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Orbital Correspondence Analysis in Maximum Symmetry: Formulation and Conceptual Framework

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A recently proposed method for the analysis of the course of chemical reactions, based on the maximal use of available symmetry, is formulated as a set of procedural rules. The application of these rules is illustrated with a simple prototype reaction:

$$CH_2 + C_2H_4 \rightarrow \text{cyclo–}C_3H_6.$$

They are then derived, using the formalism of time-dependent perturbation theory within the Born-Oppenheimer approximation, thus bringing out the method's underlying assumptions and its relation to the widely used Woodward-Hoffmann procedure.

Key words: Orbital correspondence in maximum symmetry – Woodward-Hoffmann rules

1. Introduction

A method is concurrently being proposed by one of us [1], in which the course of a chemical reaction is analyzed in terms of the correspondence between the symmetry species of the molecular orbitals of reactants and products, within the symmetry point group common to both. Though closely related to the well known procedures of Woodward and Hoffmann [2], and Longuet-Higgins and Abrahamson [3], *Orbital Correspondence Analysis in Maximum Symmetry* (OCAMS) differs from it in several essentials:

a) All symmetry elements common to the reactant and product systems, including those which are not preserved along the reaction path, are considered explicitly;

b) Symmetry elements which are not used in the Woodward-Hoffmann analysis "because they do not bisect bonds made or broken in the process" [2a], are not ignored;

c) The requirements imposed by symmetry on the geometry of the reaction path emerge directly from the analysis, and need not be deduced by trial and error from successive analyses with models simulating alternate pathways.

Our present objective is to establish the connection between the heuristic point of view motivating the primary exposition of the OCAMS procedure [1], which stresses its utility for the analysis of organic reactions, and quantum mechanical first-principles. In the following section we will reformulate the principal ideas underlying the method as a set of operational rules, illustrating their application with a very simple reaction, the cyclo-addition of singlet methylene to ethylene, which has been the subject of thorough theoretical investigation [4, 5]. This will be followed, in Section 3, by a derivation of these rules within the framework of time-dependent perturbation theory. They will be shown to have theoretical plausibility, in the sense that they can be obtained from a rigorous starting point by means of a sequence of well defined, if bold, assumptions and simplifications.

2. The OCAMS Procedure and Its Application

The reactant and product systems are set up in a common symmetry point-group. If one of them belongs to a non-commutative symmetry point group, *i.e.* one that has degenerate representations, its symmetry is reduced by a slight distortion to that of the other system.

The molecular orbitals are stacked in the usual way, in order of increasing energy, and each is assigned to a symmetry species on the basis of its transformation properties within the group.

The "allowedness" and geometrical requirements of the reaction are deduced as follows:

2.1. Direct Correspondence

Molecular orbitals of reactants and products which have similar transformation properties in the symmetry point group common to both are said to be in direct correspondence. If all the occupied orbitals of the two species correspond directly with each other[1], the reaction is "allowed" under a totally symmetric displacement.

In this special case the direct correspondences, drawn so as to obey the non-crossing rule in the common group, will continue to do so along any totally symmetric pathway. More generally, however, symmetry is reduced along the reaction path below that of the original group, so several of its representations will map onto each of those of the ensuing subgroup. Two crossing *correspondence lines* between orbital-pairs that belong to different representations of the parent group will still cross after symmetry has been reduced to that of a subgroup in which they belong to the same representation, in contrast to *correlation lines* which necessarily avoid such crossings. What really matters, of course, is that the correlation between the *electronic configurations* of reactants and products must be maintained along the reaction path [3]. This correlation is identical whether it has been established, once and for all, by a correspondence diagram or by a set of correlation diagrams, each of which takes explicit note of the avoided crossings along pathways characterized by a different subgroup.

Fig. 1 shows the reactants, ethylene + methylene, and the product, cyclopropane, in the geometry suitable for direct, concerted, cycloaddition. Both systems have C_{2v} symmetry, that of the product having been reduced from D_{3h} by a slight elongation of the two newly formed sigma-bonds. The stacking of the molecular

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[1] In open-shell states the singly and doubly occupied orbitals must correspond separately, the former remaining above the latter.

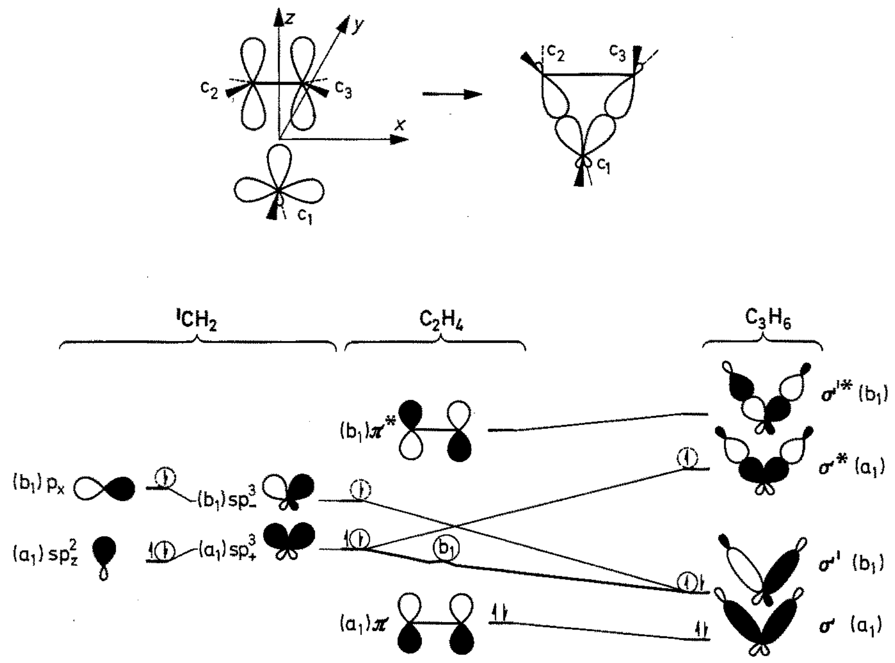

Fig. 1. $^1CH_2 + C_2H_4$ – direct approach (C_{2v})

orbitals and their assignment to symmetry species of C_{2v} are self-evident. We note that the occupied a_1 orbitals of reactant and product correspond, but the HOMO of the reactant corresponds with the LUMO of the product (both a_1) and *vice versa* (both b_1). The ground-state reaction is thus ruled to be "forbidden" under a totally symmetric displacement.

As a result of the HOMO↔LUMO correspondence, the first excited singlet states of reactant and product do correlate, $(a_1^2 a_1^1 b_1^{*1}) \leftrightarrow (a_1^2 b_1^1 a_1^{*1})$, so the concerted photochemical cycloaddition would be characterized as "allowed". The same would be true of the analogous triplet reaction, provided that the same orbital sequence is maintained for the triplets as for the singlets[2].

2.2. *Correspondence Induced by Displacement along a Symmetry Coordinate*

Reactant and product orbitals which transform as different symmetry species, Γ_r and Γ_p respectively, can be brought into correspondence by a displacement along a symmetry coordinate, i.e. one that belongs to an irreducible representation, Γ_d, such that the direct product $\Gamma_r \times \Gamma_d \times \Gamma_p$ contains the totally symmetric representation. For the commutative groups to which the method restricts itself, $\Gamma_r \times \Gamma_d \times \Gamma_p$ must equal the totally symmetric representation, so the requirement

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[2] Methylene is anomalous in that its first triplet lies below the closed shell singlet. Cycloaddition of this triplet to ethylene with formation of the highly unstable triplet of cyclopropane, though formally allowed, would hardly be expected.

for an "inducing" displacement is

$$\Gamma_d = \Gamma_r \times \Gamma_p \tag{1}$$

From Fig. 1, the correspondence that must be induced to allow concerted, ground-state cycloaddition is between $\Gamma_r = a_1$ and $\Gamma_p = b_1$; the inducing displacement must therefore be a symmetry coordinate of species b_1. Clearly, however, a displacement that transforms as b_1 is symmetric only with respect to the identity and to reflection in the xz plane, i.e. it reduces the symmetry of the system from C_{2v} to C_s. Any such distortion brings the methylene group closer to one end of the ethylenic double bond than to the other, so that concerted cycloaddition, formally allowed by symmetry, is prevented by the geometry of the permitted inducing displacement.

Examples of reactions in which the inducing displacement leads to concerted bond formation and rupture have been noted, as has an example in which two separate correspondences had to be induced by displacements of two different symmetry species [1]. In the latter case, if

$$\left.\begin{array}{r}\Gamma_{r'} \times \Gamma_{p'} = \Gamma_{d'} \\ \text{and} \qquad \\ \Gamma_{r''} \times \Gamma_{p''} = \Gamma_{d''}\end{array}\right\} \tag{2}$$

simultaneous, or consecutive, displacements along both d' and d'' are required, with the result that the overall displacement must be one that is not a symmetry coordinate in the original symmetry point group, but rather belongs to a reducible representation, Γ_d^{red} such that

$$\Gamma_d^{red} = \Gamma_{d'} + \Gamma_{d''} \tag{3}$$

2.3. Composite Displacements

A distortion Γ_d^{red} which, like that of Eq. (3), belongs to a reducible representation, can also induce a correspondence between orbitals r and p, provided the direct product: $\Gamma_r \times \Gamma_{d'} \times \Gamma_{d''} \times \Gamma_p$ contains the totally symmetric representation. For commutative groups, this requirements reduces to:

$$\Gamma_d^{red} \approx \Gamma_{d'} \times \Gamma_{d''} = \Gamma_r \times \Gamma_p \equiv \Gamma_d \tag{4}$$

i.e., the reducible representation Γ_d^{red} is simulated by the irreducible representation Γ_d.

A composite displacement of this kind is illustrated in Fig. 2. A twist of one CH_2 group about the molecular axis of ethylene allows that reactant to bond antarafacially to methylene. This motion can be constituted by combining a rotation about the molecular axis (b_2) with a twist of the two CH_2 groups about the same axis (a_2). Clearly, the composite displacement labelled "b_1" belongs to the reducible representation ($b_2 + a_2$), but it induces the $a_1 \rightarrow b_1$ correspondence required by Fig. 1, as if it were a symmetry coordinate of species: $b_2 \times a_2 = b_1$ and formally allows concerted antarafacial cycloaddition. The question whether an "allowed" mechanism of this kind can actually occur is beyond the scope of OCAMS, since it is a matter of energetics rather than symmetry.

A composite displacement will in general be sought only when simple displacements of appropriate symmetry cannot be found. The search can be systema-

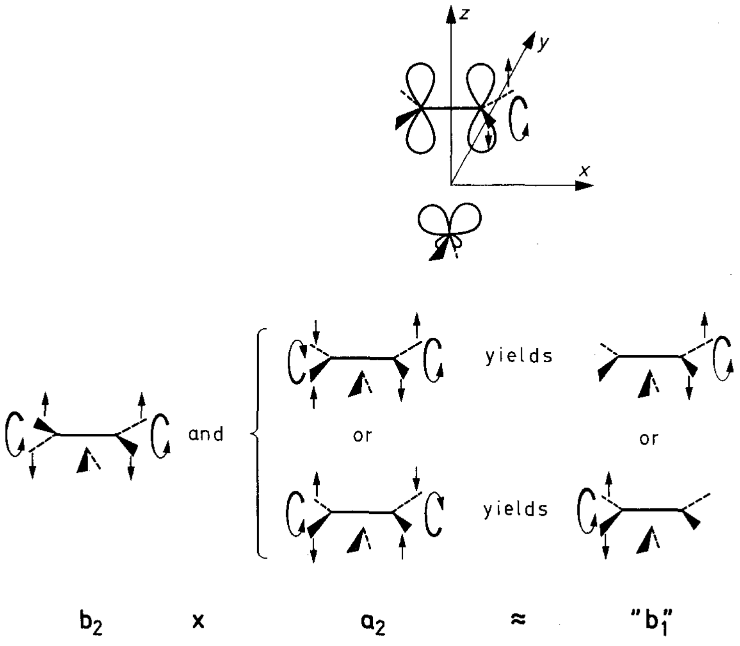

Fig. 2. Composite motion for antarafacial reaction of ethylene

tized by using the character table in a straightforward manner to determine all pairs of irreducible representations that have the desired product. Then, having established the symmetry requirements, one can go on to construct, out of symmetry coordinates obeying these requirements, composite motions which also satisfy the geometric specifications of the reaction. This way of progressing, which can, of course, be generalized to higher order, reduces the amount of trial and error involved to a minimum[3]. It should be borne in mind, however, that the successive application of even a few distortions of different symmetry species very rapidly destroys the symmetry of the system altogether, so that all reactions eventually become "symmetry-allowed".

It may be noted in passing that the degree to which symmetry is reduced by a composite displacement depends, in a rather delicate manner, on the nature of the simple displacements which make it up. If motion along any one of the symmetry coordinates is continued until the system is transformed into an intermediate with the same symmetry as reactants and products, one can, in a sense, regard the composite displacement as a two step process, in each step of which the symmetry of the system is reduced only to the degree required by the simple displacement effective in that step. The present method does not distinguish between displacements which are genuine distortions and those which merely represent a reorientation of the reactants or products from one possible conformation to

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[3] This does not mean that the use of common sense is discouraged.

another. It is in the latter situation that the distinction between symmetry coordinates which genuinely break the symmetry of the system and those which describe reorientations that leave the system in a group of high symmetry, is most valuable.

2.4. Reduction of Symmetry by the Reaction

If the product system has lower symmetry than that of the reactants, the original symmetry can be restored by the construction of an appropriate superposition of product states, to which the rules enunciated in the preceding sections are then applied. Alternatively, if it belongs to a higher – but still commutative – symmetry point group, one can treat the reaction within the group of higher symmetry by forming an appropriate superposition of reactant states. In the most general case, both the reactant and the product have to be raised in symmetry by forming appropriate linear combinations, in order to obtain a common symmetry group. This is illustrated for our model reaction in Fig. 3. It was shown in Section 2.2 that motion along a symmetry coordinate of the proper symmetry species for allowing concerted cycloaddition (b_1) destroys the equivalence of the two carbon atoms of ethylene for reaction with that of methylene. We then presume that the reaction should proceed by means of a pathway which is unsymmetrical with respect to bonding with these two, originally equivalent, carbon atoms. The product of the first step of the reaction is thus taken to be a three-carbon chain intermediate.

C_{2v} symmetry with respect to the symmetry elements of the reactant system is restored by taking linear combinations of corresponding orbitals of the two possible products. The phase of each combination is chosen so that it retains its transformation properties in C_{2v} geometry, i.e. before the choice of the particular mode of bonding has been made. Thus $(\sigma_{12}+\sigma_{13})$ was chosen because the alternative $(\sigma_{12}-\sigma_{13})$, has a nodal plane through the p_z orbital of C_1 while the reactants are still symmetrically disposed. Similarly $(\pi_{13}-\pi_{12})$ was chosen rather than $(\pi_{13}+\pi_{12})$ because the latter is neither symmetric nor antisymmetric to C_z and σ_{yz} in the C_{2v} orientation.

Inspection of Fig. 3 confirms, as suggested by Fig. 1, that stepwise cycloaddition, via a three-carbon chain intermediate generated by mutual approach of the two reactants in the xy-plane, is allowed[4].

3. A Formal Derivation of the OCAMS Procedure

3.1. Motivation and Preliminary Considerations

We shall attempt to derive the procedural rules of OCAMS from a rigorous starting point, by means of a sequence of well-defined and reasonable approximations. The derivation provides a general theoretical framework within which detailed quantitative investigation of the validity of the approximations involved

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[4] Semi-empirical calculations confirm that the reaction path does indeed have the character indicated above, but suggest that the intermediate is too unstable to have a finite lifetime, and collapses immediately to cyclopropane [4, 5].

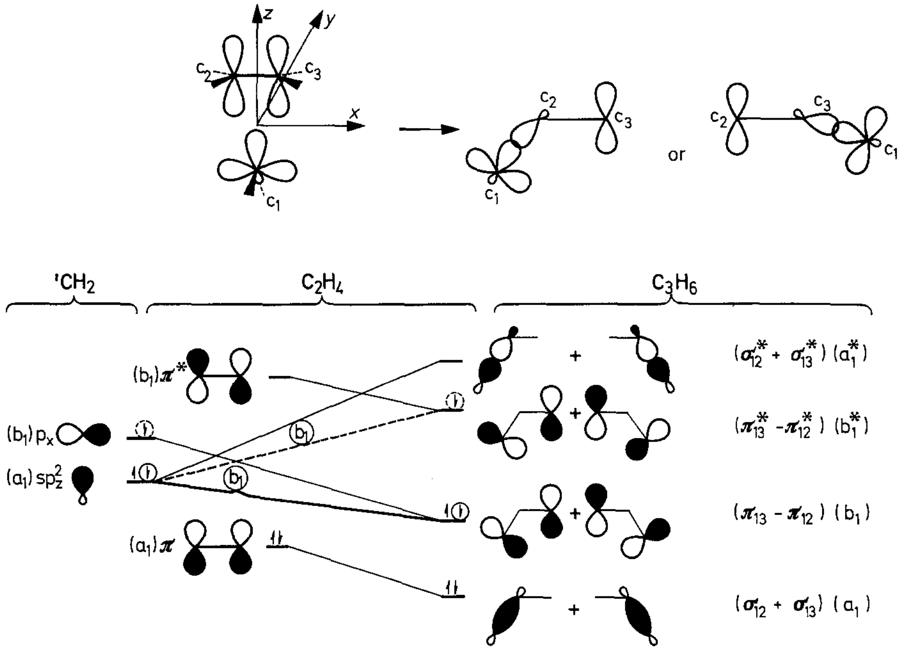

Fig. 3. $^1CH_2 + C_2H_4$ – Formation of 3-carbon chain intermediate (C_{2v})

can in principle be carried out in any particular system of choice. The framework established also enables a more detailed comparison with the Woodward-Hoffmann scheme to be made than is otherwise possible, thus assessing in more general terms the main advantages of the present approach[5].

The main assumptions to be invoked in the ensuing discussion are generally accepted in similar contexts, so their validity does not seem to require explicit consideration. Specifically, the present discussion does not attempt to provide a quantitative justification, or even a firm theoretical foundation, for the molecular orbital correlation procedure. The experimental success of this approach, which has been extensively documented over the past decade, is its best justification.

The main ingredients of the method formulated in Section 2 are the symmetry properties of the molecular orbitals occupied in the reactant and product and those of the displacement inducing the reaction. Such features are characteristic of treatments couched in terms of some kind of perturbation theory, in which the reactant and product are initial and final states (incoming and outgoing channels) respectively. A way should therefore be found of associating the displacement with the perturbation.

The approach to be developed is based on the essential idea that the nuclear framework can be partitioned into an effectively static part, which can be treated within a proper Born-Oppenheimer framework, and a dynamic part, consisting

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[5] The practical advantages of OCAMS, particularly in those cases where its conclusions are in conflict with those of the Woodward-Hoffmann rules, will be discussed elsewhere [6].

of those atoms whose motion is crucial to the course of the reaction. It could, of course, be refined by introducing the dynamics of all nuclei on an initially equal footing, and then partitioning those that are really relevant from those that are not. The essentially static nuclei are those that determine the symmetry point group to be used in the analysis, whereas the remainder, by moving, give rise to a distortion which is crucially significant to the course of the reaction.

Actually, even the "static" nuclei are not literally static. Some totally symmetric relaxation of the nuclear framework does take place and may be of considerable quantitative significance. Moreover, for some reactions, to be referred to as allowed in zero order, no distortion whatever is needed. In this latter case, if we were to regard all the nuclei as static, we would – at best – be describing resonance between two electronic wavefunctions of the same symmetry. A genuine reaction can take place only under an appropriate perturbation of the Hamiltonian describing the initial system. The totally symmetric relaxation of the essentially static part is always important, and it may be the main contributor to the transition probability of a zero-order reaction.

We shall first (Sects. 3.2–3.4) develop a formalism for dealing with the relatively simple situation encountered when the reactants and products can be oriented so as to have the same symmetry properties. Distortions which reduce the symmetry along the reaction path are allowed, provided that the system again becomes totally symmetric when the reaction is complete. It will then be shown (Sect. 3.5) how a permanent reduction in the symmetry of the products, as compared with that of the reactants, can be dealt with. This will be done by making the assumption, fundamental to measurement theory in quantum mechanics, according to which the breakdown in symmetry is a consequence of the measurement process itself. It follows that the products obtained are in a state which is a superposition of the various equivalent Born-Oppenheimer states, each of which is of lower symmetry than the superposition.

3.2. The Transition Amplitude

The simplest way of obtaining an expression for the transition amplitude that exhibits the qualitative features relevant to the present discussion is a time-dependent perturbation theory treatment. One could, equivalently, start from Lippmann's formal treatment of reactive scattering [7], which has been the basis of a discussion of the Woodward-Hoffmann and other symmetry rules by George and Ross [8].

The reaction is assumed to involve some nuclear motion which is explicitly time-dependent and gives rise to the electronic transition between the state of the reactants and that of the products. The evolution operator in the interaction representation

$$U_I(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^{t} V_I(\tau) U_I(\tau, t_0) d\tau \qquad (5)$$

gives rise to the transition between the initial (reactant) and final (product) states with the transition amplitude

$$T_{r\to p}=\langle\Psi_p|U_I(t,t_0)|\Psi_r\rangle \tag{6}$$

where $t\to\infty$ to obtain a well defined expression. Iterating the evolution operator one obtains

$$\begin{aligned}T_{r\to p}=&\langle\Psi_p|\Psi_r\rangle-\frac{i}{\hbar}\int_{t_0}^{t}d\tau\langle\Psi_p|V_I(\tau)|\Psi_r\rangle\\&+\left(\frac{i}{\hbar}\right)^2\int_{t_0}^{t}d\tau\int_{t_0}^{\tau}d\tau'\,\langle\Psi_p|V_I(\tau)V_I(\tau')|\Psi_r\rangle+\cdots\end{aligned} \tag{7}$$

The form of the various terms of this formal expansion will be sufficient for the discussion that follows. An explicit summation to infinite order of the terms that give rise to transitions between initial and final states of various symmetries might have some formal aesthetic appeal, but does not really contribute to the qualitative discussion which follows.

3.3. The Independent Particle Model

At this stage we introduce the basic assumption of the independent particle model, according to which the wavefunctions of both reactant and product can be written as antisymmetrized products of single electron orbitals. The distortion amounts to placing some of the nuclei in new positions, and can therefore be written as a sum of electron-nuclear attraction terms, involving attractions to the nuclei in the new positions and corrections for the missing nuclei in the positions originally assumed in writing H_0. The distortion is therefore a single-particle operator and this fact is sufficient to account for the factorization of the zero- and first-order terms in the expression for the transition amplitude into single-electron factors. The simplest way of obtaining this kind of factorization to any higher order, is to invoke the more restrictive (and fundamentally less satisfactory) assumption that the wavefunction can be written as a Hartree-type simple product of single electron orbitals. This assumption has been surprisingly successful in the context of Hückel-type treatments with appropriate effective Hamiltonians. It is this success, rather than any formal argument, which makes it an acceptable assumption in the present context as well.

At this stage one should recognize that the assumptions made so far lead into the orbital symmetry considerations which follow. It is well known that the more rigorous requirement of state-symmetry conservation is less restrictive and in certain situations the only valid requirement. These situations exhibit a breakdown of the strict independent particle model and require an extended scheme, involving some type of explicit consideration of correlation effects, such as configuration interaction.

3.4. Formulation of the OCAMS *Symmetry Rules*

Let us assume that $\mathscr{H}'$ and $\mathscr{H}''$, the Born-Oppenheimer Hamiltonians of the reactants and products respectively, belong to the same symmetry point group, G, and proceed to a discussion of the symmetry properties of the distortions, which can be uniquely written in terms of irreducible tensor operators with respect to G. Denoting the distortions with respect to $\mathscr{H}'$ and $\mathscr{H}''$, respectively, by V' and V'', one obtains

$$V' = \sum_{\Gamma, m} V'_{\Gamma, m}; \quad V'' = \sum_{\Gamma, m} V''_{\Gamma, m} \tag{8}$$

where the sums are over irreducible representations of the group. The only term which is not identical in V' and V'' is that corresponding to the identity representation. This follows from the fact that the difference between $\mathscr{H}'$ and $\mathscr{H}''$ is totally symmetric (as each one of them is) and that the distortions V' and V'' are simply related by the obvious requirement

$$\mathscr{H}' + V' = \mathscr{H}'' + V'' \tag{9}$$

If the sums contain only the totally symmetric representation, the total Hamiltonian still has the same symmetry as $\mathscr{H}'$ and $\mathscr{H}''$. In general, however, V' and V'' will contain terms, common to both, belonging to additional irreducible representations.

Returning now to the probability amplitude, it is obvious that the leading term suffices to account for the direct (zero-order) correspondences and those induced by displacement along a symmetry coordinate. The zero-order correspondences are induced by the totally symmetric component of the perturbation, with the obvious selection-rule that the direct product of Γ_r and Γ_p, the symmetry species of the corresponding molecular orbitals of the reactant and product respectively, should contain the identity. The non-totally symmetric terms of V' induce the further correspondences which are associated with the symmetry breaking distortions of the original Hamiltonian. Correspondences which require a distortion belonging to one of the irreducible components of V' are allowed in first-order. Further correspondences are made by the higher-order terms, in a manner which depends straightforwardly on the new irreducible representation, which can be obtained by forming direct products of those that appear in V'. Obviously, although a quantitative study may require a summation of the various terms in the perturbation expansion to high-order, the correspondences that are actually introduced are exhausted after a finite and usually small number of terms have been inspected.

It might be tempting to explore the quantitative advantages of the retention of maximum symmetry in the analysis of reactions in which the expected distortion is not too large. In those cases, the fact that a distinction between correspondences induced in different orders of perturbation theory is made may have some dynamic consequences, such as a preference for reactions which require, say, first order correspondences only. Although these considerations may have some potential interest, they can be extremely hazardous. In our model reaction, for example, we could have chosen an alternative orientation of the reactants to that of Fig. 1. Still in C_{2v} symmetry, we could have rotated the CH_2 molecule by 90° and obtained the conformation shown in Fig. 4. The OCAMS analysis would have then shown the excited state reaction to be "allowed in first-order", requiring an a_2 distortion, rather than "allowed in zero-order" as indicated by Fig. 1. Clearly the a_2 displacement called for is a rotation of the methylene molecule by

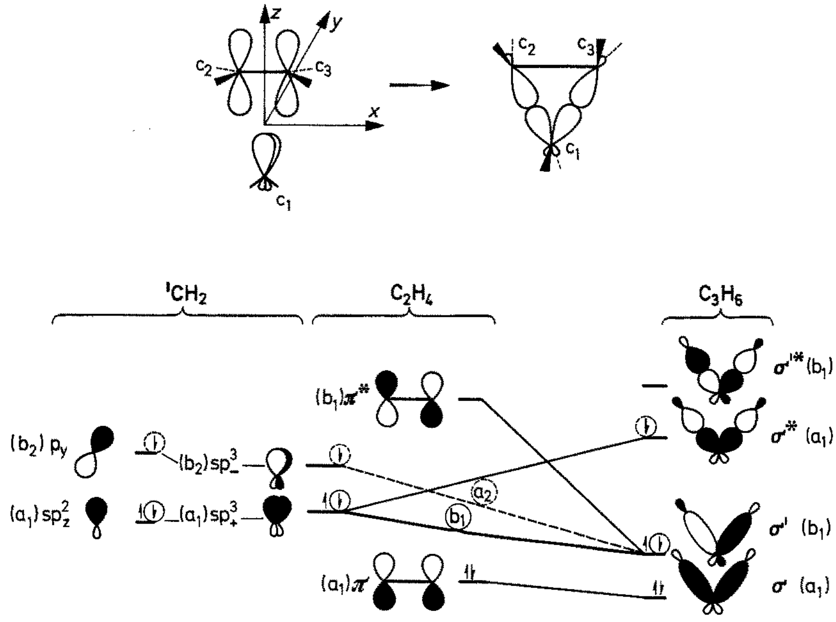

Fig. 4. $^1CH_2C_2H_4$ – Alternative orientation (Methylene in *xz* plane)

90°, back to the orientation of Fig. 1. It costs no energy, and can hardly be considered to be a distortion, since its only function is to correct an initially poor choice of the mutual orientation of the reactants, even – though this is not necessarily always the case – regenerating the original C_{2v} symmetry.

3.5. Superposition of Product States

If the straightforward Born-Oppenheimer Hamiltonian of the product does not belong to the same symmetry group as that of the reactants, one can always restore the higher symmetry by explicitly introducing nuclear dynamics. What must be done is to allow for the various equivalent nuclear conformations to be realized by a slight extension of the Born-Oppenheimer scheme, comprising the superposition of the corresponding wavefunctions. The nuclear component of each one of them can be assumed to be a product of well-localized functions (in the limit, δ functions) which are totally non-overlapping, so that no interference between the various terms occurs. Thus, the total wavefunction is still degenerate in energy with each of the equivalent Born-Oppenheimer states out of which it is constructed, but has the higher symmetry actually needed for direct correlation with the reactant. The actual transition probability to each one of the equivalent Born-Oppenheimer product states is equal to the total transition probability computed, divided by the number of equivalent states.

A formal way of raising the symmetry of the reactants and/or products so as to make them identical, with a minimal amount of extension of the Born-Oppenheimer framework, is suggested by the following considerations. Assume that the reactant possesses some kind of binary symmetry element, such as a plane of symmetry[6]. If the product does not have that symmetry element, then, of course, the two orientations of the product related to one another by the reflection in the plane considered are equally likely. Furthermore, in a strict sense, the actual product is a superposition of the two, having the same symmetry properties as the *total* (rather than the electronic) wavefunction of the reactant. The observation of one or the other product in an actual experiment is interpreted, in this strict sense, as a consequence of the measurement process itself. In order to avoid abandoning the Born-Oppenheimer framework altogether, we employ the following explicit extension of the concept of isodynamic operations originally introduced by Altmann [11] in his discussion of the symmetry groups of non-rigid molecules.

The Born-Oppenheimer Hamiltonian $\mathscr{H}$ of the reactants, commuting with the binary operation $\mathscr{R}$, bifurcates into $\mathscr{H}_1$ and $\mathscr{H}_2$, such that $\mathscr{R}\mathscr{H}_1=\mathscr{H}_2\mathscr{R}$. $\mathscr{H}_1$ and $\mathscr{H}_2$ thus refer to isodynamic systems with electronic eigenfunctions ψ_1 and ψ_2. The following relations will be relevant in the discussion to follow:

$$\left.\begin{aligned}&\mathscr{R}^2=1\\&\mathscr{H}_1\psi_1=E\psi_1;\quad \mathscr{H}_2\psi_2=E\psi_2\\&\mathscr{R}\psi_1=\psi_2\end{aligned}\right\}\tag{10}$$

To obtain a symmetrized Hamiltonian which is also degenerate with $\mathscr{H}_1$ and $\mathscr{H}_2$ we introduce the spin-like projection operators α and β which satisfy $\alpha^2=\alpha$, $\beta^2=\beta$, $\alpha\cdot\beta=0$, the spin-like functions ζ and η such that

$$\alpha\zeta=\zeta;\quad \alpha\eta=0;\quad \beta\zeta=0;\quad \beta\eta=\eta\tag{11}$$

and the operator ρ satisfying $\rho\zeta=\eta$; $\rho\eta=\zeta$.
The symmetrized Hamiltonian

$$\tilde{\mathscr{H}}=\alpha\cdot\mathscr{H}_1+\beta\cdot\mathscr{H}_2\tag{12}$$

is easily shown to be invariant under the operator $\tilde{\mathscr{R}}=\rho\mathscr{R}$. The common eigenfunctions of $\tilde{\mathscr{H}}$ and $\tilde{\mathscr{R}}$ are

$$\tilde{\psi}_{\pm}=\zeta\psi_1\pm\eta\psi_2\tag{13}$$

such that

$$\left.\begin{aligned}&\tilde{\mathscr{H}}\tilde{\psi}_{\pm}=E\tilde{\psi}_{\pm}\\ \text{and}\qquad &\tilde{\mathscr{R}}\tilde{\psi}_{\pm}=\pm\tilde{\psi}_{\pm}\end{aligned}\right\}\tag{14}$$

As $\mathscr{H}_1$ and $\mathscr{H}_2$ can be reduced to $\tilde{\mathscr{H}}$, the Hamiltonian symmetrical with respect to $\mathscr{R}$, $\tilde{\mathscr{H}}$ reduces to $\mathscr{H}\cdot(\alpha+\beta)$. The doubling of eigenstates of $\tilde{\mathscr{H}}$ in comparison with $\mathscr{H}$ can be eliminated by requiring a continuous one to one correspondence, such that to each state ψ there corresponds a state $\tilde{\psi}$ having the same eigenvalue with respect to $\tilde{\mathscr{R}}$ that ψ has with respect to $\mathscr{R}$.

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[6] The formal extension to elements of higher than binary symmetry is straightforward.

Having formally extended the Born-Oppenheimer approximation so as to enable the treatment of the reactants and products within the same symmetry group we now see that this is in full correspondence with the informal treatment outlined in Section 2.4. Instead of, loosely, referring to specific linear combinations of electronic orbitals corresponding to *different* Born-Oppenheimer Hamiltonians, we more properly refer to linear combinations of states which are eigenfunctions of an explicit Hamiltonian. All the advantages of the Born-Oppenheimer approximation have been preserved. The present treatment thus shows that the formally imprecise treatment of Section 2.4 is fully reliable, in the sense that its conclusions are in complete accord with those of the more rigorous formulation.

3.6. Choice of the Symmetry Group for the Analysis

It should be borne in mind that although the use of symmetry is often helpful, it cannot lead to conclusions in conflict to those dictated by theoretical considerations that are independent of the symmetry properties. The amount of symmetry taken into account is thus entirely a matter of convenience. If the molecular orbitals are classified according to their symmetry species with respect to a larger group, then one has more information about them. If the reaction is "allowed in zero-order" within this classification, it will certainly also be "allowed" within any lower one. The introduction of a distortion belonging to a given irreducible representation of the original symmetry group leads to reduction in the symmetry of the total Hamiltonian to that of a subgroup within which the appropriate distortion is totally symmetric.

Such reductions in symmetry have been considered in the context of normal mode analysis, where the question asked was: What is the symmetry group of a normal mode which belongs to a particular irreducible representation of the molecular equilibrium symmetry group? [9]. A general group theoretical analysis has been presented by Melvin (10). His conclusion is that if the Hamiltonian, which belongs to symmetry point group G, is distorted along a coordinate the irreducible representation of which, within G, is Γ, then the distorted Hamiltonian has *at least* the symmetry of the kernel of the representation Γ with respect to G.[7] If the distortion belongs to a non-degenerate representation, it has just this symmetry. However, a distortion which is a component of a degenerate representation may have higher symmetry. This occurs if, for an operator which does not belong to the kernel, the distortion happens to be totally symmetric, though the other components of the representation Γ are not. As a result, the corresponding representation matrix, in the appropriate basis, has a row containing 1 in the diagonal and zeros elsewhere. Now, however, the symmetry group, which, of course, is a subgroup of G, is *not* an invariant subgroup. The operator which augments the kernel actually distinguishes between the various components of an originally degenerate representation. This operator must therefore belong to a class of the group which is not completely included in the subgroup. Such a situation cannot, of course, occur if the original group is restricted to be commutative, as can always

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[7] The kernel is the set of operators whose characters for Γ are the same as the character of the identity element for Γ, and it forms an invariant subgroup of G.

be ensured by imposing a slight restriction on the group. An informal way of avoiding the use of non-commutative groups is to lower the symmetry of the original system so as to lift any degeneracy that may occur.

4. Comparison of OCAMS with the Woodward-Hoffmann Procedure

The OCAMS procedure can very simply be shown to be no less restrictive than the Woodward-Hoffmann procedure, in the sense that any reaction which is allowed by the present treatment is "Woodward-Hoffmann-allowed". This follows from the fact that allowed reactions require orbital correspondences which are either direct or are induced by a distortion that simulates the reaction path. The symmetry elements that remain in the distorted system comprise the "Woodward-Hoffmann subgroup". The representations of the original group contained in the distortion are mapped onto the identity representation of the subgroup. Assume that, within the symmetry group used in the OCAMS procedure for some particular system,

$$\Gamma_r \times \Gamma_1 \times \ldots \Gamma_p \supset \Gamma_I \tag{15}$$

where Γ_r and Γ_p are the symmetry species of the reactants and products, respectively, and Γ_I is the identity representation. Subducing to the Woodward-Hoffmann subgroup:

$$\Gamma_r \to \gamma_r, \quad \Gamma_p \to \gamma_p, \quad \Gamma_I \to \gamma_I \tag{16}$$

but also $\Gamma_1, \Gamma_2, \ldots \to \gamma_1$, so that $\gamma_r \times \gamma_p = \gamma_I$ which is only possible if $\gamma_r = \gamma_p$.

The reverse process, i.e., induction from the Woodward-Hoffmann subgroup to the OCAMS group, is also unique, at least as long as both groups are commutative.

It may be relevant to stress that this kind of correspondence between the results of the two approaches depends on each one of them being carried out in a completely consistent way. This means that all the conserved symmetry elements included in the OCAMS procedure should also be considered within the Woodward-Hoffmann approach. Thus we prefer to regard the *full* Woodward-Hoffmann procedure as that which requires consideration of *all* the symmetry elements retained along the reaction path, and the *restricted* procedure to be that in which some of these symmetry elements are discarded.

In a sense, then, the main advantage of the retention of maximum symmetry is that a fuller description of the reaction is obtained. The roles of the various molecular orbitals and of the necessary distortions is much clearer and the stereochemical as well as energetic (i.e. kinetic) consequences can be considered in a more detailed way. Furthermore, certain stages of the analysis are more systematic and straightforward, and therefore require less trial and error than in the original version of Woodward and Hoffmann. These features may be of value if an attempt to produce an automatic code is made.

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