

## 1.26: Group theory and Molecular Electronic States

Firstly, it is important that you understand the difference between a *molecular orbital* and an *electronic state*.

A strict definition of a molecular orbital is that it is a ‘one electron wavefunction’, i.e. a solution to the Schrödinger equation for the molecule. A complete one electron wavefunction (orbital) is a product of a spatial function, describing the orbital angular momentum and ‘shape’ of the orbital, and a spin function, describing the spin angular momentum.

$$\Psi = \Psi_{\text{spatial}}\Psi_{\text{spin}} \quad (26.1)$$

In common usage, the word ‘orbital’ is often used to refer only to the spatial part of the ‘true’ orbital. For example, in atoms we generally talk about ‘*s* orbitals’ or ‘*p* orbitals’ rather than ‘*s* spatial wavefunctions’ and ‘*p* spatial wavefunctions’. In this context, two electrons with opposite spins may occupy one spatial orbital. A more rigorous way of saying this would be to state that a given spatial wavefunction may be paired with two different spin wavefunctions (one corresponding to a ‘spin up’ electron and one to a ‘spin down’ electron).

An electronic state is defined by the electron configuration of the system, and by the quantum numbers of each electron contributing to that configuration. Each electronic state corresponds to one of the energy levels of the molecule. These energy levels will obviously depend on the molecular orbitals that are occupied, and their energies, but they also depend on the way in which the electrons within the various molecular orbitals interact with each other. Interactions between the electrons are essentially determined by the relative orientations of the magnetic moments associated with their orbital and spin angular momenta, which is where the dependence on quantum numbers comes in. A given electron configuration will often give rise to a number of different electronic states if the electrons may be arranged in different ways (with different quantum numbers) within the occupied orbitals.

Last year you were introduced to the idea of atomic states, and learnt how to label the states arising from a given electron configuration using term symbols of the form  $^{2S+1}L_J$ . Term symbols of this form define the spin, orbital and total angular momenta of the state, which in turn determine its energy. Molecular states, containing contributions from a number of molecular orbitals, are more complicated. For example, a given molecular orbital will generally contain contributions from several different atomic orbitals, and as a result, electrons cannot easily be assigned an *l* quantum number. Instead of using term symbols, molecular states are usually labeled according to their symmetry (the exception to this is linear molecules, for which conventional term symbols may still be used, albeit with a few modifications from the atomic case).

We can determine the symmetry of an electronic state by taking the direct product of the irreducible representations for all of the electrons involved in that state (the irreducible representation for each electron is simply the irreducible representation for the molecular orbital that it occupies). Usually we need only consider unpaired electrons. Closed shell species, in which all electrons are paired, almost always belong to the totally symmetric irreducible representation in the point group of the molecule.

An example is the molecular orbitals of butadiene, which belongs to the  $C_{2h}$  point group. Since all electrons are paired, the overall symmetry of the state is  $A_g$ , and the label for the state once the spin multiplicity is included is  $^1A_g$ . We could have arrived at the same result by taking the direct product of the irreducible representations for each electron. There are two electrons in orbitals with  $A_u$  symmetry, and two in orbitals with  $B_g$  symmetry, so overall we have:

$$A_u \otimes A_u \otimes B_g \otimes B_g = A_g \quad (26.2)$$

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