

ANGULAR MOMENTUM: ADDING 3 SPINS

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 5.13d.

Messiah, Albert (1958), Quantum Mechanics, Volume 2, Chapter 13.

In finding the ground state of an atom, we first need to eliminate those states that violate the Pauli exclusion principle. This involves finding states where the combined spin and orbital wave functions are antisymmetric. In the example of carbon, this wasn't too difficult to do since there are only two outer electrons, so we can add their angular momenta using the Clebsch-Gordan coefficients. However, so far we've seen only examples involving the addition of two angular momenta and, in fact, tables of the C-G coefficients are always given only for this case.

In the case of nitrogen, there are 3 electrons in the outer p shell, so we need to add together 3 angular momenta. We can do this in two stages. First, we combine two of the three angular momenta which we can do using C-G coefficients as before. This gives us a compound state that has a particular value of total angular momentum J and J_z value of M . We can now combine this compound state (which is treated as a single state) with the remaining component to get the final result.

There is, however, more than one way we can do this, since we can choose any one of the three electrons as the odd man out when doing the initial combination of the other two. The results will sometimes vary depending on which electron is chosen.

To see what this means, we need to look a bit more closely at what we're doing with this two-stage process. What we're finding is a state which is an eigenstate of the operators J^2 and J_z with eigenvalues $J(J+1)$ and M respectively. Since we're also specifying the initial angular momenta of the three electrons, this state should also be an eigenstate of j_i^2 for $i = 1, 2, 3$.

But what of the intermediate compound angular momentum? To make things definite, we'll look at combining j_1 and j_2 in the first stage, giving a compound state with momentum J_{12} and z component M_{12} . Since J_{12} is formed from j_1 and j_2 , its value must lie in the range $|j_1 - j_2| \dots j_1 + j_2$. For a given value of J_{12} , the final value of J (the grand total) must then lie in the range $|J_{12} - j_3| \dots J_{12} + j_3$ and the final z component must be $M = M_{12} + m_3$.

For example, suppose we consider the 3 p electrons in nitrogen. All three have $l = 1$ so we can form compound states with a total L of 0, 1, 2

or 3. Let's see how we might form the compound state $|22\rangle$. That is, we want $J = 2$ and $M = 2$. The largest possible values of M_{12} and m_3 are 2 and 1, respectively, so the possible combinations are $M_{12} = 2, m_3 = 0$ and $M_{12} = 1, m_3 = 1$. The first combination can arise only when $J_{12} = 2$, while the second can arise from either $J_{12} = 2$ or $J_{12} = 1$. Therefore, there are two possible values of J_{12} , so we have two ways of forming the final $|22\rangle$ state, as we can go via either of these values of J_{12} to get there. To keep things clear, we'll write a state as $|J_{12}, 22\rangle$ to show which route we took to get it.

As equations, we can therefore write:

$$\begin{aligned} (1) \quad & |1, 22\rangle = a_1 |11\rangle_{12} |11\rangle_3 \\ (2) \quad & |2, 22\rangle = b_1 |22\rangle_{12} |10\rangle_3 + b_2 |21\rangle_{12} |11\rangle_3 \end{aligned}$$

The subscripts on the kets on the RHS indicate which electrons contribute to that ket, and the coefficients a and b are constants. These equations are the same as those for adding two angular momenta, so the coefficients are just the C-G coefficients and can be read off a table.

In the first equation $a_1 = 1$, and in the second, we are combining $J_{12} = 2$ with $j_3 = 1$, so we get the coefficients from the 2×1 C-G table. The results are

$$\begin{aligned} (3) \quad & |1, 22\rangle = |11\rangle_{12} |11\rangle_3 \\ (4) \quad & |2, 22\rangle = \sqrt{\frac{2}{3}} |22\rangle_{12} |10\rangle_3 - \frac{1}{\sqrt{3}} |21\rangle_{12} |11\rangle_3 \end{aligned}$$

We can now expand the J_{12} states using C-G coefficients, since they are formed from the sum of two angular momenta. In all cases, they are states formed from the sum of $j_1 = 1$ and $j_2 = 1$, so we use the 1×1 table. We have

$$\begin{aligned} (5) \quad & |11\rangle_{12} = \frac{1}{\sqrt{2}} |11\rangle_1 |10\rangle_2 - \frac{1}{\sqrt{2}} |10\rangle_1 |11\rangle_2 \\ (6) \quad & |22\rangle_{12} = |11\rangle_1 |11\rangle_2 \\ (7) \quad & |21\rangle_{12} = \frac{1}{\sqrt{2}} |11\rangle_1 |10\rangle_2 + \frac{1}{\sqrt{2}} |10\rangle_1 |11\rangle_2 \end{aligned}$$

The overall states are then

(8)

$$|1, 22\rangle = \frac{1}{\sqrt{2}} |11\rangle_1 |10\rangle_2 |11\rangle_3 - \frac{1}{\sqrt{2}} |10\rangle_1 |11\rangle_2 |11\rangle_3$$

(9)

$$|2, 22\rangle = \sqrt{\frac{2}{3}} |11\rangle_1 |11\rangle_2 |10\rangle_3 - \frac{1}{\sqrt{6}} |11\rangle_1 |10\rangle_2 |11\rangle_3 - \frac{1}{\sqrt{6}} |10\rangle_1 |11\rangle_2 |11\rangle_3$$

The most general $|22\rangle$ state is a linear combination of these two:

$$(10) \quad |22\rangle = A |1, 22\rangle + B |2, 22\rangle$$

where A and B are chosen to satisfy whatever constraints have been placed on the problem (including normalization).

It can be seen from these equations that the $|22\rangle$ state is neither symmetric nor antisymmetric under all exchanges of electrons. The $|1, 22\rangle$ state is antisymmetric under exchange of 1 and 2, while the $|2, 22\rangle$ state is symmetric under the same exchange but there is no symmetry under exchange with electron 3.

The two states $|1, 22\rangle$ and $|2, 22\rangle$ span the space of $|22\rangle$ states. If we derived the eigenstates by combining electrons 2 and 3 or 1 and 3 initially, we'd get different basis states, but the space spanned by them is the same.

For example, suppose we choose to pair electrons 2 and 3 initially. We would then get

$$(11) \quad |1, 22\rangle_{23} = |11\rangle_1 |11\rangle_{23}$$

$$(12) \quad |2, 22\rangle_{23} = \sqrt{\frac{2}{3}} |10\rangle_1 |22\rangle_{23} - \frac{1}{\sqrt{3}} |11\rangle_1 |21\rangle_{23}$$

Expanding the J_{23} states we get

(13)

$$|1, 22\rangle_{23} = \frac{1}{\sqrt{2}} |11\rangle_1 |11\rangle_2 |10\rangle_3 - \frac{1}{\sqrt{2}} |11\rangle_1 |10\rangle_2 |11\rangle_3$$

(14)

$$|2, 22\rangle_{23} = \sqrt{\frac{2}{3}} |10\rangle_1 |11\rangle_2 |11\rangle_3 - \frac{1}{\sqrt{6}} |11\rangle_1 |11\rangle_2 |10\rangle_3 - \frac{1}{\sqrt{6}} |11\rangle_1 |10\rangle_2 |11\rangle_3$$

We can write these basis states in terms of the previous ones:

$$(15) \quad |1, 22\rangle_{23} = \frac{\sqrt{3}}{2} |2, 22\rangle - \frac{1}{2} |1, 22\rangle$$

$$(16) \quad |2, 22\rangle_{23} = -\frac{1}{2} |2, 22\rangle - \frac{\sqrt{3}}{2} |1, 22\rangle$$

Thus one basis can be written in terms of the other, which shows they span the same space.

We can do the same exercise for the $|11\rangle$ state, though it gets a bit more complicated. Doing the sums shows that J_{12} can be 0, 1 or 2, so we have, after looking up the C-G coefficients:

$$(17) \quad |0, 11\rangle = |00\rangle_{12} |11\rangle_3$$

$$(18) \quad |1, 11\rangle = \frac{1}{\sqrt{2}} |11\rangle_{12} |10\rangle_3 - \frac{1}{\sqrt{2}} |10\rangle_{12} |11\rangle_3$$

$$(19) \quad |2, 11\rangle = \sqrt{\frac{3}{5}} |22\rangle_{12} |1-1\rangle_3 - \sqrt{\frac{3}{10}} |21\rangle_{12} |10\rangle_3 + \frac{1}{\sqrt{10}} |20\rangle_{12} |11\rangle_3$$

Then we can expand the J_{12} states to get the final forms

$$(20)$$

$$|0, 11\rangle = \frac{1}{\sqrt{3}} |11\rangle_1 |1-1\rangle_2 |11\rangle_3 - \frac{1}{\sqrt{3}} |10\rangle_1 |10\rangle_2 |11\rangle_3 + \frac{1}{\sqrt{3}} |1-1\rangle_1 |11\rangle_2 |11\rangle_3$$

$$(21)$$

$$|1, 11\rangle = \frac{1}{2} |11\rangle_1 |10\rangle_2 |11\rangle_3 - \frac{1}{2} |10\rangle_1 |11\rangle_2 |11\rangle_3 -$$

$$(22)$$

$$\frac{1}{2} |11\rangle_1 |1-1\rangle_2 |11\rangle_3 + \frac{1}{2} |1-1\rangle_1 |11\rangle_2 |11\rangle_3$$

$$(23)$$

$$|2, 11\rangle = \sqrt{\frac{3}{5}} |11\rangle_1 |11\rangle_2 |1-1\rangle_3 - \sqrt{\frac{3}{20}} |11\rangle_1 |10\rangle_2 |10\rangle_3 -$$

$$(24)$$

$$- \sqrt{\frac{3}{20}} |10\rangle_1 |11\rangle_2 |10\rangle_3 + \frac{1}{\sqrt{60}} |11\rangle_1 |1-1\rangle_2 |11\rangle_3 +$$

$$(25)$$

$$\sqrt{\frac{2}{30}} |10\rangle_1 |10\rangle_2 |11\rangle_3 + \frac{1}{\sqrt{60}} |1-1\rangle_1 |11\rangle_2 |11\rangle_3$$

Again, there are no overall symmetries, although the first and third eigenstates are symmetric under exchange of 1 and 2, and the second eigenstate is antisymmetric.

Finally, we look at the $|00\rangle$ state. In this case, J_{12} must be 1, since there is no way to combine a J_{12} of 0 or 2 with $j_3 = 1$ to get an overall $J = 0$ state. We therefore have

$$(26) \quad |1, 00\rangle = \frac{1}{\sqrt{3}} |11\rangle_{12} |1-1\rangle_3 - \frac{1}{\sqrt{3}} |10\rangle_{12} |10\rangle_3 + \frac{1}{\sqrt{3}} |1-1\rangle_{12} |11\rangle_3$$

Expanding the J_{12} states we get

$$(27) \quad |1, 00\rangle = \frac{1}{\sqrt{6}} |11\rangle_1 |10\rangle_2 |1-1\rangle_3 - \frac{1}{\sqrt{6}} |10\rangle_1 |11\rangle_2 |1-1\rangle_3 -$$

$$(28) \quad \frac{1}{\sqrt{6}} |11\rangle_1 |1-1\rangle_2 |10\rangle_3 + \frac{1}{\sqrt{6}} |1-1\rangle_1 |11\rangle_2 |10\rangle_3 +$$

$$(29) \quad \frac{1}{\sqrt{6}} |10\rangle_1 |1-1\rangle_2 |11\rangle_3 - \frac{1}{\sqrt{6}} |1-1\rangle_1 |10\rangle_2 |11\rangle_3$$

This state is fully antisymmetric, since swapping any two electrons reverses the sign of the state. Since this is the only antisymmetric orbital angular momentum state in the list of possibilities for nitrogen, this must be the ground state. The total angular momentum is $J_{TOT} = 0 + \frac{3}{2}$. Thus the ground state for nitrogen is ${}^4S_{3/2}$.

We can add together any number of angular momenta in the same way, by choosing an initial pair to combine, then pairing the compound state with the next individual state and so on. At each stage we are adding only 2 spins, so we can always use the C-G tables to form the sums.

PINGBACKS

Pingback: Hund's rules

Pingback: Dysprosium electron configuration