

Physics 571 Lecture #27

1 Spectroscopic notation

Decades ago, atomic physicists came up with a method of labeling atomic energy levels. A level is determined by its orbital, spin, and total angular momenta and also by its parity. We keep track of these four items in the following symbol:

$$2S+1 \text{L}_J^{\Pi}$$

The total orbital angular momentum is labeled as L. It is an upper case letter, and in the usual cryptic atomic physics manner, if $L = 0$, then L is really S. If $L=1$, then L is really P. If $L = 2$, then L is really D. Values of L greater than 2 are labeled alphabetically as F, G, H, and so on for $L=3, 4, 5$, etc.

The total spin of the system is labeled as S (not to be confused with the S used to label the value of the orbital angular momentum — I know, this is like an Abbott and Costello routine). To the upper left of the orbital angular momentum symbol we write the value of $2S+1$. Sometimes this is called the multiplicity, and in many situations this tells the total number of J values allowed in a *term* (see below).

The total spin (S) and the total orbital angular momentum (L) add together to make the total angular momentum, J. The allowed values of J are $L+S, \dots, L-S$, in integer steps. The addition and allowed values of angular momentum are related to the fact that space is quantized.

The parity of the state is noted on the upper right-hand side of the symbol. If the parity is even, then we don't write anything. If it is odd, we write a little "o". The parity depends on whether the state is even or odd with respect to inversion of the coordinates in the usual way. You know, in one dimension a function has even parity is $f(x) = f(-x)$ and it has odd parity if $f(-x) = -f(x)$. The sine function has odd parity. The cosine function has even parity. It is possible to show that the stationary states in an atom (the solutions to the time independent Schrödinger equation) have definite parity. They are either even or odd. When you are thinking about parity in a multi-electron atom, you add up the ℓ values of all the individual electrons (the *real* sum, not the goofy quantum mechanical sum — you know, $1+1=2$ and NOT $1+1=0,1,2$). If this number is even, then the state has even parity. If it is odd, the state has odd parity. Actually, the more technically correct statement is that $\Pi = (-1)^{\sum \ell}$. When $\Pi = 1$ the parity is even and when $\Pi = -1$ the parity is odd.

Sometimes you will see something that looks like an energy level symbol without the J value or parity specified, like 2D (read "doublet D") or 1P (read "singlet P"). These are called terms. A quantum mechanical state is specified by the quantum numbers n, ℓ, s, m_ℓ , and m_s for each electron. In our spectroscopic notation, each energy level has $2J + 1$ "magnetic" sub-levels. If we specify a particular sub-level, then we have identified a state.

2 Hydrogen

Let's consider a few examples. First let's think about hydrogen. There is one electron. It has an angular momentum ℓ and a spin s . Let's put the electron in the ground state. The electron configuration is $1s$, meaning that $n = 1$ and $\ell = 0$. If you were a chemist you would say the electron is in the s orbital of the first shell. The total orbital angular momentum is just $L = 0$ because $\ell = 0$. The total spin angular momentum is $S = \frac{1}{2}$ because $s = \frac{1}{2}$. The total angular momentum

ranges from $L + S$ to $L - S$ in integer steps. Of course, there is only one possible value: $J = \frac{1}{2}$. Because $\ell = 0$, we have $\Pi = (-1)^0 = 1$ so the state has even parity.

The full spectroscopic notation for the ground state has both the electron configuration and the level identification. So for the ground state of hydrogen, the spectroscopic notation is

$$1s \quad ^2S_{1/2}.$$

If you were reading this to someone you would say, “one ess doublet ess one half.”

Let’s suppose that the electron is in its first excited state and the electron configuration is $2p$. This means that $n = 2$ and $\ell = 1$. Following the cryptic explanations above, we have $L = 1$ and $S = \frac{1}{2}$. But now we have two possible values for the total angular momentum: $J = \frac{1}{2}, \frac{3}{2}$. The state also has odd parity. So the spectroscopic notation for these two levels would be

$$2p \quad ^2P_{3/2}^\circ \quad \text{and} \quad 2p \quad ^2P_{1/2}^\circ.$$

Once again, if you were reading the first state you would say, “two pea doublet pea three halves.”

3 In Helium

In helium, things are a little more interesting. There are two electrons in the atom, so we have to add up their contributions to the various angular momenta.

The ground state is easy. The electron configuration is $1s^2$. Both electrons have $\ell = 0$ and $s = 1/2$. The allowed value for L is 0. The possible values for S are 0 and 1. But we can only really have $S=0$, meaning that the little individual electron spins are oppositely aligned. Otherwise, all of the quantum numbers for the two electrons would be exactly the same, in violation of the Pauli exclusion principle. With $L = 0$ and $S = 0$ we also have $J = 0$. The parity of the state is even ($\sum \ell = 0$). The spectroscopic notation for the ground level is

$$1s^2 \quad ^1S_0,$$

pronounced, “one ess squared singlet ess zero.” Occasionally you may run into an old-timer who will say, “one ess squared singlet ess naught.”

The excited state is a little more interesting. Let’s consider the electron configuration of $1s2p$. In this case we can have $S = 0$ and 1, and $L = 0$. When $L = 1$ and $S = 0$, you have $J = 1$ and odd parity:

$$1s2p \quad ^1P_1^\circ.$$

When $L = 1$ and $S = 1$, you have $J = 0, 1$, or 2, all with odd parity:

$$1s2p \quad ^3P_2^\circ \quad \text{and} \quad 1s2p \quad ^3P_1^\circ \quad \text{and} \quad 1s2p \quad ^3P_0^\circ.$$

Notice that there is one level in the singlet P term and there are three levels in the triplet P term. That is how the $2S + 1$ number on the upper left of the term came to be known as the multiplicity. It tells you (in many cases) the number of levels in a term. (Note that this does not work for the triplet S term from the $1s2s$ configuration. The system is not perfect.)

4 Two equivalent p electrons

Now let’s tackle something a little harder—the case of two equivalent p electrons. Try not to laugh too much at how arcane this appears to be. This stuff really is helpful. Every atom has an infinite

Table 1: All of the possible ways to arrange two equivalent p electrons. Arrangements that violate the Pauli Exclusion Principle (such as up-up in the same m_ℓ) are not listed.

m_ℓ			$\sum m_\ell$	$\sum m_s$	
+1	0	-1			
$\uparrow\downarrow$			+2	0	Δ
\uparrow	\uparrow		+1	+1	+
\uparrow	\downarrow		+1	0	Δ
\downarrow	\uparrow		+1	0	+
\downarrow	\downarrow		+1	-1	+
\uparrow		\uparrow	0	+1	+
\uparrow		\downarrow	0	0	Δ
\downarrow		\uparrow	0	0	+
\downarrow		\downarrow	0	-1	+
	$\uparrow\downarrow$		0	0	\times
	\uparrow	\uparrow	-1	+1	+
	\uparrow	\downarrow	-1	0	Δ
	\downarrow	\uparrow	-1	0	+
	\downarrow	\downarrow	-1	-1	+
		$\uparrow\downarrow$	-2	0	Δ

number of levels, and we have to keep track of them somehow. And besides being a historical vestige from long ago, this system is useful for knowing which states go where, what their properties are, which levels will radiate to which other levels, and so on.

For two equivalent p electrons (equivalent because they are in the same n level), we have $\ell_1 = 1, \ell_2 = 1, s_1 = \frac{1}{2}$, and $s_2 = \frac{1}{2}$. So you can have $L = 0, 1, 2$ and $S = 0, 1$. Depending on each L and S value, you have a range of possible J values.

But we need to be careful. Some of these combinations of L and S violate the Pauli exclusion principle. So we need to make a table, like the one shown in Table 1. Here we record the m_ℓ and m_s for both electrons. The table has three bins ($m_\ell = -1, 0, 1$) and the m_s values are represented by up and down arrows. We also record the total M_L and the total M_S .

Once the table is filled out, we can assign these different arrangements to terms using Hund's rules. We start with the largest M_L . In the table, this is 2. We can only get this if $L = 2$, so this will be a D term. Our next job is to find the multiplicity of the term. So for this highest value of M_L , we choose the highest value of M_S . It is 0. That means our first term is a 2D . The $L = 2$ angular momentum in the 2D term will have five sub-levels with $M_L = 2, 1, 0, -1, -2$, all with $M_S = 0$. We can identify these in the table with the symbol Δ . You will notice that there are two levels with $M_L = 1$ and $M_S = 0$. Which one should you choose? The answer is that it doesn't matter. Choose one of them. The other one will belong to a different term.

We repeat the process with the remaining levels. What is the highest remaining M_L ? It is 1. For $M_L = 1$, what is the highest value of M_S ? It is also 1. This will give us a 3P term. So I need to identify nine arrangements from the table with this term: $M_L = 1, 0, -1$ for each of the possible values of M_S . These arrangements are marked with the "+" symbol in the last column of Table 1.

Once again we repeat. There is only one arrangement left. It has $M_L = 0$ and $M_S = 0$. This gives a 1S term, and it can have only one arrangement. We mark it with a " \times " symbol. A few

comments are perhaps in order.

1. The number of arrangements for each term is equal to the number of states for the term. For example, the 3P term has nine arrangements in Table 1. For the 3P_2 level, there are five sub-levels, $m_J = 2, 1, 0, -1, -2$. For the 3P_1 level, there are three sub-levels, $m_J = 1, 0, -1$. For the 3P_0 level, there is one sub level, $m_J = 0$. The total is 9 levels.
2. The proper way to find the sub-levels belonging to a particular term is to start with the “pure” state $\ell_1 = 1, m_{\ell_1} = 1, \ell_2 = 1, m_{\ell_2} = 1$ and to apply the lowering operator $L_{1-} + L_{2-}$. With proper normalization, this will give the $L = 2, M_L = 1$, and $M_S = 0$ state as a linear combination of the two states that have $M_L = 1$ and $M_S = 0$, with appropriate Clebsch-Gordon coefficients.