The Salem-Klopman Equation

Using perturbation theory, Klopman[230] and Salem[241] derived an expression for the energy (ΔE) gained and lost when the orbitals of one reactant overlap with those of another. Their equation has the following form:

$$\Delta E = \pm \underbrace{\sum_{ab}(q_a + q_b)\beta_{ab}S_{ab}}_{\text{first term}} + \underbrace{\sum_{k<l}\frac{Q_kQ_l}{\varepsilon R_{kl}}}_{\text{second term}} + \underbrace{\sum_{r}^{\text{occ.}}\sum_{s}^{\text{unocc.}}\pm\sum_{s}^{\text{occ.}}\sum_{r}^{\text{unocc.}}\frac{2(\Sigma_{ab}c_{ra}c_{sb}\beta_{ab})^2}{E_r \pm E_s}}_{\text{third term}} \qquad 3.13$$

q_a and q_b are the electron populations (often loosely called electron densities) in the atomic orbitals a and b,
β and S are the resonance and overlap integrals from Equations 1.5 and 1.7,
Q_k and Q_l are the total charges on atoms k and l,
ε is the local dielectric constant,
R_{kl} is the distance between the atoms k and l,
c_{ra} is the coefficient of atomic orbital a in molecular orbital r, where r refers to the molecular orbitals on one molecule and s refers to those on the other
E_r is the energy of molecular orbital r and
E_s is the energy of molecular orbital s.

The derivation of this equation involves, as one might expect, many approximations and assumptions, which we shall not go into. It is valid only because S will always be small for the overlap of orbitals of p character. The integral S has the form shown in Figs. 1.13 and 1.23: for a C C bond being formed by p orbitals overlapping in a σ sense, it reaches a maximum value of 0.27 at a distance of 1.74 Å and then rapidly falls off. Thus, any
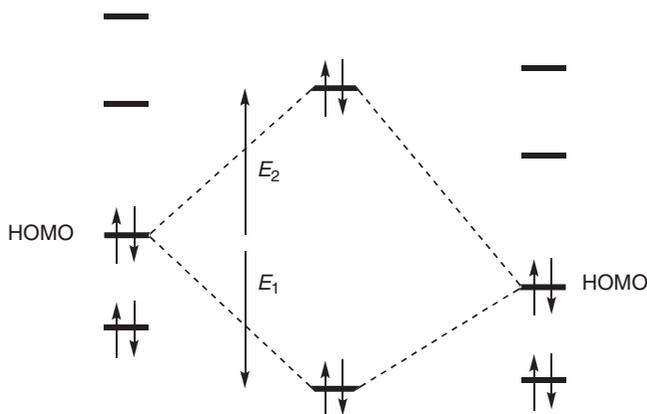

Fig. 3.5 The interaction of the HOMO of one molecule with the HOMO of another

reasonable estimate of the distance apart of the atoms in the transition structure cannot fail to make S small. The integral β is roughly proportional to S, so the third term of Equation 3.13 above is the second-order term. With S always small, the higher-order terms are naturally very small indeed, and we neglect them. This is why a *second-order* perturbation treatment works. Let us now look at each of the three terms of Equation 3.13.

(i) *The first term* is the first-order, closed-shell repulsion term, and comes from the interaction of the filled orbitals of the one molecule with the filled orbitals of the other (as in Fig. 3.5). It is always antibonding in effect.

   This term will usually be large relative to the other two terms   it represents a good deal of the enthalpy of activation for many reactions. Apart from this, its main effect on chemical reactivity can probably be identified with the well known observation that, on the whole, the smaller the number of bonds to be made or broken at a time, in a chemical reaction, the better. If a reaction can take place in several, not too difficult stages, it will probably go in stages, rather than in one concerted process. The concerted process, whatever it is, must involve the making (or breaking) of more than one bond, and for every bond to be made (or broken), we must have an energy-raising contribution from the first term of Equation 3.13. Another important reason for the general preference for stepwise reactions is, of course, the much more favourable entropy term when a relatively small number of events happen at once.

   The interaction of a filled orbital with a filled orbital, as in Fig. 3.5, leads to a small antibonding effect, but there are *many* filled orbitals interacting strongly with *many* filled orbitals, and the total effect is the sum of many small ones. The overall effect of the first term of Equation 3.13 is, therefore, rather unpredictable, but it seems that adding up a lot of small items very often averages out the total effect. Thus, if a molecule can be attacked at two possible sites, we can hope that the first term will be nearly the same for attack at each site. Similarly, if there are two possible orientations in a cycloaddition, the first term may not be very different in the two orientations. This appears not to be the case for the other two terms, and it is therefore with them that we shall mainly be concerned in explaining differential reactivity of this kind. In practice it is not obvious that we can rely on a benign first term, but we often do, and we seem to be able to get away with it. We shall, therefore, be largely ignoring the first term from now on, because frontier orbital theory is mainly used to explain features of *differential* reactivity. We are on weak ground in doing so, and we should not forget it.

(ii) *The second term* is simply the Coulombic repulsion or attraction. This term, which contains the products of the total charges, Q, on each atom, is obviously important when ions or polar molecules are reacting together. Its contribution to the energy is inversely proportional both to the dielectric constant and to the distance apart of the two charges.

(iii) *The third term* represents the interaction of all the filled orbitals with all the unfilled of correct symmetry (Fig. 3.6). It is the second-order perturbation term, and is only true if $E_r \neq E_s$. (When $E_r = E_s$, the interaction is better described in charge-transfer terms, and the perturbation is then first order of the form $\Sigma_{ab}2c_{ra}c_{sb}\beta_{ab}$.) Here we can see again, this time in simple arithmetical terms, that it is the HOMO and the LUMO which are most important   they are the orbitals with the smallest value of $E_r - E_s$, and hence they make a disproportionately large contribution to the third term of Equation 3.13.

In summary:

As two molecules collide, three major forces operate.

 (i) *The occupied orbitals of one repel the occupied orbitals of the other.*
(ii) *Any positive charge on one attracts any negative charge on the other (and repels any positive).*
(iii) *The occupied orbitals (especially the HOMOs) of each interact with the unoccupied orbitals (especially the LUMOs) of the other, causing an attraction between the molecules.*