Molecular Term Symbols

15th May 2008

I. Term Symbols for Molecules: Applying MO Diagrams

Excitations between molecular electronic states provide information about properties of molecules. As noted in Engel and Reid, molecular electronic transitions are induced by UV/VIS radiation, and so these transitions involve much more energy compared to the vibrational-rotational spectroscopies that require microwave and infrared frequencies. However, much as in the case of IR spectroscopy, electronic spectroscopy of molecules includes a "fine structure" arising from vibrational-rotational transitions associated with changes in electronic states.

Before discussing electronic spectroscopy, we will investigate the description of molecular electronic states in terms of **molecular term symbols** as in the case of atomic electronic transitions. This should highlight the fact that multiple states are possible given a particular molecular electronic configuration based on the angular momentum and spin. Recall the discussion of Engel and Reid, Section 21.8 for a more detailed discussion of the importance of orbital and spin angular momentum in determining the energetics of atoms (and molecules).

Molecular Term Symbols: Diatomic Molecules

- As with atoms, M_L and M_S are the "good" quantum numbers (**L** and **S** commute with Hamiltonian for diatomic molecules

- Only **unfilled subshells** contribute to the term orbital and spin angular momentum

- For first and second row diatomics, MO's are either of σ or π type.

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- M_L and M_S are generated as follow:

    - $M_L = \sum_i m_{l_i}$

    - $M_S = \sum_i m_{s_i}$

- For MO's with σ symmetry, $m_l = 0$

- For MO's with π symmetry, $m_l = \pm 1$

    - Note that there is no $m_l = 0$ for π MO's since the P_z atomic orbital is associated with the σ MO

- As in the atomic case, $-L \le M_L \le L$ and $-S \le M_S \le S$.

- We need to determine the maximum values of M_L and M_S and generate term symbols

- The values of M_L corresponding to the various total angular momentum values possible are labelled with Λ.

- The possible values of Λ can be 0, 1, 2, 3, ...

    - As with the atomic case, each numerical value of Λ corresponds to a letter, in the molecular case being Greek letters.

- The term symbols are of the form: $^{2S+1}\Lambda$

Λ	0	1	2	3
Symbol	Σ	Π	Δ	Φ

Examples

Ground state of dihydrogen (hydrogen molecule), H_2:

$M_L^{max} = 0 + 0 = 0$
$M_S^{max} = 1/2 - 1/2 = 0$

Table 1. Microstates for Ground State H_2.

M_L	M_S
	0
0	$(0^+, 0^-)$

For homonuclear diatomic molecules, recall, there is inversion symmetry. This can be thought of as simple multiplication of functions of even or odd symmetry. Thus, for a pair of electrons in the same σ_g MO, the product would be $(gerade)(gerade)$, which is (even)(even) = even; thus the symmetry is gerade.

In general:
(g)(g) = g
(g)(u) = u
(u)(u) = g

Thus, this is a $^1\Sigma_g$ molecular term.

Ground state of Oxygen (O_2).

MO diagram of oxygen:
$M_L^{max} = 1 + 1 = 2$
$M_S^{max} = 1/2 + 1/2 = 1$

M_L	M_S		
	-1	0	1
2	$-----$	$(1^+, 1^-)$	$-----$
1	$-----$	$-----$	$-----$
0	$(1^-, -1^-)$	$(1^+, -1^-), (1^-, -1^+)$	$(1^+, -1^+)$
-1	$-----$	$-----$	$-----$
-2	$-----$	$(-1^+, -1^-)$	$-----$

The molecular terms are thus: $^1\mathbf{\Delta_g}$, $^3\mathbf{\Sigma_g}$, and $^1\mathbf{\Sigma_g}$.

Ground State of B_2

MO diagram of B_2:
$M_L^{max} = 1 + 1 = 2$
$M_S^{max} = 1/2 + 1/2 = 1$

M_L	M_S		
	-1	0	1
2	$- - - - -$	$(1^+, 1^-)$	$- - - - -$
1	$- - - - -$	$- - - - -$	$- - - - -$
0	$(1^-, -1^-)$	$(1^+, -1^-), (1^-, -1^+)$	$(1^+, -1^+)$
-1	$- - - - -$	$- - - - -$	$- - - - -$
-2	$- - - - -$	$(-1^+, -1^-)$	$- - - - -$

The molecular terms are thus: $^1\mathbf{\Delta_g}$, $^3\mathbf{\Sigma_g}$, and $^1\mathbf{\Sigma_g}$.

This is not too surprising, as B_2 and O_2 share the "same" molecular electronic structure (both are paramagnetic)!

C_2 **Molecular Term Symbol**
?

Transitions

See Figure 26.1 for potential energy curves for the five lowest-lying bound states of O_2.

As the energy states become higher in energy, the bond length increases, ultimately leading to the dissociated state of two individual atoms. This makes sense since excited states have more anti-bonding character. They have less bonding order, less bonding energy, longer bond, and lower vibrational frequency.

Selection Rules
The selection rules for diatomic molecular transitions are well-defined. For nuclei with atomic numbers less than about 40, the selection rules are:

$$\begin{aligned} \Delta\Lambda &= 0, \pm 1 \\ \Delta S &= 0 \end{aligned}$$

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The $\Delta\Lambda = 0$ applies to Σ to Σ transitions, and the ± 1 transition to $\Sigma -¿$ Π. For homonuclear diatomic molecules, "g" to "u" (and vise versa) are allowed. Forbidden are "u" to "u" and "g" to "g".

Keep in mind that these selection rules can be derived by applying the criterion for the transition dipole moment (which is more generally associated with Fermi's Golden Rule for quantum transitions).

Also bear in mind that the electronic energy within the Born-Oppenheimer approximation is a function of internuclear separation. We can visualize such **potential energy curves** (as we have done previously) as:
   Vibrational Fine Structure

Electronic transitions in molecules are accompanied by vibrational transitions as well. The process is pictured as a **vertical** transition between electronic states. This underlying assumption is again the Born-Oppenheimer approximation. The assumption here is one of electronic dynamics being much faster than that of the nuclei. Consequantly, during a vertical transition between electronic states, the nuclear positions remain constant. **Electronic transitions occur on a timescale that is much shorter than the timescales associated with molecular vibrations**.

Thus, though we have selection rules for electronic transitions, what constraints are contributed by the vibrational level change that occurs during this transition?

The Franck-Condon principle allows us to arrive at a criterion describing the change in vibrational states during an electronic transition. The development rests on the determination of the transition dipole moment within the Born-Oppenheimer approximation:

$$\psi(\mathbf{r}_1, ..., \mathbf{r}_n, \mathbf{R}_1, ..., \mathbf{R}_m) = \psi^{electronic}(\mathbf{r}_1, ..., \mathbf{r}_n, \mathbf{R}_1^{fixed}, ..., \mathbf{R}_m^{fixed}) \, \phi^{vib-rot}(\mathbf{R}_1, ..., \mathbf{R}_m)$$

The transition dipole moment criterion is:

$$\mu^{fi} = \int \psi_f^*(\mathbf{r}_1, ..., \mathbf{r}_n, \mathbf{R}_1, ..., \mathbf{R}_m) \hat{\mu} \psi_i(\mathbf{r}_1, ..., \mathbf{r}_n, \mathbf{R}_1, ..., \mathbf{R}_m) \, d\tau \neq 0$$

The subscripts and superscripts "f" and "i" refer to final and initial states;

the dipole moment operator $\hat{\mu}$ is given by :

$$\hat{\mu} \quad = \quad -e \sum_{i=1}^{n} \mathbf{r}_i$$

This is a function of the coordinates of the electrons only!.

Substituting the Born-Oppenheimer wavefunction (product of eletronic and vibrational wavefunctions) in to the transition dipole equation leads to:

$$\mu^{fi} \quad = \quad \int (\phi_f^{vib-rot}(\mathbf{R}_1, ..., \mathbf{R}_m))^* \, (\phi_f^{vib-rot}(\mathbf{R}_1, ..., \mathbf{R}_m)) \, d\tau \quad \int \psi_f^{electronic} \hat{\mu} \psi_i^{electronic} \, d\tau$$

We see that the first integral represents the overlap between the vibrational wave functions of the intial and final states.

The square of the magnitude of the first integral on the right hand side is called the Franck-Condon factor and is a measure of the expected intensity of an electronic transition.

$$S^2 \quad = \quad \left| \int (\phi_f^{vib-rot}(\mathbf{R}_1, ..., \mathbf{R}_m))^* \, (\phi_f^{vib-rot}(\mathbf{R}_1, ..., \mathbf{R}_m)) \, d\tau \right|^2$$

The Franck-Condon factor shows, **the probability of a vibrational-electronic transition is governed by the overlap between the final and initial vibrational wave functions at fixed internuclear distances**. Moreover, in the simplest sense, we can take the initial states to be ground molecular electronic states. This obviates the need to account for transitions between all energy levels of the intial state.

Keep in mind that within the Franck-Condon formulation, there are several transitions with sufficiently large factors (overlap between vibrational wavefunctions) to generate multiple spectral lines. However, a limited number (or perhaps just one) transition will have a dominant intensity due to the greatest overlap between relevant wavefuntions.

For transition from a ground electronic and vibrational state, discrete energy spectrum for transitions to lower-lying excited states; continuous energy spectrum to anti-bonding states.

Transitions Between Ground and Excited States

For transitions from ground singlet states to excited singlet or triplet states, three types of transitions are possible:

- Radiative Transitions: photons absorbed or emitted (Fluorescence)

- Nonradiative Transitions: energy transfer between **internal** degrees of freedom of a molecule or to surrondings.

- Intersystem Crossing (singlet-triplet). (Phosphorescence)

Singlet-Singlet Transitions: Absorption and Fluorescence

Fluorescence is a radiative transition from the lowest vibrational state of excited states back to the ground state. Consider the following figure:
The fluorescence process involves:

- Absorption from the lowest vibrational level of the ground state to the various vibrational levels of the excited (singlet state)

- Internal conversion of energy (non-radiative): molecules in the excited vibrational levels of the excited state collide with other moleceuls (crystal, gas, liquid)

- Non-radiative transitions occur much more rapidly compared to radiative transitions from excited vibrational levels of the excited state

- Thus, most molecules are found in the ground vibrational level in the excited state

- Once in the ground vibrational level of the excited state, the molecule undergoes radiative transition to any vibrational level in the ground state

Intersystem Crossing and Phosphorescence

Though we have discussed the selection rule for molecule electronic transitions as given $\Delta S = 0$, it is generally possible to have transitions between singlet and triplet states in molecules.