Chapter 3

Review of Molecular Orbital and Configuration-Mixing Ideas

Chapters 1 and 2 describe what a potential surface is and how a reaction path moves along the surface. In this chapter we discuss briefly how to obtain such surfaces. Knowledge of the procedure is important because it relates to the actual *numerical* evaluation of potential energy surfaces and, furthermore, because it makes one think about those electronic configurations that are likely to be important in describing chemical reactions. These ideas are presented more thoroughly in Appendix A.

Consider again the hypothetical dissociation of H_2O. At its equilibrium geometry this molecule has molecular orbitals with a_1, b_2, and b_1 symmetries. The $1s_O$, σ_{OH}, σ_{OH}^*, and lone pair orbitals in the molecular plane all have a_1 symmetry. Another σ_{OH} and σ_{OH}^* orbital pair has b_2 symmetry, and the p_O orbital directed perpendicular to the molecular plane has b_1 symmetry. As we saw above, the $\sigma_{OH} \rightarrow \sigma_{OH}^*$, $a_1 \rightarrow b_2$, or $b_2 \rightarrow a_1$ orbital excitations of H_2O may play important roles in the asymmetric dissociation to give OH + H. Hence, we expect that the $1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2$, $1a_1^2 2a_1^2 1b_2 3a_1^2 1b_1^2 4a_1$, and $1a_1^2 2a_1 1b_2^2 3a_1^2 1b_1^2 2b_2$ configurations should be important in describing this fragmentation. Although the orbitals having a_1 and b_2 symmetry can only be labeled as a' once the C_{2v} symmetry is broken (b_1 becomes a''), we can immediately tell that the first configuration above cannot possibly describe OH + H because all orbitals are doubly occupied, whereas the radical fragments OH + H have two singly occupied orbitals. The other two configurations do have the correct orbital occupancy to describe OH + H. However, at the equilibrium geometry of H_2O, this first configuration dominates the electronic wavefunction because it has two pairs of bonding electrons. Hence, as H_2O fragments, a substantial change in the electronic structure is expected to occur when moving from one dominant configuration to another.

Before proceeding further to specific examples, one must learn how to construct wavefunctions whose energies give us the desired potential energy surfaces. In the conventional molecular orbital model of electronic structure (Cook, 1978; Pilar, 1968) there are three levels of analysis of wavefunctions:

the orbital, configuration, and state-function levels. The electronic wavefunction of a given state is usually expressed as a linear combination of configurations, each of which is expressed in terms of Slater determinants over molecular orbitals (see Appendix A). In some circumstances, the state wavefunctions of the reactants and products may be smoothly connected (correlated) by way of the reaction coordinate, though the orbitals or orbital occupancies (configurations) of reactants and products may not correlate smoothly. Recall that we are directed to correlate or to connect orbitals, configurations, or states by the observation that Q_r is totally symmetric (except where ψ_0 is degenerate or when second-order Jahn-Teller effects dominate), and hence, movements along Q_r cannot change the symmetry of ψ_0.

3.1 Molecular Orbitals: Symmetry of the Fock Operator

Let us recall from Chapter 1 how Hartree-Fock (HF) molecular orbitals, which are probably the most widely used orbitals, are obtained. (For those readers who wish to review the fundamental steps involved in *ab initio* molecular orbital calculations, a brief overview is provided in Appendix A.) A Fock operator can be constructed from a particular orbital occupancy that is assumed to dominate the true wavefunction at the geometry at which one is located [we now write the operators in atomic units as in Pilar (1968)]:

$$F = -\frac{1}{2}\nabla_r^2 - \sum_a \frac{Z_a}{|\mathbf{r} - \mathbf{R}_a|} + \sum_\mu \int \phi_\mu^*(\mathbf{r}_2) \frac{1 - P_{12}}{|\mathbf{r} - \mathbf{r}_2|} \phi_\mu(\mathbf{r}_2) \, d\mathbf{r}_2 \qquad (3.1)$$

in which μ extends over all of the spin orbitals that appear in the presumed dominant electronic configuration. Clearly, the first two terms in F commute with the symmetry operations of the molecule because they depend on $\mathbf{R}_a$ in a symmetrical manner. If the ϕ_μ are nondegenerate and symmetry-adapted (this will often be true in so-called symmetry-restricted HF calculations), $\phi_\mu^*(\mathbf{r}_2)\phi_\mu(\mathbf{r}_2)$ is totally symmetric: therefore, even the coulomb part of the last term in F will commute with all symmetry operations. To show that the exchange part is also symmetric is more difficult.

Consider the commutator of the exchange operator K with any symmetry operation σ

$$[\sigma, K]\phi(\mathbf{r}) = \sigma(\mathbf{r}) \int K(\mathbf{r}, \mathbf{r}_2)\phi(\mathbf{r}_2) \, d\mathbf{r}_2 - \int K(\mathbf{r}, \mathbf{r}_2)\sigma(\mathbf{r}_2)\phi(\mathbf{r}_2) \, d\mathbf{r}_2 \qquad (3.2)$$

in which the kernel $K(\mathbf{r}, \mathbf{r}_2)$ is defined as

Now using the fact that symmetry operators are unitary ($\sigma^+ = \sigma^{-1}$), we obtain

$$\int K(\mathbf{r}, \mathbf{r}_2)\sigma(\mathbf{r}_2)\phi(\mathbf{r}_2)\, d\mathbf{r}_2 = \int [\sigma^{-1}(\mathbf{r}_2)K(\mathbf{r}, \mathbf{r}_2)]\phi(\mathbf{r}_2)\, d\mathbf{r}_2 \tag{3.4}$$

and hence

$$[\sigma, K]\phi(\mathbf{r}) = \int [\sigma(\mathbf{r}) - \sigma^{-1}(\mathbf{r}_2)]K(\mathbf{r}, \mathbf{r}_2)\phi(\mathbf{r}_2)\, d\mathbf{r}_2. \tag{3.5}$$

From equation 3.3 it should be clear that $K(\mathbf{r}, \mathbf{r}_2)$ contains $\mathbf{r}$ and $\mathbf{r}_2$ in a symmetrical manner. Moreover, for abelian point groups (those with no degenerate representations; see Cotton, 1963), $\sigma^{-1} = \sigma$. Therefore, $\sigma(\mathbf{r}) - \sigma^{-1}(\mathbf{r}_2)$ operating on $K(\mathbf{r}, \mathbf{r}_2)$ would give zero, and the commutator $[\sigma, K]$ vanishes. For nonabelian groups σ^{-1} is no longer σ. However, if the sum over occupied spin orbitals $\{\sigma_\mu\}$ has equal occupancy for sets of (degenerate) orbitals that are related to one another by symmetry (i.e., $\sigma\phi_\mu = \phi_{\mu'}$), then the overall sum arising in $\sigma(\mathbf{r})K(\mathbf{r}, \mathbf{r}_2)$ will be the same (although not term-by-term) as that in $\sigma^{-1}(\mathbf{r}_2)K(\mathbf{r}, \mathbf{r}_2)$ and again $[\sigma, K] = 0$. The main point is that $[\sigma, F] = 0$ implies that the eigenfunctions of F, which are the Hartree-Fock molecular orbitals, will also be eigenfunctions of σ and, hence, will be symmetry adapted. As a result, all of the rules for correlating states (ψ_0, ψ_k) that are discussed above immediately apply also to these Hartree-Fock orbitals since F has all of the same symmetry as h_e. This means that symmetry conservation applies to orbitals and to total wavefunctions.

Now let us review how the Hartree-Fock equations are solved for the molecular orbitals. First, an atomic-orbital basis set consisting most likely of orbitals of the Slater ($r^{n-1}e^{-\zeta r}Y_{lm}$) or the Gaussian ($x^a y^b z^c e^{-\alpha r^2}$) type is chosen. These basis functions generally are located on each of the nuclei in the molecule being studied. Minimal, double-zeta, or extended bases including polarization functions are common choices. Tabulations of good basis sets are available for the ground-state normal chemical-valence states of most first- and second-row atoms as they occur in molecules. For example, good Gaussian bases are given by Huzinaga (1965) and by Dunning (1970, 1971). If the state of interest has unusual behavior (i.e., ionic states, Rydberg states, or many low-lying excited states), it is necessary to explore the effect of adding more and more atomic basis functions. The importance of this basis-set selection step cannot be overemphasized; without a good basis, one has little chance of achieving meaningful results.

Once an atomic basis is obtained, all one-electron (kinetic energy, overlap, and electron-nuclear interactions) and two electron ($\langle ab|cd \rangle$) integrals are evaluated (with a computer). At this stage in the calculation ...

symmetry-adapted functions $\{X_b\}$ and to generate the one- and two-electron integrals over these symmetry functions.

The matrix elements of the Fock operator are then constructed (Roothaan, 1951) within the symmetry-adapted basis. This is done symmetry-by-symmetry since F is block-diagonal. To construct each block of F *all* (i.e., those belonging to all symmetries) of the *occupied* spin orbitals $\{\phi_\mu\}$ must be available. However, these Hartree-Fock molecular orbitals are not yet known, so an iteration process is used (Cook, 1978). With the aid of a computer one can guess the form of the occupied molecular orbitals; this is done by specifying the expansion coefficients $\{C_{\mu b}\}$ of ϕ_μ in the symmetry-adapted basis:

$$\phi_\mu = \sum_b X_b C_{\mu b}. \tag{3.6}$$

The guess can be made either on chemical grounds (e.g., $\phi_1 = 1s_0$ for H_2O) or, as in most computer programs, by first solving the equation

$$F\phi_\mu = \epsilon_\mu \phi_\mu \tag{3.7}$$

ignoring the coulomb and exchange contributions to F. The orbitals that result from the latter procedure are usually not chemically reasonable because they respond to only the isolated nuclei—no electron repulsion (screening) effects were included. Nevertheless, these initial orbitals can be used to construct a new F operator whose matrix elements (in the symmetry-adapted basis) are defined by

$$F_{cb} = \left\langle X_c \left| -\frac{1}{2}\nabla_r^2 - \sum_a \frac{Z_a}{|\mathbf{r} - \mathbf{R}_a|} \right| X_b \right\rangle$$

$$+ \sum_\mu \sum_{d,f} C_{\mu d} C_{\mu f} [\langle X_c X_d | X_b X_f \rangle - \langle X_c X_d | X_f X_b \rangle \delta_{s_\mu s_c}], \tag{3.8}$$

(Roothaan, 1951) in which μ runs over the occupied *spin* orbitals and $\delta_{s_\mu s_c}$ indicates that the spin (α, β) of ϕ_μ must match that of X_c for the exchange term to contribute. The form of the Fock matrix given in equation 3.8 is appropriate for performing a spin-unrestricted Hartree-Fock (UHF) calculation. There are two different F matrices for the α and β spin orbitals. Therefore, the molecular orbitals computed for α and β spin generally differ. Numerous techniques exist that attempt to overcome this somewhat inconvenient fact (different orbitals for different spins), so a single Fock matrix can be used to generate spatial orbitals that are appropriate for both α and β spins. We will

of their solutions for special cases. These are treated in a clear manner by Cook (1978).

Having formed $\mathbf{F}$ (using the crude $\{C_{\mu,d}\}$), we solve

$$\mathbf{F}\mathbf{C}_\mu = \epsilon_\mu \mathbf{S}\mathbf{C}_\mu. \tag{3.9}$$

in which $\mathbf{S}$ is the overlap matrix, for a new set of $\{\mathbf{C}_\mu\}$ coefficients that are then used to form a new $\mathbf{F}$ and, subsequently, a new set $\{\mathbf{C}_\mu\}$. This iterative self-consistent-field (SCF) procedure is continued until the $\{\mathbf{C}_\mu\}$ no longer vary from iteration to iteration.

The results of such an SCF calculation are a set of occupied and unoccupied (virtual) orbitals $\{\phi_\mu\}$ and orbital energies $\{\epsilon_\mu\}$. For example, for a double-zeta basis of H_2O, there are fourteen χ_c functions (eight s and six p). Hence, $\mathbf{F}$ is a 14×14 matrix having fourteen eigenvalues and fourteen eigenvectors. Of the fourteen SCF orbitals, only five are occupied in the ground state $(1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2)$; nine are virtual or unoccupied orbitals. Keep in mind that the words *occupied* and *virtual* only refer to the occupancy which *you* guessed to start the SCF procedure. We saw earlier that as H_2O is pulled apart to give OH + H, the occupancy changes. Thus, for OH + H it would be more natural to use the "open shell" configuration to define occupancy.

3.2. When Can Orbital Energies be Added?

Before closing this discussion of orbitals, let us review (Cook, 1978; Pilar, 1968) the expression for the total electronic energy E_{HF} in the Hartree-Fock approximation:

$$E_{HF} = \sum_\mu \epsilon_\mu - \frac{1}{2}\sum_{\mu,\nu}\langle \mu\nu | \widetilde{\mu\nu}\rangle, \tag{3.10}$$

in which μ and ν run over the occupied spin orbitals and $\langle \mu\nu | \widetilde{\mu\nu}\rangle$ represents the coulomb interaction integrals minus the exchange integrals (Cook, 1978) over the Hartree-Fock molecular orbitals. It is important to note that the sum of the occupied orbital energies does *not* give E_{HF}, because, through F, each ϵ_μ contains interactions between ϕ_μ and *all* other ϕ_ν orbitals. Hence, the sum $\Sigma_\mu \epsilon_\mu$ doubly counts the electron-electron interactions. As a result, the second term in equation 3.10 is needed. Although $E_{HF} + \frac{1}{2}\Sigma_{a,b}(Z_a Z_b / R_{ab})$ is not equal to the sum of orbital energies plus the nuclear repulsion energies, the *changes* in this energy accompanying molecular distortion can, for *neutral* molecules, often be approximated well by the changes in $\Sigma_\mu \epsilon_\mu$. This approximation works

on different centers. That is, the *subtracted* electron-electron repulsions involving orbitals on different atoms cancel the repulsions of the corresponding nuclei (at least at large bond length). This cancellation does not occur for ions because there are "extra" or "missing" electrons whose repulsions are not cancelled. One more thing must be stressed at this time: even though the shape of the HF-level potential energy surface might be well represented by the shape of $\Sigma_\mu \epsilon_\mu$, the entire Hartree-Fock picture rests on a guess of *the* dominant electronic configuration occupancy *and* the assumption that ψ_0 and E_0 could be accurately represented by a single determinant wavefunction. If the guess is wrong, or if the correct electronic wavefunction requires more than one configuration to describe reality qualitatively (e.g., in H_2O as it fragments into $OH + H$), the shape of the Hartree-Fock surface will probably not be correct.

3.3. Configuration Construction and Mixing

In the preceding sections the means by which molecular orbitals are defined, calculated, and correlated by symmetry along the reaction coordinate have been described. This information is not, however, sufficient to allow a statement about how the *wavefunctions* are to be symmetry-correlated—other information is needed about how the orbitals are occupied in the state wavefunction ψ_0. This amounts to specifying the electronic configurations that are important in describing ψ_0 throughout the entire range of the reaction coordinate. Many sophisticated *ab initio* computer programs (Shavitt, 1978) have configuration-selection subroutines that choose those configurations of the proper symmetry whose energies (expectation values) are low in order to represent the ground or low-lying excited states accurately.

In most chemical reactions, by using information about the orbital energy variations and estimates of electron repulsion energies, we can guess those few configurations likely to dominate ψ_0. For the asymmetric fragmentation of H_2O, we expect both the $(1-4)(a')^2(1a'')^2$ and the $(3a')^2 \rightarrow 3a'5a'$ configurations to be important. The former configuration dominates ψ_0 near the equilibrium geometry of H_2O, whereas the latter dominates for $OH + H$. For the $OH + H$ geometry the $(1-4)(a')^2(1a'')^2$ configuration corresponds to $OH^- + H^+$. At the equilibrium geometry of H_2O, the $(3a')^2 \rightarrow 3a'5a'$ configuration describes a singly excited state of H_2O that has one OH bond broken (i.e., $\sigma_{OH}^2 \sigma_{OH'} \sigma_{OH'}^*$).

In general, we first consider how the orbitals of the reactants and products symmetry-correlate along the reaction coordinate. This is done by simply ordering the orbitals of reactants and products by their energies and by connecting the orbitals of the same symmetry by "correlation lines." Then we attempt to write down all occupancies (configurations) of these orbitals that are

electronic energy. From this list of dominant configurations, a qualitative diagram can be drawn displaying their energies (expectation values) as functions of the reaction coordinate. This diagram is referred to as a configuration-correlation diagram (CCD); it is the configuration-space analog of the orbital-correlation diagram (OCD).

The step of constructing the configuration-correlation diagram brings us closer to the goal of predicting how the total electronic energy varies along the reaction coordinate. However, we still must consider the fact that configurations of the same symmetry must be combined (in the configuration interaction step) to give the correct electronic wave functions. In quantitative calculations done on modern computers, the Slater-Condon rules (see Condon and Shortley, 1957, or Cook, 1978) are used to evaluate the Hamiltonian matrix elements

$$H_{ij} = \langle \Phi_i | H | \Phi_j \rangle \tag{3.11}$$

between the important configurations $\{\Phi_i\}$ whose overall space and spin symmetry is correct. The eigenvalues of the H matrix then give the *total* electronic energies of those states that arise from the configurations $\{\Phi_i\}$. These total state energies, when plotted as functions of the reaction coordinate, generate the state-correlation diagram (SCD), which finally allows something to be said about the shape of the potential energy surfaces along the reaction coordinate—in particular, whether large or small reaction barriers are expected.

If *ab initio* calculations are not being done on a computer, a qualitatively correct picture of the state-correlation diagram can still be achieved by using the configuration-correlation diagram. The reasoning is that, when the energies of two configurations *cross* on the configuration-correlation diagram, the states that arise from the mixing of these two configurations will have energies that aviod one another because of configuration interaction (see Shavitt, 1977). Thus, simply by converting all of the crossings that occur in the configuration-correlation diagram to avoided crossings, an approximate state-correlation diagram is obtained.

Before considering how a state-correlation diagram for a chemical reaction is used, it is valuable to review the essential characteristics of the reaction coordinate. It is a totally symmetric motion on the potential surface, except when ψ_0 is degenerate or when low-lying excited states of another symmetry are present that can couple ($\langle \psi_k | \partial V / \partial Q | \psi_0 \rangle$) to ψ_0, in which cases the reaction coordinate becomes symmetric once the symmetry is lowered. The important point is that, by labeling the wavefunctions with *only* those symmetry elements that are preserved along the entire reaction path, the reaction coordinate is *always* symmetric and, hence, the symmetry of ψ_0 remains constant. This means that whenever we guess a reaction coordinate, the symmetries of the orbitals, configurations, and states should be labeled using only those sym-

sidering the C_{2v} insertion of an atom (say Mg) into the bond of H_2, only the elements of the C_{2v} point group must be used, which means that the ^1S, $^3P_{2,1,0}$, and ^1P states of Mg must be labeled according to how they transform under C_{2v}. Being able to do this is crucial to the use of symmetry correlation concepts as a tool for understanding reactivity.

3.4. Approximate Symmetry

In this section one more point concerning the preserved symmetry elements will be made. The symmetries of the active orbitals (those orbitals involved in the bond-breaking and bond-forming process) are determined by the potential energy field influencing the electrons in these orbitals. This field depends in turn upon how the nuclei and the passive-occupied orbitals are arranged in space. However, those nuclei and passive orbitals that are spatially far from an active orbital will have little influence on the potential field at this active site. As a result, the shape (nodal characteristics and symmetry) of this active orbital will be little influenced by nuclei and orbitals that are far from it. For example, we do not expect the carbonyl π and π^* orbitals of H_2CO (formaldehyde) to be qualitatively different from those of $(H_3C)_2CO$ (acetone) or even $H_3C(CO)H$ (acetaldehyde). In fact, we expect the π and π^* orbitals to maintain their odd character under reflection through the plane containing the C(CO)H group to a very high extent. Certainly the *quantitative* nature of the π orbital, which is more highly localized on the oxygen, and the π^* orbital, which is polarized toward the carbon, will be differently influenced by substituents. However, the basic orbital *nodal characteristics*, which is really the most important aspect of symmetry used, remains largely intact. Thus, approximate *local* symmetry is almost as good as true overall molecular symmetry.