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Intermolecular Orbital Theory of the Interaction between Conjugated Systems. I. General Theory[1]

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Abstract: The interaction between two conjugated molecules with overlapping p orbitals is described in terms of the π electrons of the separate systems. New (*inter*molecular) orbitals are built out of the interacting molecular orbitals. The interaction energy is expanded in terms of the small overlap S, and analytical energy expressions are obtained in terms of $S_{rr'}$ between pairs of atoms r, r' and of an interaction integral $\eta_{rr'}$. For molecules in their ground state, the total energy of interaction is the sum of a repulsion energy due to the "exclusion shell" around each carbon atom and an attractive energy due to the mixing between occupied orbitals on one molecule and unoccupied orbitals on the other. Both of these terms are second order in the overlap. If one molecule is excited, an additional, first-order energy arises from the stabilization of the excited electron and the destabilization of the hole. The general principle is established that a thermal reaction A + B is favored if there is strong interaction between the top occupied orbital(s) on one molecule and the lowest unoccupied orbital(s) on the other (and conversely). On the other hand, a photochemical reaction A* + B is favored if the orbital of the excited electron (generally the lowest previously unoccupied orbital of A) interacts strongly with an orbital of neighboring or slightly higher energy (generally the lowest unoccupied orbital of B), equally, if the orbital of the hole (top occupied orbital of A) interacts strongly with an orbital of neighboring or slightly lower energy (generally the top occupied orbital of B).

The study of the interaction between conjugated molecules forms an important part of the investigation of organic reaction mechanisms and of molecular photochemistry. The typical Diels–Alder addition occurs most readily between a conjugated system and a dienophile in which the reacting double bond belongs also to a conjugated chain. Recently a great amount of interest has been focused on intermolecular cycloadditions of conjugated systems, whether thermal or photochemical. In an adjacent field, the spectral behavior and the structure of the excimers of aromatic molecules have excited the curiosity of physical chemists and organic chemists alike.

The theory of the mechanism of these interactions has advanced considerably in the last few years. Among the proposals put forward are the following. (1) The Diels–Alder reaction[2a] should be a concerted, but asymmetric, addition with one bond closure occurring faster than the others.[2b] Furthermore the preference for *endo* rather than *exo* adducts appears due to a secondary interaction between the β' atomic orbital, adjacent to the reacting double bond, and a β orbital of the diene.[3]

(2) Concerning cycloadditions in general, thermal reactions should proceed when $m + n$, the total number of π electrons in the newly formed ring, is of the form $4q + 2$, whereas photochemical reactions will be allowed for $m + n = 4q$.[4] Exceptions to these selection rules should occur only *via* multistep mechanisms.

(3) Little is known, finally, about the structure of excited dimers in solution, although they are often as-

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[1] Research supported in part by National Institutes of Health Grant GM-12343.

[2] (a) See, for instance, A. Wasserman, "Diels–Alder Reactions," Elsevier Publishing Co., New York, N. Y., J. Sauer, *Angew. Chem.*, **79**, 76 (1967); (b) R. B. Woodward and T. Katz, *Tetrahedron*, **5**, 70 (1959); see also J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **83**, 4947 (1961).

[3] R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 4388 (1965).

[4] R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

sumed to have a planar "sandwich" structure. It has been suggested recently that excimers actually have a configuration "similar to that of adjacent parallel molecules in the crystal lattice."[5] What appears to be certain, in any case, is that resonance interaction between transition dipole moments in the interacting molecules (exciton splitting) fails entirely to reproduce the experimental spectral shifts, and that overlap must be introduced explicitly to understand the stability of excimers.[6] For instance, the first-order Davydov splitting cannot account for the fluorescence of benzene excimers in solution;[6e] the shift of dimer singlet energies is far too small in the zero-overlap approximation. Similar results are obtained for solutions of naphthalene, anthracene, pyrene, and perylene.[6b] Overlap is now believed to be an essential feature.[6b,d,g]

One way in which overlap can be introduced is to mix molecular exciton states with charge-resonance states by configuration interaction,[6b,c,e] but a molecular orbital wave function is equivalent to a mixture of excitation-resonance and charge-resonance wave functions. Thus a direct molecular orbital approach, including all π electrons of the two systems, may be a more adequate method for calculating the energies and spectral shifts of these dimers.[6a,d,f] Recent experimental results[7] which emphasize the importance of the charge-resonance component point in the same direction.

At present the only available molecular orbital approach which is general enough to be applied to the study of all such interactions is Hoffmann's "extended Hückel theory."[8] For a single molecule this simple but powerful theory includes all electrons, both π and σ, in a one-electron treatment in which the complete secular determinant, with overlap included, is diagonalized. There is no difficulty, in principle, in extending this treatment to the interaction of two molecules (considered as one composite system) with overlapping orbitals. This has been performed by Hoffmann himself on butadiene plus ethylene,[4] by Chestnut, *et al.*, on the benzene excimer,[6d] by Polak and Paldus on ethylene dimers,[6f] and recently by Herndon and Hall on various Diels–Alder additions.[9] However, the numerical resolution of a large secular equation does not provide any information on the important atom–atom or orbital–orbital interactions, nor on the interaction energy as a function of the various atomic overlaps. It is difficult, without repeating the entire diagonalization at many different interatomic distances, to establish whether a given bond closure is more favorable than another one, and whether a given reaction must proceed symmetrically or not. Furthermore for very large molecules, the secular determinant procedure itself becomes unwieldy. The interaction of two pyrene molecules requires the resolution of a 132×132 determinant for each dimer configuration when there is no plane of symmetry allowing for its factorization. One is then obliged to consider only highly symmetric configuration of approach[4] or to restrict the number of electrons in the calculation.[9]

Our purpose in this paper is to try and develop a theory which provides explicit expressions for the interaction energy of two conjugated molecules as a function of the various atomic orbital overlaps (a reaction surface of sorts). Such a theory should provide insight into the important orbital interactions and should allow ready calculation of reaction paths. The essential features of the proposed theory are as follows.

(1) The wave functions are built out of "*intermolecular*" *orbitals* covering the entire system of interacting molecules. As we have already pointed out, for excited states a molecular orbital wave function is equivalent to a mixture of exciton and charge-resonance wave functions. One-electron energies will therefore be similar to those obtained in procedures[6b,c,e] which use such a mixture.

The Hamiltonian is an effective one-electron Hamiltonian. Two-electron energies, such as the weak exciton stabilization energy in excimers, can be obtained through a configuration interaction calculation. Introduction of explicit two-electron terms in the Hamiltonian will be required if large charge–charge interactions are present.

(2) *The molecular orbitals and experimental energies of the separate molecules are chosen as starting point.* We therefore make use of what is known about the separate molecules and seek only the small changes brought about by the interaction.

(3) *Perturbation theory is used to determine the changes in the molecular orbitals and in the energies of states.*

(4) Expansion in powers of the overlap allows for explicit analytical energy expressions which are numerically tractable.

The results of such calculations should be no different from those of a numerical "extended Hückel"[8] or similar calculation. However the calculations are much less elaborate and the effects involved should be much more transparent. In particular, it will be possible to compare stabilization energies brought about by bond closures in various configurations of approach.

In the following and further papers, the theory will be applied successively to intermolecular cycloadditions and excited complexes of conjugated molecules. An attempt will be made to establish the validity of the various proposals put forward in this introduction. If necessary, new proposals will be put forward.

Assumptions

The assumptions are as follows. (1) Both conjugated molecules are assumed to have well-separated bands of σ and π orbitals. This is known not to be strictly true, in particular for the smaller olefinic systems such as ethylene,[10] but should be a good approximation for the larger conjugated systems. It is reasonable to consider that the major interactions will arise from the less tightly bound manifold of π orbitals (and π

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(5) R. L. Barnes and J. B. Birks, *Proc. Roy. Soc.* (London), **A291**, 570 (1966).

(6) (a) J. Koutecký and J. Paldus, *Collection Czech. Chem. Commun.*, 27, 599 (1962); (b) J. N. Murrell and J. Tanaka, *Mol. Phys.*, 7, 363 (1964); (c) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **41**, 3131 (1964); **42**, 1675 (1965); T. Azumi and H. Azumi, *Bull. Chem. Soc. Japan*, **39**, 1829 (1966); 40, 279 (1967); (d) D. B. Chestnut, C. J. Fritchie, and H. E. Simmons, *J. Chem. Phys.*, **42**, 1127 (1965); (e) M. T. Vala, I. H. Hillier, S. A. Rice, and J. Jortner, *ibid.*, **44**, 23 (1966); I. Hillier, L. Glass, and S. A. Rice, *ibid.*, **45**, 3015 (1966); (f) R. Polak and J. Paldus, *Theoret. Chim. Acta*, **4**, 37 (1966); M. G. Sucre and A. Tallet, *ibid.*, **7**, 277 (1967); (g) see, however, J. B. Birks, *Chem. Phys. Letters*, **1**, 304 (1967).

(7) E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, **45**, 397 (1966).

(8) R. Hoffmann, *ibid.*, **39**, 1397 (1963); for a similar theory, see J. A. Pople and D. P. Santry, *Mol. Phys.*, 7, 269 (1963).

(9) W. C. Herndon and L. H. Hall, *Theoret. Chim. Acta*, 7, 4 (1967).

(10) M. B. Robin, R. R. Hart, and N. A. Kuebler, *J. Chem. Phys.*, **44**, 2664 (1966).

electrons) on the two molecules, the σ bonds acting only as a *hard core* which forbids too close an approach. Indeed there is yet no indication whatsoever that consideration of the *reactant* σ electrons is necessary to describe aromatic excimer formation or the incipient steps of cycloadditions. It is not unreasonable to assume that significant rehybridization takes place only after the course of intermolecular addition or complexing has been determined by the initial overlap of p orbitals. However, special cases will arise where the σ interactions are important: photochemical reactions involving excitation to σ antibonding orbitals, or from σ bonding orbitals, etc.

(2) The states of the composite pair are described in terms of one-electron orbitals. These *intermolecular orbitals* are due to the interaction, *via* overlap, of the π molecular orbitals of the two molecules (see, for example, Figure 3).

(3) The total effective one-electron Hamiltonian has the usual form defined in Hückel theory

$$H = \sum_i h(i) \qquad h = t + v + v' \tag{1}$$

Here t is the kinetic energy operator, v some average effective potential field of the nuclei and electrons of the first molecule, and v' the average potential due to the second molecule[11] (henceforth the prime notation refers to the second molecule).

The matrix elements between molecular orbitals on the same molecule are

$$\int\psi_j h\psi_k \, d\tau = \int\psi_j(t + v)\psi_k \, d\tau + \int\psi_j v'\psi_k \, d\tau \approx \delta_{jk}E_j$$

$$\int\psi_{j'} h\psi_{k'} \, d\tau = \int\psi_{j'}(t + v')\psi_{k'} \, d\tau + \int\psi_{j'} v\psi_{k'} \, d\tau \approx \delta_{j'k'}E_{j'} \tag{2}$$

where E_j is the one-electron *Hückel energy* of orbital ψ_j, and we have used the fact that the potential v' (v) is small in the region of the first (second) molecule.

The matrix element of h between orbitals on the two molecules is

$$\int\psi_j h\psi_{j'} \, d\tau = \int\psi_j {}^1/_2(t + v)\psi_{j'} \, d\tau + \int\psi_j {}^1/_2(t + v')\psi_{j'} \, d\tau + \int\psi_j {}^1/_2(v + v')\psi_{j'} \, d\tau$$

or

$$h_{jj'} = {}^1/_2E_jS_{jj'} + {}^1/_2E_{j'}S_{jj'} + \int\psi_j {}^1/_2(v + v')\psi_{j'} \, d\tau \tag{3}$$

where $S_{jj'}$ is the overlap integral between π orbital ψ_j and π orbital $\psi_{j'}$. Since the potential $v + v'$ is large only in the region *between* the two molecules, the matrix element

$$I_{jj'} = \int\psi_j {}^1/_2(v + v')\psi_{j'} \, d\tau \tag{4}$$

can be considered to represent the *interaction energy* between an electron in ψ_j and an electron in $\psi_{j'}$. It might be tempting to write $\int\psi_j h\psi_{j'} \, d\tau = \beta_{jj'}$ and apply ordinary Hückel theory to the two systems considered as a supermolecule, neglecting overlap. However, we are primarily interested in the *change in energy* when the two molecules come together, and this arises solely from the Coulombic interaction potential,[12] whereas h contains the kinetic energy. Furthermore we shall see that explicit neglect of overlap integrals fails to lead to any repulsion energy whatsoever.

(4) The Hückel molecular orbitals of the separate systems are expanded in the usual LCAO form (atomic orbitals ϕ_r, $\phi_{r'}$), This expansion leads to expressions involving atomic matrix elements of the overlap and interaction energy between the 2p orbitals on the two systems

$$\begin{aligned} S_{rr'} &= \int\phi_r\phi_{r'} \, d\tau \\ \eta_{rr'} &= \int\phi_r {}^1/_2(v + v')\phi_{r'} \, d\tau \end{aligned} \tag{5}$$

The matrix element $\eta_{rr'}$ is negative (the major effect in $v + v'$ is the attractive nuclear field) and will be roughly proportional to the overlap integral $S_{rr'}$. For certain quantitative calculations it will be convenient to write the proportionality explicitly

$$\eta_{rr'}/\beta = kS_{rr'} \tag{6}$$

where β is the resonance integral in the isolated molecules and k is a dimensionless constant, but all the qualitative conclusions are independent of this assumption.

(5) Several restrictive remarks are in order. To neglect explicit Coulombic repulsion terms e^2/r_{12} in the interaction between the molecules has several important consequences. (a) The interaction between net charges on the two systems is neglected; this prohibits the prediction of meaningful reaction paths for highly polar molecules. (b) The "first-order" energy of interaction (with $1/R^3$ behavior) between an excited molecule and an identical partner in its ground state is neglected. The corresponding exciton stabilization energy, however, is now well known to give only small energies, far too weak generally to explain excimer formation in solution.[6] In the present theory the exciton stabilization can be accounted for, if necessary, through a configuration interaction calculation.

(c) The theory does not distinguish between the *inter*molecular contributions to singlet and triplet energies. The over-all energies of the singlet and triplet corresponding to a given one-electron excitation are different, however, because *we use distinct experimental energies at infinite separation.* This is somewhat equivalent to neglecting intermolecular correlation *vs.* intramolecular correlation. Some justification is provided by the helium–helium system.[13] There the energy curves for the lowest excited singlet and triplet are nearly parallel.

$$({}^1\Sigma u^+) \quad r_e = 1.040 \text{ Å} \quad D_e = 3.07 \text{ eV}$$

$$({}^3\Sigma u^+) \quad r_e = 1.045 \text{ Å} \quad D_e = 2.62 \text{ eV}$$

Note also that single configurations built out of molecular orbitals will not, in general, correlate correctly with some separate-molecule state at infinite distances. To obtain this correlation correctly, it is necessary to mix in other configurations. Hence the theory is valid only at distances which are not too large.

(6) The crucial assumption of the theory concerns the atomic orbital overlap integral $S_{rr'}$. All $S_{rr'}$'s are taken to be *small compared with unity* (*i.e.*, ≤ 0.2). We shall now show that this surprising assumption is particularly justified for the interaction between conjugated molecules. They come together with as little inter-

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(11) See, for example, L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966.

(12) H. C. Longuet-Higgins, *Proc. Roy. Soc.*, (London), **A235**, 537 (1956).

(13) M. L. Ginter, *J. Chem. Phys.*, **42**, 561 (1965).

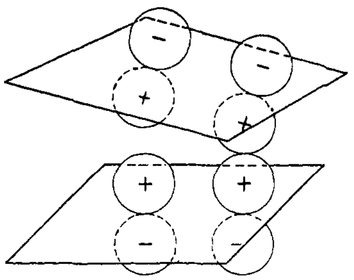

Figure 1. Approach of two conjugated molecules.

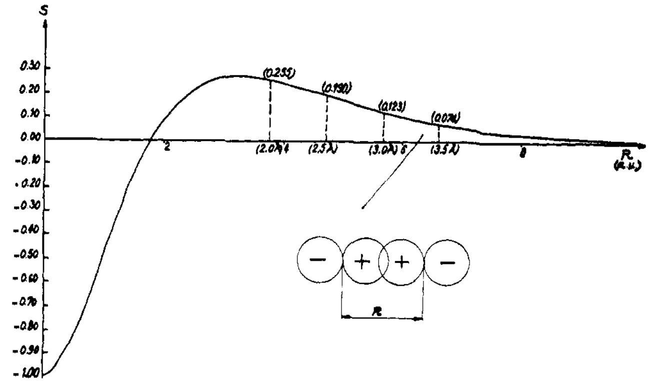

Figure 2. (2pσ, 2pσ) overlap between carbon orbitals.

ference as possible between the σ(CH, CC) cores on either side, to avoid having a very large repulsion. Thus the carbon 2p orbitals, which are sticking out from each molecule, can overlap significantly. The general tendency then for the molecules is to come together with their planes *roughly* parallel and opposed (Figure 1). Such an approach is accepted for the Diels–Alder reaction and must occur in most concerted cycloadditions. The carbon 2p orbitals are then brought approximately into a "σ"-type overlap.

Now the "σ" overlap S between two "end-to-end" p orbitals has a very particular behavior, as shown in Figure 2. Here the overlap integral has been calculated between two SCF orbitals for the ^{5}S valence-state of carbon.[14] As the orbitals are brought together, the integral first increases, as would be expected, but then *levels off and starts decreasing after reaching a maximum value of 0.270.* At the distance of 1 Å the overlap integral is zero! The reason for this behavior is apparent from a consideration of the orbital lobes. At large distances only the two lobes of same positive sign overlap, and S increases as the orbitals come closer, but, at a distance 2.5 Å, the positive lobe of one orbital starts overlapping the negative lobe of the other (and conversely). Therefore S increases less and less, until it reaches a maximum at 1.74 Å. As the distance decreases even further, the overlap becomes more and more "negative," reaching the value -1.00 when the two nuclei coincide.

It is clear that in the significant range of distances (2.5–3.5 Å), where the core repulsive wall is small, the overlap is smaller than 0.2. Only when the angle between the molecular planes is large may the overlap be somewhat greater. (In the extreme case of a 90° angle, the overlap integral between two positive half-lobes at right angles might at very best reach a slightly larger value than the maximum for positive lobes pointing at each other.)

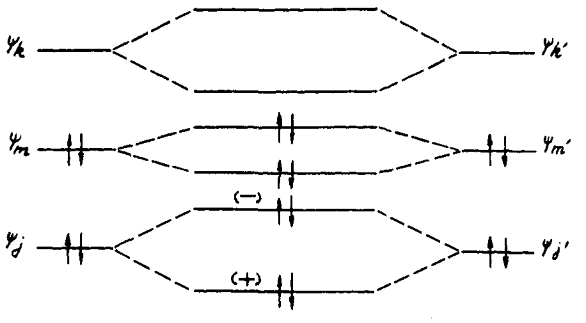

Figure 3. Interaction between degenerate pairs of orbitals belonging to identical molecules.

(7) Except in exceptional cases, only those matrix elements $\eta_{rr'}$ and $S_{rr'}$, between orbital ϕ_r and its *nearest neighbor* $\phi_{r'}$ on the opposite molecule, are conserved. Exceptions will arise when three atomic centers interact mutually.

Under these conditions we can develop expressions for the absolute π interaction energies of both ground and excited states for any configuration of the approaching molecules.

The Interaction Energy between Molecules in Their Ground States

Let us begin by supposing that the interacting molecules are identical closed shells with the same pattern of Hückel orbital energies. The first effect to consider is the "first-order" interaction energy between pairs of degenerate orbitals (ψ_j, $\psi_{j'}$). As shown in Figure 3, each pair of orbitals is split in the usual fashion, giving two new (intermolecular) orbitals which correspond to a + or − combination of the initial pair. The relative position of the + and − orbitals is determined by the sign of $I_{jj'}$; for negative $I_{jj'}$ the positive combination has the lower energy.

The four electrons initially in ψ_j and $\psi_{j'}$ now have a total energy, shown in eq 7, where (2) has been used.

$$2\int\left(\frac{\psi_j + \psi_{j'}}{\sqrt{2 + 2S_{jj'}}}\right)h\left(\frac{\psi_j + \psi_{j'}}{\sqrt{2 + 2S_{jj'}}}\right)\mathrm{d}\tau + 2\int\left(\frac{\psi_j - \psi_{j'}}{\sqrt{2 - 2S_{jj'}}}\right)h\left(\frac{\psi_j - \psi_{j'}}{\sqrt{2 - 2S_{jj'}}}\right)\mathrm{d}\tau = (E_j + E_{j'})\left(\frac{1}{1 + S_{jj'}} + \frac{1}{1 - S_{jj'}}\right) + 2h_{jj'}\left(\frac{1}{1 + S_{jj'}} - \frac{1}{1 - S_{jj'}}\right) \quad (7)$$

Assumption 6 allows us to expand (7) *in powers of* $S_{jj'}$;[15] thus (7) becomes, to second order in $S_{jj'}$

$$2(E_j + E_{j'})(1 + S_{jj'}{}^2) - 4h_{jj'}S_{jj'} = 2(E_j + E_{j'}) - 4I_{jj'}S_{jj}$$

where (3) and (4) have been used. The quantity $2(E_j + E_{j'})$ is simply the energy of the same four elec-

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(14) R. B. Hermann, *J. Chem. Phys.*, **42**, 1027 (1965). A similar curve can be found in J. D. Roberts, "Molecular Orbital Calculations," W. A. Benjamin, Inc., New York, N. Y., 1962, p 30.

(15) If all $S_{rr'}$ are small, $S_{jj'}$ is also small. The maximum value of $S_{jj'}$ should occur if all $S_{rr'}$ have their maximum value S_{max}; then $S_{jj'} = S_{\mathrm{max}}\Sigma_{rr'}c_{jr'}c_{j'r'}$ (see eq 14), which is smaller or equal to S_{max}.

trons in the noninteracting molecules. The total interaction energy due to the splitting of all degenerate pairs of occupied orbitals is then

$$E_{\text{int}}^{(\text{I})} = -4\sum_{j=j'}^{\text{occ}} I_{jj'}S_{jj'} \tag{8}$$

In such a calculation one can distinguish two different orders of development: orders of magnitude in the overlap integral $S_{jj'}$, and orders of "perturbation" in the interaction energy $^1/_2(v + v')$ (or $I_{jj'}$). However, as the interaction integral $I_{jj'}$ contains the overlap density $\psi_j\psi_{j'}$, the "first-order" interaction energy in (8) is only *second order* in the overlap; the destabilizing effect of the antibonding electrons is almost compensated by the stabilizing effect of the bonding pair. It is therefore necessary to pursue the calculation *to second order in the perturbing interaction energy* (by mixing orbitals of different energy) so that all terms of order $S_{jj'}^2$, in particular those in $I_{jj'}^2$, are included.

The mixing of two orbitals ψ_j and $\psi_{j'}$ of different energy leads to the secular determinant

$$\begin{vmatrix} E_j - E & H_{jj'} - S_{jj'}E \\ H_{jj'} - S_{jj'}E & E_{j'} - E \end{vmatrix} = 0$$

giving

$$E^2(1 - S_{jj'}^2) - E(E_j + E_{j'} - 2S_{jj'}H_{jj'}) + E_jE_{j'} - H_{jj'}^2 = 0 \tag{9}$$

Only if the energy difference $E_{j'} - E_j$ is large relative to the matrix element $\text{H}_{jj'} - S_{jj'}E$ can we obtain the energy root E in the usual perturbation form.[16]

$$E_j^{(2)} = E_j - \frac{(H_{jj'} - S_{jj'}E_j)^2}{E_{j'} - E_j} \tag{10}$$

Here $E_j^{(2)}$ is the perturbed orbital energy of ψ_j. We must therefore divide the "second-order" contributions into two distinct parts: (1) mixing of ψ_j(occupied) with $\psi_{j'}$(occupied) and (2) mixing of ψ_j(occupied) with $\psi_{k'}$(unoccupied) and of $\psi_{j'}$(occupied) with ψ_k(unoccupied). In the first case the energy difference $E_{j'} - E_j$ may well be small or of the same order as $H_{jj'} - S_{jj'}E$ and we must use (9). In the second case the difference $E_{j'} - E_j$ is at least equal to the lowest excitation energy of one molecule, ~3 eV, which we shall assume to be significantly larger than $H_{jj'} - S_{jj'}E$.

For the mixing between occupied orbitals we calculate directly the *sum* of the new energies of ψ_j and $\psi_{j'}$ from (9)

$$E_j^{(2)} + E_{j'}^{(2)} = \frac{E_j + E_{j'} - 2S_{jj'}H_{jj'}}{1 - \text{S}_{jj'}^2} = E_j + E_{j'} - 2S_{jj'}I_{jj'}$$

where the usual expansion in powers of $S_{jj'}$ and (3) have been used. Hence the total interaction energy for all the electrons is

$$E_{\text{int}}^{(\text{II})} = -4\sum^{\text{occ}}\sum_{j\neq j'}^{\text{occ}} I_{jj'}S_{jj'} \tag{11}$$

For the mixing between one occupied orbital ψ_j and all unoccupied orbitals $\psi_{k'}$ of the second molecule, eq 10 leads to the following interaction energy[17] shown below.

$$-\sum_{k'}^{\text{unocc}}\frac{(H_{jk'} - S_{jk'}E_j)^2}{E_{k'} - E_j} = -\sum_{k'}^{\text{unocc}}\frac{(I_{jk'} + {}^1/_2(E_{k'} - E_j)S_{jk'})^2}{E_{k'} - E_j}$$

The total energy due to this effect is obtained by summing over all occupied orbitals

$$E_{\text{int}}^{(\text{III})} = -2\sum_j^{\text{occ}}\sum_{k'}^{\text{unocc}}\frac{[I_{jk'} + {}^1/_2(E_{k'} - E_j)S_{jk'}]^2}{E_{k'} - E_j} - 2\sum_{j'}^{\text{occ}}\sum_{k}^{\text{unocc}}\frac{[I_{kj'} + {}^1/_2(E_k - E_{j'})S_{kj'}]^2}{E_k - E_{j'}} \tag{12}$$

The combination of (8), (11), and (12) gives an over-all interaction energy (eq 13). It is clear that this result is

$$E_{\text{int}} = -2\sum_j^{\text{occ}}\sum_{\substack{\text{all}\\ j'}} I_{jj'}S_{jj'} - 2\sum_{j'}^{\text{occ}}\sum_{\substack{\text{all}\\ j}} I_{jj'}S_{jj'} - 2\sum_j^{\text{occ}}\sum_{k'}^{\text{unocc}}\left[\frac{I_{jk'}^2}{E_{k'} - E_j} + \frac{1}{4}(E_{k'} - E_j)S_{jk'}^2\right] - 2\sum_{j'}^{\text{occ}}\sum_{k}^{\text{unocc}}\left[\frac{I_{kj'}^2}{E_k - E_{j'}} + \frac{1}{4}(E_k - E_{j'})S_{kj'}^2\right] \tag{13}$$

independent of whether the molecules are identical or not. If they are different molecules, with no accidental orbital degeneracy, (8) disappears but the summation in (11) now includes all occupied j, and all occupied j', and (13) is still obtained.

The last step of the calculation is the development of the molecular orbitals in a linear combination of atomic orbitals, $\psi_j = \sum_r c_{jr}\phi_r$. Hence

$$\begin{aligned} I_{jj'} &= \sum_r\sum_{r'} c_{jr}c_{j'r'}\eta_{rr'} \\ S_{jj'} &= \sum_s\sum_{s'} c_{js}c_{j's'}S_{ss'} \end{aligned} \tag{14}$$

where (r, r') and (s, s') are pairs of interacting atoms on the two molecules. Since $\sum_{\text{all } j'} c_{j'r'}c_{j's'} = \delta_{r's'}$ (δ = Kronecker symbol), the first two terms of (13) give

$$-\sum_{rr'}\sum_{ss'}(p_{rs}\delta_{r's'} + p_{r's'}\delta_{rs})\eta_{rr'}S_{ss'}$$

where p_{rs} is the bond order between atoms r and s of the first molecule, and $p_{r's'}$ is the bond order between atoms r' and s' of the second molecule. If we suppose that different atoms r and s do not interact with the same atom r' or s' (no three-center interactions), this expression reduces to the contributions from $r = s$, $r' = s'$.

$$-\sum_r\sum_{r'}(q_r + q_{r'})\eta_{rr'}S_{rr'}$$

Here q_r is the Hückel charge density at atom r. Finally, therefore

$$E_{\text{int}} = -\sum_{rr'}(q_r + q_{r'})\eta_{rr'}S_{rr'} - 2\sum_j^{\text{occ}}\sum_{k'}^{\text{unocc}}\left[\frac{(\sum_{rr'} c_{jr}c_{k'r'}\eta_{rr'})^2}{E_{k'} - E_j} + \frac{1}{4}(E_{k'} - E_j) \times (\sum_{rr'} c_{jr}c_{k'r'}S_{rr'}{}')^2\right] - 2\sum_{j'}^{\text{occ}}\sum_{k}^{\text{unocc}}\left[\frac{(\sum_{rr'} c_{kr}c_{j'r'}\eta_{rr'})^2}{E_k - E_{j'}} + \frac{1}{4}(E_k - E_{j'})(\sum_{rr'} c_{kr}c_{j'r'}S_{rr'})^2\right] \tag{15}$$

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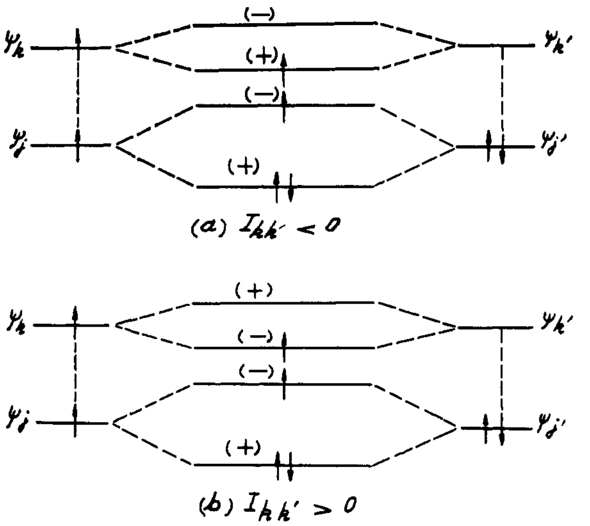
[16] Rigorously, eq 10 can be derived from (9) only if $(E_{j'} - E_j)^2 \gg 4(H_{jj'} - S_{jj'}E_j)(H_{jj'} - S_{jj'}E_{j'})$. Note that the present development assumes that the simultaneous mixing of *three* orbitals is negligible *i.e.*, that we need not go to third-order perturbation theory.

[17] This is a well-known result of perturbation theory: see H. F. Hameka, "Advanced Quantum Chemistry," Addison-Wesley Publishing Co., Reading, Mass., 1965, p 75; J. I. Musher and L. Salem, *J. Chem. Phys.*, **44**, 2943 (1966).



(a) $I_{kk'} < 0$

(b) $I_{kk'} > 0$

Figure 4. Interaction between two identical molecules, one excited and one in its ground state.

Equation 15 gives the interaction energy between two conjugated molecules in their ground states. We see that it comprises two major terms. (1) The first is a *repulsive* term, $-\sum_{rr'}(q_r + q_{r'})\eta_{rr'}S_{rr'}$, roughly proportional to the square of the overlap and strictly proportional to the π charge densities on the interacting atoms. This repulsion arises because each conjugated molecule has a closed-shell structure in which all the bonding orbitals are full.[18] The larger the π charge density q_r on an atom, the larger the size of the "exclusion shell" into which other electrons are forbidden to penetrate. (2) The second is an *attractive* term due essentially to the mixing of the occupied orbitals of one molecule with the unoccupied orbitals on the other. This attraction takes place because conjugated molecules, although closed shells from the strict point of view of occupancy of bonding orbitals, are also open shells since they possess a half-filled band of π levels.

Equation 15 therefore illustrates the *dual nature of conjugated molecules:* closed shells, but yet availability of low-lying antibonding orbitals. Hence we can understand the great reactivity of these molecules as arising from the existence of half-filled bands of π electrons, even though the valency shell of each carbon atom is full.

The Interaction Energy When One Molecule Is Excited

When one molecule is excited, it is necessary to distinguish the interaction of *identical* molecules from that of different molecules.

Let us suppose that the interacting molecules are identical, and that one molecule is in the excited (singlet or triplet) state corresponding to the one-electron (nondegenerate) excitation $\psi_j \rightarrow \psi_k$. The two possible diagrams for the relevant interacting orbitals are shown in Figure 4; (a) for $I_{kk'} < 0$ and (b) for $I_{kk'} > 0$. (We can always assume, without loss of generality, an arbitrary order for the +, − combination of the lowest pair.) We can now calculate the *change in interaction energy*, ΔE_{int}, due to the excitation, from the case (Figure 2) where both molecules were in their ground state.

$$\Delta E_{\text{int}} = \int\left(\frac{\psi_k \pm \psi_{k'}}{\sqrt{2 \pm 2S_{kk'}}}\right)h\left(\frac{\psi_k \pm \psi_{k'}}{\sqrt{2 \pm 2S_{kk'}}}\right)\mathrm{d}\tau - \int\left(\frac{\psi_j - \psi_{j'}}{\sqrt{2 - 2S_{jj'}}}\right)h\left(\frac{\psi_j - \psi_{j'}}{\sqrt{2 - 2S_{jj'}}}\right)\mathrm{d}\tau - (E_k - E_j) \quad (16)$$

Here the upper sign refers to case a, the lower sign to case b, and the excitation energy $(E_k - E_j)$ represents the change in energy of the noninteracting molecules. Developing (16) in the usual way (see previous section) and using (3) and (4) we get

$$\Delta E_{\text{int}} = \pm I_{kk'}(1 \mp S_{kk'}) + I_{jj'}(1 + S_{jj'}) \quad (17)$$

But $I_{jj'}$ is negative and can be written $-|I_{jj'}|$, and similarly for $I_{kk'}$ in case a. The change in interaction energy can therefore be written, in all cases

$$\Delta E_{\text{int}}^{(\text{I})} = -(|I_{kk'}| + |I_{jj'}|) + (I_{jj'}S_{jj'} - I_{kk'}S_{kk'}) \quad (18)$$

The major term in eq 18 is the term $-(|I_{kk'}| + |I_{jj'}|)$, which is first order in the overlap. Essentially, the interaction energy between an excited molecule and a ground-state molecule *contains a term linear in the overlap.* This term will be predominant (relative to E_{int}) for small values of the intermolecular overlap.

To (18) we must add the contributions arising from the mixing of ψ_j and ψ_k with orbitals of different energy in the second molecule. It is difficult to use (9) here to calculate the interaction of ψ_j with the other occupied orbitals (or of ψ_k with the other unoccupied ones). *If*, however, orbitals ψ_j and ψ_k are both well separated in energy from all the other orbitals in the molecule,[16] we can apply eq 10 to *all* the "second-order" mixings.

$$\Delta E_{\text{int}}^{(\text{I})} = \sum_{\substack{\text{all } j' \\ (\neq j)}}\frac{(H_{jj'} - S_{jj'}E_j)^2}{E_{j'} - E_j} - \sum_{\substack{\text{all } j' \\ (\neq k)}}\frac{(H_{kj'} - S_{kj'}E_j)^2}{E_{j'} - E_k} = \sum_{\substack{\text{all } j' \\ (\neq j)}}\frac{[I_{jj'} + {}^1\!/_2(E_{j'} - E_j)S_{jj'}]^2}{E_{j'} - E_j} - \sum_{\substack{\text{all } j' \\ (\neq k)}}\frac{[I_{kj'} + {}^1\!/_2(E_{j'} - E_k)S_{kj'}]^2}{E_{j'} - E_k} \quad (19)$$

The first term represents the loss of "second-order" stabilization, relative to the situation where both molecules are in the ground state, due to the loss of one electron in ψ_j; and the second term represents the additional stabilization due to the electron in ψ_k. Combining (18) and (19) we get (for identical molecules)

$$\Delta E_{\text{int}} = -(|I_{kk'}| + |I_{jj'}|) + \sum_{\text{all } j'}(I_{jj'}S_{jj'} - I_{kj'}S_{kj'}) + \sum_{\substack{\text{all } j' \\ (\neq j)}}\left[\frac{I_{jj'}^2}{E_{j'} - E_j} + {}^1\!/_4(E_{j'} - E_j)S_{jj'}^2\right] - \sum_{\substack{\text{all } j' \\ (\neq k)}}\left[\frac{I_{kj'}^2}{E_{j'} - E_k} + {}^1\!/_4(E_{j'} - E_k)S_{kj'}^2\right] \quad (20)$$

Again we must emphasize that this result is true, as far as the terms of order S^2 are concerned, only if ψ_j and ψ_k are well separated from the other molecular orbitals; only then will eq 10 be equivalent to 9.

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[18] The "atomic" nature of this repulsion is due to the atomic subdivision which is inherent in Hückel theory.

If the molecules are *different*, with no accidental degeneracy between E_j or E_k and any $E_{j'}$, eq 18 disappears, and only 19 subsists, where the summations are over all j' without restriction. The results for ΔE_{int} is then eq 20 *without the linear term* $-(|I_{kk'}| + I_{jj'}|)$ and where there is no need to specify that the j''s are different from j or k.

There remains to establish the expression for the interaction energy in terms of the atomic matrix elements η and S. We have the simplification

$$\sum_{\text{all } j'}(I_{jj'}S_{jj'} - I_{kj'}S_{kj'}) = \sum_{rr'}\sum_{ss'}(c_{jr}c_{js}\delta_{r's'} - c_{kr}c_{ks}\delta_{r's'})\eta_{rr'}S_{ss'} = \sum_{rr'}(c_{jr}^2 - c_{kr}^2)\eta_{rr'}S_{rr'}$$

The final result for the interaction energy E_{int}^* between an excited conjugated molecule and an identical partner in its ground state is eq 21. For *identical* molecules

$$E_{\text{int}}^* = E_{\text{int}} + \Delta E_{\text{int}} \tag{21}$$

$$\begin{aligned}\Delta E_{\text{int}}^{(j \rightarrow k)} = {} & -(|\sum_{rr'}c_{jr}c_{j'r'}\eta_{rr'}| + |\sum_{rr'}c_{kr}c_{k'r'}\eta_{rr'}|) + \\ & \sum_{rr'}(c_{jr}^2 - c_{kr}^2)\eta_{rr'}S_{rr'} + \sum_{\substack{\text{all } j' \\ (\neq j)}}\left[\frac{(\sum_{rr'}c_{jr}c_{j'r'}\eta_{rr'})^2}{E_{j'} - E_j} + \right. \\ & \left. {}^1\!/_4(E_{j'} - E_j)(\sum_{rr'}c_{jr}c_{j'r'}S_{rr'})^2\right] - \\ & \sum_{\substack{\text{all } j' \\ (\neq k)}}\left[\frac{(\sum_{rr'}c_{kr}c_{j'r'}\eta_{rr'})^2}{E_{j'} - E_k} + {}^1\!/_4(E_{j'} - E_k)(\sum c_{kr}c_{j'r'}S_{rr'})^2\right]\end{aligned}$$

the linear term is the all-important one, and the other terms can often be neglected in searching for the qualitative behavior of an interacting system. For *different* molecules the linear term disappears, and only the second, third, and fourth terms of (21), which are second order in S, subsist. It is then important to check that there is no degeneracy or near-degeneracy between ψ_j, or ψ_k, and any $\psi_{j'}$. The term $(c_{jr}^2 - c_{kr}^2)\eta_{rr'}S_{rr'}$ represents the effect of the change in size of the exclusion shell around atom r upon excitation.

Equations 15 and 21 are the fundamental expressions which yield the interaction energy of two conjugated molecules, whether one is excited or not. The author would like to emphasize that, in spite of their apparent complexity, these equations are *extremely tractable.* Detailed examples (part II[19]) will show how little arithmetical effort goes into the evaluation of the interaction energy.

The Important Case of Interacting Alternant Hydrocarbons

The characteristic properties of alternant hydrocarbons[11] are familiar to most chemists and we shall not dwell on them. Let us assume that the interacting molecules are even alternants and see how this affects formulas 15 and 21. First the charge density q_r is uniformly equal to 1. In the second place, let us associate with the unoccupied orbitals

$$\begin{aligned}\psi_k &= \sum{}^*c_{jr}\phi_r - \sum{}^\circ c_{js}\phi_s \\ \psi_{k'} &= \sum c_{j'r'}\phi_{r'} - \sum{}^\circ c_{j's'}\phi_{s'}\end{aligned} \tag{22a}$$

and the conjugate orbitals[11]

$$\begin{aligned}\psi_j &= \sum{}^*c_{jr}\phi_r + \sum{}^\circ c_{js}\phi_s \\ \psi_{j'} &= \sum{}^*c_{j'r'}\phi_{r'} + \sum{}^\circ c_{j's'}\phi_{s'}\end{aligned} \tag{22b}$$

(No nonbonding orbitals are assumed to be present.) In (22) the summations over starred (*) and unstarred (°) atoms are separate. Let us also remark that

$$E_{k'} - E_j = \epsilon_{k'} - \epsilon_j = -(\epsilon_{j'} + \epsilon_j)$$

where the ϵ's denote *binding* energies. We can then write, for typical terms of (15), eq 23, where we have

$$\begin{aligned}-2\sum_j^{\text{occ}}\sum_{k'}^{\text{unocc}}\frac{\left(\sum_{rr'}c_{jr}c_{k'r'}\eta_{rr'}\right)^2}{E_{k'} - E_j} &= 2\sum_j^{\text{occ}}\sum_{k'}^{\text{unocc}}\frac{\left[\sum_{rr'}(c_{jr}^* + c_{jr}^\circ)(c_{j'r'}^* - c_{j'r'}^\circ)\eta_{rr'}\right]^2}{\epsilon_j + \epsilon_{j'}} \\ -2\sum_{j'}^{\text{occ}}\sum_{k}^{\text{unocc}}\frac{\left(\sum_{rr'}c_{kr}c_{j'r'}\eta_{rr'}\right)^2}{E_k - E_{j'}} &= 2\sum_{j'}^{\text{occ}}\sum_{j}^{\text{unocc}}\frac{\left[\sum_{rr'}(c_{jr}^* - c_{j'r}^\circ)(c_{j'r'}^* + c_{j'r'}^\circ)\eta_{rr'}\right]^2}{\epsilon_{j'} + \epsilon_j}\end{aligned} \tag{23}$$

employed provisionally the same index (r, r') for starred and unstarred atoms. Combination of expressions of this type leads to the final equation for the ground-state energy (eq 24), where the notation $(^{*\circ} - {}^{\circ *})$ represents

$$\begin{aligned}E_{\text{int}} = {} & -2\sum_{rr'}\eta_{rr'}S_{rr'} + \sum_j^{\text{occ}}\sum_{j'}^{\text{occ}} \\ & \left\{4\frac{\left(\sum_{rr'}c_{jr}^*c_{j'r'}^*\eta_{rr'} - \sum_{ss'}c_{js}^\circ c_{j's'}^\circ\eta_{ss'}\right)^2 + (^{*\circ} - {}^{\circ *})^2}{\epsilon_j + \epsilon_{j'}} + \right. \\ & (\epsilon_j + \epsilon_{j'})\left[\left(\sum_{rr'}c_{jr}^*c_{j'r'}^*S_{rr'} - \right.\right. \\ & \left.\left.\left.\sum_{ss'}c_{js}^\circ c_{j's'}^\circ S_{ss'}\right)^2 + (^{*\circ} - {}^{\circ *})\right]^2\right\}\end{aligned} \tag{24}$$

a term similar to the one immediately preceding it, but with a different ordering of coefficients.

For the interaction between two identical molecules, one of which is *excited*, there will be two important cases. These correspond to the lowest possible excited states in conjugated molecules:[11] the (singlet or triplet) *p* excited state, corresponding to the transition between top occupied (ψ_m) and lowest unoccupied (ψ_{m+1}) orbitals, and the (singlet or triplet) α excited state, corresponding to one combination of the *degenerate* transitions $\psi_{m-1} \rightarrow \psi_{m+1}$ and $\psi_m \rightarrow \psi_{m+2}$. Let us write, in the usual manner

$$\psi_{m+2} = \sum a_r^*\phi_r - \sum a_s^\circ\phi_s \tag{25}$$

$$\psi_{m+1} = \sum b_r^*\phi_r - \sum b_s^\circ\phi_s \text{ (lowest unoccupied orbital)}$$

$$\psi_m = \sum b_r^*\phi_r + \sum b_s^\circ\phi_s \text{ (top occupied orbital)}$$

$$\psi_{m-1} = \sum a_r^*\phi_r + \sum a_s^\circ\phi_s$$

Assume first that one molecule is in an excited (singlet or triplet) p state. We can then transform (21), in which now $j = m$, $k = m + 1$. We notice (1) that $c_{m,r}^2 = c_{m+1,r}^2$ for all r; (2) that the following relation holds

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[19] L. Salem, *J. Am. Chem. Soc.*, **90**, 553 (1968).

$$\left|\sum_{\tau\tau'} c_{j\tau}c_{j'\tau'}\eta_{\tau\tau'}\right| + \left|\sum_{\tau\tau'} c_{k\tau}c_{k'\tau'}\eta_{\tau\tau'}\right| = \left|\sum_{\tau\tau'}(b_\tau^* + b_\tau^\circ)(b_{\tau'}^* + b_{\tau'}^\circ)\eta_{\tau\tau'}\right| + \left|\sum_{\tau\tau'}(b_\tau^* - b_\tau^\circ)(b_{\tau'}^* - b_{\tau'}^\circ)\eta_{\tau\tau'}\right|$$

(note that $|A + B| + |A - B|$ is equal to the larger of the two quantities $2|A|$ and $2|B|$); and (3) that the terms in the summation over j' can be transformed (after separating the contributions from occupied and unoccupied j') and combined in a manner similar to (23) by using the pairing property. One finds a sum involving the interaction of ψ_m with the unoccupied orbitals of the second molecule (and ψ_{m+1} with the occupied ones), and a second sum comprising the interaction of ψ_m with the occupied orbitals of the second molecule (and ψ_{m+1} with the unoccupied ones). The final result is shown in eq 26, where the abbreviated

$$\Delta E_{\text{int}}^{(\text{p})} = -2 \times \text{the larger of } \left(\begin{array}{l}\left|\sum_{\tau\tau'} b_\tau^* b_{\tau'}^* \eta_{\tau\tau'} + \sum_{ss'} b_s^\circ b_{s'}^\circ \eta_{ss'}\right| \\ \left|\sum_{\tau s'} b_\tau^* b_{s'}^\circ \eta_{\tau s'} + \sum_{s\tau'} b_s^\circ b_{\tau'}^* \eta_{s\tau'}\right|\end{array}\right) - \sum_{j'}^{\text{occ}}\left\{2\frac{\left(\sum_{\tau\tau'} b_\tau^* c_{j'\tau'}^* \eta_{\tau\tau'} - \sum_{ss'} b_s^\circ c_{j'\tau'}^\circ \eta_{ss'}\right)^2 + (*^\circ - {}^\circ*)}{\epsilon_m + \epsilon_{j'}} + \frac{1}{2}(\epsilon_m + \epsilon_{j'})\left[\left(\sum_{\tau\tau'} b_\tau^* c_{j'\tau'}^* S_{\tau\tau'} - \sum_{ss'} b_s^\circ c_{j's'}^\circ S_{ss'}\right)^2 + (*^\circ - {}^\circ*)^2\right]\right\} - \sum_{\substack{j'\\(\neq m)}}^{\text{occ}}\left\{2\frac{\left(\sum_{\tau\tau'} b_\tau^* c_{j'\tau'}^* \eta_{\tau\tau'} + \sum_{ss'} b_s^\circ c_{j's'}^\circ \eta_{ss'}\right)^2 + (*^\circ + {}^\circ*)^2}{\epsilon_m - \epsilon_{j'}} + \frac{1}{2}(\epsilon_m - \epsilon_{j'})\left[\left(\sum_{\tau\tau'} b_\tau^* c_{j'\tau'}^* S_{\tau\tau'} + \sum_{ss'} b_s^\circ c_{j's'}^\circ S_{ss'}\right)^2 + (*^\circ + {}^\circ*)^2\right]\right\} \quad (26)$$

notation is the same as in eq 24 and where the reader is again reminded that the validity of the second-order expression (terms in braces) is subject to the level m being *well separated* from all the other ones.

In the case where the molecules are different, the linear term in (26) disappears and the last summation then includes all occupied j', even $j' = m'$.

If one molecule is in an excited (singlet or triplet) α state, the change in interaction energy ΔE_{int} follows again simply from (21). It suffices to note that in the state $^1/_2(\psi_{m-1} \rightarrow \psi_{m+1} - \psi_m \rightarrow \psi_{m+2})$ orbital ψ_{m-1} loses an electron "one-half of the time" while orbital ψ_m loses an electron the "other half of the time;" similarly orbital ψ_{m+1} gains an electron one-half of the time and ψ_{m+2} gains an electron the other half. The energy changes are therefore *the same* as if "half the time" the first molecule was in the state $\psi_m \rightarrow \psi_{m+1}$ (p state) and "half the time" in the state $\psi_{m-1} \rightarrow \psi_{m+2}$. In the latter case, ΔE_{int} is given by (26) where the b_r coefficients are replaced by a_r, and ϵ_m by ϵ_{m-1}. Hence, over-all eq 27 obtains. The formulas are rather lengthy, but again, even for large systems, the summation over j' is readily

$$\Delta E_{\text{int}}^{(\alpha)} = \frac{1}{2}\Delta E_{\text{int}}^{(\text{p})} + \text{the larger of } \left(\begin{array}{l}\left|\sum_{\tau\tau'} a_\tau^* a_{\tau'}^* \eta_{\tau\tau'} + \sum_{ss'} a_s^\circ a_{s'}^\circ \eta_{ss'}\right| \\ \left|\sum_{\tau s} a_\tau^* a_s^\circ \eta_{\tau s'} + \sum_{s\tau'} a_s^\circ a_{\tau'}^* \eta_{s\tau'}\right|\end{array}\right) - \frac{1}{2} \times \sum_{j'}^{\text{occ}}\left\{2\frac{\left(\sum_{\tau\tau'} a_\tau^* c_{j'\tau'}^* \eta_{\tau\tau'} - \sum_{ss'} a_s^\circ c_{j's'}^\circ \eta_{ss'}\right)^2 + (*^\circ - {}^\circ*)^2}{\epsilon_{m-1} + \epsilon_{j'}} + \frac{1}{2}(\epsilon_{m-1} + \epsilon_{j'})\left[\left(\sum_{\tau\tau'} a_\tau^* c_{j'\tau'}^* S_{\tau\tau'} - \sum_{ss'} a_s^\circ c_{j's'}^\circ S_{ss'}\right)^2 + (*^\circ - {}^\circ*)^2\right]\right\} - \frac{1}{2}\sum_{\substack{j'\\(\neq m-1)}}^{\text{occ}}\left\{2\frac{\left(\sum_{\tau\tau'} a_\tau^* c_{j'\tau'}^* \eta_{\tau\tau'} + \sum_{ss'} a_s^\circ c_{j's'}^\circ \eta_{ss}\right)^2 + (*^\circ - {}^\circ*)^2}{\epsilon_{m-1} - \epsilon_{j'}} + \frac{1}{2}(\epsilon_{m-1} - \epsilon_{j'})\left[\left(\sum_{\tau\tau'} a_\tau^* c_{j'\tau'}^* S_{\tau\tau'} + \sum_{ss'} a_s^\circ c_{j's'}^\circ S_{ss'}\right)^2 + (*^\circ - {}^\circ*)^2\right]\right\} \quad (27)$$

evaluated. Note that eq 27 applies equally well if the first molecule is in the β *state* corresponding to the strongly allowed transition $^1/_2(\psi_{m-1} \rightarrow \psi_{m+1} + \psi_{m-2} \rightarrow \psi_m)$.

Again, if the molecules are different, the linear term disappears and last summation includes all occupied j'.

Special care is required if nonbonding orbitals are present (see, for instance, the ion plus neutral cycloaddition in part II).[19]

Summary of Important Equations and General Rules of Behavior

Equations 15 and 21, or 24, 26, and 27 for alternant hydrocarbons, as they stand, give the *exact* energy of interaction up to order S^2. Equation 24 can be verified, for instance, in the simple case of two interacting ethylene molecules; expansion of the complete four-by-four secular determinant for the four interacting molecular orbitals and neglect of terms of high order leads to (24). All these expressions, furthermore, have the particular feature that two similar sums, one with terms in $\eta_{\tau\tau'}$ *divided* by an energy, and one with the same sums but involving $S_{\tau\tau'}$ and *multiplied by* $^1/_4$ times the same energy factor, occur in each one of them.

Let us compare two such sums, for instance

$$\sum_j^{\text{occ}}\sum_k^{\text{unocc}}\frac{\left[\sum_{\tau\tau'} c_{j\tau}c_{k'\tau'}\eta_{\tau\tau'}\right]^2}{E_{k'} - E_j}$$

and

$$\sum_j^{\text{occ}}\sum_{k'}^{\text{unocc}}\frac{1}{4}(E_{k'} - E_j)\left[\sum_{\tau\tau'} c_{j\tau}c_{k'\tau'}S_{\tau\tau'}\right]^2$$

which occur in (15). Since Hückel orbital energies are comprised roughly between $\alpha - 2\beta$ and $\alpha + 2\beta$, an average excitation energy is of the order of 2β. Hence the ratio of a term in the first sum to the corresponding term in the second sum is

$$\frac{\eta_{\tau\tau'}^2}{2\beta}\Big/\frac{1}{4}(2\beta)S_{\tau\tau'}^2 = \frac{1}{\beta^2}\left(\frac{\eta_{\tau\tau'}}{S_{\tau\tau'}}\right)^2 \quad (28)$$

Now the ratio $\eta_{\tau\tau'}/S_{\tau\tau'}$ can be estimated by remarking that, if $\eta_{rr'}/S_{rr'}$ is roughly constant with distance, it should be approximatly equal to β/S_0, where S_0 is the overlap integral between adjacent π orbitals in benzene ($\sim$0.25).[20]

$$\eta_{rr'}/S_{rr'} \approx 4\beta \tag{29}$$

A more reliable value for $\eta_{rr'}/S_{rr'}$ is obtained by comparing (3), for two isolated carbon p atomic orbitals

$$\int\phi_r h\phi_{r'}\,\mathrm{d}\tau = \alpha S_{rr'} + \eta_{rr'} \quad (\alpha = \int\phi_r h\phi_r\,\mathrm{d}\tau) \tag{30}$$

with Hoffmann's semiempirical equation[8]

$$\int\phi_r h\phi_{r'}\,\mathrm{d}\tau = \frac{1.75}{2}(\alpha + \alpha)S_{rr'} \tag{31}$$

where $\alpha = -11.4$ eV. Hence $\eta_{rr'}/S_{rr'} = -8.55$ eV. With the benzene spectroscopic value $\beta = -3$ eV for the resonance integral[11]

$$\eta_{rr'}/S_{rr'} = 2.85\beta \tag{32}$$

For this value of the ratio $\eta_{rr'}/S_{rr'}$, the term in the first sum is still eight times larger than the second.[21] It seems therefore legitimate, if this calculation is reliable, to neglect the $S_{rr'}{}^2$ terms in comparison with the $\eta_{rr'}{}^2$ terms.

Under these conditions the energy expressions simplify. We write below the five useful expressions, two of which are valid in the general case and three for even-alternant hydrocarbons. In the latter case, if an arbitrary pair of interacting atoms is chosen as belonging to the starred (*) set of their respective molecules, then the topology of most interactions (see II,[19] III) is such that only pairs of atoms which are *both starred* (* *) or *both unstarred* (° °) interact. For alternant hydrocarbons, therefore, the formulas below are restricted to this type of interaction.

(A) *General Case*

Molecules in their ground states

$$E_{\mathrm{int}} = -\sum_{rr'}(q_r + q_{r'})\eta_{rr'}S_{rr'} - 2\sum_{j}^{\mathrm{occ}}\sum_{k'}^{\mathrm{unocc}}\frac{\left(\sum_{rr'}c_{jr}c_{k'r'}\eta_{rr'}\right)^2}{E_{k'} - E_j} - 2\sum_{j'}^{\mathrm{occ}}\sum_{k}^{\mathrm{unocc}}\frac{\left(\sum_{rr'}c_{kr}c_{j'r'}\eta_{rr'}\right)^2}{E_k - E_{j'}} \tag{15a}$$

Identical molecules, one of which is excited ($E_{\mathrm{int}}{}^* = E_{\mathrm{int}} + \Delta E_{\mathrm{int}}$)

$$\Delta E_{\mathrm{int}}{}^{(j\rightarrow k)} = -\left(\left|\sum_{rr'}c_{jr}c_{j'r'}\eta_{rr'}\right| + \left|\sum_{rr'}c_{kr}c_{k'r'}\eta_{rr'}\right|\right) + \sum_{rr'}(c_{jr}{}^2 - c_{kr}{}^2)\eta_{rr'}S_{rr'} + \sum_{\substack{\mathrm{all}\ j' \\ (\neq j)}}\frac{\left(\sum_{rr'}c_{jr}c_{j'r'}\eta_{rr'}\right)^2}{E_{j'} - E_j} - \sum_{\substack{\mathrm{all}\ j' \\ (\neq k)}}\frac{\left(\sum_{rr'}c_{kr}c_{j'r'}\eta_{rr'}\right)^2}{E_{j'} - E_k} \tag{21a}$$

(The linear term in $\eta_{rr'}$ disappears if the molecules are different, with no accidental degeneracy between ψ_j or ψ_k and any $\psi_{j'}$.)

(B) *Two Even-Alternant Hydrocarbons* (* * and ° ° interactions only)

Molecules in their ground states

$$E_{\mathrm{int}} = -2\sum_{rr'}\eta_{rr'}S_{rr'} + 4\sum_{j}^{\mathrm{occ}}\sum_{j'}^{\mathrm{occ}}\frac{\left(\sum_{rr'}c_{jr}{}^*c_{j'r'}{}^*\eta_{rr'} - \sum_{ss'}c_{js}{}^\circ c_{j's'}{}^\circ\eta_{ss'}\right)^2}{\epsilon_j + \epsilon_{j'}} \tag{24a}$$

Identical molecules, one of which is in excited p(L$_\mathrm{a}$) state

$$\Delta E_{\mathrm{int}}{}^{(\mathrm{p})} = -2\left|\sum_{rr'}b_r{}^*b_{r'}{}^*\eta_{rr'} + \sum_{ss'}b_s{}^\circ b_{s'}{}^\circ\eta_{ss'}\right| - 2\sum_{j'}^{\mathrm{occ}}\frac{\left(\sum_{rr'}b_r{}^*c_{j'r'}{}^*\eta_{rr'} - \sum_{ss'}b_s{}^\circ c_{j's'}{}^\circ\eta_{ss'}\right)^2}{\epsilon_m + \epsilon_{j'}} - 2\sum_{\substack{j' \\ (\neq m)}}^{\mathrm{occ}}\frac{\left(\sum_{rr'}b_r{}^*c_{j'r'}{}^*\eta_{rr'} + \sum_{ss'}b_s{}^\circ c_{j's'}{}^\circ\eta_{ss'}\right)^2}{\epsilon_m - \epsilon_{j'}} \tag{26a}$$

(The linear term disappears if the molecules are different with no accidental degeneracy between E_j or E_k and any $E_{j'}$; the last term breaks down if ψ_m is not well separated from all $\psi_{j'}$.)

Identical molecules, one of which is in excited α(L$_\mathrm{b}$) state

$$\Delta E_{\mathrm{int}}{}^{(\alpha)} = \frac{1}{2}\Delta E_{\mathrm{int}}{}^{(\mathrm{p})} - \left|\sum_{rr'}a_r{}^*a_{r'}{}^*\eta_{rr'} + \sum_{ss'}a_s{}^*a_{s'}{}^*\eta_{ss'}\right| - \sum_{j'}^{\mathrm{occ}}\frac{\left(\sum_{rr'}a_r{}^*c_{j'r'}{}^*\eta_{rr'} - \sum_{ss'}a_s{}^\circ c_{j's'}{}^\circ\eta_{ss'}\right)^2}{\epsilon_{m-1} + \epsilon_{j'}} - \sum_{j'(\neq m-1)}^{\mathrm{occ}}\frac{\left(\sum_{rr'}a_r{}^*c_{j'r'}{}^*\eta_{rr'} + \sum_{ss'}a_s{}^\circ c_{j's'}{}^\circ\eta_{ss'}\right)^2}{\epsilon_{m-1} - \epsilon_{j'}} \tag{27a}$$

(Again the linear terms disappear if the molecules are different with no degeneracy between E_{m-1} or E_{m+2} and any $E_{j'}$; the last term breaks down if ψ_{m-1} is not well separated from all $\psi_{j'}$.)

In all these equations the coefficients c_{jr} are the ordinary Hückel atomic orbital coefficients (b_r for the top bonding orbital, a_r for the next-to-top-bonding one) and ϵ_j the Hückel *binding* energies (ϵ_m, top bonding orbital). For a given configuration of the interacting molecules, knowledge of these quantities allows the numerical calculation of the interaction energy in terms of the various overlaps $S_{rr'}$ and interaction integrals $\eta_{rr'}$. The $\eta_{rr'}$'s can also be expressed in terms of $S_{rr'}$ *via* (6). *In the following work, the parameter k of eq 6 is taken equal to 3.*

At the outset, two conclusions emerge from the general equations (15a and 21a). (1) In the interaction between two molecules in their ground states, the repulsion energy term $-\sum_{rr'}(q_r + q_{r'})\eta_{rr'}S_{rr'}$ is rather uniformly distributed over pairs of interacting atoms. The quantity $q_r + q_{r'}$ which multiplies $\eta_{rr'}S_{rr'}$ will always be near 2 so that the coefficient of each $\eta_{rr'}S_{rr'}$ will be nearly the same. Whether a given thermal reaction is favored or not, and proceeds along a given pathway, *must therefore depend on the interaction between top occupied orbitals on one molecule and lowest unoccupied orbitals of the other* (and conversely).

Fukui was the first to stress the role of these "frontier

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[20] Note that this relationship can only give an order of magnitude for $\eta_{rr'}/S_{rr'}$, since β contains the kinetic energy, whereas η does not, and since β is relative to a pπ, rather than a pσ, overlap.

[21] Note that, for the value of $\eta_{rr'}/S_{rr'}$ given by (32), second-order perturbation theory, as developed previously,[16] is valid. The ratio of a typical matrix element $\Sigma c_{jr}c_{k'r'}\eta_{rr'}$ over the energy difference $E_{k'} - E_j$ is no larger than $2.85\beta S_{rr'}$ divided by β (the smallest possible excitation energy), which is still small for $S_{rr'} \sim 0.1$.

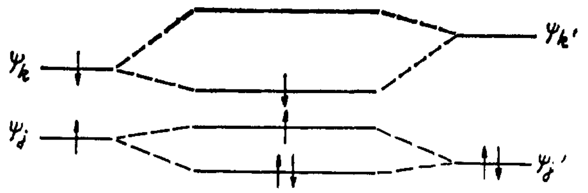

Figure 5. Favorable interaction between an excited molecule and a different neighbor.

orbitals" (highest occupied orbital of the diene and lowest occupied orbital of the dienophile) in his study of Diels–Alder reactivity.[22] Fukui has also emphasized[23,24] the importance of a perturbation treatment of the interaction between conjugated molecules and has developed such a treatment, including both σ and π electrons, together with orbital rehybridization, but neglecting overlap explicitly. He was thus able to confirm or predict the *syn* or *anti* character of various two-center reactions.

However, it is clear from eq 15a that the repulsive terms due to orbital overlap must be included in a quantitative evaluation of interaction energies, and that they can possibly influence the course of a reaction: for instance, a significant decrease in π charge density on an atom, and hence a decrease in the size of the shell into which other electrons are forbidden to penetrate, can lead to a significant decrease of its repulsion with other atoms.[25]

(2) In the interaction between an excited molecule (excitation $\psi_j \rightarrow \psi_k$) and a molecule in its ground state, two cases must be considered. If the molecules are *identical*,[26] the existence of a substantial decrease in the interaction energy ($\Delta E_{\text{int}} < 0$) due to the excitation *depends essentially on the magnitude of the interaction between the orbital ψ_j which loses the electron and its degenerate partner $\psi_{j'}$, and between the orbital ψ_k which gains the electron and its partner, $\psi_{k'}$.* Indeed, the interaction energy in the presence of an excited electron (Figure 4a, for instance) is smaller than the ground-state interaction energy by (a) the energy decrease of this electron in the intermolecular orbital $\psi_k + \psi_{k'}$; (b) the energy increase of the "hole" which it leaves in the intermolecular orbital $\psi_j - \psi_{j'}$. Mathematically these effects are contained in the term $-(|\sum_{rr'} c_{jr}c_{j'r'}\cdot\eta_{rr'}| + |\sum_{rr'} c_{kr}c_{k'r'}\eta_{rr'}|)$ of eq 21a. If the molecules are *different*, the interaction energy change is determined by the second-order terms in (21a). In particular, a photochemical reaction will be favored, *via* a large negative ΔE_{int}, if either (1) there is a strong interaction between the orbital ψ_j which loses the electron and an orbital in the second molecule of neighboring, but *lower* energy, or (2) there is a strong interaction between the orbital ψ_k into which the electron jumps and an orbital in the second molecule of neighboring, but *higher*, energy. Again these effects will either raise the energy of the hole or lower the energy of the excited electron (Figure 5), thus providing a substantial decrease in interaction energy. In Figure 5 the relevant orbitals of the second molecule, $\psi_{j'}$ and $\psi_{k'}$ are, respectively, the top occupied and lowest unoccupied orbitals. This is very often the case. Otherwise B would have an excited state below that of A, and A would in principle transfer its excitation energy to B.

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[22] K. Fukui in "Molecular Orbitals in Chemistry, Physics, and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press Inc., New York, N. Y., 1964, p 573, where an expression very similar to the second and third terms of (15a) appears. The same idea is used by R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, 87, 4388 (1965), in their study of the *endo–exo* relationship.

[23] K. Fukui, *Bull. Chem. Soc. Japan*, 39, 498 (1966).

[24] K. Fukui and H. Fujimoto, *ibid.*, 39, 2116 (1966).

[25] This "*size*" effect is entirely distinct from any attractive or repulsive effects which might arise from the net charge density on the interacting atoms. These two-electron interactions have not been included in the theory, although they should be in a more rigorous theory (see the discussion of part II[19]). The size effect observed here is such that two atoms with charge density 0.90 will repel less than two atoms with charge 1.10, although the Coulombic repulsions are the same.

[26] Or also if the molecules are different but with an accidental degeneracy between ψ_j or ψ_k and some $\psi_{j'}$.