

# Mapping Analysis of Concerted Reactions

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**Abstract:** A new analysis of concerted reactions, based on the assumption that nuclear motion is prevented from altering the nodal structure of orbitals by a substantial energy barrier, is developed. A unitary transform  $R$ , constrained to be a topological identity, maps the wave function of the reactant system into the geometry of the product system. The overlap of the mapped function with the ground state of the products is an indication whether the stereochemical reaction path associated with the mapping is allowed in the sense of Hoffmann and Woodward. Portions of the charge distribution are merely reoriented by the mapping; a procedure for identifying these portions and describing them in terms of bonds is presented.

The predictions of the stereochemical course of reactions provided by the Woodward–Hoffmann rules have been thoroughly tested and have proved highly reliable.<sup>2</sup> While the familiar analyses dealt with systems for which symmetry allowed an easy construction of the necessary correlation diagrams, most experimental tests involved systems without useful symmetry. Strictly speaking then, the analysis in its original form does not apply to these experimentally interesting cases. This is not to say that the correlation diagrams for these systems would not be of the form suggested by the symmetry arguments; however, to establish the similarity would require the laborious and costly exploration of the reaction energy surface by MO calculations. Such large calculations would seem to be required for the correlation diagram analysis of any type of stereoelectronic process falling outside the classes of reactions discussed by Woodward and Hoffmann. In view of this argument and considering the possibility that even in reactions which are easily handled by symmetry arguments, the geometries of useful symmetry may never be physically achieved,<sup>3</sup> it seems clear that a more general analysis should be sought, which incorporates the Hoffmann–Woodward results without using the restrictive symmetry analysis.

It is the purpose of this paper to describe such an analysis, based on the nodal structure of occupied orbitals. The conceptual base of the new method is outlined in part I; part II contains a mathematical formulation of the central mapping operator. In part III, a localization method is developed which allows the identification of portions of the charge distribution which are merely reoriented during a reaction, and exert only a minor influence on the reaction. The accompanying report describes some applications to systems in which use of the simplest Woodward–Hoffmann methods is difficult.

## I. Conceptual Basis of the Mapping Analysis of Concerted Reactions

The central assumption of the mapping method is that nuclear motion may twist, stretch, and bend molecular

(1) Chemistry Department, University of Virginia, Charlottesville, Va. 22901.

(2) (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395, 2511 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046, 4389 (1965); (b) but see an exception: J. I. Brauman and D. M. Golden, *ibid.*, **90**, 1920 (1968).

(3) R. F. Bryan, G. A. Doorakian, H. H. Freedman, and H. P. Weger, *ibid.*, **92**, 399 (1970).

orbitals, but will not introduce new nodes into the orbitals.<sup>4</sup> The assumption is illustrated in Figure 1 by the behavior of a mythical two-electron species  $XY$ . The wave function is represented by a doubly occupied orbital  $\phi = \alpha\psi_0 + (1 - \alpha^2)^{1/2}\psi_1$ , where  $\psi_0 = 1/\sqrt{2} \cdot (1sX + 1sY)$  and  $\psi_1 = 1/\sqrt{2}(1sX - 1sY)$ . The atomic basis functions  $1sX$  and  $1sY$  are assumed to be orthogonal; the energy is then given by

$$W = W_X + W_Y + Z_X Z_Y e^2 / a_0 D + a^2(J + K) + (1 - a^2)(J - K)$$

where  $W_X$  and  $W_Y$  are the energies of the isolated one-electron atoms  $X$  and  $Y$ , the term  $Z_X Z_Y e^2 / a_0 D$  is the repulsion between the nuclei, and the remaining terms represent the energy of interaction of the electrons;  $J$  and  $K$  are the coulomb and exchange integrals, respectively. As  $\alpha$  tends to zero and the node in  $\psi_1$  is introduced into the wave function, the energy rises sharply. This energy barrier inhibits strongly any nuclear motion which requires the introduction of a new node into an orbital. The prohibition of newly formed nodes may be expressed simply in the language of topology; the mapping  $R$  which produces the orbitals of  $B$  from the orbitals of  $A$  in the reaction  $A \rightarrow B$  must be a topological identity. In other words, the hypersurface  $\Pi_i \phi_i^B$  can be obtained from  $\Pi_j \psi_j^A$  without cutting or piercing the latter surface. A new node in the wave function between atoms  $A$  and  $B$  will change the sign of the expression  $\Sigma(a \text{ on } A, b \text{ on } B) P_{ab} P_{ab}'$  from positive to negative; here the prime indicates that the density matrix has been altered by some transformation. A topological identity will associate a positive sign with the expression, meaning that bonding (or antibonding) is maintained.

$$R(A \Pi_i \phi_i^K) \longrightarrow (A \Pi_i \phi_i^L)$$

In the usage of Woodward and Hoffmann, which we follow in this case, the stereochemical path which determines  $R$  is "allowed" only if the orbitals occupied in the ground state of  $B$  are obtained by mapping. It follows that the overlap between the mapped function and the ground-state function of  $B$  is a useful indication of whether the path is allowed. The overlap  $S = (A \Pi_i \phi_i^K | A \Pi_j \phi_j^0)$  will equal unity if the process is allowed, and

(4) These ideas are implicit in a study of rearrangements of  $C_3H_7^+$  systems: C. Trindle and O. Sinanoğlu, *ibid.*, **91**, 4054 (1969).

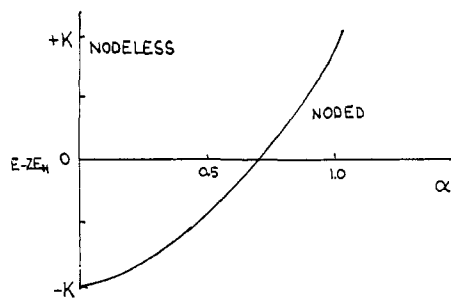


Figure 1. The energy of a hypothetical system is shown as a function of the configuration mixing parameter  $\alpha$  which indicates the sizable barrier to the introduction of a new node into the wave function.

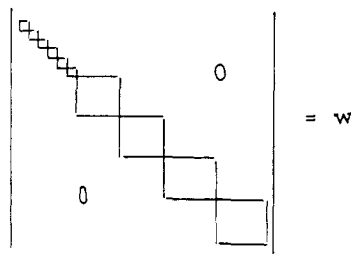


Figure 3. The block diagonal form of the topological identity  $M$  is indicated schematically for  $C_4H_6$ .

Figure 2. The state overlap is shown as a function of the configuration mixing parameter  $\lambda$ . Normal ranges of  $\lambda$  are enclosed by the boxes. Within these ranges the overlap of functions with like nodal structure exceeds 0.95, while the overlap of functions with unlike nodal structure does not exceed 0.30.

equal zero if an excited state of **B** is obtained by mapping.

If we deal with an approximate mapping operator, the orbitals of **B** will not be exactly reproduced. We would expect values of the overlap to be intermediate between 0 and 1. For example, consider an orbital of **B**,  $\psi^0 = (X_a + X_b)/\sqrt{2}$  where  $X_a$  and  $X_b$  are orthogonalized atomic orbitals. The approximate mapping will produce an orbital

$$\psi^\lambda = (1 + \lambda^2)^{-1/2}(X_a + \lambda X_b)$$

If  $\lambda > 0$  then  $\psi^0$  and  $\psi^\lambda$  have like nodal structures, while if  $\lambda < 0$  the nodal structures are unlike. The behavior of the overlap with changes in  $\lambda$  is shown in Figure 2. The boxes enclose normal ranges for  $\lambda$ , and make apparent that  $S$  is greater than 0.95 for functions of like nodal structure and is less than 0.30 for functions of dissimilar nodal structure. The square of the overlap is a more clear-cut measure; between  $(0.95)^2$  and  $(0.30)^2$  is a full order of magnitude. We will see that the square of the overlap is convenient in the mathematical formulation of the problem. From the preceding arguments we can hypothesize that nodal structure is conserved during concerted reactions, and that the overlap between the mapped function and the ground-state function of the products is a useful indication whether a reaction is allowed. The next task is to formulate the mapping operator in a way consistent with these suggestions.

## II. Mathematical Expression of an Approximate Mapping Operator

Given orbitals occupied in state **K** of **A** and orbitals occupied in the ground state **0** of **B**, we seek a mapping  $R$  which is a topological identity and produces or-

bitals similar to those of **B** by its action on the orbitals of **A**. We may start from an expression of the overlap between arbitrarily mapped orbitals and the ground-state function of **B**; the overlap is easily evaluated by the method of corresponding orbitals.<sup>5</sup> The matrix  $D^\dagger D$  is formed, where  $D_{ij} = (\phi_i^K/\psi_j^0)$ , and diagonalized;  $U^\dagger D^\dagger D U = (\delta_{ij} d_i)$ . The overlap is given by  $S = \prod_i (d_i)^{1/2}$ .

We will find it convenient to work with the trace of  $D^\dagger D$ , since this quantity is invariant to unitary transform of the matrix; it may be interpreted as the sum of squares of the overlaps between the corresponding orbitals of **A** and **B**,  $\text{Tr} D^\dagger D = \sum_i d_i$ . We obtain the following expression for an element of  $D^\dagger D$ . In terms of the elements of the  $R$  transform and the LCAO coefficients of the orbitals

$$(D^\dagger D)_{Kl} = \sum_{\nu\sigma\mu m} C_{K\nu}^A R_{\nu\sigma} C_{m\sigma}^B C_{ml}^B R_{\mu l} C_{l\mu}^A$$

if we assume an orthogonalized basis set (as in most approximate MO methods).<sup>6</sup> The trace is

$$\sum_K (D^\dagger D)_{KK} = \sum_{\nu\sigma\mu m} C_{K\nu}^A R_{\nu\sigma} C_{m\sigma}^B C_{ml}^B R_{\mu l} C_{K\mu}^A =$$

$$1/4 \text{Tr}(\mathbf{R} \mathbf{P}^A \mathbf{R}^\dagger \mathbf{P}^B)$$

The elements of  $\mathbf{R}$  may be determined by requiring the trace to be a maximum, subject to the condition that  $\mathbf{R}$  be a topological identity. This condition will be satisfied by the use of some simple but drastic assumptions.

In this report we take the very simple view that  $\mathbf{R}$  may reflect the stretches, bends, and twists associated with a reaction, but charge transfer will be disallowed. A twist at a certain center can be considered to simply reorient the p-type basis functions on that center. Similarly, bends and (to some extent) stretches have the effect of rehybridizing the basis functions on the affected center. Thus we can be confident of representing the major results of nuclear motion by a series of transformations of the basis functions on each center. The form of a mapping transform will be block diagonal with blocks of dimension  $4 \times 4$  for each first-row atom such as carbon, a single diagonal element for hydrogen atoms, etc. Figure 3 shows a sample  $\mathbf{R}$  matrix for butadiene-cyclobutene.

We can be assured that the one-center transforms comprise a topological identity by considering the sign

(5) H. F. King, R. E. Stanton, H. Kim, R. E. Wyatt, and R. G. Parr, *J. Chem. Phys.*, **47**, 1936 (1967).

(6) (a) J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965); **44**, 3289 (1966); (b) Quantum Chemistry Program Exchange, Chemistry Department, Room 204, Indiana University, Bloomington, Ind. 47401.

of the expression

$$\sum_{a \text{ on } A} \sum_{b \text{ on } B} (\mathbf{P}^{AB})_{ab} (\mathbf{P}^{AB})_{ab} = \sum_{a \text{ on } A} \sum_{b \text{ on } B} \sum_{\mu, \nu} \mathbf{P}_{ab}^{A\mu} \mathbf{t}_{\mu a}^A \mathbf{P}_{\nu b}^{B\mu} \mathbf{t}_{\nu b}^B$$

Here the one-center transforms are labeled by a superscript indicating the atom on which the transform is defined. The density matrices are also labeled with superscripts indicating the atoms involved. The expression can be rewritten in the following way

$$\sum_{\mu \text{ on } A} \sum_{b \text{ on } B} (\mathbf{tP})_{\mu b}^{AB} (\mathbf{tP})_{\mu b}^{AB} \geq 0$$

Since the latter is simply a sum of squares, it must be positive or zero, assuring that the one-center transforms do not affect the nodal structure.

We wish to determine the elements of  $\mathbf{R}$  by implementation of the condition that  $\text{Tr}(\mathbf{D}^{\neq} \mathbf{D})$  be a maximum. Direct construction of  $\mathbf{R}$  is beyond our reach at this time, but we have devised an iterative method similar to the Jacobi procedure for diagonalizing a square symmetric matrix. Consider a model transform  $\mathbf{R}_{\alpha\beta}^{(2)}$  which may be specified by two indices  $\alpha$  and  $\beta$  referring to two basis functions  $\mathbf{X}_{\alpha}$  and  $\mathbf{X}_{\beta}$  on center  $J$ , and a single angle of rotation  $\omega_{\alpha\beta}$ . The two-dimensional rotation is given by

$$\mathbf{I} \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos \omega & 0 & -\sin \omega \\ 0 & 0 & 1 & 0 \\ 0 & \sin \omega & 0 & \cos \omega \end{vmatrix}$$

For concreteness the indices 2 and 4 on carbon  $J$  have been used. The action of  $\mathbf{R}$  on  $\text{Tr}(\mathbf{D}^{\neq} \mathbf{D})$  is written

$$\sigma = \text{Tr}(\mathbf{D}^{\neq} \mathbf{D}) \longrightarrow \sum_{\substack{J\sigma\nu \\ J\neq I \\ I\mu\lambda}} \mathbf{R}_{I\mu\lambda}^{(2)} \mathbf{P}_{I\lambda J\sigma}^A \mathbf{P}_{J\sigma I\mu}^B + \sum_{\substack{K\mu\lambda \\ K\neq I \\ I\mu\lambda}} \mathbf{P}_{K\mu I\mu}^A \mathbf{R}_{I\mu\lambda}^{(2)} \mathbf{P}_{I\lambda K\mu}^B + \sum_{\sigma\nu\mu\lambda} \mathbf{R}_{I\mu\lambda}^{(2)} \mathbf{P}_{I\lambda I\sigma} \mathbf{R}_{J\sigma\nu}^{(2)} \mathbf{P}_{I\nu I\mu}^B$$

We extremize  $\text{Tr}(\mathbf{D}^{\neq} \mathbf{D})$  with respect to the angle  $\omega_{\alpha\beta}$  by setting its derivative to zero. After some manipulation, including neglect of second powers of  $\sin \omega_{\alpha\beta}$ , we recover an expression for  $\tan(\omega_{\alpha\beta})$ .

$$\tan \omega_{\alpha\beta}^I = \frac{\sum_{J\nu\neq I\alpha,\beta} (\mathbf{P}_{I\beta J\nu}^A \mathbf{P}_{I\alpha J\nu}^B - \mathbf{P}_{I\alpha J\nu}^A \mathbf{P}_{I\beta J\nu}^B)}{\sum_{J\nu\neq I\alpha,\beta} (\mathbf{P}_{I\beta J\nu}^A \mathbf{P}_{I\beta J\nu}^B + \mathbf{P}_{I\alpha J\nu}^A \mathbf{P}_{I\alpha J\nu}^B)} = \frac{A}{B}$$

$$\sin \omega_{\alpha\beta}^I = A/(A^2 + B^2)^{1/2} \quad \cos \omega_{\alpha\beta}^I = B/(A^2 + B^2)^{1/2}$$

This solution may lead to minimal as well as maximal  $\sigma$ , so we must check on the second derivative, adjusting  $\omega_{\alpha\beta}^I$  so that it is negative. This one-parameter transform is the basis for an iterative process; a sequence of such transformations, with systematic variation of the indices, is applied to  $\sigma$  until  $\sigma$  converges within some tolerance, or all angles  $\omega_{\alpha\beta}$  approach zero.

The products of this calculation are (1) wave functions mapped from reactants toward products; (2) the overlap of the mapped wave function with the ground-state function of the products; and (3) a set of roots  $d_{ii}$  which may be interpreted as the square of the overlaps of corresponding orbitals in the mapped and ground state sets. These roots indicate to what extent indi-

vidual orbitals are simply reoriented during the reaction—such orbitals will be associated with roots very near unity even for the approximate mapping operator we have available. Smaller roots indicate that the mapping has not accurately reflected a reorganization of the charge in a certain orbital.

The portion of the charge density which is merely reoriented during a reaction could be interpreted as representing the bonds which do not participate in the reaction. A mathematical means of transforming the reoriented portion of the charge into parts corresponding to bonds is developed in the following section.

### III. Localization Formalism

Given a set of orbitals, the feasibility of a localized description and the distribution of bonds can be deduced from the bond index matrix.<sup>7</sup> However, the same information can be gotten at a glance from transformed orbitals determined by some localization criterion.<sup>8</sup> The localization methods referred to in ref 8, with the exception of that described in ref 8c, are not applicable to the wave functions with which we deal.<sup>9</sup> In view of the substantial amounts of computer time required by the method of Trindle and Sinanoğlu,<sup>8c</sup> at least in the context of the mapping calculation, we present a population localization method similar in spirit to that of Magnasco and Perico<sup>8d</sup> but suitable to wave functions expressed in orthogonalized bases. The new method should be even faster than that described in ref 8d since we use a steepest ascents approach rather than the series of two-dimensional rotations employed by Magnasco and Perico.

Following the ideas of Magnasco and Perico we assume that the amount of charge in an orbital, confined to a previously chosen set of atomic orbitals expected to participate in a bond, is a useful measure of the localization of that orbital. In an orthogonal basis we cannot use the definition of partial Mulliken populations; the bond index is a suitable parallel quantity. The bond index  $W_{ab}$  is given by

$$W_{ab} = P_{ab}^2 = 4 \sum_{ij \text{ occ}} C_{ia} C_{ib} C_{ja} C_{jb} \quad (1)$$

where  $P$  is the bond order, and the  $C$ 's are LCAO expansion coefficients for the orbitals; the sum is taken over all occupied MO's.  $W_{ab}$  may be interpreted as the charge in atomic orbital "a" involved in bonding with atomic orbital "b." We define a local orbital bond index for the  $i$ th MO, choosing a set of atomic orbitals  $G_i$  expected to be involved in the  $i$ th bond.

$$B_i = 4 \sum_{ab \text{ in } G_i} C_{ia}^2 C_{ib}^2 \quad (2)$$

The total localization measure is simply  $B = \sum B_i$ . This quantity is always positive; maximizing it is equiv-

(7) C. Trindle, *J. Amer. Chem. Soc.*, **91**, 219 (1969).

(8) (a) S. F. Boys, *Rev. Mod. Phys.*, **32**, 296 (1960); S. F. Boys and J. M. Foster, *ibid.*, **32**, 300 (1960); S. F. Boys in "Quantum Theory of Atoms, Molecules and the Solid State," P. O. Löwdin, Ed., Academic Press, New York, N. Y., 1966; (b) C. Edmiston and K. Reudenberg, *J. Chem. Phys.*, **43**, 597 (1965); (c) C. Trindle and O. Sinanoğlu, *ibid.*, **49**, 65 (1968); (d) V. Magnasco and A. Perico, *ibid.*, **47**, 971 (1967); (e) W. H. Adams, *ibid.*, **34**, 89 (1961); **37**, 2009 (1962); **42**, 4030 (1965).

(9) These are semiempirically determined SCF wave functions expressed in an orthogonal basis, such as are obtained by the CNDO method and many related refinements. Magnasco and Perico's original method is applicable to extended Hückel functions or others expressed in an overlapping basis.

alent to confining the orbitals to the sets  $G_i$  or localizing them to the  $i$  bonds.

It is possible to develop a  $2 \times 2$  iterative method for the maximization of  $B$  similar to the method used by Magnasco and Perico, but we wish to explore the potentially faster steepest ascents approach. The technique discussed below is similar to that used by Taylor in his implementation of the Lennard-Jones and Pople coulomb localization criterion.<sup>10</sup> Let the localization transform be approximated by  $\mathbf{T} \simeq \mathbf{I} + \epsilon\mathbf{A}$ ;  $\mathbf{I}$  is the identity and  $\mathbf{A}$  a first-order correction. The number  $\epsilon$  is used as an ordering parameter. Since  $(\mathbf{I} + \epsilon\mathbf{A}) \cdot (\mathbf{I} + \epsilon\mathbf{A})^\dagger = \mathbf{I} + \epsilon(\mathbf{A} + \mathbf{A}^\dagger) + \mathcal{O}(\epsilon^2)$  we demand that  $\mathbf{A}^{\text{tr}} = -\mathbf{A}$  to assure that  $\mathbf{T}$  is unitary to first order in the correction  $\mathbf{A}$ .  $\mathbf{A}$  is thus traceless and skew-symmetric. The effect of  $\mathbf{I} + \epsilon\mathbf{A}$  on the localization measure  $\mathbf{B}$  is shown below.

$$B' = B + 4 \sum_{i>k} \left\{ \sum_{ab \text{ in } G_i} C_{Ka} C_{ia} C_{ib}^2 - \sum_{ab \text{ in } G_K} C_{ia} C_{Ka} C_{Ka}^2 C_{Kb}^2 \right\} \mathbf{A}_{iK} + \mathcal{O}(\mathbf{A}^2) \quad (3)$$

The variation of  $B'$  must be zero, subject to the constraint that  $2 \sum_{i>K} \mathbf{A}_{iK}^2$  be constant. Thus, by the method of undetermined multipliers

$$\delta B' = 4 \sum_{i>K} \left\{ \sum_{ab \text{ in } G_i} C_{Ka} C_{ia} - \sum_{ab \text{ in } G_K} C_{ia} C_{Ka} C_{Kb}^2 \right\} \delta \mathbf{A}_{iK} = 0$$

$$\lambda \delta [2 \sum_{i>K} (\mathbf{A}_{iK})^2] = 4 \lambda \sum_{i>K} \mathbf{A}_{iK} = 0 \quad (4)$$

These equations are satisfied if

$$\mathbf{A}_{iK} = \sum_{ab \text{ in } G_i} C_{Ka} C_{ia} C_{ib}^2 - \sum_{ab \text{ in } G_K} C_{ia} C_{Ka} C_{Kb}^2 \quad (5)$$

While the antisymmetry of  $\mathbf{A}$  guarantees unitarity of  $\mathbf{T}$  to first order in  $\mathbf{A}$ , often the departure from unitarity is unacceptable, particularly in the initial, long steps of localization.  $\mathbf{T}$  may be unitized by forming the product  $\mathbf{T}\mathbf{T}^\dagger$  which may be represented as  $\mathbf{I} + \mathbf{q}$ . Define  $\mathbf{Q}^{-1/2}$  by its Taylor series;  $\mathbf{Q}^{-1/2} = \mathbf{I} - 1/2\mathbf{q} + 3/8\mathbf{q}^2 - \dots$ . The product  $\tilde{\mathbf{A}} = \mathbf{Q}^{-1/2}(\mathbf{I} + \mathbf{A})$  is unitary. The unitized matrix  $\tilde{\mathbf{A}}$  is applied to the matrix or orbitals, and localizes them to some extent. In an iterative process, a new transformation matrix is constructed with the new coefficients, etc., until  $B$  converges to its maximum.

The formulas 2 through 5 are suitable for a single-determinant wave function composed of doubly occupied orbitals, encountered in most simple SCF calculations. However, in this context we are concerned with sets of corresponding orbitals; these orbitals arise from any different-orbital-different-spin or multiconfigurational wave function, as well as from the mapping analysis, which is our main interest. It is a simple matter to extend the localization to sets  $a$  and  $b$  of corresponding orbitals. Let the localization measure be

$$B = \sum_{i \text{ occ}} B_i = 1/2 \sum_{i \text{ occ}} [4 \sum_{ab \text{ in } G_i} (a_{ia}^2 a_{ib}^2 + b_{ia}^2 b_{ib}^2)] \quad (6)$$

After an analysis exactly parallel to that given above, we

(10) W. J. Taylor, *J. Chem. Phys.*, **48**, 2385 (1968).

find

$$A_{iK} = 1/2 \left\{ \sum_{ab \text{ in } G_i} (a_{Ka} a_{ia} a_{ib}^2 + b_{Ka} b_{ia} b_{ib}^2) - \sum_{ab \text{ in } G_K} (a_{ia} a_{Ka} a_{Kb}^2 + b_{ia} b_{Ka} b_{Kb}^2) \right\} \quad (7)$$

The matrix  $\tilde{\mathbf{A}}$  derived from eq 7 is applied to both sets  $a$  and  $b$ , with this restriction. The sum over  $i$  in (6) and the indices  $i$  and  $K$  in (7) range over orbitals which have like roots in the matrix  $\mathbf{D}^\dagger \mathbf{D}$  discussed in part II, and the matrix  $\tilde{\mathbf{A}}$  is applied to these orbitals only.

#### IV. Choice of the Local Sets of Basis Functions $G_i$

From the derivations, it appears that the local orbitals determined by the population criterion would be dependent on the makeup of the sets  $G_i$  of atomic orbitals chosen to represent each bond or lone pair. The choices are arbitrary, in principle, but in practice this is rarely a problem. In systems expected to be largely localized, so that all bonds are two-center entities, the choice is straightforward. CC bonds in alkanes would contain all the valence atomic orbitals on the bonded carbons, for example. Small amounts of delocalization such as found in formic acid or butadiene will not invalidate this simple approach.

If intuition fails, the bond indices can provide direct aid. Generally the compass of a set  $G_i$  is inadequate if the sum  $\sum_{ab \text{ in } G_i} W_{ab}$  is not near one. For example, the total  $\pi$  bond index between adjacent carbons in benzene is 0.50 while the  $\pi$  bond index between a terminal carbon and its neighbor in butadiene is 0.87; localization of the  $\pi$  orbitals in benzene to two-center bonds fails, but the  $\pi$  orbitals in butadiene are substantially localizable. (Benzene  $\pi$  orbitals may be localized to (nonunique) three-center bonds.)

#### Summary

The conceptual basis and an approximate mathematical formulation of a new analysis of concerted reactions are described. The central assumption of this mapping analysis is that the distortions producing a product wave function from a reactant wave function by a certain reaction route may not include the introduction of new nodes, if the reaction is to be allowed (in the usage of Hoffmann and Woodward). The Woodward-Hoffmann analyses based on symmetry arguments are special cases of this assumption. A mapping operator which obeys the stricture that no change in nodal structure is permitted is constructed. The overlap between the mapped function and the wave function of the desired function is a criterion of the allowed character of a reaction. A product of the mapping is the identification of a portion of the charge distribution which is reoriented but not substantially reorganized during the reaction. A localization method for resolving this passive segment of the charge into bonds and lone pairs which are transferrable from product to reactant is developed. Applications of these new methods of analysis are described in the accompanying paper.