

## 9.5: Diatomic Term Symbols

A term symbol for a diatomic molecule contains a great deal of information about symmetry properties of the wavefunction which describes the electronic state. The symmetry properties are closely related to the values of the quantum numbers which specify the wavefunction. The pattern used to assign a symbol to a value for a quantum number is very similar to the pattern used for atomic systems. The major difference is that the quantum numbers must reflect the cylindrical symmetry of diatomic molecules rather than the spherical symmetry of atoms.

Quantum Number	One Electron		Many Electrons	
	Atom ( <i>l</i> )	Molecule ( $\lambda$ )	Atom ( <i>L</i> )	Molecule ( $\Lambda$ )
0	s	$\sigma$	S	$\Sigma$
1	p	$\pi$	P	$\Pi$
2	d	$\delta$	D	$\Delta$
3	f	$\phi$	F	$\Phi$

Just as there is a  $(2l+1)$  degeneracy in the spherical wavefunctions, there is also an important degeneracy pattern in the wavefunctions of diatomic molecules.  $\Sigma$  and  $\sigma$  states are singly degenerate whereas all other are doubly degenerate. Why this is should become apparent as we develop the united atom method for decomposing spherical symmetry to cylindrical symmetry.

$\lambda$ or $\Lambda$	Wavefunction Symmetry		Degeneracy
0	$\sigma$	$\Sigma$	1
1	$\pi$	$\Pi$	2
2	$\delta$	$\Delta$	2
3	$\phi$	$\Phi$	2

There are three methods commonly used to derive terms symbols for diatomic molecules. All of the methods are based on determining the quantum number  $\Lambda$  and the total spin quantum number. In the case of homonuclear diatomic molecules, the inversion symmetry is also important.

$\Sigma$  states have another important symmetry designation.  $\Sigma$  states can have either + or - symmetry depending on whether or not the state is symmetric with respect to reflection through a plane containing the internuclear axis. Symmetric states are designated as  $\Sigma^+$  state and antisymmetric ones are  $\Sigma^-$ .  $\Pi$ ,  $\Delta$  and all other states with  $L \neq 0$  are doubly degenerate as they have both + and - components.

There is always an odd number of S states generated for the United Atom method or the Separated Atom method. They will come in pairs of  $\Sigma^+$ ,  $\Sigma^-$  and the odd remaining state will have +/- symmetry as determined by the **Wigner-Witmer rule**. For this, one must consider the associated atomic state (using either the United Atom or the Separated Atom method). The +/- symmetry is determined by whether the indicated sum is even or odd according to the following table.

Method	Sum	Value	Parity
United Atom	$L + \sum l_i$	even	+
		odd	-
Separated Atom	$L_A + \sum l_A + L_B + \sum l_B$	even	+
		odd	-

## United Atom Method

Think of the molecule as an atom with the same number of electrons. The atom will have spherical symmetry. The task is to reduce the spherical symmetry of the atomic wavefunction to the cylindrical symmetry of the diatomic molecule. In this case, the z-axis of the unified atom becomes the internuclear axis of the molecule. Thus, the quantum numbers will transform as

$$\begin{aligned} M_L &\rightarrow \Lambda \\ S &\rightarrow \Lambda \end{aligned}$$

### ✓ Example 9.5.1

What molecular terms are predicted for the OH radical?

#### Solution

The unified atom with the same number of electrons as OH is fluorine. The ground state designation for atomic fluorine is  $^2P$ . For this state,  $L = 1$  and so  $m_L$  can be -1, 0 or +1. The only values of  $m_L$  are 0 and 1. Therefore, the predicted terms will be  $\Sigma$  and  $\Pi$ . The multiplicity will be the same as the unified atom ( $S = \frac{1}{2}$ ). The  $\Sigma$  state will be symmetric with respect to reflection through a plane containing the z-axis since

$$L + \sum l_i$$

is even for fluorine. So the expected terms are

$$^2\Sigma^+ \text{ and } ^2\Pi.$$

As it turns out, the ground state of OH is  $^2\Pi$ . The only way to confirm the ground state, however, is to use the molecular orbital method.

## Separated Atom Method

A second method for determining molecular term symmetries is the separated atom method. This method is similar to the atomic term symbol method of writing out an exhaustive list of microstates and then accounting for each one. The quantum numbers which are important are determined from the sums of the z-component quantum numbers of the atomic wavefunctions. Thus, the values of  $\Lambda$  which are possible will be given by all possible combinations of  $m_L$ . Values of the same magnitude are then paired to make the two degenerate components for any values of  $\Lambda > 0$ .

### ✓ Example 9.5.2

What molecular terms arise for HLi, formed from a ground state hydrogen atom and a ground state lithium atoms?

#### Solution

The ground state of lithium is  $^2S$ . For this set of atoms, we can construct the following table to combine values of  $m_L$  to form values of  $\Lambda$  and values of S as well.

	H ( $^2S$ )	Li ( $^2S$ )	$\Lambda$ and S
$M_L$	0	0	0
S	$\frac{1}{2}$	$\frac{1}{2}$	1, 0

It is clear that the only value of  $\Lambda$  that can be generated from these separated atom states is  $\Lambda = 0$ , or a  $\Sigma$  state. The sum of  $L_A + L_B + \Sigma l_A + \Sigma l_B$  is given by  $0 + 0 + 0 + 0 = 0$ , which is even. Hence, the  $\Sigma$  state has  $\Sigma^+$  symmetry. So the resulting states are  $^1\Sigma_g^+$  and  $^3\Sigma_g^+$ . The ground state of  $Li_2$  is  $^1\Sigma_g^+$ , but this can only be confirmed by the use of the molecular orbital method.

### ✓ Example 9.5.3

What molecular terms are predicted for the OH radical?

#### Solution

The ground state atomic term for O is  $^3P$  and that for H is  $^2S$ . The following table shows the possible combinations of  $m_L$  to form  $\Lambda$  and the combinations of S which form the familiar Clebsch series of resultant S values.

	H ( $^2S$ )	O ( $^3P$ )	$\Lambda$ and S
$M_L$	0	+1, 0, -1	+1, 0, -1
S	$\frac{1}{2}$	1	$\frac{3}{2}, \frac{1}{2}$

The combination of a P term and an S term gives one  $\Pi$  ( $\Lambda = \pm 1$ ) and one  $\Sigma$  ( $\Lambda = 0$ ) term. The sum  $L_A + L_B + \Sigma l_A + \Sigma l_B$  is given by  $1 + 0 + 4 + 0$  and is clearly odd. Therefore, the  $\Sigma$  state will be of  $\Sigma^-$  symmetry. The spin quantum numbers which are possible are  $\frac{3}{2}$  and  $\frac{1}{2}$ . Therefore, the possible term symbols are  $^4\Pi$ ,  $^4\Sigma^-$ ,  $^2\Pi$  and  $^2\Sigma^-$ . (The ground state of the OH radical happens to be of  $^2\Pi$  symmetry, but again, this can only be confirmed using a molecular orbital approach.) Notice that there is no g/u symmetry indicated in this case because the molecule does not include an inversion center being a heteronuclear diatomic molecule!

### ✓ Example 9.5.3

What molecular terms arise for CO formed from a ground state carbon atom and a ground state oxygen atom?

#### Solution

The ground state of both C and O is  $^3P$ . the following table summarizes the decomposition of the two atomic states from spherical to cylindrical symmetry.

	C ( $^3P$ )	O ( $^3P$ )	$\Lambda$ and S
$M_L$	+1, 0, -1	+1, 0, -1	$\pm 2, \pm 1, \pm 1, 0, 0, 0$
S	1	1	2, 1, 0

The resultant state are  $\Delta$ ,  $2\Pi$  and  $3\Sigma$ . Of the three  $\Sigma$  states, two will form a pair of  $\Sigma^+/\Sigma^-$ . The last S state must have its +/- symmetry determined by the Wigner-Witmer rule.

$$L_C + L_O + \Sigma l_C + \Sigma l_O = 1 + 1 + 2 + 4 = 8 \text{ (even)}$$

So the final  $\Sigma$  state is  $\Sigma^+$ . The spin states generated are quintet, triplet and singlet. So the set of molecular states generated are

$$^5\Delta, ^5\Pi, ^5\Pi, ^5\Sigma^+, ^5\Sigma^-, ^5\Sigma^+$$

$$^3\Delta, ^3\Pi, ^3\Pi, ^3\Sigma^+, ^3\Sigma^-, ^3\Sigma^+$$

$$^1\Delta, ^1\Pi, ^1\Pi, ^1\Sigma^+, ^1\Sigma^-, ^1\Sigma^+$$

The ground state of CO is in fact  $^1\Sigma^+$ , but as always, this can only be reliably predicted using the molecular orbital method.

The number of states generated from separated atoms increases rapidly as the angular momentum in the separated atoms increases.

### Molecular Orbital Method

The molecular orbital method requires the construction of a molecular orbital diagram. As was the case in the atomic term symbol problem, the molecular terms can be constructed considering only partially filled subshells. The quantum numbers will then be given by the vectorial sums of the one-electron quantum numbers. Consider the orbital diagram for the oxygen molecule.

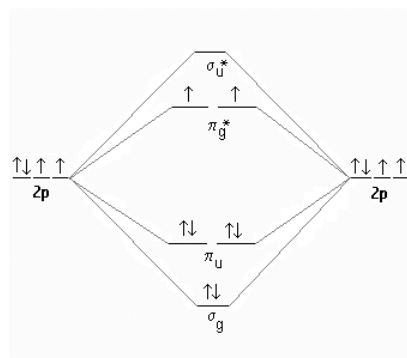


Figure 9.5.1

The only important electrons in this case are the two  $\pi_g^*$  electrons. (Ignore all of the ones in completely filled subshells - just as was done in the case of atoms as these always contribute  $\Lambda = 0$  and  $S = 0$ .) The orbital angular momentum  $\lambda$  of one of the  $\pi_g^*$  electrons will cancel that of the other as one will have a value of  $\lambda = -1$  and the other has  $\lambda = +1$ . (This is similar to the atomic case where one electron was in an orbital with  $m_l = -1$  and the other in an orbital with  $m_l = +1$ . The sum of the two is zero.) Thus,  $\Lambda$  will be 0. Hence the predicted term will be a  $\Sigma$  state.

Since one of the  $\pi_g^*$  orbitals is symmetric with respect to reflection through a plane containing the nuclei and the other is antisymmetric, the predicted term will be antisymmetric with respect to this symmetry operation.

$$(sym) \times (antisym) = antisym$$

Thus, the state will be of  $\Sigma^-$  symmetry. In a similar manner, the gerade/ungerade symmetry can be determined by the product of the one-electron orbital symmetries.

$$(g) \times (g) = g$$

Finally, the spin multiplicity can be determined in the usual way.

$$S = s_1 + s_2, s_1 + s_2 - 1, \dots, s_1 - s_2$$

$$S = 1 \text{ and } 0$$

The predicted terms for this electronic configuration are  $^3\Sigma_g^-$  and  $^1\Sigma_g^-$ . The ground state of  $O_2$  is  $^3\Sigma_g^-$ . And since this result was generated using the molecular orbital method, the result is reliable that this is indeed the ground state of the  $O_2$  molecule!

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