

Atoms

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Griffiths problem 5.12

		S	L	J	term symbol
H	(1s)	$\frac{1}{2}$	0	$\frac{1}{2}$	$^2S_{1/2}$
He	(1s) ²	0	0	0	1S_0
Li	(1s) ² (2s)	$\frac{1}{2}$	0	$\frac{1}{2}$	$^2S_{1/2}$
Be	(1s) ² (2s) ²	0	0	0	1S_0
B	(1s) ² (2s) ² (2p)	$\frac{1}{2}$	1	$\frac{1}{2}, \frac{3}{2}$	
C	(1s) ² (2s) ² (2p) ²	0, 1	0, 1, 2	0, 1, 2, 3	
N	(1s) ² (2s) ² (2p) ³	$\frac{1}{2}, \frac{3}{2}$	0, 1, 2, 3	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$	

Griffiths problem 5.13

(a) For He, Hund's first rule predicts that triplet states ($S = 1$) will have less energy than corresponding singlet states ($S = 0$). This is confirmed by the figure on Griffiths page 213.

(b) For C, Hund's first rule predicts that the lowest energy state will have $S = 1$ (triplet). Hund's second rule says that, for a given spin, the highest possible L has least energy. So you'd think that for C that would be $L = 2$, yet in fact the correct result is $L = 1$. Why?

The spin triplet is symmetric under exchange, so the spatial state must be antisymmetric under exchange. If we add together the two p electron orbital angular momenta, we could get $L = 0$, or 1, or 2, but the $L = 2$ states are symmetric. To see this, note that the "top of the ladder" state $|2, +2\rangle_J = |1, +1\rangle_{(A)}|1, +1\rangle_{(B)}$ is obviously symmetric, so all the states produced from it by applying the symmetric operator $\hat{L}_- = \hat{L}_-^{(A)} + \hat{L}_-^{(B)}$ will also be symmetric.

(c) For B, C, and N, the (2p) subshell is half-filled or less, so the lowest energy has $J = |L - S|$. For B, this means $J = \frac{1}{2}$ so the term symbol is $^2P_{1/2}$.

(d) For carbon, we already have $S = 1$ (first rule) and $L = 1$ (second rule). According to the third rule, $J = 0$ so the proper term symbol for carbon is 3P_0 .

How about nitrogen? Well, now we've got to add *three* angular momenta. Hund's first rule says that the ground state will have the highest spin, namely $S = \frac{3}{2}$, which is a quadruplet and spin symmetric (it includes, for example, the state $|\uparrow\uparrow\uparrow\rangle$). This means that the spatial function must be antisymmetric.

I can think of two ways to proceed from here: (1) Start with the angular momentum and find the exchange symmetry. (2) Start with the exchange symmetry and find the angular momentum.

(1) *Start with the angular momentum and find the exchange symmetry.* Sum the three spatial angular momenta and look to see which sums are antisymmetric. These are then the only possible total angular momenta.

In general this involves adding first two triplets [$L = 1$] to form a quintet [$J_{\text{partial}} = 2$], a triplet [$J_{\text{partial}} = 1$], and a singlet [$J_{\text{partial}} = 0$], then adding to this the third triplet [$L = 1$] to form one heptet [$J = 3$], two quintets [$J = 2$], three triplets [$J = 1$], and one singlet [$J = 0$]. (For three triplets there are $3^3 = 27$ states; for one heptet plus two quintets plus three triplets plus one singlet there are $7 + 2 \times 5 + 3 \times 3 + 1 = 27$ states. . . so far so good.)

In general, you would do this using the table of Clebsch-Gordan coefficients, and it would be a lot of work. But Jocienne Nelson, class of 2014, pointed out this shortcut: If you're adding three building-block levels to make a state, then the simple balls-in-buckets picture says you have to use three different building blocks. We have only three building blocks available: $|1, +1\rangle$, $|1, 0\rangle$, and $|1, -1\rangle$. Thus the sum of m s must be zero.

Of those 27 states, which ones have an m_J of zero? They are $|3, 0\rangle_J$, $|2, 0\rangle_J$, $|1, 0\rangle_J$ and $|0, 0\rangle_J$. Now we do a proof by contradiction: If $|1, 0\rangle_J$ were antisymmetric under interchange, then $\hat{J}_-|1, 0\rangle_J \propto |1, -1\rangle_J$ would also be antisymmetric under interchange, because

$$\hat{J}_- = \hat{L}_-^{(A)} + \hat{L}_-^{(B)} + \hat{L}_-^{(C)}$$

is symmetric under interchange. But we know that states antisymmetric under interchange have $m_J = 0$, so $|1, -1\rangle_J$ *can't* be antisymmetric under interchange. Thus our initial assumption that $|1, 0\rangle_J$ was antisymmetric under interchange must be wrong.

This argument can be repeated for $|3, 0\rangle_J$ and for $|2, 0\rangle_J$, but not for $|0, 0\rangle_J$, because this state lowers to nothingness. Thus the total orbital angular momentum must be zero (S).

(2) *Start with the exchange symmetry and find the angular momentum.* We find antisymmetric combinations of the building blocks, and then find the total angular momentum of the combination. (This method suggested by Noah Forman, class of 2007.)

There is only one completely antisymmetric combination of $|1, +1\rangle$, $|1, 0\rangle$, and $|1, -1\rangle$, namely

$$\frac{1}{\sqrt{6}} [+ |1, +1\rangle_{(A)}|1, 0\rangle_{(B)}|1, -1\rangle_{(C)} - |1, +1\rangle_{(A)}|1, -1\rangle_{(B)}|1, 0\rangle_{(C)} + |1, -1\rangle_{(A)}|1, +1\rangle_{(B)}|1, 0\rangle_{(C)} \\ - |1, -1\rangle_{(A)}|1, 0\rangle_{(B)}|1, +1\rangle_{(C)} + |1, 0\rangle_{(A)}|1, -1\rangle_{(B)}|1, +1\rangle_{(C)} + |1, 0\rangle_{(A)}|1, +1\rangle_{(B)}|1, -1\rangle_{(C)}].$$

To this state we apply the “total angular momentum squared” operator

$$(\hat{L}^{(A)} + \hat{L}^{(B)} + \hat{L}^{(C)}) \cdot (\hat{L}^{(A)} + \hat{L}^{(B)} + \hat{L}^{(C)}) \\ = (\hat{L}^{(A)})^2 + (\hat{L}^{(B)})^2 + (\hat{L}^{(C)})^2 + 2\hat{L}^{(A)} \cdot \hat{L}^{(B)} + 2\hat{L}^{(B)} \cdot \hat{L}^{(C)} + 2\hat{L}^{(A)} \cdot \hat{L}^{(C)}$$

If $(\hat{L}^{(A)})^2$ is applied to the above state, the result is of course $\ell(\ell + 1) = 2$ times that state (using $\hbar = 1$). Similarly for $(\hat{L}^{(B)})^2$ or $(\hat{L}^{(C)})^2$. But

$$\begin{aligned}
\hat{\vec{L}}^{(A)} \cdot \hat{\vec{L}}^{(B)} &= \hat{L}_x^{(A)} \hat{L}_x^{(B)} + \hat{L}_y^{(A)} \hat{L}_y^{(B)} + \hat{L}_z^{(A)} \hat{L}_z^{(B)} \\
&= \frac{1}{4}(\hat{L}_+^{(A)} + \hat{L}_-^{(A)})(\hat{L}_+^{(B)} + \hat{L}_-^{(B)}) - \frac{1}{4}(\hat{L}_+^{(A)} - \hat{L}_-^{(A)})(\hat{L}_+^{(B)} - \hat{L}_-^{(B)}) + \hat{L}_z^{(A)} \hat{L}_z^{(B)} \\
&= \frac{1}{2}(\hat{L}_-^{(A)} \hat{L}_+^{(B)} + \hat{L}_+^{(A)} \hat{L}_-^{(B)}) + \hat{L}_z^{(A)} \hat{L}_z^{(B)}
\end{aligned}$$

Recall that

$$\begin{aligned}
\hat{L}_+ |\ell, m\rangle &= \sqrt{\ell(\ell+1) - m(m+1)} |\ell, m+1\rangle \\
\hat{L}_+ |1, +1\rangle &= 0 \\
\hat{L}_+ |1, 0\rangle &= \sqrt{2} |1, +1\rangle \\
\hat{L}_+ |1, -1\rangle &= \sqrt{2} |1, 0\rangle \\
\hat{L}_- |\ell, m\rangle &= \sqrt{\ell(\ell+1) - m(m-1)} |\ell, m-1\rangle \\
\hat{L}_- |1, +1\rangle &= \sqrt{2} |1, 0\rangle \\
\hat{L}_- |1, 0\rangle &= \sqrt{2} |1, -1\rangle \\
\hat{L}_- |1, -1\rangle &= 0.
\end{aligned}$$

A little additional work shows that if $\hat{\vec{L}}^{(A)} \cdot \hat{\vec{L}}^{(B)}$ is applied to the above state, the result is -1 times that state. And because of the exchange symmetry of the state, the same is true of $\hat{\vec{L}}^{(B)} \cdot \hat{\vec{L}}^{(C)}$ or $\hat{\vec{L}}^{(A)} \cdot \hat{\vec{L}}^{(C)}$.

Thus when the whole battery $(\hat{\vec{L}}^{(A)} + \hat{\vec{L}}^{(B)} + \hat{\vec{L}}^{(C)})^2$ is applied, the result is 0. And there it is... the only completely antisymmetric state has angular momentum $L = 0$.

Using either method, we have $L = 0$. We already had $S = \frac{3}{2}$, so $J = \frac{3}{2}$, and the term symbol for nitrogen's ground state is ${}^4S_{3/2}$.