CHAPTER 11

MOLECULAR ORBITAL THEORY

Molecular orbital theory is a conceptual extension of the orbital model, which was so successfully applied to atomic structure. As was once playfuly remarked, “a molecue is nothing more than an atom with more nuclei.” This may be overly presumptuous, but we do attempt, as far as posssible, to exploit analogies with atomic structure. Our understanding of atomic orbitals began with the exact solutions of a prototype problem–the hydrogen atom. We will begin our study of homonuclear diatomic molecules beginning with another exactly solvable prototype, the hydrogen molecule-ion H_2^+.

The Hydrogen Molecule-Ion

The simplest conceivable molecule would be made of two protons and one electron, namely H_2^+. This species actually has a transient existence in electrical discharges through hydrogen gas and has been detected by mass spectrometry. It also has been detected in outer space. The Schrödinger equation for H_2^+ can be solved exactly within the Born-Oppenheimer approximation. For fixed internuclear distance R, this reduces to a problem of one electron in the field of two protons, designated A and B. We can write

$$\left\{-\frac{1}{2}\nabla^2 - \frac{1}{r_\mathrm{A}} - \frac{1}{r_\mathrm{B}} + \frac{1}{R}\right\}\psi(\mathbf{r}) = E\,\psi(\mathbf{r}) \tag{1}$$

where r_A and r_B are the distances from the electron to protons A and B, respectively. This equation was solved by Burrau

(1927), after separating the variables in prolate spheroidal coordinates. We will write down these coordinates but give only a pictorial account of the solutions. The three prolate spheroidal coordinates are designated μ, ν, ϕ. the first two are defined by

$$\mu = \frac{r_{\mathrm{A}} + r_{\mathrm{B}}}{R}, \qquad \nu = \frac{r_{\mathrm{A}} - r_{\mathrm{B}}}{R} \tag{2}$$

while ϕ is the angle of rotation about the internuclear axis. The surfaces of constant μ and ν are, respectively, confocal ellipsoids and hyperboloids of revolution with foci at A and B. The two-dimensional analog should be familiar from analytic geometry, an ellipse being the locus of points such that the sum of the distances to two foci is a constant. Analogously, a hyperbola is the locus whose *difference* is a constant. Fig. 1 shows several surfaces of constant μ, ν and ϕ. The ranges of the three coordinates are $\mu = \{1, \infty\}$, $\nu = \{-1, 1\}$, $\phi = \{0, 2\pi\}$. The prolate-spheroidal coordinate system conforms to the natural symmetry of the H_2^+ problem in the same way that spherical polar coordinates were the appropriate choice for the hydrogen atom.

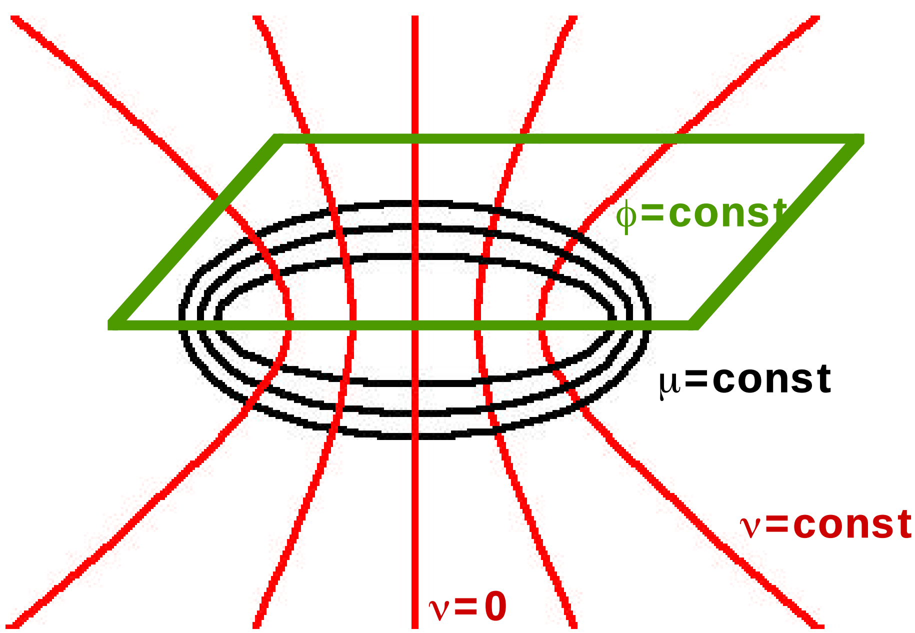

Figure 1. Prolate spheroidal coordinates.

The first few solutions of the H_2^+ Schrödinger equation are sketched in Fig. 2, roughly in order of increasing energy. The ϕ-dependence of the wavefunction is contained in a factor

$$\Phi(\phi) = e^{i\lambda\phi}, \qquad \lambda = 0, \pm 1, \pm 2 \ldots \tag{3}$$

which is identical to the ϕ-dependence in atomic orbitals. In fact, the quantum number λ represents the component of orbital angular momentum along the internuclear axis, the only component which has a definite value in systems with axial (cylindrical) symmetry. The quantum number λ determines the basic shape of a diatomic molecular orbital, in the same way that l did for an atomic orbital. An analogous code is used, σ for $\lambda = 0$, π for $\lambda = \pm 1$, δ for $\lambda = \pm 2$, and so on. We are already familiar with σ- and π-orbitals from valence-bond theory. A second classification of the H_2^+ eigenfunctions pertains to their symmetry with respect to inversion through the center of the molecule, also known as *parity*. If $\psi(-\mathbf{r}) = \psi(\mathbf{r})$, the function is classified *gerade* or even parity, and the orbital designation is given a subscript g, as in σ_g or π_g. If $\psi(-\mathbf{r}) = -\psi(\mathbf{r})$, the function is classified as *ungerade* or odd parity, and we write instead σ_u or π_u. Atomic orbitals can also be classified by inversion symmetry. However, all s and d AO's are g, while all p and f orbitals are u, so no subscript is necessary. The MO's of a given symmetry are numbered in order of increasing energy, for example $1\sigma_g$, $2\sigma_g$, $3\sigma_g$.

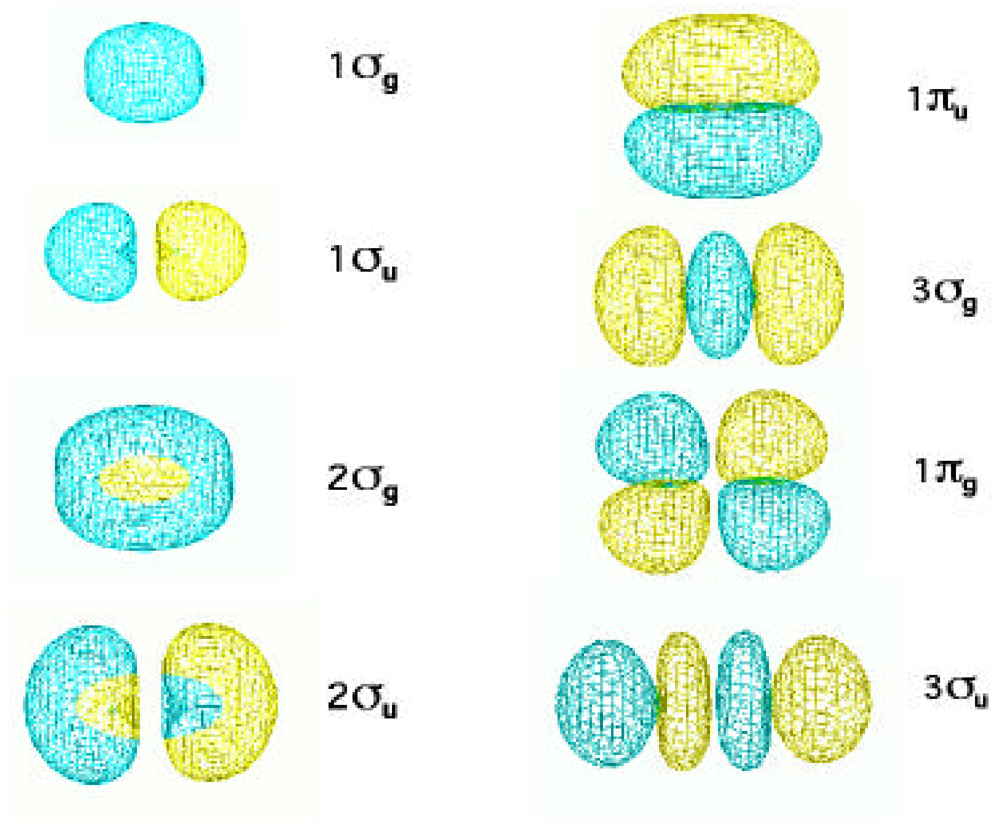

Figure 2. H_2^+ molecular orbitals.

The lowest-energy orbital, as we have come to expect, is nodeless. It obviously must have cylindrical symmetry ($\lambda = 0$) and inversion symmetry (g). It is designated $1\sigma_g$ since it is the first orbital of this classification. The next higher orbital has a nodal plane, with $\nu = 0$, perpendicular to the axis. This function still has cylindrical symmetry (σ) but now changes sign upon inversion (u). It is designated $1\sigma_u$, as the first orbital of this type. The next higher orbital has an inner ellipsiodal node. It has the same symmetry as the lowest orbital and is designated $2\sigma_g$. Next comes the $2\sigma_u$ orbital, with both planar and ellipsoidal nodes. Two degenerate π-orbitals come next, each with a nodal plane containing the internuclear axis, with ϕ=const. Their classification is $1\pi_u$. The second $1\pi_u$-

orbital, not shown in Fig. 2, has the same shape rotated by 90°. The $3\sigma_g$ orbital has two hyperbolic nodal surfaces, where $\nu = \pm$const. The $1\pi_g$, again doubly-degenerate, has two nodal planes, $\nu = 0$ and ϕ=const. Finally, the $3\sigma_u$, the last orbital we consider, has three nodal surfaces where ν=const.

An MO is classified as a *bonding orbital* if it promotes the bonding of the two atoms. Generally a bonding MO has a significant accumulation of electron charge in the region between the nuclei and thus reduces their mutual repulsion. The $1\sigma_g$, $2\sigma_g$, $1\pi_u$ and $3\sigma_g$ are evidently bonding orbitals. An MO which does *not* significantly contribute to nuclear shielding is classified as an *antibonding orbital*. The $1\sigma_u$, $2\sigma_u$, $1\pi_g$ and $3\sigma_u$ belong in this category. Often an antibonding MO is designated by σ^* or π^*.

The actual ground state of H_2^+ has the $1\sigma_g$ orbital occupied. The equilibrium internuclear distance R_e is 2.00 bohr and the binding energy D_e is 2.79 eV, which represents quite a strong chemical bond. The $1\sigma_u$ is a repulsive state and a transition from the ground state results in dissociation of the molecule.

The LCAO Approximation

In Fig. 3, the $1\sigma_g$ and $1\sigma_u$ orbitals are plotted as functions of z, along the internuclear axis. Both functions have cusps, discontinuities in slope, at the positions of the two nuclei A and B. The $1s$ orbitals of hydrogen atoms have the same cusps. The shape of the $1\sigma_g$ and $1\sigma_u$ suggests that they can be approximated by a sum and difference, respectively, of hydrogen $1s$ orbitals, such that

$$\psi(1\sigma_{g,u}) \approx \psi(1s_A) \pm \psi(1s_B) \tag{4}$$

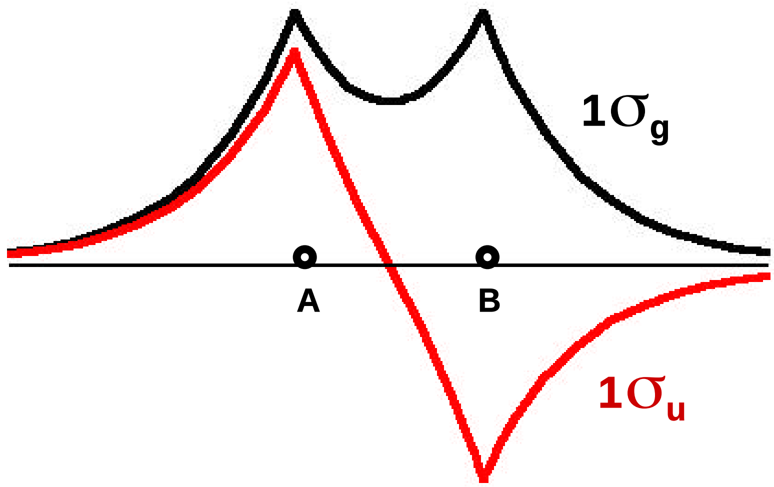

Figure 3. H_2^+ orbitals along internuclear axis.

This *linear combination of atomic orbitals* is the basis of the so-called LCAO approximation. The other orbitals pictured in Fig. 2 can likewise be approximated as follows:

$$\psi(2\sigma_{g,u}) \approx \psi(2s_A) \pm \psi(2s_B)$$
$$\psi(3\sigma_{g,u}) \approx \psi(2p\sigma_A) \pm \psi(2p\sigma_B)$$
$$\psi(1\pi_{u,g}) \approx \psi(2p\pi_A) \pm \psi(2p\pi_B) \qquad (5)$$

The $2p\sigma$ atomic orbital refers to $2p_z$, which has the axial symmetry of a σ-bond. Likewise $2p\pi$ refers to $2p_x$ or $2p_y$, which are positioned to form π-bonds. An alternative notation for diatomic molecular orbitals which specifies their atomic origin and bonding/antibonding character is shown here:

$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$3\sigma_g$	$3\sigma_u$	$1\pi_u$	$1\pi_g$
$\sigma 1s$	$\sigma^* 1s$	$\sigma 2s$	$\sigma^* 2s$	$\sigma 2p$	$\sigma^* 2p$	$\pi 2p$	$\pi^* 2p$

Almost all applications of molecular-orbital theory are based on the LCAO approach, since the exact H_2^+ functions are far too complicated to work with.

The relationship between MO's and their constituent AO's can be represented in a correlation diagram, show in Fig. 4.

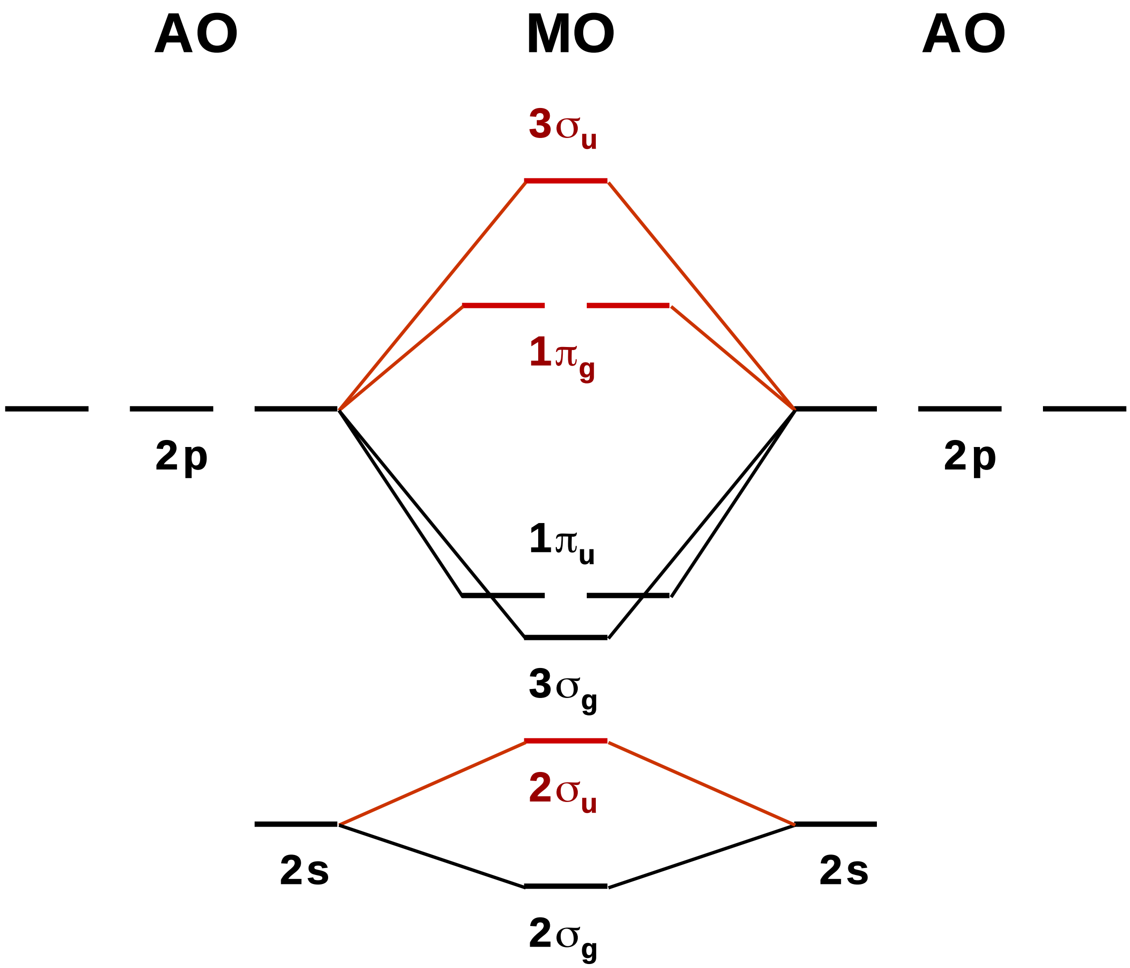

Figure 4. Molecular-orbital correlation diagram. The $1s \rightarrow 1\sigma_g$, $1\sigma_u$ is similar to the $2s$ correlations.

MO Theory of Homonuclear Diatomic Molecules

A sufficient number of orbitals is available for the *Aufbau* of the ground states of all homonuclear diatomic species from H_2 to Ne_2. Table 1 summarizes the results. The most likely order in which the MO's are filled is given by

$$1\sigma_g < 1\sigma_u < 2\sigma_g < 2\sigma_u < 3\sigma_g \sim 1\pi_u < 1\pi_g < 3\sigma_u$$

The relative order of $3\sigma_g$ and $1\pi_u$ depends on which other MO's are occupied, much like the situation involving the $4s$ and $3d$ atomic orbitals. The results of photoelectron spectroscopy indicate that $1\pi_u$ is lower up to and including N_2, but $3\sigma_g$ is lower thereafter.

The term symbol Σ, Π, $\Delta\ldots$, analogous to the atomic S, P, D... symbolizes the axial component of the total orbital angular momentum. When a π-shell is filled (4 electrons) or half-filled (2 electrons), the orbital angular momentum cancels to zero and we find a Σ term. The spin multiplicity is completely analogous to the atomic case. The total parity is again designated by a subscript g or u. Since the many electron wavefunction is made up of products of individual MO's, the total parity is odd only if the molecule contains an *odd* number of u orbitals. Thus a σ_u^2 or a π_u^2 subshell transforms like g.

For Σ terms, a $\pm$ superscript denotes the sign change of the wavefunction under a reflection in a plane containing the internuclear axis. This is equivalent to a sign change in the variable $\phi \to -\phi$. This symmetry is needed when we deal with spectroscopic selection rules. In a spin-paired π_u^2 subshell the triplet spin function is symmetric so that the orbital factor must be antisymmetric, of the form

$$\frac{1}{\sqrt{2}}\Big(\pi_x(1)\pi_y(2) - \pi_y(1)\pi_x(2)\Big) \tag{6}$$

This will change sign under the reflection, since $x \to x$ but $y \to -y$. We need only remember that a π_u^2 subshell will give the term symbol ${}^3\Sigma_g^-$.

The net bonding effect of the occupied MO's is determined by the *bond order*, half the excess of the number bonding minus the number antibonding. This definition brings the MO results into correspondence with the Lewis (or valence-bond) concept of single, double and triple bonds. It is also possible in MO theory to have a bond order of 1/2, for example, in H_2^+ which is held together by a single bonding orbital. A bond order of zero generally indicates no stable chemical bond, although helium and neon atoms can still form clusters held together by much weaker van der Waals forces. Molecular-orbital theory successfully accounts for the transient stability of a ${}^3\Sigma_u^+$ excited state of He_2, in which one of the antibonding electrons is promoted to an excited bonding orbital. This species has a lifetime of about 10^{-4} sec, until it emits a photon and falls back into the unstable ground state. Another successful prediction of MO theory concerns the relative binding energy of the positive ions N_2^+ and O_2^+, compared to the neutral molecules. Ionization weakens the N-N bond since a bonding electron is lost, but it strengthens the O-O bond since an antibonding electron is lost.

One of the earliest triumphs of molecular orbital theory was the prediction that the oxygen molecule is paramagnetic. Fig. 5 shows that liquid O_2 is a magnetic substance, attracted to the region between the poles of a permanent magnet. The paramagnetism arises from the half-filled $1\pi_g^2$ subshell. According to Hund's rules the two electrons singly occupy the two degenerate $1\pi_g$ orbitals with their spins aligned *parallel*. The term symbol is ${}^3\Sigma_g^-$ and the molecule thus has a nonzero spin angular momentum and a net magnetic moment, which is attracted to an external magnetic field. Linus Pauling invented the paramagnetic oxygen analyzer, which is extensively used in medical technology.

Figure 5. Demonstration showing blue liquid O_2 attracted to the poles of a permanent magnet. From http://jchemed.chem.wisc.edu/jcesoft/cca/CCA2/STHTM/PARANIO/9.HTM

Variational Computation of Molecular Orbitals

Thus far we have approached MO theory from a mainly descriptive point of view. To begin a more quantitative treatment, recall the LCAO approximation to the H_2^+ ground state, Eq (4), which can be written

$$\psi = c_A \, \psi_A + c_B \, \psi_B \tag{7}$$

Using this as a trial function in the variational principle (4.53), we have

$$E(c_A, c_B) = \frac{\int \psi \, \hat{H} \, \psi \, d\tau}{\int \psi^2 \, d\tau} \tag{8}$$

where $\hat{H}$ is the Hamiltonian from Eq (1). In fact, these equations can be applied more generally to construct *any* molecular orbital, not just solutions for H_2^+. In the general case,

$\hat{H}$ will represent an effective one-electron Hamiltonian determined by the molecular environment of a given orbital. The energy expression involves some complicated integrals, but can be simplified somewhat by expressing it in a standard form. Hamiltonian matrix elements are defined by

$$H_{AA} = \int \psi_A \, \hat{H} \, \psi_A \, d\tau$$

$$H_{BB} = \int \psi_B \, \hat{H} \, \psi_B \, d\tau$$

$$H_{AB} = H_{BA} = \int \psi_A \, \hat{H} \, \psi_B \, d\tau \tag{9}$$

while the overlap integral is given by

$$S_{AB} = \int \psi_A \, \psi_B \, d\tau \tag{10}$$

Presuming the functions ψ_A and ψ_B to be normalized, the variational energy (8) reduces to

$$E(c_A, c_B) = \frac{c_A^2 \, H_{AA} + 2c_A c_B \, H_{AB} + c_B^2 \, H_{BB}}{c_A^2 + 2c_A c_B \, S_{AB} + c_B^2} \tag{11}$$

To optimize the MO, we find the minimum of E wrt variation in c_A and c_B, as determined by the two conditions

$$\frac{\partial E}{\partial c_A} = 0, \qquad \frac{\partial E}{\partial c_B} = 0 \tag{12}$$

The result is a *secular equation* determining two values of the energy:

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & H_{BB} - E \end{vmatrix} = 0 \tag{13}$$

For the case of a homonuclear diatomic molecule, for example H_2^+, the two Hamiltonian matrix elements H_{AA} and H_{BB} are equal, say to α. Setting $H_{AB} = \beta$ and $S_{AB} = S$, the secular equation reduces to

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = (\alpha - E)^2 - (\beta - ES)^2 = 0 \tag{14}$$

with the two roots

$$E^{\pm} = \frac{\alpha \pm \beta}{1 \pm S} \tag{15}$$

The calculated integrals α and β are usually negative, thus for the bonding orbital

$$E^{+} = \frac{\alpha + \beta}{1 + S} \qquad \text{(bonding)} \tag{16}$$

while for the antibonding orbital

$$E^{-} = \frac{\alpha - \beta}{1 - S} \qquad \text{(antibonding)} \tag{17}$$

Note that $(E^{-} - \alpha) > (\alpha - E^{+})$, thus the energy increase associated with antibonding is slightly greater than the energy decrease for bonding.