10.2: The Orbital Approximation and Orbital Configurations

You should be able to recognize from the form of the electronic Hamiltonian, Equation that the electronic Schrödinger equation, Equation, cannot be solved. The problem, as for the case of atoms, is the electron-electron repulsion terms. Approximations must be made, and these approximations are based on the idea of using one-electron wavefunctions to describe multi-electron systems, in this case molecules just as is done for multi-electron atoms. Initially two different approaches were developed. Heitler and London originated one in 1927, called the **Valence Bond Method**, and Robert Mulliken and others developed the other somewhat later, called the **Molecular Orbital Method**. By using configuration interaction, both methods can provide equivalent electronic wavefunctions and descriptions of bonding in molecules, although the basic concepts of the two methods are different. We will develop only the molecular orbital method because this is the method that is predominantly employed now. The wavefunction for a single electron in a molecule is called a molecular orbital in analogy with the one-electron wavefunctions for atoms being called atomic orbitals.

To describe the electronic states of molecules, we construct wavefunctions for the electronic states by using molecular orbitals. These wavefunctions are approximate solutions to the Schrödinger equation. A mathematical function for a molecular orbital is constructed, *[Math Processing Error]*, as a linear combination of other functions, *[Math Processing Error]*, which are called basis functions because they provide the basis for representing the molecular orbital.

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The variational method is used to find values for parameters in the basis functions and for the constant coefficients in the linear combination that optimize these functions, i.e. make them as good as possible. The criterion for quality in the variational method is making the ground state energy of the molecule as low as possible. Here and in the rest of this chapter, the following notation is used: *[Math Processing Error]* is a general spin function (can be either *[Math Processing Error]* or *[Math Processing Error]*), *[Math Processing Error]* is the basis function (this usually represents an atomic orbital), *[Math Processing Error]* is a molecular orbital, and *[Math Processing Error]* is the electronic state wavefunction (representing a single Slater determinant or linear combination of Slater determinants).

The ultimate goal is a mathematical description of electrons in molecules that enables chemists and other scientists to develop a deep understanding of chemical bonding and reactivity, to calculate properties of molecules, and to make predictions based on these calculations. For example, an active area of research in industry involves calculating changes in chemical properties of pharmaceutical drugs as a result of changes in chemical structure.

Just as for atoms, each electron in a molecule can be described by a product of a spatial orbital and a spin function. These product functions are called spin orbitals. Since electrons are fermions, the electronic wavefunction must be antisymmetric with respect to the permutation of any two electrons. A Slater determinant containing the molecular spin orbitals produces the antisymmetric wavefunction. For example for two electrons,

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Solving the Schrödinger equation in the orbital approximation will produce a set of spatial molecular orbitals, each with a specific energy, *[Math Processing Error]*. Following the Aufbau Principle, 2 electrons with different spins (*[Math Processing Error]* and *[Math Processing Error]*, consistent with the Pauli Exclusion Principle) are assigned to each spatial molecular orbital in order of increasing energy. For the ground state of the 2n electron molecule, the n lowest energy spatial orbitals will be occupied, and the electron configuration will be given as *[Math Processing Error]*. The electron configuration also can be specified by an orbital energy level diagram as shown in Figure *[Math Processing Error]*. Higher energy configurations exist as well, and these configurations produce excited states of molecules. Some examples are shown in Figure *[Math Processing Error]*.

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ε_5 ——— ——— ——— ———

ε_4 ——— ——— ——— ———

ε_3 ——— ——— ——— ———

ε_2 ——— ——— ——— ———

ε_1 ——— ——— ——— ———
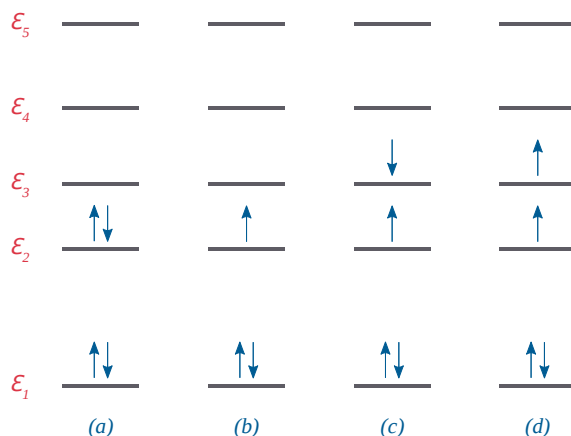
(a)　　(b)　　(c)　　(d)

Figure *[Math Processing Error]*: a) The lowest energy configuration of a closed-shell system. b) The lowest energy configuration of an open-shell radical. c) An excited singlet configuration. d) An excited triplet configuration. (CC BY-SA 4.0; Ümit Kaya via LibreTexts)

Molecular orbitals usually are identified by their symmetry or angular momentum properties. For example, a typical symbol used to represent an orbital in an electronic configuration of a diatomic molecule is *[Math Processing Error]*. The superscript in symbol means that this orbital is occupied by two electrons; the prefix means that it is the second sigma orbital with *gerade* symmetry.

Diatomic molecules retain a component of angular momentum along the internuclear axis. The molecular orbitals of diatomic molecule therefore can be identified in terms of this angular momentum. A Greek letter, e.g. *[Math Processing Error]* or *[Math Processing Error]*, encodes this information, as well as information about the symmetry of the orbital. A *[Math Processing Error]* means the component of angular momentum is 0, and there is no node in any plane containing the internuclear axis, so the orbital must be symmetric with respect to reflection in such a plane. A *[Math Processing Error]* means there is a node and the wavefunction is antisymmetric with respect to reflection in a plane containing the internuclear axis. For homonuclear diatomic molecules, a *g* or a *u* is added as a subscript to designate whether the orbital is symmetric or antisymmetric with respect to the center of inversion of the molecule.

A homonuclear diatomic molecule has a center of inversion in the middle of the bond. This center of inversion means that *[Math Processing Error]* with the origin at the inversion center. Inversion takes you from *[Math Processing Error]* to *[Math Processing Error]*. For a heteronuclear diatomic molecule, there is no center of inversion so the symbols g and u are not used. A prefix 1, 2, 3, etc. simply means the first, second, third, etc. orbital of that type. We can specify an electronic configuration of a diatomic molecule by these symbols by using a superscript to denote the number of electrons in that orbital, e.g. the lowest energy configuration of *[Math Processing Error]* is

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