

## 10.10: Electronic States

The electronic configuration of an atom or molecule is a concept imposed by the orbital approximation. Spectroscopic transitions and other properties of atoms and molecules result from the states and not from the configurations, although it is useful to think about both the configuration and the state whenever possible. While a single determinant wavefunction generally is adequate for closed-shell systems (i.e. all electrons are paired in spatial orbitals), the best descriptions of the electronic states, especially for excited states and free radicals that have unpaired electrons, involve configuration interaction using multiple determinants. In these descriptions different configurations are mixed together and the picture of an orbital configuration disintegrates, and other properties, such as orbital and spin angular momentum and symmetry, are needed to identify and characterize the electronic states of molecules.

While a component of orbital angular momentum is preserved along the axis of a linear molecule, generally orbital angular momentum is quenched due to the irregular shapes of molecules. Angular momentum is quenched because circular motion is not possible when the potential energy function does not have circular symmetry.

The spin orbitals, however, still can be eigenfunctions of the spin angular momentum operators because the spin-orbit coupling usually is small. The resulting spin state depends on the orbital configuration. For a closed-shell configuration, the spin state is a singlet and the spin angular momentum is 0 because the contributions from the  $\alpha$  and  $\beta$  spins cancel. For an open shell configuration, which is characteristic of free radicals, there is an odd number of electrons and the spin quantum number  $s = \frac{1}{2}$ . This configuration produces a doublet spin state since  $2S + 1 = 2$ . Excited configurations result when electromagnetic radiation or exposure to other sources of energy promotes an electron from an occupied orbital to a previously unoccupied orbital. An excited configuration for a closed shell system produces two states, a singlet state ( $2S + 1 = 0$ ) and a triplet state ( $2S + 1 = 3$ ) depending on how the electron spins are paired. The z-components of the angular momentum for 2 electrons can add to give +1, 0, or -1 in units of  $\hbar$ . The three spin functions for a triplet state are

$$\alpha(1)\alpha(2) \quad (10.10.1)$$

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \quad (10.10.2)$$

$$\beta(1)\beta(2) \quad (10.10.3)$$

and the singlet spin function is

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (10.10.4)$$

The singlet and triplet states differ in energy even though the electron configuration is the same. This difference results from the antisymmetry condition imposed on the wavefunctions. The antisymmetry condition reduces the electron-electron repulsion for triplet states, so triplet states have the lower energy.

The electronic states of molecules therefore are labeled and identified by their spin and orbital angular momentum and symmetry properties, as appropriate. For example, the ground state of the hydrogen molecule is designated as  $X^1 \sum_g^+$ . In this symbol, the  $X$  identifies the state as the ground state, the superscript 1 identifies it as a singlet state, the sigma says the orbital angular momentum is 0, and the g identifies the wavefunction as symmetric with respect to inversion. Other states with the same symmetry and angular momentum properties are labeled as A, B, C, etc in order of increasing energy or order of discovery. States with different spin multiplicities from that of the ground state are labeled with lower case letters, a, b, c, etc.

For polyatomic molecules the symmetry designation and spin multiplicity are used. For example, an excited state of naphthalene is identified as  $^1B_{1u}$ . The superscript 1 identifies it as a singlet state, The letter  $B$  and subscript 1 identifies the symmetry with respect to rotations, and the subscript u says the wavefunction is antisymmetric with respect to inversion.

Good quality descriptions of the electronic states of molecules are obtained by using a large basis set, by optimizing the parameters in the functions with the variational method, and by accounting for the electron-electron repulsion using the self-consistent field method. Electron correlation effects are taken into account with configuration interaction (CI). The CI methodology means that a wavefunction is written as a series of Slater Determinants involving different configurations, just as we discussed for the case of atoms. The limitation in this approach is that computer speed and capacity limit the size of the basis set and the number of configurations that can be used.

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