# 9.1: Electronic Configurations

Atoms, linear molecules, and non-linear molecules have orbitals which can be labeled either according to the symmetry appropriate for that isolated species or for the species in an environment which produces lower symmetry. These orbitals should be viewed as regions of space in which electrons can move, with, of course, at most two electrons (of opposite spin) in each orbital. Specification of a particular occupancy of the set of orbitals available to the system gives an **electronic configuration**. For example, $1s^2 2s^2 2p^4$ is an electronic configuration for the Oxygen atom (and for the F^{+1} ion and the N^{-1} ion); $1s^2 2s^2 2p^3 3p^1$ is another configuration for O, F^{+1}, or N^{-1}. These configurations represent situations in which the electrons occupy low-energy orbitals of the system and, as such, are likely to contribute strongly to the true ground and low-lying excited states and to the low-energy states of molecules formed from these atoms or ions.

Specification of an electronic configuration does not, however, specify a particular electronic state of the system. In the above $1s^2 2s^2 2p^4$ example, there are many ways (fifteen, to be precise) in which the 2p orbitals can be occupied by the four electrons. As a result, there are a total of fifteen states which cluster into three energetically distinct **levels**, lying within this single configuration. The $1s^2 2s^2 2p^3 3p^1$ configuration contains thirty-six states which group into six distinct energy levels (the word **level** is used to denote one or more state with the same energy). Not all states which arise from a given electronic configuration have the same energy because various states occupy the degenerate (e.g., 2p and 3p in the above examples) orbitals differently. That is, some states have orbital occupancies of the form

$$2p_1^2 2p_0^1 2p_{-1}^1$$

while others have

$$2p_1^2 2p_0^2 2p_{-1}^0$$
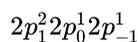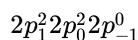
as a result, the states can have quite different coulombic repulsions among the electrons (the state with two doubly occupied orbitals would lie higher in energy than that with two singly occupied orbitals). Later in this Section and in Appendix G techniques for constructing wavefunctions for each state contained within a particular configuration are given in detail. Mastering these tools is an important aspect of learning the material in this text.

In summary, an atom or molecule has many orbitals (core, bonding, non-bonding, Rydberg, and antibonding) available to it; occupancy of these orbitals in a particular manner gives rise to a configuration. If some orbitals are partially occupied in this configuration, more than one state will arise; these states can differ in energy due to differences in how the orbitals are occupied. In particular, if degenerate orbitals are partially occupied, many states can arise and have energies which differ substantially because of differences in electron repulsions arising in these states. Systematic procedures for extracting all states from a given configuration, for labeling the states according to the appropriate symmetry group, for writing the wavefunctions corresponding to each state and for evaluating the energies corresponding to these wavefunctions are needed. Much of Chapters 10 and 11 are devoted to developing and illustrating these tools.