

## Section 2 Simple Molecular Orbital Theory

In this section, the conceptual framework of molecular orbital theory is developed. Applications are presented and problems are given and solved within qualitative and semi-empirical models of electronic structure. Ab Initio approaches to these same matters, whose solutions require the use of digital computers, are treated later in Section 6. Semi-empirical methods, most of which also require access to a computer, are treated in this section and in Appendix F.

Unlike most texts on molecular orbital theory and quantum mechanics, this text treats polyatomic molecules before linear molecules before atoms. The finite point-group symmetry (Appendix E provides an introduction to the use of point group symmetry) that characterizes the orbitals and electronic states of non-linear polyatomics is more straightforward to deal with because fewer degeneracies arise. In turn, linear molecules, which belong to an axial rotation group, possess fewer degeneracies (e.g., orbitals or states are no more degenerate than  $s$ ,  $p$ , or  $d$  orbitals or states; all are doubly degenerate) than atomic orbitals and states (e.g.,  $p$  orbitals or states are 3-fold degenerate,  $d$ 's are 5-fold, etc.). Increased orbital degeneracy, in turn, gives rise to more states that can arise from a given orbital occupancy (e.g., the  $2p^2$  configuration of the C atom yields fifteen states, the  $2p^2$  configuration of the NH molecule yields six, and the  $\pi^*$  configuration of ethylene gives four states). For these reasons, it is more straightforward to treat low-symmetry cases (i.e., non-linear polyatomic molecules) first and atoms last.

It is recommended that the reader become familiar with the point-group symmetry tools developed in Appendix E before proceeding with this section. In particular, it is important to know how to label atomic orbitals as well as the various hybrids that can be formed from them according to the irreducible representations of the molecule's point group and how to construct symmetry adapted combinations of atomic, hybrid, and molecular orbitals using projection operator methods. If additional material on group theory is needed, Cotton's book on this subject is very good and provides many excellent chemical applications.

### Chapter 4

*Valence Atomic Orbitals on Neighboring Atoms Combine to Form Bonding, Non-Bonding and Antibonding Molecular Orbitals*

#### I. Atomic Orbitals

In Section 1 the Schrödinger equation for the motion of a single electron moving about a nucleus of charge  $Z$  was explicitly solved. The energies of these orbitals relative to an electron infinitely far from the nucleus with zero kinetic energy were found to depend strongly on  $Z$  and on the principal quantum number  $n$ , as were the radial "sizes" of these hydrogenic orbitals. Closed analytical expressions for the  $r$ ,  $\theta$ , and  $\phi$  dependence of these orbitals are given in Appendix B. The reader is advised to also review this material before undertaking study of this section.

## A. Shapes

*Shapes of atomic orbitals play central roles in governing the types of directional bonds an atom can form.*

All atoms have sets of bound and continuum s,p,d,f,g, etc. orbitals. Some of these orbitals may be unoccupied in the atom's low energy states, but they are still present and able to accept electron density if some physical process (e.g., photon absorption, electron attachment, or Lewis-base donation) causes such to occur. For example, the Hydrogen atom has 1s, 2s, 2p, 3s, 3p, 3d, etc. orbitals. Its negative ion  $H^-$  has states that involve 1s2s, 2p<sup>2</sup>, 3s<sup>2</sup>, 3p<sup>2</sup>, etc. orbital occupancy. Moreover, when an H atom is placed in an external electronic field, its charge density polarizes in the direction of the field. This polarization can be described in terms of the orbitals of the isolated atom being combined to yield distorted orbitals (e.g., the 1s and 2p orbitals can "mix" or combine to yield sp hybrid orbitals, one directed toward increasing field and the other directed in the opposite direction). Thus in many situations it is important to keep in mind that each atom has a full set of orbitals available to it even if some of these orbitals are not occupied in the lowest-energy state of the atom.

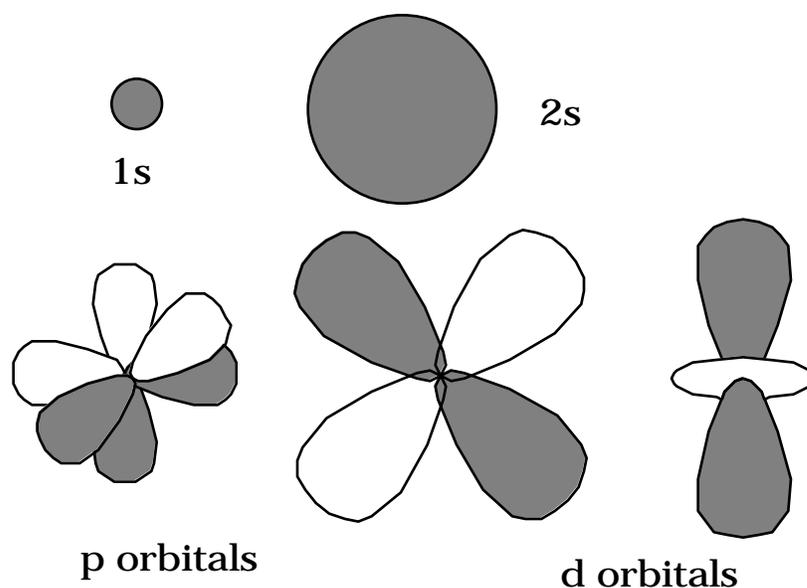
## B. Directions

*Atomic orbital directions also determine what directional bonds an atom will form.*

Each set of p orbitals has three distinct directions or three different angular momentum m-quantum numbers as discussed in Appendix G. Each set of d orbitals has five distinct directions or m-quantum numbers, etc; s orbitals are unidirectional in that they are spherically symmetric, and have only  $m = 0$ . Note that the degeneracy of an orbital  $(2l+1)$ , which is the number of distinct spatial orientations or the number of m-values, grows with the angular momentum quantum number  $l$  of the orbital without bound.

It is because of the energy degeneracy within a set of orbitals, that these distinct directional orbitals (e.g., x, y, z for p orbitals) may be combined to give new orbitals

which no longer possess specific spatial directions but which have specified angular momentum characteristics. The act of combining these degenerate orbitals does not change their energies. For example, the  $2^{-1/2}(p_x + ip_y)$  and  $2^{-1/2}(p_x - ip_y)$  combinations no longer point along the x and y axes, but instead correspond to specific angular momenta ( $+1\hbar$  and  $-1\hbar$ ) about the z axis. The fact that they are angular momentum eigenfunctions can be seen by noting that the x and y orbitals contain dependences of  $\cos(\phi)$  and  $\sin(\phi)$ , respectively. Thus the above combinations contain  $\exp(i\phi)$  and  $\exp(-i\phi)$ , respectively. The sizes, shapes, and directions of a few s, p, and d orbitals are illustrated below (the light and dark areas represent positive and negative values, respectively).



### C. Sizes and Energies

*Orbital energies and sizes go hand-in-hand; small 'tight' orbitals have large electron binding energies (i.e., low energies relative to a detached electron). For orbitals on neighboring atoms to have large (and hence favorable to bond formation) overlap, the two orbitals should be of comparable size and hence of similar electron binding energy.*

The size (e.g., average value or expectation value of the distance from the atomic nucleus to the electron) of an atomic orbital is determined primarily by its principal quantum number  $n$  and by the strength of the potential attracting an electron in this orbital to the

atomic center (which has some  $l$ -dependence too). The energy (with negative energies corresponding to bound states in which the electron is attached to the atom with positive binding energy and positive energies corresponding to unbound scattering states) is also determined by  $n$  and by the electrostatic potential produced by the nucleus and by the other electrons. Each atom has an infinite set of orbitals of each  $l$  quantum number ranging from those with low energy and small size to those with higher energy and larger size.

Atomic orbitals are solutions to an orbital-level Schrödinger equation in which an electron moves in a potential energy field provided by the nucleus and all the other electrons. Such one-electron Schrödinger equations are discussed, as they pertain to qualitative and semi-empirical models of electronic structure in Appendix F. The spherical symmetry of the one-electron potential appropriate to atoms and atomic ions is what makes sets of the atomic orbitals degenerate. Such degeneracies arise in molecules too, but the extent of degeneracy is lower because the molecule's nuclear coulomb and electrostatic potential energy has lower symmetry than in the atomic case. As will be seen, it is the symmetry of the potential experienced by an electron moving in the orbital that determines the kind and degree of orbital degeneracy which arises.

Symmetry operators leave the electronic Hamiltonian  $\mathbf{H}$  invariant because the potential and kinetic energies are not changed if one applies such an operator  $\mathbf{R}$  to the coordinates and momenta of all the electrons in the system. Because symmetry operations involve reflections through planes, rotations about axes, or inversions through points, the application of such an operation to a product such as  $\mathbf{H}$  gives the product of the operation applied to each term in the original product. Hence, one can write:

$$\mathbf{R}(\mathbf{H}) = (\mathbf{R}\mathbf{H})(\mathbf{R}).$$

Now using the fact that  $\mathbf{H}$  is invariant to  $\mathbf{R}$ , which means that  $(\mathbf{R}\mathbf{H}) = \mathbf{H}$ , this result reduces to:

$$\mathbf{R}(\mathbf{H}) = \mathbf{H}(\mathbf{R}),$$

which says that  $\mathbf{R}$  commutes with  $\mathbf{H}$ :

$$[\mathbf{R}, \mathbf{H}] = 0.$$

Because symmetry operators commute with the electronic Hamiltonian, the wavefunctions that are eigenstates of  $\mathbf{H}$  can be labeled by the symmetry of the point group of the molecule (i.e., those operators that leave  $\mathbf{H}$  invariant). It is for this reason that one constructs symmetry-adapted atomic basis orbitals to use in forming molecular orbitals.

## II. Molecular Orbitals

*Molecular orbitals (mos) are formed by combining atomic orbitals (aos) of the constituent atoms. This is one of the most important and widely used ideas in quantum chemistry. Much of chemists' understanding of chemical bonding, structure, and reactivity is founded on this point of view.*

When aos are combined to form mos, core, bonding, nonbonding, antibonding, and Rydberg molecular orbitals can result. The mos  $\psi_i$  are usually expressed in terms of the constituent atomic orbitals  $\psi_a$  in the linear-combination-of-atomic-orbital-molecular-orbital (LCAO-MO) manner:

$$\psi_i = \sum_a C_{ia} \psi_a.$$

The orbitals on one atom are orthogonal to one another because they are eigenfunctions of a hermitian operator (the atomic one-electron Hamiltonian) having different eigenvalues. However, those on one atom are not orthogonal to those on another atom because they are eigenfunctions of different operators (the one-electron Hamiltonia of the different atoms). Therefore, in practice, the primitive atomic orbitals must be orthogonalized to preserve maximum identity of each primitive orbital in the resultant orthonormalized orbitals before they can be used in the LCAO-MO process. This is both computationally expedient and conceptually useful. Throughout this book, the atomic orbitals (aos) will be assumed to consist of such orthonormalized primitive orbitals once the nuclei are brought into regions where the "bare" aos interact.

Sets of orbitals that are not orthonormal can be combined to form new orthonormal functions in many ways. One technique that is especially attractive when the original functions are orthonormal in the absence of "interactions" (e.g., at large interatomic distances in the case of atomic basis orbitals) is the so-called symmetric orthonormalization (SO) method. In this method, one first forms the so-called overlap matrix

$$S_{\mu\nu} = \langle \psi_\mu | \psi_\nu \rangle$$

for all functions  $\psi_\mu$  to be orthonormalized. In the atomic-orbital case, these functions include those on the first atom, those on the second, etc.

Since the orbitals belonging to the individual atoms are themselves orthonormal, the overlap matrix will contain, along its diagonal, blocks of unit matrices, one for each set of individual atomic orbitals. For example, when a carbon and oxygen atom, with their core

1s and valence 2s and 2p orbitals are combined to form CO, the 10x10  $S_{\mu}$  matrix will have two 5x5 unit matrices along its diagonal (representing the overlaps among the carbon and among the oxygen atomic orbitals) and a 5x5 block in its upper right and lower left quadrants. The latter block represents the overlaps  $\langle C_{\mu} | O_{\nu} \rangle$  among carbon and oxygen atomic orbitals.

After forming the overlap matrix, the new orthonormal functions  $\phi'_{\mu}$  are defined as follows:

$$\phi'_{\mu} = (S^{-1/2})_{\mu} \phi_{\mu}$$

As shown in Appendix A, the matrix  $S^{-1/2}$  is formed by finding the eigenvalues  $\{\epsilon_i\}$  and eigenvectors  $\{V_{i\mu}\}$  of the  $S$  matrix and then constructing:

$$(S^{-1/2})_{\mu} = \sum_i V_{i\mu} V_i (\epsilon_i)^{-1/2}$$

The new functions  $\{\phi'_{\mu}\}$  have the characteristic that they evolve into the original functions as the "coupling", as represented in the  $S_{\mu}$  matrix's off-diagonal blocks, disappears.

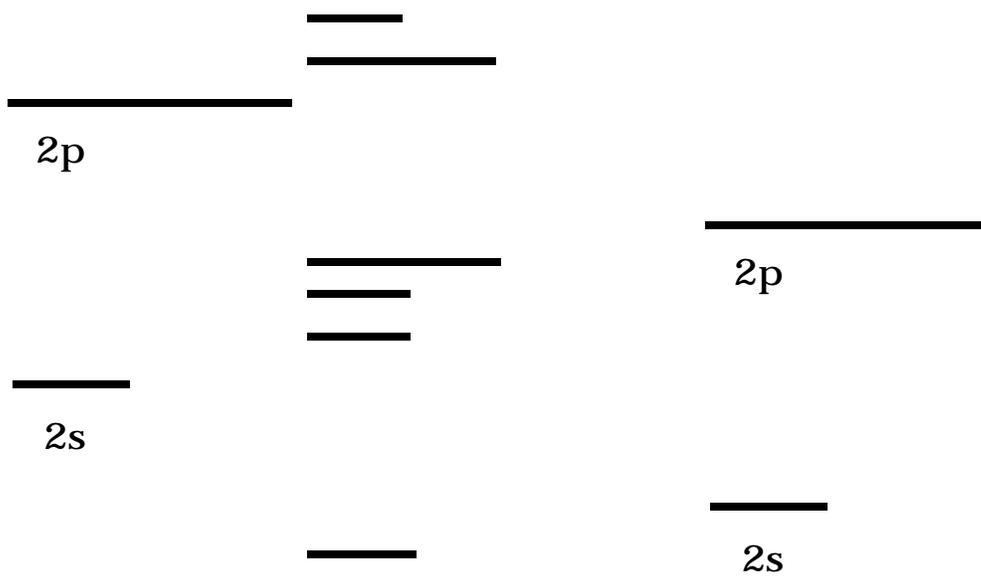
Valence orbitals on neighboring atoms are coupled by changes in the electrostatic potential due to the other atoms (Coulomb attraction to the other nuclei and repulsions from electrons on the other atoms). These coupling potentials vanish when the atoms are far apart and become significant only when the valence orbitals overlap one another. In the most qualitative picture, such interactions are described in terms of off-diagonal Hamiltonian matrix elements ( $h_{ab}$ ; see below and in Appendix F) between pairs of atomic orbitals which interact (the diagonal elements  $h_{aa}$  represent the energies of the various orbitals and are related via Koopmans' theorem (see Section 6, Chapter 18.VII.B) to the ionization energy of the orbital). Such a matrix embodiment of the molecular orbital problem arises, as developed below and in Appendix F, by using the above LCAO-MO expansion in a variational treatment of the one-electron Schrödinger equation appropriate to the mos  $\{\phi_i\}$ .

In the simplest two-center, two-valence-orbital case (which could relate, for example, to the  $Li_2$  molecule's two 2s orbitals), this gives rise to a 2x2 matrix eigenvalue problem ( $h_{11}, h_{12}, h_{22}$ ) with a low-energy mo ( $E = (h_{11} + h_{22})/2 - 1/2[(h_{11} - h_{22})^2 + 4h_{12}^2]^{1/2}$ ) and a higher energy mo ( $E = (h_{11} + h_{22})/2 + 1/2[(h_{11} - h_{22})^2 + 4h_{12}^2]^{1/2}$ ) corresponding to bonding and antibonding orbitals (because their energies lie below and above the lowest and highest interacting atomic orbital energies, respectively). The mos themselves are expressed  $\phi_i = \sum_a C_{ia} \phi_a$  where the LCAO-MO coefficients  $C_{ia}$  are obtained from the normalized eigenvectors of the  $h_{ab}$  matrix. Note that the bonding-antibonding orbital energy splitting depends on  $h_{ab}^2$  and on the energy difference ( $h_{aa} - h_{bb}$ ); the best bonding (and

worst antibonding) occur when two orbitals couple strongly (have large  $h_{ab}$ ) and are similar in energy ( $h_{aa} \approx h_{bb}$ ).

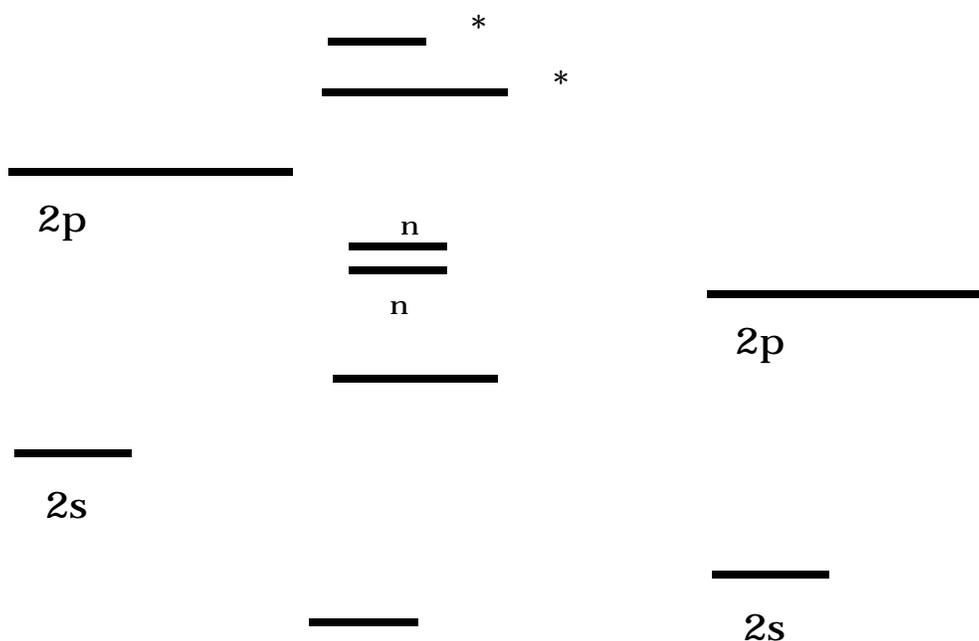


### Homonuclear Bonding With 2s and 2p Orbitals



### Heteronuclear Bonding With 2s and 2p Orbitals

In both the homonuclear and heteronuclear cases depicted above, the energy ordering of the resultant mos depends upon the energy ordering of the constituent aos as well as the strength of the bonding-antibonding interactions among the aos. For example, if the 2s-2p atomic orbital energy splitting is large compared with the interaction matrix elements coupling orbitals on neighboring atoms  $h_{2s,2s}$  and  $h_{2p,2p}$ , then the ordering shown above will result. On the other hand, if the 2s-2p splitting is small, the two 2s and two 2p orbitals can all participate in the formation of the four mos. In this case, it is useful to think of the atomic 2s and 2p orbitals forming sp hybrid orbitals with each atom having one hybrid directed toward the other atom and one hybrid directed away from the other atom. The resultant pattern of four mos will involve one bonding orbital (i.e., an in-phase combination of two sp hybrids), two non-bonding orbitals (those directed away from the other atom) and one antibonding orbital (an out-of-phase combination of two sp hybrids). Their energies will be ordered as shown in the Figure below.



Here  $n$  is used to denote the non-bonding  $\sigma$ -type orbitals and  $\sigma$ ,  $\sigma^*$ ,  $\pi$ , and  $\pi^*$  are used to denote bonding and antibonding  $\sigma$ - and  $\pi$ -type orbitals.

Notice that the total number of  $\sigma$  orbitals arising from the interaction of the 2s and 2p orbitals is equal to the number of aos that take part in their formation. Notice also that this is true regardless of whether one thinks of the interactions involving bare 2s and 2p atomic orbitals or hybridized orbitals. The only advantage that the hybrids provide is that they permit one to foresee the fact that two of the four mos must be non-bonding because

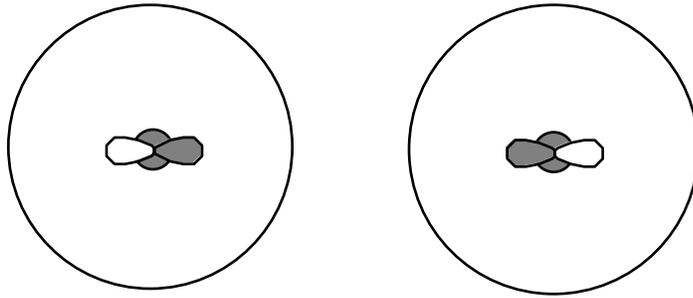
two of the four hybrids are directed away from all other valence orbitals and hence can not form bonds. In all such qualitative MO analyses, the final results (i.e., how many MOs there are of any given symmetry) will not depend on whether one thinks of the interactions involving atomic or hybrid orbitals. However, it is often easier to "guess" the bonding, non-bonding, and antibonding nature of the resultant MOs when thought of as formed from hybrids because of the directional properties of the hybrid orbitals.

### C. Rydberg Orbitals

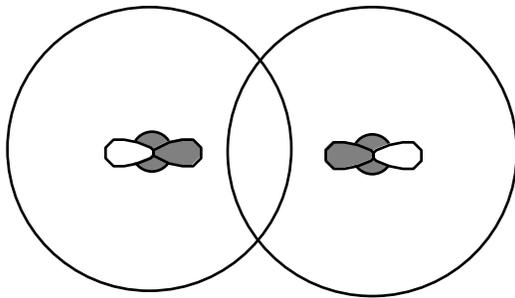
*It is essential to keep in mind that all atoms possess 'excited' orbitals that may become involved in bond formation if one or more electrons occupies these orbitals. Whenever an atom with principal quantum number one or more units higher than that of the conventional atom becomes involved in bond formation, Rydberg MOs are formed.*

Rydberg orbitals (i.e., very diffuse orbitals having principal quantum numbers higher than the atoms' valence orbitals) can arise in molecules just as they do in atoms. They do not usually give rise to bonding and antibonding orbitals because the valence-orbital interactions bring the atomic centers so close together that the Rydberg orbitals of each atom subsume both atoms. Therefore as the atoms are brought together, the atomic Rydberg orbitals usually pass through the internuclear distance region where they experience (weak) bonding-antibonding interactions all the way to much shorter distances at which they have essentially reached their united-atom limits. As a result, molecular Rydberg orbitals are molecule-centered and display little, if any, bonding or antibonding character. They are usually labeled with principal quantum numbers beginning one higher than the highest  $n$  value of the constituent atomic valence orbitals, although they are sometimes labeled by the  $n$  quantum number to which they correlate in the united-atom limit.

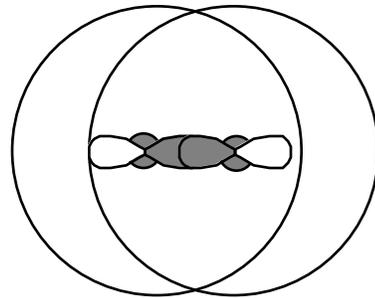
An example of the interaction of 3s Rydberg orbitals of a molecule whose 2s and 2p orbitals are the valence orbitals and of the evolution of these orbitals into united-atom orbitals is given below.



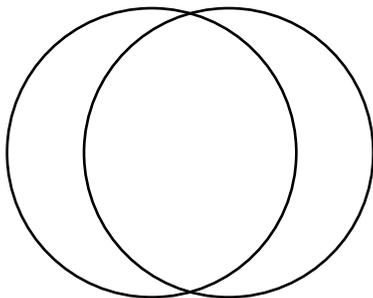
2s and 2p Valence Orbitals and 3s Rydberg Orbitals For Large R Values



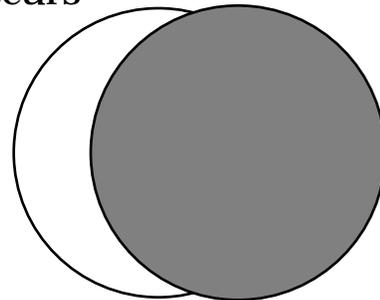
Overlap of the Rydberg Orbitals Begins



Rydberg Overlap is Strong and Bond Formation Occurs



The In-Phase (  $3s + 3s$  ) Combination of Rydberg Orbitals Correlates to an s-type Orbital of the United Atom



The Out-of-Phase Combination of Rydberg Orbitals (  $3s - 3s$  ) Correlates to a p-type United-Atom Orbital

## D. Multicenter Orbitals

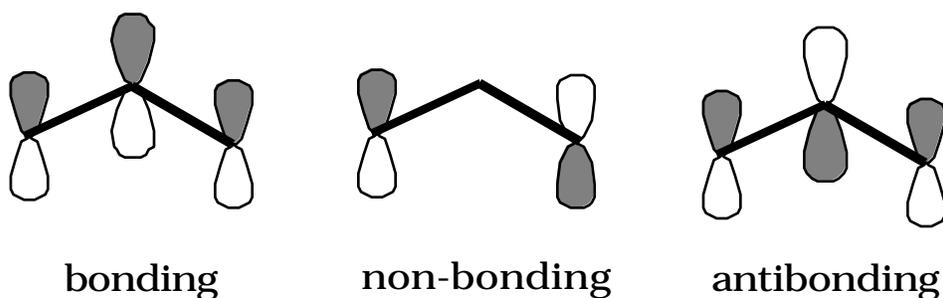
*If aos on one atom overlap aos on more than one neighboring atom, mos that involve amplitudes on three or more atomic centers can be formed. Such mos are termed delocalized or multicenter mos.*

Situations in which more than a pair of orbitals interact can, of course, occur. Three-center bonding occurs in Boron hydrides and in carbonyl bridge bonding in transition metal complexes as well as in delocalized conjugated orbitals common in unsaturated organic hydrocarbons. The three p orbitals on the allyl radical (considered in the absence of the underlying orbitals) can be described qualitatively in terms of three p aos on the three carbon atoms. The couplings  $h_{12}$  and  $h_{23}$  are equal (because the two CC bond lengths are the same) and  $h_{13}$  is approximated as 0 because orbitals 1 and 3 are too far away to interact. The result is a 3x3 secular matrix (see below and in Appendix F):

$$\begin{array}{ccc} h_{11} & h_{12} & 0 \\ h_{21} & h_{22} & h_{23} \\ 0 & h_{32} & h_{33} \end{array}$$

whose eigenvalues give the molecular orbital energies and whose eigenvectors give the LCAO-MO coefficients  $C_{ia}$ .

This 3x3 matrix gives rise to a bonding, a non-bonding and an antibonding orbital (see the Figure below). Since all of the  $h_{aa}$  are equal and  $h_{12} = h_{23}$ , the resultant orbital energies are:  $h_{11} + 2 h_{12}$ ,  $h_{11}$ , and  $h_{11} - 2 h_{12}$ , and the respective LCAO-MO coefficients  $C_{ia}$  are (0.50, 0.707, 0.50), (0.707, 0.00, -0.707), and (0.50, -0.707, 0.50). Notice that the sign (i.e., phase) relations of the bonding orbital are such that overlapping orbitals interact constructively, whereas for the antibonding orbital they interact out of phase. For the nonbonding orbital, there are no interactions because the central C orbital has zero amplitude in this orbital and only  $h_{12}$  and  $h_{23}$  are non-zero.



### Allyl System Orbitals

#### E. Hybrid Orbitals

*It is sometimes convenient to combine aos to form hybrid orbitals that have well defined directional character and to then form mos by combining these hybrid orbitals. This recombination of aos to form hybrids is never necessary and never provides any information that could be achieved in its absence. However, forming hybrids often allows one to focus on those interactions among directed orbitals on neighboring atoms that are most important.*

When atoms combine to form molecules, the molecular orbitals can be thought of as being constructed as linear combinations of the constituent atomic orbitals. This clearly is the only reasonable picture when each atom contributes only one orbital to the particular interactions being considered (e.g., as each Li atom does in  $\text{Li}_2$  and as each C atom does in the orbital aspect of the allyl system). However, when an atom uses more than one of its valence orbitals within particular bonding, non-bonding, or antibonding interactions, it is sometimes useful to combine the constituent atomic orbitals into hybrids and to then use the hybrid orbitals to describe the interactions. As stated above, the directional nature of hybrid orbitals often makes it more straightforward to "guess" the bonding, non-bonding, and antibonding nature of the resultant mos. It should be stressed, however, that exactly the same quantitative results are obtained if one forms mos from primitive aos or from hybrid orbitals; the hybrids span exactly the same space as the original aos and can therefore contain no additional information. This point is illustrated below when the  $\text{H}_2\text{O}$  and  $\text{N}_2$  molecules are treated in both the primitive ao and hybrid orbital bases.

## Chapter 5

*Molecular Orbitals Possess Specific Topology, Symmetry, and Energy-Level Patterns*

In this chapter the symmetry properties of atomic, hybrid, and molecular orbitals are treated. It is important to keep in mind that both symmetry and characteristics of orbital energetics and bonding "topology", as embodied in the orbital energies themselves and the interactions (i.e.,  $h_{j,k}$  values) among the orbitals, are involved in determining the pattern of molecular orbitals that arise in a particular molecule.

## I. Orbital Interaction Topology

*The pattern of mo energies can often be 'guessed' by using qualitative information about the energies, overlaps, directions, and shapes of the aos that comprise the mos.*

The orbital interactions determine how many and which mos will have low (bonding), intermediate (non-bonding), and higher (antibonding) energies, with all energies viewed relative to those of the constituent atomic orbitals. The **general patterns** that are observed in most compounds can be summarized as follows:

- i. If the energy splittings among a given atom's aos with the same principal quantum number are small, hybridization can easily occur to produce hybrid orbitals that are directed toward (and perhaps away from) the other atoms in the molecule. In the first-row elements (Li, Be, B, C, N, O, and F), the 2s-2p splitting is small, so hybridization is common. In contrast, for Ca, Ga, Ge, As, and Br it is less common, because the 4s-4p splitting is larger. Orbitals directed toward other atoms can form bonding and antibonding mos; those directed toward no other atoms will form nonbonding mos.
- ii. In attempting to gain a qualitative picture of the electronic structure of any given molecule, it is advantageous to begin by hybridizing the aos of those atoms which contain more than one ao in their valence shell. Only those aos that are not involved in  $\pi$ -orbital interactions should be so hybridized.
- iii. Atomic or hybrid orbitals that are not directed in a  $\pi$ -interaction manner toward other aos or hybrids on neighboring atoms can be involved in  $\sigma$ -interactions or in nonbonding interactions.
- iv. Pairs of aos or hybrid orbitals on neighboring atoms directed toward one another interact to produce bonding and antibonding orbitals. The more the bonding orbital lies below the lower-energy ao or hybrid orbital involved in its formation, the higher the antibonding orbital lies above the higher-energy ao or hybrid orbital.

For example, in formaldehyde,  $\text{H}_2\text{CO}$ , one forms  $sp^2$  hybrids on the C atom; on the O atom, either  $sp$  hybrids (with one p orbital "reserved" for use in forming the  $\sigma$  and  $\pi^*$  orbitals and another p orbital to be used as a non-bonding orbital lying in the plane of the molecule) or  $sp^2$  hybrids (with the remaining p orbital reserved for the  $\sigma$  and  $\pi^*$  orbitals) can be used. The H atoms use their 1s orbitals since hybridization is not feasible for them. The C atom clearly uses its  $sp^2$  hybrids to form two CH and one CO  $\sigma$  bonding-antibonding orbital pairs.

The O atom uses one of its  $sp$  or  $sp^2$  hybrids to form the CO  $\sigma$  bond and antibond. When  $sp$  hybrids are used in conceptualizing the bonding, the other  $sp$  hybrid forms a lone pair orbital directed away from the CO bond axis; one of the atomic p orbitals is involved in the CO  $\sigma$  and  $\pi^*$  orbitals, while the other forms an in-plane non-bonding orbital. Alternatively, when  $sp^2$  hybrids are used, the two  $sp^2$  hybrids that do not interact with the C-atom  $sp^2$  orbital form the two non-bonding orbitals. Hence, the final picture of bonding, non-bonding, and antibonding orbitals does not depend on which hybrids one uses as intermediates.

As another example, the 2s and 2p orbitals on the two N atoms of  $\text{N}_2$  can be formed into pairs of  $sp$  hybrids on each N atom plus a pair of p atomic orbitals on each N atom. The  $sp$  hybrids directed toward the other N atom give rise to bonding  $\sigma$  and antibonding  $\sigma^*$  orbitals, and the  $sp$  hybrids directed away from the other N atom yield nonbonding orbitals. The p orbitals, which consist of 2p orbitals on the N atoms directed perpendicular to the N-N bond axis, produce bonding  $\pi$  and antibonding  $\pi^*$  orbitals.

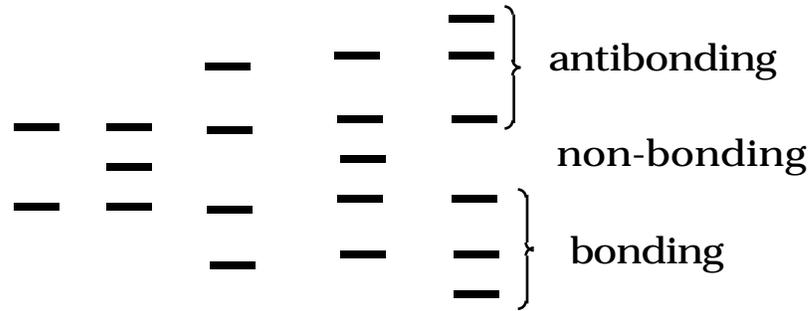
v. In general,  $\sigma$  interactions for a given pair of atoms interacting are stronger than  $\pi$  interactions (which, in turn, are stronger than  $\pi^*$  interactions, etc.) for any given sets (i.e., principal quantum number) of aos that interact. Hence,  $\sigma$  bonding orbitals (originating from a given set of aos) lie below  $\pi$  bonding orbitals, and  $\pi^*$  orbitals lie above  $\pi$  orbitals that arise from the same sets of aos. In the  $\text{N}_2$  example, the  $\sigma$  bonding orbital formed from the two  $sp$  hybrids lies below the  $\pi$  bonding orbital, but the  $\pi^*$  orbital lies below the  $\sigma^*$  orbital. In the  $\text{H}_2\text{CO}$  example, the two CH and the one CO bonding orbitals have low energy; the CO  $\sigma$  bonding orbital has the next lowest energy; the two O-atom non-bonding orbitals have intermediate energy; the CO  $\pi^*$  orbital has somewhat higher energy; and the two CH and one CO antibonding orbitals have the highest energies.

vi. If a given ao or hybrid orbital interacts with or is coupled to orbitals on more than a single neighboring atom, multicenter bonding can occur. For example, in the allyl radical the central carbon atom's p orbital is coupled to the p orbitals on both neighboring atoms;

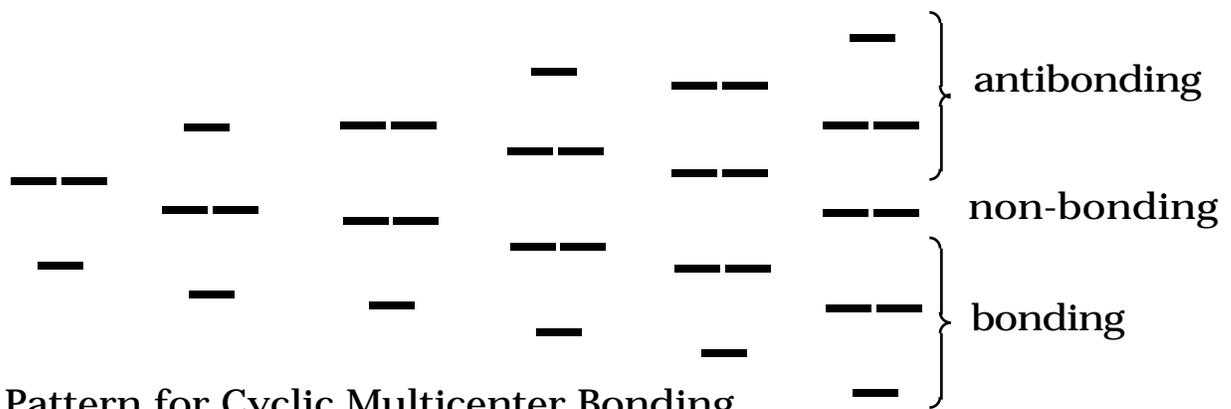
in linear  $\text{Li}_3$ , the central Li atom's 2s orbital interacts with the 2s orbitals on both terminal Li atoms; in triangular  $\text{Cu}_3$ , the 2s orbitals on each Cu atom couple to each of the other two atoms' 4s orbitals.

vii. Multicenter bonding that involves "linear" chains containing N atoms (e.g., as in conjugated polyenes or in chains of Cu or Na atoms for which the valence orbitals on one atom interact with those of its neighbors on both sides) gives rise to mo energy patterns in which there are  $N/2$  (if N is even) or  $N/2 - 1$  non-degenerate bonding orbitals and the same number of antibonding orbitals (if N is odd, there is also a single non-bonding orbital).

viii. Multicenter bonding that involves "cyclic" chains of N atoms (e.g., as in cyclic conjugated polyenes or in rings of Cu or Na atoms for which the valence orbitals on one atom interact with those of its neighbors on both sides and the entire net forms a closed cycle) gives rise to mo energy patterns in which there is a lowest non-degenerate orbital and then a progression of doubly degenerate orbitals. If N is odd, this progression includes  $(N-1)/2$  levels; if N is even, there are  $(N-2)/2$  doubly degenerate levels and a final non-degenerate highest orbital. These patterns and those that appear in linear multicenter bonding are summarized in the Figures shown below.



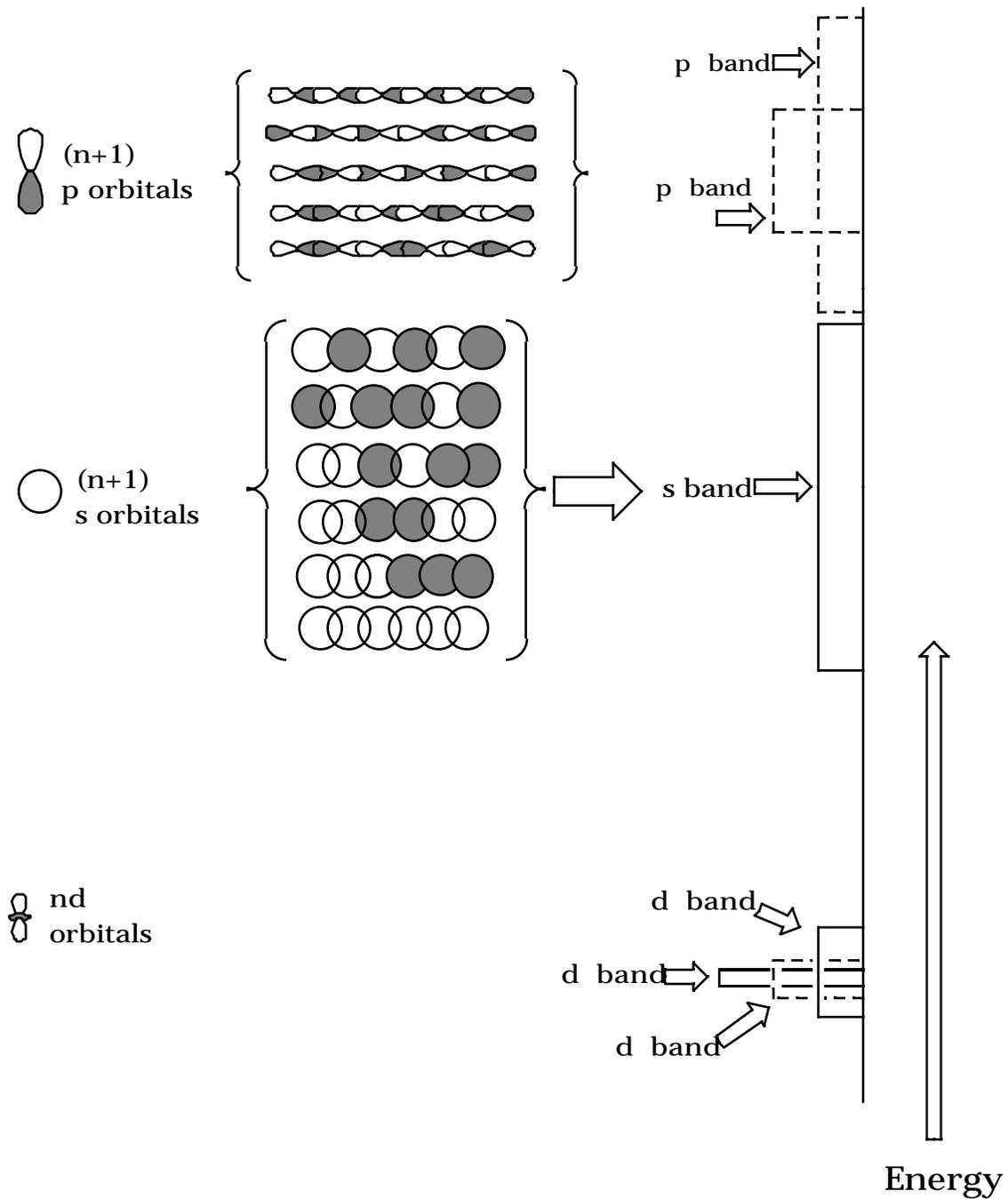
**Pattern for Linear Multicenter  
Bonding Situation:  $N=2, 3, \dots, 6$**



**Pattern for Cyclic Multicenter Bonding  
 $N= 3, 4, 5, \dots, 8$**

ix. In extended systems such as solids, atom-based orbitals combine as above to form so-called 'bands' of molecular orbitals. These bands are continuous rather than discrete as in the above cases involving small polyenes. The energy 'spread' within a band depends on the overlap among the atom-based orbitals that form the band; large overlap gives rise to a large band width, while small overlap produces a narrow band. As one moves from the bottom (i.e., the lower energy part) of a band to the top, the number of nodes in the corresponding band orbital increases, as a result of which its bonding nature decreases. In the figure shown below, the bands of a metal such as Ni (with 3d, 4s, and 4p orbitals) is illustrated. The d-orbital band is narrow because the 3d orbitals are small and hence do not overlap appreciably; the 4s and 4p bands are wider because the larger 4s and 4p orbitals overlap to a greater extent. The d-band is split into  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  components corresponding to the nature of the overlap interactions among the constituent atomic d orbitals. Likewise, the p-band is split into  $p_x$  and  $p_y$  components. The widths of the  $p_x$  and  $p_y$  components of each band are larger than those of the  $d$  components because the corresponding  $p$  overlap interactions

are stronger. The intensities of the bands at energy  $E$  measure the densities of states at that  $E$ . The total integrated intensity under a given band is a measure of the total number of atomic orbitals that form the band.



## II. Orbital Symmetry

*Symmetry provides additional quantum numbers or labels to use in describing the mos. Each such quantum number further sub-divides the collection of all mos into sets that have vanishing Hamiltonian matrix elements among members belonging to different sets.*

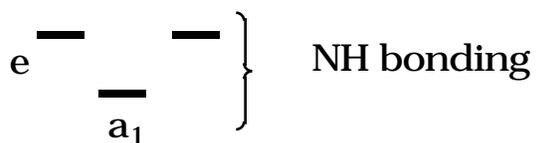
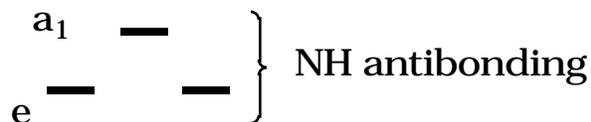
Orbital interaction "topology" as discussed above plays a most- important role in

determining the orbital energy level patterns of a molecule. Symmetry also comes into play but in a different manner. Symmetry can be used to characterize the core, bonding, non-bonding, and antibonding molecular orbitals. Much of this chapter is devoted to how this can be carried out in a systematic manner. Once the various mos have been labeled according to symmetry, it may be possible to recognize additional degeneracies that may not have been apparent on the basis of orbital-interaction considerations alone. Thus, topology provides the basic energy ordering pattern and then symmetry enters to identify additional degeneracies.

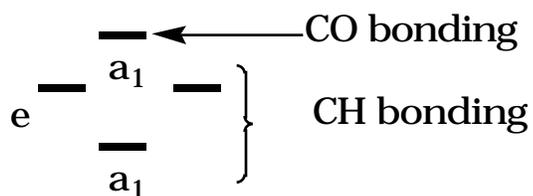
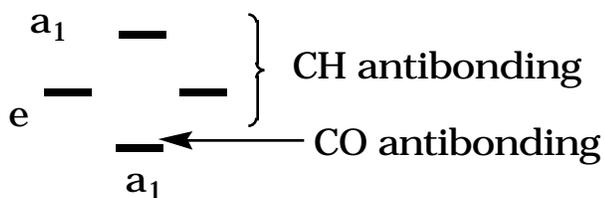
For example, the three NH bonding and three NH antibonding orbitals in  $\text{NH}_3$ , when symmetry adapted within the  $C_{3v}$  point group, cluster into  $a_1$  and e mos as shown in the Figure below. The N-atom localized non-bonding lone pair orbital and the N-atom 1s core orbital also belong to  $a_1$  symmetry.

In a second example, the three CH bonds, three CH antibonds, CO bond and antibond, and three O-atom non-bonding orbitals of the methoxy radical  $\text{H}_3\text{C-O}$  also cluster into  $a_1$  and e orbitals as shown below. In these cases, point group symmetry allows one to identify degeneracies that may not have been apparent from the structure of the orbital interactions alone.





### Orbital Character and Symmetry in NH<sub>3</sub>

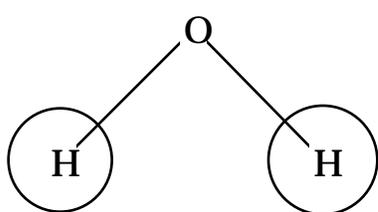


### Orbital Character and Symmetry in H<sub>3</sub>CO Radical

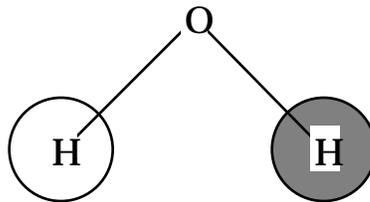


The three resultant molecular orbital energies are, of course, identical to those obtained without symmetry above. The three LCAO-MO coefficients, now expressing the mos in terms of the symmetry adapted orbitals are  $C_{is} = (0.707, 0.707, 0.0)$  for the bonding orbital,  $(0.0, 0.0, 1.00)$  for the nonbonding orbital, and  $(0.707, -0.707, 0.0)$  for the antibonding orbital. These coefficients, when combined with the symmetry adaptation coefficients  $C_{sa}$  given earlier, express the three mos in terms of the three aos as  $\psi_i = \sum_{sa} C_{is} C_{sa} \phi_{sa}$ ; the sum  $\sum_{sa} C_{is} C_{sa}$  gives the LCAO-MO coefficients  $C_{ia}$  which, for example, for the bonding orbital, are  $(0.707^2, 0.707, 0.707^2)$ , in agreement with what was found earlier without using symmetry.

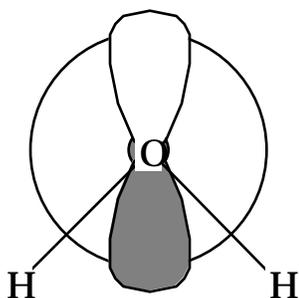
The low energy orbitals of the  $H_2O$  molecule can be used to illustrate the use of symmetry within the primitive ao basis as well as in terms of hybrid orbitals. The 1s orbital on the Oxygen atom is clearly a nonbonding core orbital. The Oxygen 2s orbital and its three 2p orbitals are of valence type, as are the two Hydrogen 1s orbitals. In the absence of symmetry, these six valence orbitals would give rise to a 6x6 secular problem. By combining the two Hydrogen 1s orbitals into  $0.707(1s_L + 1s_R)$  and  $0.707(1s_L - 1s_R)$  symmetry adapted orbitals (labeled  $a_1$  and  $b_2$  within the  $C_{2v}$  point group; see the Figure below), and recognizing that the Oxygen 2s and  $2p_z$  orbitals belong to  $a_1$  symmetry (the z axis is taken as the  $C_2$  rotation axis and the x axis is taken to be perpendicular to the plane in which the three nuclei lie) while the  $2p_x$  orbital is  $b_1$  and the  $2p_y$  orbital is  $b_2$ , allows the 6x6 problem to be decomposed into a 3x3 ( $a_1$ ) secular problem, a 2x2 ( $b_2$ ) secular problem and a 1x1 ( $b_1$ ) problem. These decompositions allow one to conclude that there is one nonbonding  $b_1$  orbital (the Oxygen  $2p_x$  orbital), bonding and antibonding  $b_2$  orbitals (the O-H bond and antibond formed by the Oxygen  $2p_y$  orbital interacting with  $0.707(1s_L - 1s_R)$ ), and, finally, a set of bonding, nonbonding, and antibonding  $a_1$  orbitals (the O-H bond and antibond formed by the Oxygen 2s and  $2p_z$  orbitals interacting with  $0.707(1s_L + 1s_R)$  and the nonbonding orbital formed by the Oxygen 2s and  $2p_z$  orbitals combining to form the "lone pair" orbital directed along the z-axis away from the two Hydrogen atoms).



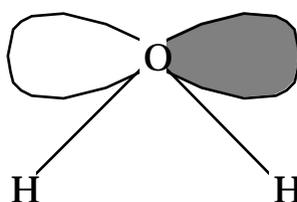
$a_1$  Hydrogen Orbitals



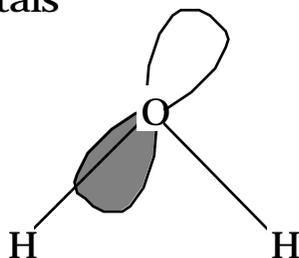
$b_2$  Hydrogen Orbitals



Oxygen  $a_1$  Orbitals



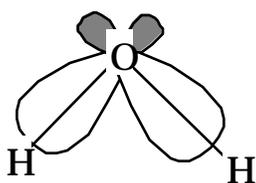
Oxygen  $b_2$  Orbital



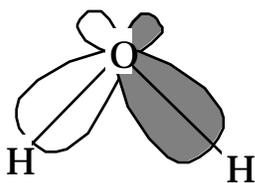
Oxygen  $b_1$  Orbital

Alternatively, to analyze the  $\text{H}_2\text{O}$  molecule in terms of hybrid orbitals, one first combines the Oxygen  $2s$ ,  $2p_z$ ,  $2p_x$  and  $2p_y$  orbitals to form four  $sp^3$  hybrid orbitals. The valence-shell electron-pair repulsion (VSEPR) model of chemical bonding (see R. J. Gillespie and R. S. Nyholm, *Quart. Rev.* 11, 339 (1957) and R. J. Gillespie, *J. Chem. Educ.* 40, 295 (1963)) directs one to involve all of the Oxygen valence orbitals in the hybridization because four  $\sigma$ -bond or nonbonding electron pairs need to be accommodated about the Oxygen center; no  $\pi$  orbital interactions are involved, of course. Having formed the four  $sp^3$  hybrid orbitals, one proceeds as with the primitive aos; one forms symmetry adapted orbitals. In this case, the two Hydrogen  $1s$  orbitals are combined exactly as above to form  $0.707(1s_L + 1s_R)$  and  $0.707(1s_L - 1s_R)$ . The two  $sp^3$  hybrids which lie in the

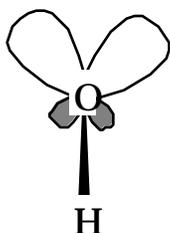
plane of the H and O nuclei ( label them L and R) are combined to give symmetry adapted hybrids:  $0.707(L+R)$  and  $0.707(L-R)$ , which are of  $a_1$  and  $b_2$  symmetry, respectively ( see the Figure below). The two  $sp^3$  hybrids that lie above and below the plane of the three nuclei (label them T and B) are also symmetry adapted to form  $0.707(T+ B)$  and  $0.707(T- B)$ , which are of  $a_1$  and  $b_1$  symmetry, respectively. Once again, one has broken the  $6 \times 6$  secular problem into a  $3 \times 3$   $a_1$  block, a  $2 \times 2$   $b_2$  block and a  $1 \times 1$   $b_1$  block. Although the resulting bonding, nonbonding and antibonding  $a_1$  orbitals, the bonding and antibonding  $b_2$  orbitals and the nonbonding  $b_1$  orbital are now viewed as formed from symmetry adapted Hydrogen orbitals and four Oxygen  $sp^3$  orbitals, they are, of course, exactly the same molecular orbitals as were obtained earlier in terms of the symmetry adapted primitive aos. The formation of hybrid orbitals was an intermediate step which could not alter the final outcome.



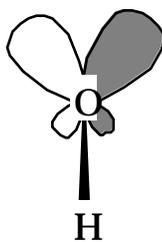
**L + R  $a_1$  Hybrid  
Symmetry Orbital**



**L - R  $b_2$  Hybrid  
Symmetry Orbital**



**T + B Hybrid  
Symmetry Orbital  
Seen From the Side**



**T - B Hybrid  
Symmetry Orbital  
Seen From the Side**

That no degenerate molecular orbitals arose in the above examples is a result of the fact that the  $C_{2v}$  point group to which  $H_2O$  and the allyl system belong (and certainly the  $C_s$  subgroup which was used above in the allyl case) has no degenerate representations. Molecules with higher symmetry such as  $NH_3$ ,  $CH_4$ , and benzene have energetically degenerate orbitals because their molecular point groups have degenerate representations.

## B. Linear Molecules

*Linear molecules belong to the axial rotation group. Their symmetry is intermediate in complexity between nonlinear molecules and atoms.*

For linear molecules, the symmetry of the electrostatic potential provided by the nuclei and the other electrons is described by either the  $C_{\infty v}$  or  $D_{\infty h}$  group. The essential difference between these symmetry groups and the finite point groups which characterize the non-linear molecules lies in the fact that the electrostatic potential which an electron feels is invariant to rotations of any amount about the molecular axis (i.e.,  $V(\phi + \alpha) = V(\phi)$ , for any angle increment  $\alpha$ ). This means that the operator  $C_{\infty}$  which generates a rotation of the electron's azimuthal angle  $\phi$  by an amount  $\alpha$  about the molecular axis commutes with the Hamiltonian  $[H, C_{\infty}] = 0$ .  $C_{\infty}$  can be written in terms of the quantum mechanical operator  $L_z = -i\hbar \frac{\partial}{\partial \phi}$  describing the orbital angular momentum of the electron about the molecular (z) axis:

$$C_{\infty} = \exp(i L_z / \hbar).$$

Because  $C_{\infty}$  commutes with the Hamiltonian and  $C_{\infty}$  can be written in terms of  $L_z$ ,  $L_z$  must commute with the Hamiltonian. As a result, the molecular orbitals of a linear molecule must be eigenfunctions of the z-component of angular momentum  $L_z$ :

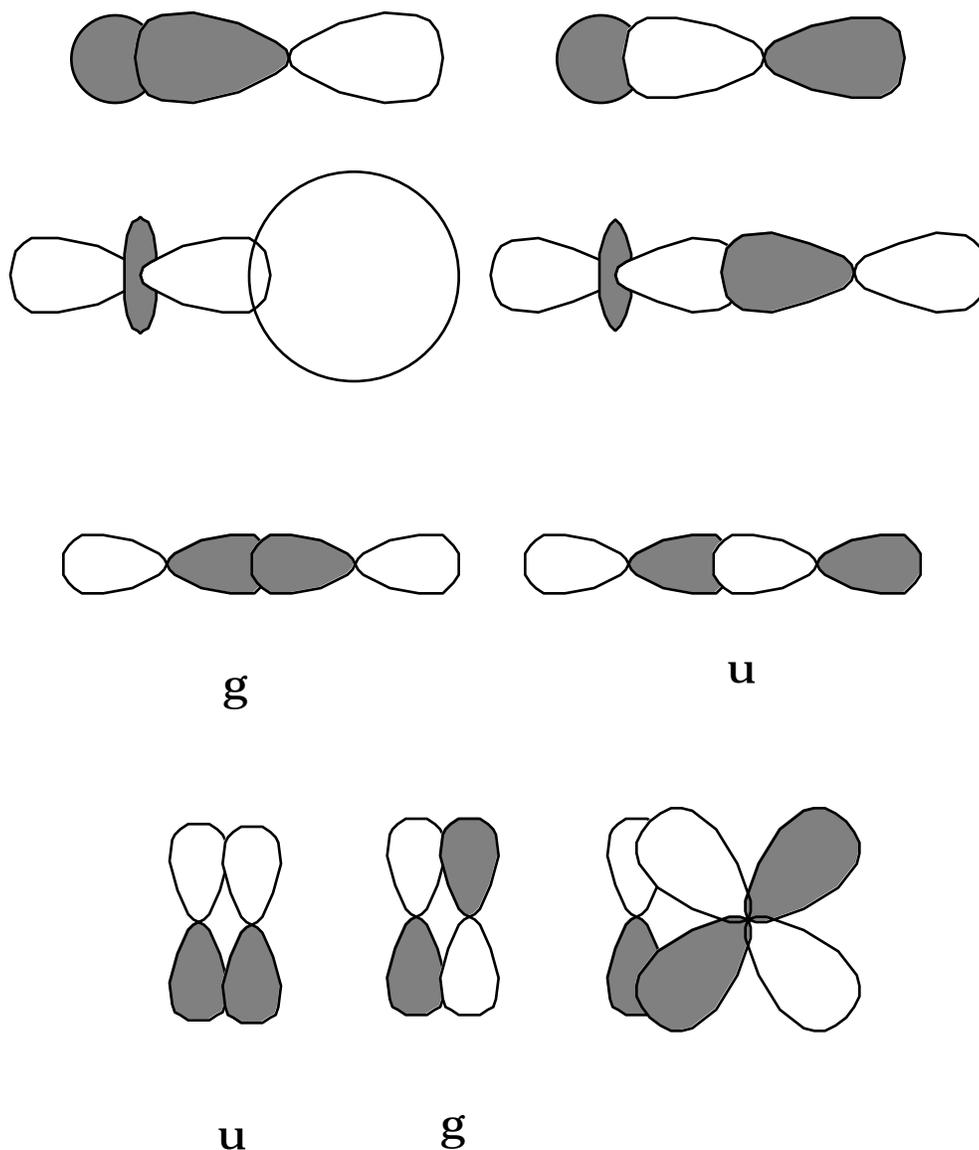
$$-i\hbar \frac{\partial}{\partial \phi} \psi = m\hbar \psi.$$

The electrostatic potential is not invariant under rotations of the electron about the x or y axes (those perpendicular to the molecular axis), so  $L_x$  and  $L_y$  do not commute with the Hamiltonian. Therefore, only  $L_z$  provides a "good quantum number" in the sense that the operator  $L_z$  commutes with the Hamiltonian.

In summary, the molecular orbitals of a linear molecule can be labeled by their m quantum number, which plays the same role as the point group labels did for non-linear polyatomic molecules, and which gives the eigenvalue of the angular momentum of the orbital about the molecule's symmetry axis. Because the kinetic energy part of the Hamiltonian contains  $(\hbar^2/2m_e r^2) \nabla^2$ , whereas the potential energy part is independent of  $\phi$ , the energies of the molecular orbitals depend on the square of the m quantum number. Thus, pairs of orbitals with  $m = \pm 1$  are energetically degenerate; pairs with  $m = \pm 2$  are degenerate, and so on. The absolute value of m, which is what the energy depends on, is called the quantum number. Molecular orbitals with  $m = 0$  are called orbitals; those with  $m = 1$  are orbitals; and those with  $m = 2$  are orbitals.

Just as in the non-linear polyatomic-molecule case, the atomic orbitals which constitute a given molecular orbital must have the same symmetry as that of the molecular orbital. This means that  $\sigma$ ,  $\pi$ , and  $\delta$  molecular orbitals are formed, via LCAO-MO, from  $m=0$ ,  $m= \pm 1$ , and  $m= \pm 2$  atomic orbitals, respectively. In the diatomic  $N_2$  molecule, for example, the core orbitals are of  $\sigma$  symmetry as are the molecular orbitals formed from the  $2s$  and  $2p_z$  atomic orbitals (or their hybrids) on each Nitrogen atom. The molecular orbitals formed from the atomic  $2p_{-1}=(2p_x - i 2p_y)$  and the  $2p_{+1}=(2p_x + i 2p_y)$  orbitals are of  $\pi$  symmetry and have  $m = -1$  and  $+1$ .

For homonuclear diatomic molecules and other linear molecules which have a center of symmetry, the inversion operation (in which an electron's coordinates are inverted through the center of symmetry of the molecule) is also a symmetry operation. Each resultant molecular orbital can then also be labeled by a quantum number denoting its parity with respect to inversion. The symbols  $g$  (for gerade or even) and  $u$  (for ungerade or odd) are used for this label. Again for  $N_2$ , the core orbitals are of  $\sigma_g$  and  $\sigma_u$  symmetry, and the bonding and antibonding  $\pi$  orbitals formed from the  $2s$  and  $2p$  orbitals on the two Nitrogen atoms are of  $\pi_g$  and  $\pi_u$  symmetry.



The bonding  $\pi$  molecular orbital pair (with  $m = +1$  and  $-1$ ) is of  $\pi_u$  symmetry whereas the corresponding antibonding orbital is of  $\pi_g$  symmetry. Examples of such molecular orbital symmetries are shown above.

The use of hybrid orbitals can be illustrated in the linear-molecule case by considering the N<sub>2</sub> molecule. Because two bonding and antibonding molecular orbital pairs are involved in N<sub>2</sub> (one with  $m = +1$ , one with  $m = -1$ ), VSEPR theory guides one to form sp hybrid orbitals from each of the Nitrogen atom's 2s and 2p<sub>z</sub> (which is also the 2p orbital with  $m = 0$ ) orbitals. Ignoring the core orbitals, which are of  $\pi_g$  and  $\pi_u$  symmetry as noted above, one then symmetry adapts the four sp hybrids (two from each atom) to build one  $\sigma_g$  orbital involving a bonding interaction between two sp hybrids pointed toward one

another, an antibonding  $\sigma_u$  orbital involving the same pair of sp orbitals but coupled with opposite signs, a nonbonding  $\sigma_g$  orbital composed of two sp hybrids pointed away from the interatomic region combined with like sign, and a nonbonding  $\sigma_u$  orbital made of the latter two sp hybrids combined with opposite signs. The two  $2p_m$  orbitals ( $m = +1$  and  $-1$ ) on each Nitrogen atom are then symmetry adapted to produce a pair of bonding  $\sigma_u$  orbitals (with  $m = +1$  and  $-1$ ) and a pair of antibonding  $\sigma_g$  orbitals (with  $m = +1$  and  $-1$ ). This hybridization and symmetry adaptation thereby reduces the  $8 \times 8$  secular problem (which would be  $10 \times 10$  if the core orbitals were included) into a  $2 \times 2$   $\sigma_g$  problem (one bonding and one nonbonding), a  $2 \times 2$   $\sigma_u$  problem (one bonding and one nonbonding), an identical pair of  $1 \times 1$   $\sigma_u$  problems (bonding), and an identical pair of  $1 \times 1$   $\sigma_g$  problems (antibonding).

Another example of the equivalence among various hybrid and atomic orbital points of view is provided by the CO molecule. Using, for example, sp hybrid orbitals on C and O, one obtains a picture in which there are: two core orbitals corresponding to the O-atom 1s and C-atom 1s orbitals; one CO bonding, two non-bonding, and one CO antibonding orbitals arising from the four sp hybrids; a pair of bonding and a pair of antibonding orbitals formed from the two p orbitals on O and the two p orbitals on C. Alternatively, using  $sp^2$  hybrids on both C and O, one obtains: the two core orbitals as above; a CO bonding and antibonding orbital pair formed from the  $sp^2$  hybrids that are directed along the CO bond; and a single bonding and antibonding  $\pi^*$  orbital set. The remaining two  $sp^2$  orbitals on C and the two on O can then be symmetry adapted by forming  $\pm$  combinations within each pair to yield: an  $a_1$  non-bonding orbital (from the  $+$  combination) on each of C and O directed away from the CO bond axis; and a p orbital on each of C and O that can subsequently overlap to form the second bonding and  $\pi^*$  antibonding orbital pair.

It should be clear from the above examples, that no matter what particular hybrid orbitals one chooses to utilize in conceptualizing a molecule's orbital interactions, symmetry ultimately returns to force one to form proper symmetry adapted combinations which, in turn, renders the various points of view equivalent. In the above examples and in several earlier examples, symmetry adaptation of, for example,  $sp^2$  orbital pairs (e.g.,  $sp_L^2 \pm sp_R^2$ ) generated orbitals of pure spatial symmetry. In fact, symmetry combining hybrid orbitals in this manner amounts to forming other hybrid orbitals. For example, the above  $\pm$  combinations of  $sp^2$  hybrids directed to the left (L) and right (R) of some bond axis generate a new sp hybrid directed along the bond axis but opposite to the  $sp^2$  hybrid used to form the bond and a non-hybridized p orbital directed along the L-to-R direction. In the CO example, these combinations of  $sp^2$  hybrids on O and C produce sp hybrids on O and C and p orbitals on O and C.

### C. Atoms

*Atoms belong to the full rotation symmetry group; this makes their symmetry analysis the most complex to treat.*

In moving from linear molecules to atoms, additional symmetry elements arise. In particular, the potential field experienced by an electron in an orbital becomes invariant to rotations of arbitrary amounts about the x, y, and z axes; in the linear-molecule case, it is invariant only to rotations of the electron's position about the molecule's symmetry axis (the z axis). These invariances are, of course, caused by the spherical symmetry of the potential of any atom. This additional symmetry of the potential causes the Hamiltonian to commute with all three components of the electron's angular momentum:  $[L_x, H] = 0$ ,  $[L_y, H] = 0$ , and  $[L_z, H] = 0$ . It is straightforward to show that H also commutes with the operator  $L^2 = L_x^2 + L_y^2 + L_z^2$ , defined as the sum of the squares of the three individual components of the angular momentum. Because  $L_x$ ,  $L_y$ , and  $L_z$  do not commute with one another, orbitals which are eigenfunctions of H cannot be simultaneous eigenfunctions of all three angular momentum operators. Because  $L_x$ ,  $L_y$ , and  $L_z$  do commute with  $L^2$ , orbitals can be found which are eigenfunctions of H, of  $L^2$  and of any one component of  $\mathbf{L}$ ; it is convention to select  $L_z$  as the operator which, along with H and  $L^2$ , form a mutually commutative operator set of which the orbitals are simultaneous eigenfunctions.

So, for any atom, the orbitals can be labeled by both l and m quantum numbers, which play the role that point group labels did for non-linear molecules and did for linear molecules. Because (i) the kinetic energy operator in the electronic Hamiltonian explicitly contains  $L^2/2m_e r^2$ , (ii) the Hamiltonian does not contain additional  $L_z$ ,  $L_x$ , or  $L_y$  factors, and (iii) the potential energy part of the Hamiltonian is spherically symmetric (and commutes with  $L^2$  and  $L_z$ ), the energies of atomic orbitals depend upon the l quantum number and are independent of the m quantum number. This is the source of the  $2l+1$ - fold degeneracy of atomic orbitals.

The angular part of the atomic orbitals is described in terms of the spherical harmonics  $Y_{l,m}$ ; that is, each atomic orbital can be expressed as

$$\psi_{n,l,m} = Y_{l,m}(\theta, \phi) R_{n,l}(r).$$

The explicit solutions for the  $Y_{l,m}$  and for the radial wavefunctions  $R_{n,l}$  are given in Appendix B. The variables  $r, \theta, \phi$  give the position of the electron in the orbital in spherical coordinates. These angular functions are, as discussed earlier, related to the cartesian (i.e., spatially oriented) orbitals by simple transformations; for example, the orbitals with  $l=2$  and  $m=2,1,0,-1,-2$  can be expressed in terms of the  $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ ,  $d_{xx-yy}$ , and  $d_{zz}$  orbitals. Either set of orbitals is acceptable in the sense that each orbital is an

eigenfunction of  $H$ ; transformations within a degenerate set of orbitals do not destroy the Hamiltonian-eigenfunction feature. The orbital set labeled with  $l$  and  $m$  quantum numbers is most useful when one is dealing with isolated atoms (which have spherical symmetry), because  $m$  is then a valid symmetry label, or with an atom in a local environment which is axially symmetric (e.g., in a linear molecule) where the  $m$  quantum number remains a useful symmetry label. The cartesian orbitals are preferred for describing an atom in a local environment which displays lower than axial symmetry (e.g., an atom interacting with a diatomic molecule in  $C_{2v}$  symmetry).

The radial part of the orbital  $R_{n,l}(r)$  as well as the orbital energy  $\epsilon_{n,l}$  depend on  $l$  because the Hamiltonian itself contains  $l(l+1)\hbar^2/2m_e r^2$ ; they are independent of  $m$  because the Hamiltonian has no  $m$ -dependence. For bound orbitals,  $R_{n,l}(r)$  decays exponentially for large  $r$  (as  $\exp(-2r/a_{n,l})$ ), and for unbound (scattering) orbitals, it is oscillatory at large  $r$  with an oscillation period related to the deBroglie wavelength of the electron. In  $R_{n,l}(r)$  there are  $(n-l-1)$  radial nodes lying between  $r=0$  and  $r=\infty$ . These nodes provide differential stabilization of low- $l$  orbitals over high- $l$  orbitals of the same principal quantum number  $n$ . That is, penetration of outer shells is greater for low- $l$  orbitals because they have more radial nodes; as a result, they have larger amplitude near the atomic nucleus and thus experience enhanced attraction to the positive nuclear charge. The average size (e.g., average value of  $r$ ;  $\langle r \rangle = \int R_{n,l}^2 r^3 dr$ ) of an orbital depends strongly on  $n$ , weakly on  $l$  and is independent of  $m$ ; it also depends strongly on the nuclear charge and on the potential produced by the other electrons. This potential is often characterized qualitatively in terms of an effective nuclear charge  $Z_{\text{eff}}$  which is the true nuclear charge of the atom  $Z$  minus a screening component  $Z_{\text{sc}}$  which describes the repulsive effect of the electron density lying radially inside the electron under study. Because, for a given  $n$ , low- $l$  orbitals penetrate closer to the nucleus than do high- $l$  orbitals, they have higher  $Z_{\text{eff}}$  values (i.e., smaller  $Z_{\text{sc}}$  values) and correspondingly smaller average sizes and larger binding energies.

## Chapter 6

*Along "Reaction Paths", Orbitals Can be Connected One-to-One According to Their Symmetries and Energies. This is the Origin of the Woodward-Hoffmann Rules*

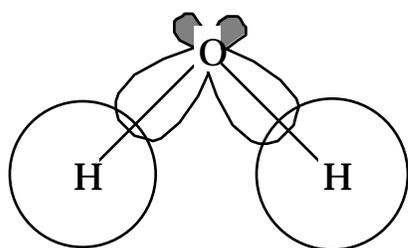
### I. Reduction in Symmetry

*As fragments are brought together to form a larger molecule, the symmetry of the nuclear framework (recall the symmetry of the coulombic potential experienced by electrons depends on the locations of the nuclei) changes. However, in some cases, certain symmetry elements persist throughout the path connecting the fragments and the product molecule. These preserved symmetry elements can be used to label the orbitals throughout the 'reaction'.*

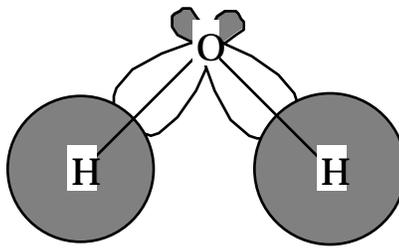
The point-group, axial- and full-rotation group symmetries which arise in non-linear molecules, linear molecules, and atoms, respectively, are seen to provide quantum numbers or symmetry labels which can be used to characterize the orbitals appropriate for each such species. In a physical event such as interaction with an external electric or magnetic field or a chemical process such as collision or reaction with another species, the atom or molecule can experience a change in environment which causes the electrostatic potential which its orbitals experience to be of lower symmetry than that of the isolated atom or molecule. For example, when an atom interacts with another atom to form a diatomic molecule or simply to exchange energy during a collision, each atom's environment changes from being spherically symmetric to being axially symmetric. When the formaldehyde molecule undergoes unimolecular decomposition to produce CO + H<sub>2</sub> along a path that preserves C<sub>2v</sub> symmetry, the orbitals of the CO moiety evolve from C<sub>2v</sub> symmetry to axial symmetry.

It is important, therefore to be able to label the orbitals of atoms, linear, and non-linear molecules in terms of their full symmetries as well in terms of the groups appropriate to lower-symmetry situations. This can be done by knowing how the representations of a higher symmetry group decompose into representations of a lower group. For example, the Y<sub>l,m</sub> functions appropriate for spherical symmetry, which belong to a 2l+1 fold degenerate set in this higher symmetry, decompose into doubly degenerate pairs of functions Y<sub>l,1</sub>, Y<sub>l,-1</sub>; Y<sub>l,1-1</sub>, Y<sub>l,-1+1</sub>; etc., plus a single non-degenerate function Y<sub>l,0</sub>, in axial symmetry. Moreover, because L<sup>2</sup> no longer commutes with the Hamiltonian whereas L<sub>z</sub> does, orbitals with different l-values but the same m-values can be coupled. As the N<sub>2</sub> molecule is formed from two N atoms, the 2s and 2p<sub>z</sub> orbitals, both of which belong to the same ( ) symmetry in the axial rotation group but which are of different symmetry in the isolated-atom spherical symmetry, can mix to form the g bonding orbital, the u antibonding, as well as the g and u nonbonding lone-pair orbitals. The fact that 2s and 2p have different l-values no longer uncouples these orbitals as it did for the isolated atoms, because l is no longer a "good" quantum number.

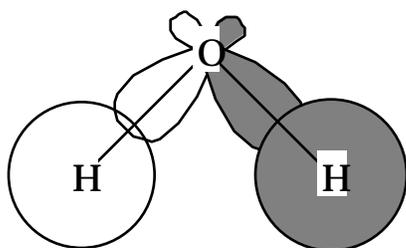
Another example of reduced symmetry is provided by the changes that occur as H<sub>2</sub>O fragments into OH and H. The bonding orbitals (a<sub>1</sub> and b<sub>2</sub>) and in-plane lone pair (a<sub>1</sub>) and the \* antibonding (a<sub>1</sub> and b<sub>2</sub>) of H<sub>2</sub>O become a' orbitals (see the Figure below); the out-of-plane b<sub>1</sub> lone pair orbital becomes a" (in Appendix IV of Electronic Spectra and Electronic Structure of Polyatomic Molecules, G. Herzberg, Van Nostrand Reinhold Co., New York, N.Y. (1966) tables are given which allow one to determine how particular symmetries of a higher group evolve into symmetries of a lower group).



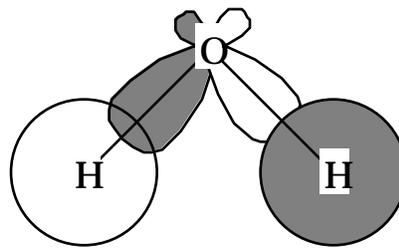
$a_1$  bonding orbital



$a_1^*$  antibonding orbital

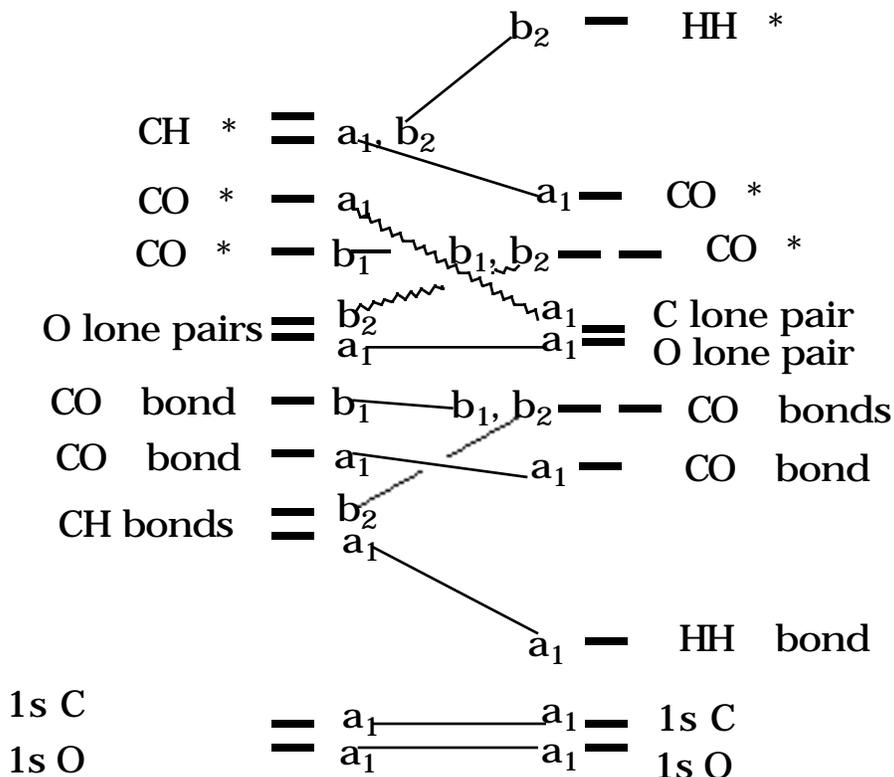


$b_2$  bonding orbital



$b_2^*$  antibonding orbital

To further illustrate these points dealing with orbital symmetry, consider the insertion of CO into  $H_2$  along a path which preserves  $C_{2v}$  symmetry. As the insertion occurs, the degenerate bonding orbitals of CO become  $b_1$  and  $b_2$  orbitals. The antibonding  $^*$  orbitals of CO also become  $b_1$  and  $b_2$ . The  $g$  bonding orbital of  $H_2$  becomes  $a_1$ , and the  $u$  antibonding  $H_2$  orbital becomes  $b_2$ . The orbitals of the reactant  $H_2CO$  are energy-ordered and labeled according to  $C_{2v}$  symmetry in the Figure shown below as are the orbitals of the product  $H_2 + CO$ .



## H<sub>2</sub>CO ==> H<sub>2</sub> + CO Orbital Correlation Diagram in C<sub>2v</sub> Symmetry

When these orbitals are connected according to their symmetries as shown above, one reactant orbital to one product orbital starting with the low-energy orbitals and working to increasing energy, an orbital correlation diagram (OCD) is formed. These diagrams play essential roles in analyzing whether reactions will have symmetry-imposed energy barriers on their potential energy surfaces along the reaction path considered in the symmetry analysis. The essence of this analysis, which is covered in detail in Chapter 12, can be understood by noticing that the sixteen electrons of ground-state H<sub>2</sub>CO do not occupy their orbitals with the same occupancy pattern, symmetry-by-symmetry, as do the sixteen electrons of ground-state H<sub>2</sub> + CO. In particular, H<sub>2</sub>CO places a pair of electrons in the second b<sub>2</sub> orbital while H<sub>2</sub> + CO does not; on the other hand, H<sub>2</sub> + CO places two electrons in the sixth a<sub>1</sub> orbital while H<sub>2</sub>CO does not. The mismatch of the orbitals near the 5a<sub>1</sub>, 6a<sub>1</sub>, and 2b<sub>2</sub> orbitals is the source of the mismatch in the electronic configurations of the ground-states of H<sub>2</sub>CO and H<sub>2</sub> + CO. These mismatches give rise, as shown in Chapter 12, to symmetry-caused energy barriers on the H<sub>2</sub>CO ==> H<sub>2</sub> + CO reaction potential energy surface.

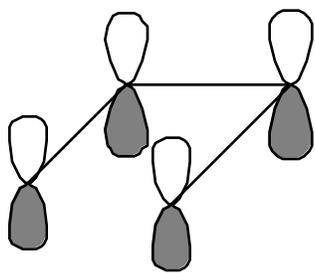
## II. Orbital Correlation Diagrams

*Connecting the energy-ordered orbitals of reactants to those of products according to symmetry elements that are preserved throughout the reaction produces an orbital correlation diagram.*

In each of the examples cited above, symmetry reduction occurred as a molecule or atom approached and interacted with another species. The "path" along which this approach was thought to occur was characterized by symmetry in the sense that it preserved certain symmetry elements while destroying others. For example, the collision of two Nitrogen atoms to produce  $N_2$  clearly occurs in a way which destroys spherical symmetry but preserves axial symmetry. In the other example used above, the formaldehyde molecule was postulated to decompose along a path which preserves  $C_{2v}$  symmetry while destroying the axial symmetries of CO and  $H_2$ . The actual decomposition of formaldehyde may occur along some other path, but if it were to occur along the proposed path, then the symmetry analysis presented above would be useful.

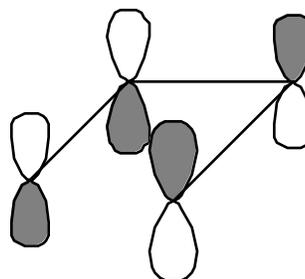
The symmetry reduction analysis outlined above allows one to see new orbital interactions that arise (e.g., the  $2s$  and  $2p_z$  interactions in the  $N + N \Rightarrow N_2$  example) as the interaction increases. It also allows one to construct orbital correlation diagrams (OCD's) in which the orbitals of the "reactants" and "products" are energy ordered and labeled by the symmetries which are preserved throughout the "path", and the orbitals are then correlated by drawing lines connecting the orbitals of a given symmetry, one-by-one in increasing energy, from the reactants side of the diagram to the products side. As noted above, such orbital correlation diagrams play a central role in using symmetry to predict whether photochemical and thermal chemical reactions will experience activation barriers along proposed reaction paths (this subject is treated in Chapter 12).

To again illustrate the construction of an OCD, consider the orbitals of 1,3-butadiene as the molecule undergoes disrotatory closing (notice that this is where a particular path is postulated; the actual reaction may or may not occur along such a path) to form cyclobutene. Along this path, the plane of symmetry which bisects and is perpendicular to the  $C_2-C_3$  bond is preserved, so the orbitals of the reactant and product are labeled as being even-e or odd-o under reflection through this plane. It is not proper to label the orbitals with respect to their symmetry under the plane containing the four C atoms; although this plane is indeed a symmetry operation for the reactants and products, it does not remain a valid symmetry throughout the reaction path.

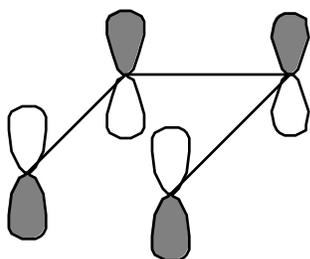


Lowest orbital of  
1,3- butadiene denoted

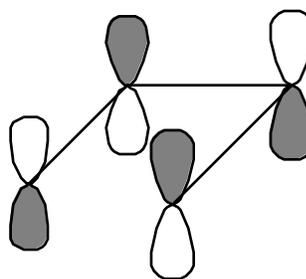
1



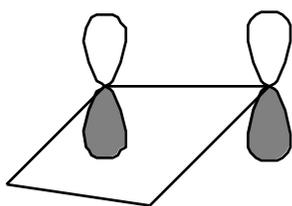
2



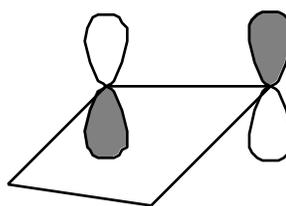
3



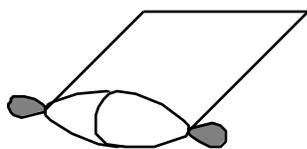
4



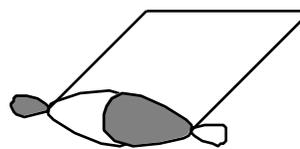
orbital of  
cyclobutene



\* orbital of  
cyclobutene

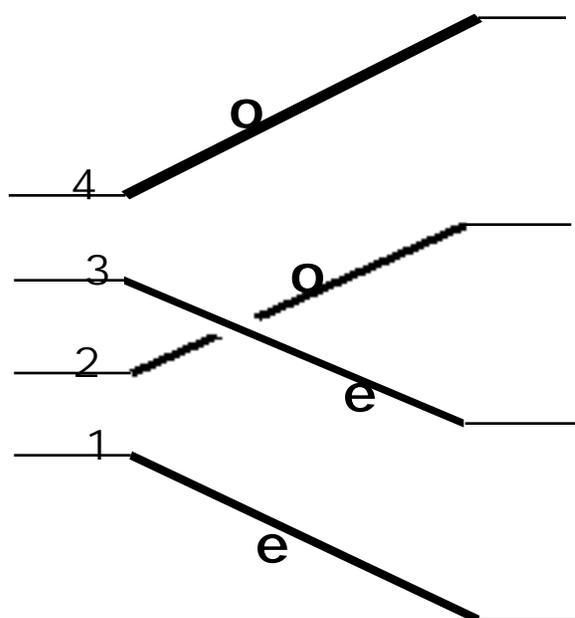


orbital of  
cyclobutene



\* orbital of  
cyclobutene

The four orbitals of 1,3-butadiene are of the following symmetries under the preserved plane (see the orbitals in the Figure above):  $\psi_1 = e$ ,  $\psi_2 = o$ ,  $\psi_3 = e$ ,  $\psi_4 = o$ . The  $\psi_1$  and  $\psi_3$  and  $\psi_2$  and  $\psi_4$  orbitals of cyclobutane which evolve from the four active orbitals of the 1,3-butadiene are of the following symmetry and energy order:  $\psi_1 = e$ ,  $\psi_2 = e$ ,  $\psi_3 = o$ ,  $\psi_4 = o$ . Connecting these orbitals by symmetry, starting with the lowest energy orbital and going through the highest energy orbital, gives the following OCD:



The fact that the lowest two orbitals of the reactants, which are those occupied by the four electrons of the reactant, do not correlate to the lowest two orbitals of the products, which are the orbitals occupied by the two and two electrons of the products, will be shown later in Chapter 12 to be the origin of the activation barrier for the thermal disrotatory rearrangement (in which the four active electrons occupy these lowest two orbitals) of 1,3-butadiene to produce cyclobutene.

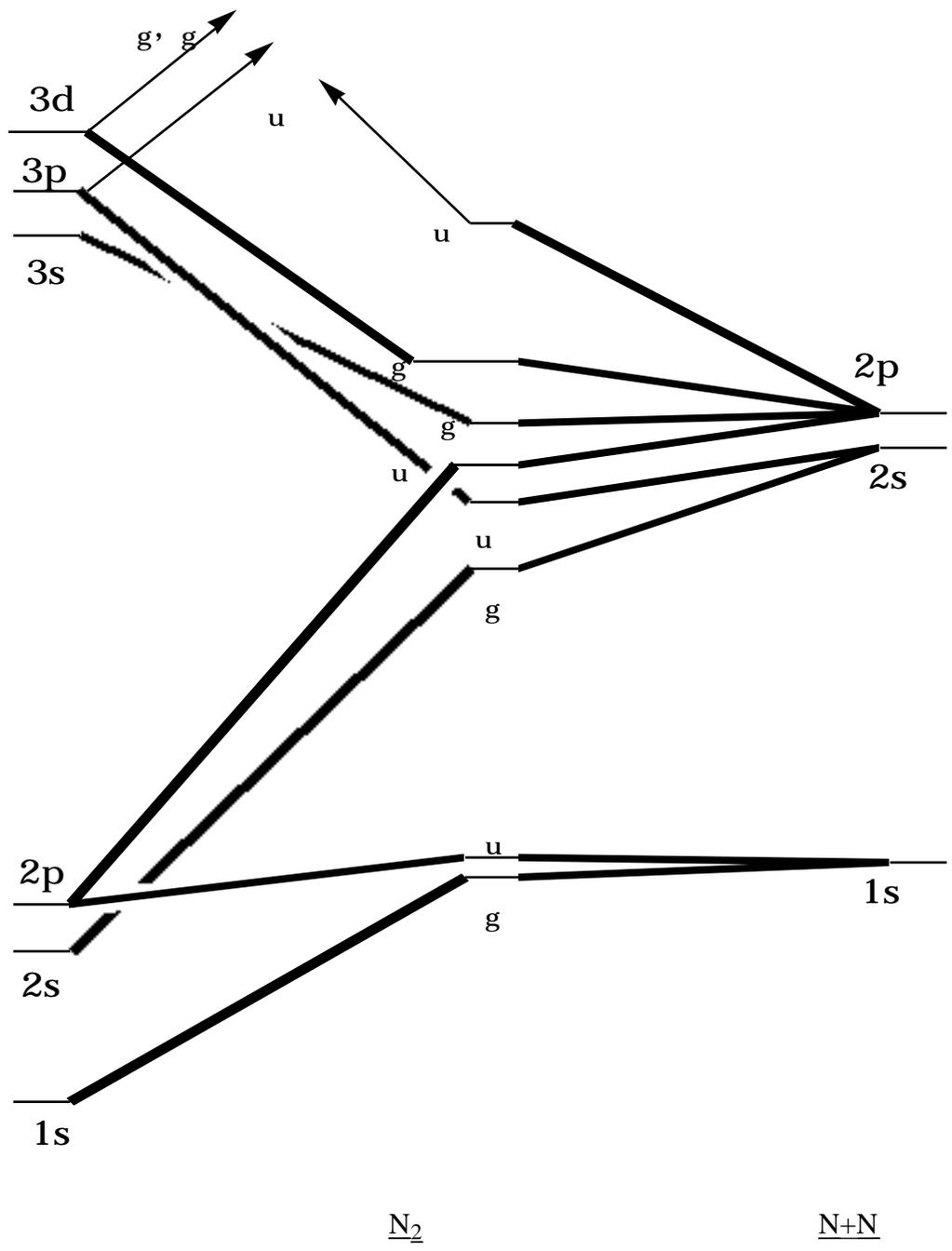
If the reactants could be prepared, for example by photolysis, in an excited state having orbital occupancy  $\psi_1^2 \psi_2^1 \psi_3^1$ , then reaction along the path considered would not have any symmetry-imposed barrier because this singly excited configuration correlates to a singly-excited configuration  $\psi_2^2 \psi_1^1 \psi_3^1$  of the products. The fact that the reactant and product configurations are of equivalent excitation level causes there to be no symmetry constraints on the photochemically induced reaction of 1,3-butadiene to produce cyclobutene. In contrast, the thermal reaction considered first above has a symmetry-imposed barrier

because the orbital occupancy is forced to rearrange (by the occupancy of two electrons) from the ground-state wavefunction of the reactant to smoothly evolve into that of the product.

It should be stressed that although these symmetry considerations may allow one to anticipate barriers on reaction potential energy surfaces, they have nothing to do with the thermodynamic energy differences of such reactions. Symmetry says whether there will be symmetry-imposed barriers above and beyond any thermodynamic energy differences. The enthalpies of formation of reactants and products contain the information about the reaction's overall energy balance.

As another example of an OCD, consider the  $N + N \Rightarrow N_2$  recombination reaction mentioned above. The orbitals of the atoms must first be labeled according to the axial rotation group (including the inversion operation because this is a homonuclear molecule). The core 1s orbitals are symmetry adapted to produce  $1_g$  and  $1_u$  orbitals (the number 1 is used to indicate that these are the lowest energy orbitals of their respective symmetries); the 2s orbitals generate  $2_g$  and  $2_u$  orbitals; the 2p orbitals combine to yield  $3_g$ , a pair of  $1_u$  orbitals, a pair of  $1_g$  orbitals, and the  $3_u$  orbital, whose bonding, nonbonding, and antibonding nature was detailed earlier. In the two separated Nitrogen atoms, the two orbitals derived from the 2s atomic orbitals are degenerate, and the six orbitals derived from the Nitrogen atoms' 2p orbitals are degenerate. At the equilibrium geometry of the  $N_2$  molecule, these degeneracies are lifted, Only the degeneracies of the  $1_u$  and  $1_g$  orbitals, which are dictated by the degeneracy of  $+m$  and  $-m$  orbitals within the axial rotation group, remain.

As one proceeds inward past the equilibrium bond length of  $N_2$ , toward the united-atom limit in which the two Nitrogen nuclei are fused to produce a Silicon nucleus, the energy ordering of the orbitals changes. Labeling the orbitals of the Silicon atom according to the axial rotation group, one finds the 1s is  $g$ , the 2s is  $g$ , the 2p orbitals are  $u$  and  $u$ , the 3s orbital is  $g$ , the 3p orbitals are  $u$  and  $u$ , and the 3d orbitals are  $g$ ,  $g$ , and  $g$ . The following OCD is obtained when one connects the orbitals of the two separated Nitrogen atoms (properly symmetry adapted) to those of the  $N_2$  molecule and eventually to those of the Silicon atom.



The fact that the separated-atom and united-atom limits involve several crossings in the OCD can be used to explain barriers in the potential energy curves of such diatomic molecules which occur at short internuclear distances. It should be noted that the Silicon atom's 3p orbitals of  $\sigma_u$  symmetry and its 3d orbitals of  $\sigma_g$  and  $\pi_g$  symmetry correlate with higher energy orbitals of  $N_2$  not with the valence orbitals of this molecule, and that the  $3\sigma_u$  antibonding orbital of  $N_2$  correlates with a higher energy orbital of Silicon (in particular, its 4p orbital).

## Chapter 7

### *The Most Elementary Molecular Orbital Models Contain Symmetry, Nodal Pattern, and Approximate Energy Information*

#### I. The LCAO-MO Expansion and the Orbital-Level Schrödinger Equation

In the simplest picture of chemical bonding, the valence molecular orbitals  $\psi_i$  are constructed as linear combinations of valence atomic orbitals  $\psi_\mu$  according to the LCAO-MO formula:

$$\psi_i = \sum_{\mu} C_{i\mu} \psi_{\mu}$$

The core electrons are not explicitly included in such a treatment, although their effects are felt through an electrostatic potential

$V$  that has the following properties:

i.  $V$  contains contributions from all of the nuclei in the molecule exerting coulombic attractions on the electron, as well as coulombic repulsions and exchange interactions exerted by the other electrons on this electron;

ii. As a result of the (assumed) cancellation of attractions from distant nuclei and repulsions from the electron clouds (i.e., the core, lone-pair, and valence orbitals) that surround these distant nuclei, the effect of  $V$  on any particular molecular orbital  $\psi_i$  depends primarily on the atomic charges and local bond polarities of the atoms over which  $\psi_i$  is delocalized.

As a result of these assumptions, qualitative molecular orbital models can be developed in which one assumes that each molecular orbital  $\psi_i$  obeys a one-electron Schrödinger equation

$$h \psi_i = \epsilon_i \psi_i$$

Here the orbital-level hamiltonian  $h$  contains the kinetic energy of motion of the electron and the potential  $V$  mentioned above:

$$[-\hbar^2/2m_e \nabla^2 + V] \psi_i = \epsilon_i \psi_i.$$

Expanding the  $\psi_i$  in the LCAO-MO manner, substituting this expansion into the above Schrödinger equation, multiplying on the left by  $\psi_i^*$ , and integrating over the coordinates of the electron generates the following orbital-level eigenvalue problem:

$$\sum_{\mu} \langle \psi_i | [-\hbar^2/2m_e \nabla^2 + V] | \mu \rangle C_{i\mu} = \epsilon_i \sum_{\mu} \langle \psi_i | \mu \rangle C_{i\mu}.$$

If the constituent atomic orbitals  $\{ \psi_{\mu} \}$  have been orthonormalized as discussed earlier in this chapter, the overlap integrals  $\langle \psi_i | \mu \rangle$  reduce to  $\delta_{i\mu}$ .

## II. Determining the Effective Potential $V$

In the most elementary models of orbital structure, the quantities that explicitly define the potential  $V$  are not computed from first principles as they are in so-called ab initio methods (see Section 6). Rather, either experimental data or results of ab initio calculations are used to determine the parameters in terms of which  $V$  is expressed. The resulting empirical or semi-empirical methods discussed below differ in the sophistication used to include electron-electron interactions as well as in the manner experimental data or ab initio computational results are used to specify  $V$ .

If experimental data is used to parameterize a semi-empirical model, then the model should not be extended beyond the level at which it has been parameterized. For example, experimental bond energies, excitation energies, and ionization energies may be used to determine molecular orbital energies which, in turn, are summed to compute total energies. In such a parameterization it would be incorrect to subsequently use these mos to form a wavefunction, as in Sections 3 and 6, that goes beyond the simple 'product of orbitals' description. To do so would be inconsistent because the more sophisticated wavefunction would duplicate what using the experimental data (which already contains mother nature's electronic correlations) to determine the parameters had accomplished.

Alternatively, if results of ab initio theory at the single-configuration orbital-product wavefunction level are used to define the parameters of a semi-empirical model, it would then be proper to use the semi-empirical orbitals in a subsequent higher-level treatment of electronic structure as done in Section 6.

### A. The Hückel Parameterization of $V$

In the most simplified embodiment of the above orbital-level model, the following additional approximations are introduced:

1. The diagonal values  $\langle \mu | -\hbar^2/2m_e \nabla^2 + V | \mu \rangle$ , which are usually denoted  $\epsilon_\mu$ , are taken to be equal to the energy of an electron in the atomic orbital  $\mu$  and, as such, are evaluated in terms of atomic ionization energies (IP's) and electron affinities (EA's):

$$\langle \mu | -\hbar^2/2m_e \nabla^2 + V | \mu \rangle = -IP_\mu,$$

for atomic orbitals that are occupied in the atom, and

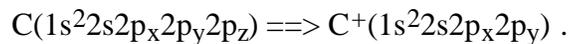
$$\langle \mu | -\hbar^2/2m_e \nabla^2 + V | \mu \rangle = -EA_\mu,$$

for atomic orbitals that are not occupied in the atom.

These approximations assume that contributions in  $V$  arising from coulombic attraction to nuclei other than the one on which  $\mu$  is located, and repulsions from the core, lone-pair, and valence electron clouds surrounding these other nuclei cancel to an extent that

$\langle \mu | V | \mu \rangle$  contains only potentials from the atom on which  $\mu$  sits.

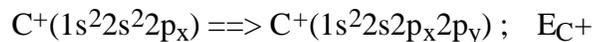
It should be noted that the IP's and EA's of valence-state orbitals are not identical to the experimentally measured IP's and EA's of the corresponding atom, but can be obtained from such information. For example, the 2p valence-state IP (VSIP) for a Carbon atom is the energy difference associated with the hypothetical process



If the energy differences for the "promotion" of C



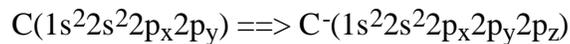
and for the promotion of  $C^+$



are known, the desired VSIP is given by:

$$IP_{2p_z} = IP_C + E_{C^+} - E_C .$$

The EA of the 2p orbital is obtained from the



energy gap, which means that  $EA_{2p_z} = EA_C$ . Some common IP's of valence 2p orbitals in eV are as follows: C (11.16), N (14.12), N<sup>+</sup> (28.71), O (17.70), O<sup>+</sup> (31.42), F<sup>+</sup> (37.28).

2. The off-diagonal elements  $\langle -\hbar^2/2m_e \nabla^2 + V | \mu \rangle$  are taken as zero if  $\mu$  and  $\nu$  belong to the same atom because the atomic orbitals are assumed to have been constructed to diagonalize the one-electron hamiltonian appropriate to an electron moving in that atom. They are set equal to a parameter denoted  $\mu_{\nu}$ , if  $\mu$  and  $\nu$  reside on neighboring atoms that are chemically bonded. If  $\mu$  and  $\nu$  reside on atoms that are not bonded neighbors, then the off-diagonal matrix element is set equal to zero.

3. The geometry dependence of the  $\mu_{\nu}$  parameters is often approximated by assuming that  $\mu_{\nu}$  is proportional to the overlap  $S_{\mu\nu}$  between the corresponding atomic orbitals:

$$\mu_{\nu} = \mu_{\nu}^0 S_{\mu\nu} .$$

Here  $\mu_{\nu}^0$  is a constant (having energy units) characteristic of the bonding interaction between  $\mu$  and  $\nu$ ; its value is usually determined by forcing the molecular orbital energies obtained from such a qualitative orbital treatment to yield experimentally correct ionization potentials, bond dissociation energies, or electronic transition energies.

The particular approach described thus far forms the basis of the so-called Hückel model. Its implementation requires knowledge of the atomic  $\mu_{\nu}$  and  $\mu_{\nu}^0$  values, which are eventually expressed in terms of experimental data, as well as a means of calculating the geometry dependence of the  $\mu_{\nu}$ 's (e.g., some method for computing overlap matrices  $S_{\mu\nu}$ ).

## B. The Extended Hückel Method

It is well known that bonding and antibonding orbitals are formed when a pair of atomic orbitals from neighboring atoms interact. The energy splitting between the bonding

and antibonding orbitals depends on the overlap between the pair of atomic orbitals. Also, the energy of the antibonding orbital lies higher above the arithmetic mean  $E_{ave} = E_A + E_B$  of the energies of the constituent atomic orbitals ( $E_A$  and  $E_B$ ) than the bonding orbital lies below  $E_{ave}$ . If overlap is ignored, as in conventional Hückel theory (except in parameterizing the geometry dependence of  $S_{\mu,\nu}$ ), the differential destabilization of antibonding orbitals compared to stabilization of bonding orbitals can not be accounted for.

By parameterizing the off-diagonal Hamiltonian matrix elements in the following overlap-dependent manner:

$$h_{\nu,\mu} = \langle \nu | -\hbar^2/2m_e \nabla^2 + V | \mu \rangle = 0.5 K (h_{\mu,\mu} + h_{\nu,\nu}) S_{\mu,\nu},$$

and explicitly treating the overlaps among the constituent atomic orbitals  $\{ \mu \}$  in solving the orbital-level Schrödinger equation

$$\mu \langle \nu | -\hbar^2/2m_e \nabla^2 + V | \mu \rangle C_{i\mu} = \epsilon_i \mu \langle \nu | \mu \rangle C_{i\mu},$$

Hoffmann introduced the so-called extended Hückel method. He found that a value for  $K=1.75$  gave optimal results when using Slater-type orbitals as a basis (and for calculating the  $S_{\mu,\nu}$ ). The diagonal  $h_{\mu,\mu}$  elements are given, as in the conventional Hückel method, in terms of valence-state IP's and EA's. Cusachs later proposed a variant of this parameterization of the off-diagonal elements:

$$h_{\nu,\mu} = 0.5 K (h_{\mu,\mu} + h_{\nu,\nu}) S_{\mu,\nu} (2 - |S_{\mu,\nu}|).$$

For first- and second-row atoms, the 1s or (2s, 2p) or (3s, 3p, 3d) valence-state ionization energies ( $\mu$ 's), the number of valence electrons (#Elec.) as well as the orbital exponents ( $e_s$ ,  $e_p$  and  $e_d$ ) of Slater-type orbitals used to calculate the overlap matrix elements  $S_{\mu,\nu}$ , corresponding are given below.

Atom	# Elec.	$e_s=e_p$	$e_d$	$s(\text{eV})$	$p(\text{eV})$	$d(\text{eV})$
H	1	1.3		-13.6		
Li	1	0.650		-5.4	-3.5	
Be	2	0.975		-10.0	-6.0	
B	3	1.300		-15.2	-8.5	
C	4	1.625		-21.4	-11.4	
N	5	1.950		-26.0	-13.4	
O	6	2.275		-32.3	-14.8	
F	7	2.425		-40.0	-18.1	
Na	1	0.733		-5.1	-3.0	
Mg	2	0.950		-9.0	-4.5	
Al	3	1.167		-12.3	-6.5	
Si	4	1.383	1.383	-17.3	-9.2	-6.0
P	5	1.600	1.400	-18.6	-14.0	-7.0
S	6	1.817	1.500	-20.0	-13.3	-8.0
Cl	7	2.033	2.033	-30.0	-15.0	-9.0

In the Hückel or extended Hückel methods no explicit reference is made to electron-electron interactions although such contributions are absorbed into the  $V$  potential, and hence into the  $\mu$  and  $\mu_s$  parameters of Hückel theory or the  $h_{\mu,\mu}$  and  $h_{\mu_s}$  parameters of extended Hückel theory. As electron density flows from one atom to another (due to electronegativity differences), the electron-electron repulsions in various atomic orbitals changes. To account for such charge-density-dependent coulombic energies, one must use an approach that includes explicit reference to inter-orbital coulomb and exchange interactions. There exists a large family of semi-empirical methods that permit explicit treatment of electronic interactions; some of the more commonly used approaches are discussed in Appendix F.