = 1$.

$$H_{HF} = \frac{2A}{\hbar^2}\mathbf{S}\cdot\mathbf{I} \qquad\qquad [\mathbf{I},\mathbf{S}] = 0$$

Before perturbation, 4 degenerate states:

$$|\,m_i, m_s\rangle := |\,i, m_i, s, m_s\rangle = |\,i, m_i\rangle \otimes |\,s, m_s\rangle$$

$$|\chi_1\rangle = |+\tfrac{1}{2},+\tfrac{1}{2}\rangle \qquad |\chi_2\rangle = |+\tfrac{1}{2},-\tfrac{1}{2}\rangle$$

$$|\chi_3\rangle = |-\tfrac{1}{2},+\tfrac{1}{2}\rangle \qquad |\chi_4\rangle = |-\tfrac{1}{2},-\tfrac{1}{2}\rangle$$

Introducing a total AM operator is a very good idea:

$$\mathbf{F} = \mathbf{I} + \mathbf{S}$$

Total angular momentum is conserved

Total F and F_z also give good quantum numbers for H_{HF}:

$$\mathbf{F} = \mathbf{I} + \mathbf{S} \qquad F^2 = I^2 + S^2 + 2\,\mathbf{S}\cdot\mathbf{I}$$

$$F_z = I_z + S_z \qquad 2\,\mathbf{S}\cdot\mathbf{I} = F^2 - I^2 - S^2$$

$$[\mathbf{F}, \mathbf{S}\cdot\mathbf{I}] = [F_z, \mathbf{S}\cdot\mathbf{I}] = 0$$

Explicitly:
$$\begin{aligned}[F_z, \mathbf{S}\cdot\mathbf{I}] &= [I_z + S_z, I_xS_x + I_yS_y + I_zS_z] \\ &= [I_z, I_x]S_x + [I_z, I_y]S_y + I_x[S_z, S_x] + I_y[S_z, S_y] \\ &= i\hbar I_yS_x - i\hbar I_xS_y + i\hbar I_xS_y - i\hbar I_yS_x = 0\end{aligned}$$

Note: $[I_z, H_{HF}] \neq 0\,, \quad [S_z, H_{HF}] \neq 0$ Need to use f and m_f quantum numbers now.

We conclude that f and $m_f = m_i + m_s$ are good quantum numbers for H_{HF}.

Matrix elements for H_{HF}

What are the matrix elements $\langle \chi_j | H_{HF} | \chi_k \rangle$ of H_{HF} in the unperturbed basis?

Rewrite in terms of raising and lowering operators:

$$2\,\mathbf{S}\cdot\mathbf{I} = I_+S_- + I_-S_+ + 2I_zS_z$$

Easily verified from definitions.

Matrix elements are now straightforward to calculate. Example:

$$\begin{aligned}
\langle \chi_1 | 2\,\mathbf{S}\cdot\mathbf{I} | \chi_1 \rangle &= \langle \tfrac{1}{2}, \tfrac{1}{2} | 2\,\mathbf{S}\cdot\mathbf{I} | \tfrac{1}{2}, \tfrac{1}{2} \rangle \\
&= \langle \tfrac{1}{2}, \tfrac{1}{2} | I_+S_- | \tfrac{1}{2}, \tfrac{1}{2} \rangle + \langle \tfrac{1}{2}, \tfrac{1}{2} | I_-S_+ | \tfrac{1}{2}, \tfrac{1}{2} \rangle + 2\langle \tfrac{1}{2}, \tfrac{1}{2} | I_zS_z | \tfrac{1}{2}, \tfrac{1}{2} \rangle \\
&= 2\langle \tfrac{1}{2}, \tfrac{1}{2} | I_zS_z | \tfrac{1}{2}, \tfrac{1}{2} \rangle \\
&= 2\cdot\tfrac{1}{2}\hbar\cdot\tfrac{1}{2}\hbar\,\langle \tfrac{1}{2}, \tfrac{1}{2} | \tfrac{1}{2}, \tfrac{1}{2} \rangle \\
&= \tfrac{1}{2}\hbar^2
\end{aligned}$$

Eigenvalues

The matrix in this basis is: (all other terms vanish)

$$H_{HF} = \frac{2A}{\hbar^2}\mathbf{S}\cdot\mathbf{I} \longrightarrow \begin{pmatrix} A/2 & & & \\ & -A/2 & A & \\ & A & -A/2 & \\ & & & A/2 \end{pmatrix}$$

Middle block is basically S_x.

$$\begin{pmatrix} -A/2 & A \\ A & -A/2 \end{pmatrix} = \frac{2A}{\hbar}S_x - \frac{A}{2}$$

Diagonalizing this gives us the new eigenstates and eigenvalues.

Eigenvalues:

$$\left\{ \frac{A}{2},\ A-\frac{A}{2},\ -A-\frac{A}{2},\ \frac{A}{2} \right\}$$

Eigenvectors:

$$\left\{ |\chi_1\rangle,\ \frac{1}{\sqrt{2}}(|\chi_2\rangle + |\chi_3\rangle),\ \frac{1}{\sqrt{2}}(|\chi_2\rangle - |\chi_3\rangle),\ |\chi_4\rangle \right\}$$

Rearranging…

$$\left\{ \underbrace{\frac{A}{2},\ \frac{A}{2},\ \frac{A}{2}}_{\text{degenerate}},\ -\frac{3A}{2} \right\}$$

$$\left\{ \underbrace{|\uparrow\uparrow\rangle,\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle),\ |\downarrow\downarrow\rangle}_{\text{“Triplet”}},\ \underbrace{\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)}_{\text{“Singlet”}} \right\}$$

Quantum numbers

The new total AM quantum numbers are constrained

For consistency, use:

$$F^2 = I^2 + S^2 + 2\,\mathbf{S}\cdot\mathbf{I}$$

Two choices:

$$f(f+1) = \frac{1}{2}\left(\frac{1}{2}+1\right)+\frac{1}{2}\left(\frac{1}{2}+1\right) + \begin{cases} 1/2 \\ -3/2 \end{cases} \Rightarrow \quad f = \begin{cases} 1 \\ 0 \end{cases}$$

Again we see that total angular momentum adds up nicely: $\frac{1}{2}+\frac{1}{2}=1\,,\quad \frac{1}{2}-\frac{1}{2}=0$

In terms of the new f quantum number, the states have a natural interpretation:

$$|f, m_f\rangle = \begin{cases} |1,1\rangle & = |\uparrow\uparrow\rangle \\ |1,0\rangle & = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle\right) \\ |1,-1\rangle & = |\downarrow\downarrow\rangle \\ |0,0\rangle & = \frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) \end{cases}$$

There are three ways to have total spin 1 and just one way to have total spin 0.

We also see that the spin 1 states are **symmetric**, while the spin 0 state is **antisymmetric**.

Addition of angular momenta

General question:
Given two spins, j_1 and j_2, what are the allowed values of total AM?

$$J = |j_1 - j_2|,\ |j_1 - j_2| + 1,\ \ldots\ , j_1 + j_2$$

Math-speak: "decompose into a direct sum of irreducible representations of SU(2)".

For each value of the total spin, we can have a z-component:

$$M = -J,\ -J + 1,\ \ldots\ , J$$

$|J, J\rangle$ is always totally symmetric.

We want to be able to answer questions like (for example):

A spin $j_1 = 3/2$ and spin $j_2 = 1$ particle have total spin $J = 3/2$ and $M = 1/2$.
Now measure the z-component of each individually.

What is the probability of finding $(m_1, m_2) = (+3/2, -1)$?
What about $(m_1, m_2) = (+1/2, 0)$? What about $(m_1, m_2) = (-1/2, 1)$?

Clebsch-Gordan coefficients

A general solution to this problem is given by the Clebsch-Gordan coefficients:

$$|J\,M\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} |j_1\,m_1\,j_2\,m_2\rangle\langle j_1\,m_1\,j_2\,m_2\,|\,J\,M\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} C^{j_1\,j_2\,J}_{m_1\,m_2\,M}\,|j_1\,m_1\,j_2\,m_2\rangle$$

Resolution of identity
in the j_1-j_2 subspace.

The **Clebsch-Gordan coefficients** are just the basis expansion coefficients.

$$C^{j_1\,j_2\,J}_{m_1\,m_2\,M} = \langle j_1\,m_1\,j_2\,m_2\,|\,J\,M\rangle \qquad C^{j_1\,j_2\,J}_{m_1\,m_2\,M} \neq 0 \;\;\Rightarrow\;\; M = m_1 + m_2$$

(conservation of AM)

These are tabulated, and you can **look them up**.

Clebsch-Gordan tables

Returning to our example question:

$$C^{j_1\, j_2\, J}_{m_1\, m_2\, M} = \langle j_1\, m_1\, j_2\, m_2 | J\, M \rangle$$

$j_1 = \frac{3}{2}, j_2 = 1$

$m=\frac{1}{2}$			
m_1, m_2 \ j	$\frac{5}{2}$	$\frac{3}{2}$	$\frac{1}{2}$
$\frac{3}{2}$, -1	$\sqrt{\frac{1}{10}}$	$\sqrt{\frac{2}{5}}$	$\sqrt{\frac{1}{2}}$
$\frac{1}{2}$, 0	$\sqrt{\frac{3}{5}}$	$\sqrt{\frac{1}{15}}$	$-\sqrt{\frac{1}{3}}$
-$\frac{1}{2}$, 1	$\sqrt{\frac{3}{10}}$	$-\sqrt{\frac{8}{15}}$	$\sqrt{\frac{1}{6}}$

$$|J, M\rangle = |\tfrac{3}{2}, +\tfrac{1}{2}\rangle$$

$$= \sqrt{\frac{2}{5}}\, |\tfrac{3}{2}, \tfrac{3}{2}, 1, -1\rangle + \sqrt{\frac{1}{15}}\, |\tfrac{1}{2}, \tfrac{3}{2}, 1, 0\rangle - \sqrt{\frac{8}{15}}\, |\tfrac{3}{2}, -\tfrac{1}{2}, 1, 1\rangle$$

$\uparrow$

$|j_1, m_1, j_2, m_2\rangle$

Use the Born rule to calculate the answers:

$$\left| \langle \tfrac{3}{2}, \tfrac{3}{2}, 1, -1 | \tfrac{3}{2}, +\tfrac{1}{2} \rangle \right|^2 = \left| \sqrt{\frac{2}{5}} \right|^2 = \frac{2}{5}$$

← Probability of finding (+3/2, -1) for the two z-components.

Similarly, the probability of finding (+1/2, 0) is 1/15 and of finding (-1/2,+1) is 8/15.