# Valence-Bond Approach to Conservation of Symmetry in Concerted Reactions

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**Abstract:** Generalized electron-pair wave functions are used to describe the electronic states involved in a concerted reaction process. For symmetry preserving reaction paths, it is shown that primitive symmetry labels for the electron pairs can be used to determine the nature of the interaction energy between reactant and product functions and to make an assessment of the relative heights of the potential energy barriers that would be encountered along various stereospecific reaction paths. A conservation of symmetry principle is introduced for the simplest form of electron-pair function, that based on the canonical valence-bond description. This provides a generalization of the Woodward–Hoffmann rules for the conservation of molecular orbital symmetry. Illustrative examples are considered and the limitations of the symmetry conservation principle are discussed.

## I. Introduction

An important tool in the study of concerted chemical reactions is the symmetry conservation principle. Woodward and Hoffmann[2] and others[3,4] have used this concept in the context of molecular orbital theory to present rules for predicting the stereospecific course of several classes of organic reactions. The method is easily applied, requires no elaborate calculations of energy surfaces, and gives correct predictions for many examples.[2] Although several alternative approaches have appeared in the literature,[5-14] no one has developed a valence-bond formulation with the same generality and simplicity as the molecular orbital scheme. In this paper, we employ generalized electron-pair wave functions to develop a simple valence-bond theory of concerted reactions, and to provide an alternative foundation for the Woodward–Hoffmann rules.

The basic idea of the Woodward–Hoffmann method in its simplest form is to define molecular orbitals which are symmetry adapted with respect to a symmetry operator that is present in both reactant and product molecular species and bisects the bonds that are formed or broken during the reaction. The reactant and product molecular orbital energy levels are classified according to symmetry and arranged in order of their probable energy values. Levels of like symmetry in the reactants and products are correlated by connecting them one-to-one starting with the levels of lowest energy. An aufbau principle is employed to fill the levels with the available electrons. A thermal reaction is considered to be "symmetry allowed" if all filled molecular energy levels of the reactants correlate with corresponding lowest energy levels of the products. A thermal reaction is considered to be "symmetry forbidden" if all filled levels of the reactants do not correlate with the corresponding lowest energy levels of the products. To treat photochemical processes, one of the electrons in the highest filled level is assumed to be promoted to the next higher level by the photoexcitation. All filled and partially filled levels are considered in a corresponding way to determine whether the photochemical reaction is "allowed" or "forbidden".

In the Woodward–Hoffmann scheme, one implicitly visualizes uniquely defined reactant molecular orbitals undergoing transformations until they have formed the corresponding unique molecular orbitals of the products, while retaining their symmetry properties throughout. Although conceptually simple, the set of orbitals obtained for the intermediate species in the reaction, in general, lose their orthogonality relationships and their uniqueness. The qualitative conclusions based on such a model of the system cannot therefore be quantitatively verified through calculations using the theory directly,[15,16] that is, calculations that make use of a single-determinantal wave function to represent the system over the entire reaction path. Instead a treatment including configuration interaction and employing a multideterminant wave function must be introduced.

It has been shown[17,18] that for certain reactions (e.g., $H_2 + D_2 \rightleftarrows 2HD$) the simplest minimum basis-set nonionic valence-bond wave function provides a good approximation to a complete molecular orbital configuration interaction treatment valid for reactants, products, and the intermediate region. This suggests that if the single molecular orbital configuration considered in the Woodward–Hoffmann scheme makes the dominant contribution to the valence-bond function, the more general validity of the latter can serve to justify the former. Furthermore, it should be possible to use the dominant configuration argument to develop a valence-bond analog of the Woodward–Hoffmann rules.

In the present paper, we introduce generalized electron-pair functions and show how primitive symmetry labels can be associated with each pair. The primitive symmetry labels are utilized to develop simple arguments for determining whether or not there is a stabilizing interaction between the reactant and product wave functions along symmetry preserving reaction paths. Because of the relation of the generalized electron-pair function to certain configuration interaction wave functions of the molecular orbital type, the resulting arguments can be used to obtain a firmer theoretical foundation for the Woodward–Hoffmann rules. Furthermore, introduction of the appropriate primitive symmetry labels for the simplest electron-pair function (i.e., one composed of canonical valence-bonds for each pair) permits one to translate the Woodward–Hoffmann scheme into valence-bond language. A simple symmetry conservation postulate for the valence-bond functions is developed for concerted reactions and applied in a manner analogous to the Woodward–Hoffmann procedure.

Section II presents the generalized electron-pair theory and shows how to determine the interaction between reactant and product wave functions. In section III, the simple valence-bond formulation is developed. The resulting symmetry conservation postulate for concerted reactions is given in section IV and applied in section V to a number of illustrative reactions that have also been treated by the

Woodward–Hoffmann rules. Section VI discusses some of the limitations of the symmetry conservation postulate that are made clear by the present approach.

## II. Interaction Energy Along Reaction Paths

In this section a generalized electron-pair function is introduced to describe the bonding in the reactants and products for a reaction to which symmetry arguments can be applied. It is shown how primitive symmetry labels can be determined for each electron pair, even when it is expressed as a general linear combination of basis orbitals. The complete set of primitive symmetry labels for the reactant and product functions is then used to find very simple rules for the interaction energy along symmetry preserving paths.

**A. Construction of Symmetry-Adapted Wave Functions.** The generalized electron-pair formalism employed in this paper consists of dividing the $n$ electrons of a molecule into $n/2$ pairs of electrons, forming $n/2$ appropriate two-electron pair functions, taking an antisymmetrized product of these $n/2$ pair functions to form an $n$-electron electron-pair function, and using a linear combination of different pair functions to form the total wave function for the system. A convenient method of handling the resulting wave functions is in terms of the geminal-product wave function formalism.[19-22] Within the context of the latter, the $n/2$ two-electron pair functions used to make up the valence-bond structure can be given the most general configuration-interaction form: that is, they can be constructed from all of the atomic orbital basis functions of the system while simultaneously satisfying the requirements of molecular symmetry. The advantage of this procedure is that it permits one to retain the qualitative valence-bond language and concepts in a general formulation that simplifies the problem of evaluating matrix elements.

The generalized pair wave function $\Psi$ for an $n$-electron system is written in terms of an antisymmetrized product of the $n/2$ pair functions or geminals, $\Lambda$, as

$$\Psi(1\ldots n) = \mathrm{A}\{\Lambda_1(1,2)\Lambda_2(3,4)\ldots\Lambda_{n/2}(n-1,n)\} \quad (1)$$

where A is the full $n$-electron antisymmetrizer, which includes a normalization factor. The valence-bond description of a covalent bond between atoms A and B corresponds to a geminal of the form

$$\Lambda(1,2) = [a(1)b(2) + b(1)a(2)] \times [\text{singlet spin}] \quad (2)$$

where $a$ and $b$ denote orbitals on centers A and B, respectively. A much better description of the AB bond can be obtained, however, by extending the orbital expansion in eq 2 to include more basis functions (e.g., a total of $M$) and to combine these via a configuration-interaction series

$$\Lambda_Q(1,2) = \sum_{ij}\hat{Q}_{ij}\chi_i(1)\chi_j(2) \times [\text{singlet spin}] \quad (3)$$

where the $\chi$ are the basis functions and $\hat{\mathbf{Q}}$ is an arbitrary $M \times M$ matrix (the full antisymmetrizer in eq 1 obviates the need for $\hat{\mathbf{Q}}$ to be either symmetric or antisymmetric). Optimal values of the elements of $\hat{\mathbf{Q}}$ can be determined, in principle, from a minimization of the total energy of the system with respect to the $\hat{Q}_{ij}$; this aspect of the problem has been discussed[19-22] but is not of concern to the present work. Taking $\chi_1 = a$ and $\chi_2 = b$, the valence bond expression in eq 2 is obtained by constraining $\hat{\mathbf{Q}}$ to have only two nonzero elements; namely, $\hat{Q}_{12} = \hat{Q}_{21} = 1$ and the remaining elements are zero. The more general form in eq 3 allows other covalent-type functions and ionic-type functions to contribute to the geminal wave function.

A symmetry transformation of the basis orbitals is now applied

$$\lambda_k(1) = \sum_j \chi_j(1)T_{jk} \quad (4)$$

to yield a set of symmetry-adapted orbitals $\lambda$ that conform to irreducible representations of the symmetry group of interest for the reaction process under consideration. The symmetry transformation $\mathbf{T}$ leaves the geminal function invariant

$$\Lambda_Q(1,2) = \sum_{ij} Q_{ij}\lambda_i(1)\lambda_j(2) \times [\text{singlet spin}] \quad (5)$$

when written in terms of the symmetry-adapted orbitals $\lambda$ and the transformed matrix $\mathbf{Q}$,

$$\mathbf{Q} = \mathbf{T}^{-1}\cdot\hat{\mathbf{Q}}\cdot\mathbf{T} \quad (6)$$

No orthogonality has been assumed to exist between the various basis functions (other than "accidental" orthogonalities like that between an s and p function located on the same center, etc.). Nevertheless, group theory dictates that the symmetry transformation T induces an orthogonality between functions belonging to different irreducible symmetry species of the symmetry group. In particular, with a twofold axis or mirror plane of symmetry, T partitions the basis set into a symmetric subset $\lambda^{\mathrm{S}}$ and an antisymmetric subset $\lambda^{\mathrm{A}}$ having the orthogonality property

$$\int d\tau_1 \lambda_i^{\mathrm{S}}(1)\lambda_k^{\mathrm{A}}(1) = 0 \quad (7)$$

while orbitals within the same symmetry subset do not acquire any new orthogonalities; hence

$$\int d\tau_1 \lambda_i^{\mathrm{S}}(1)\lambda_j^{\mathrm{S}}(1) = \text{n.n.z.} \quad (8)$$

$$\int d\tau_1 \lambda_k^{\mathrm{A}}(1)\lambda_l^{\mathrm{A}}(1) = \text{n.n.z.} \quad (9)$$

where "n.n.z." is an abbreviation for "not necessarily zero". Arranging the orbitals so that all the $\lambda^{\mathrm{S}}$ precede the $\lambda^{\mathrm{A}}$ gives $\mathbf{Q}$ the block structure

$$\mathbf{Q} = \left(\begin{array}{c|c} \mathrm{SS} & \mathrm{SA} \\ \hline \mathrm{AS} & \mathrm{AA} \end{array}\right) \quad (10)$$

where a nonzero element in a given block produces a term in eq 5 having the indicated symmetry species; e.g., from block AS, a term is generated of the form $\lambda^{\mathrm{A}}(1)\lambda^{\mathrm{S}}(2)$.

In order to obtain a pair function having the symmetry SS, the matrix $\mathbf{Q}$ is constrained to have the form

$$\mathbf{Q}^{\mathrm{SS}} = \left(\begin{array}{c|c} \mathrm{SS} & 0 \\ \hline 0 & 0 \end{array}\right) \quad (11)$$

with similar constraints necessary to obtain the pair symmetries AA and SA. Within a given symmetry block, a further constraint to a single nonzero term (e.g., $Q_{ij} = \delta_{ij}\delta_{i1}$) gives the special case of a molecular orbital description of the pair. By allowing the entire block to be nonzero, a more general configuration-interaction wave function is produced for the geminal. Use of the symmetry constrained matrix $\mathbf{Q}^{\mathrm{XY}}$ allows the geminal to be identified with the corresponding symmetry labels, $\Lambda^{\mathrm{XY}}$, where of the labels X and Y each one refers to one of the electrons in the pair. This two-term symmetry designation (XY) is the irreducible primitive symmetry classification of the geminal; an irreducible composite symmetry label is obtained through use of the group multiplication rules, e.g., SS = AA = S and SA = AS = A.

The irreducible primitive symmetry classification for an $n$-electron wave function consists of an $n$-term label, which is formed from all of the two-term primitive symmetry classifications labeling each of the pairs in the system. The order of the symbols within the label is immaterial, e.g., XYXZ is equivalent to XXYZ. Here again, an irreducible composite symmetry label can be obtained through repeated use of the group multiplication rules. Wave functions whose composite classifications belong to different irreducible symmetry classes have vanishing matrix elements with respect to the Hamiltonian. Those in the same irreducible class can interact with one another even if they have different primitive classifications.

Of primary interest is an assessment of the effect of the primitive symmetry labels on matrix elements of $\mathcal{H}$ with respect to the total $n$-electron wave functions for reactant and product species, $\Psi_R$ and $\Psi_P$, respectively, expressed in the geminal-product form of eq 1. We consider the expectation value of a $K$-particle operator $\theta_K$

$$\langle \theta_K \rangle = \langle \Psi_R(1\ldots n) | \theta_K | \Psi_P(1\ldots n) \rangle \tag{12}$$

For the molecular Hamiltonians of interest here, it is sufficient to examine the cases where $\theta_K$ is a symmetric operator with $K = 0$, 1, or 2.

For $K = 0$ or 1, eq 12 reduces to a sum of terms containing factors of the form

$$\langle \Lambda_i^{\mathrm{W}w}(1, s) | \theta_0 \text{ or } \theta_1 | \Lambda_k^{\mathrm{Y}y}(1, u) \rangle_1 \tag{13}$$

where the bracket indicates integration over the coordinates of electron 1, geminals $i.k$ derive from wave functions $R.P.$ respectively, the capital letter superscripts indicate the primitive symmetry species relevant to the integration, the small letter superscripts indicate primitive symmetries that are not relevant to this integration, and $s.u$ are other electron coordinates. The evaluation of eq 13 proceeds from the definition of $\Lambda$ in eq 5 and the symmetry induced orthogonality represented by eq 7. For the twofold axis and mirror plane symmetries of importance to this work, the consequence is that W and Y must be identical in order for the integral to be nonzero. To obtain the contribution to $\langle \theta_0 \rangle$ or $\langle \theta_1 \rangle$ the factor in eq 13 is of course multiplied by an appropriate number of overlap integrals ($\theta_0$) to account for the integration over the other $n - 1$ electrons. Each of these integrations also requires that the primitive symmetry label from $\Psi_R$ for the electron being integrated be equal to that from $\Psi_P$. Thus, the only possible nonzero terms in eq 12 for the operators $\theta_0$ or $\theta_1$ arise from the situation where $\Psi_R$ and $\Psi_P$ have an identical list of primitive symmetry labels; the order of the labels does not matter.

For $K = 2$, eq 12 reduces to a sum of terms containing factors of the following type

$$\langle\langle \Lambda_i^{\mathrm{WX}}(1, 2) | \theta_2 | \Lambda_k^{\mathrm{YZ}}(1, 2) \rangle_1 \rangle_2 \tag{14}$$

$$\langle\langle \Lambda_i^{\mathrm{WX}}(1,2) | \theta_2 | \Lambda_k^{\mathrm{Y}y}(1, u) \Lambda_l^{\mathrm{Z}z}(2,v) \rangle_1 \rangle_2 \tag{15}$$

and

$$\langle\langle \Lambda_i^{\mathrm{W}w}(1, s) \Lambda_j^{\mathrm{X}x}(2, t) | \theta_2 | \Lambda_k^{\mathrm{Y}y}(1, u) \Lambda_l^{\mathrm{Z}z}(2, v) \rangle_1 \rangle_2 \tag{16}$$

The symmetry induced orthogonality of eq 7 causes these two-electron integrals to vanish unless the product of symmetry species W·X·Y·Z contains a totally symmetric component of the symmetry group. In terms of the twofold axis or mirror plane symmetries, with the multiplication rules SS = AA = S and SA = A, these integrals are nonzero only if WX-YZ is of the form SS-SS, AA-AA, SA-SA, or SS-AA; that is, they must be identical or differ by two labels. As in the $\theta_0$ and $\theta_1$ case, the factors in eq 14-16 are multiplied by an appropriate number of overlap terms ($\theta_0$) corresponding to integration over the remaining $n - 2$ electrons. Each of the latter requires that the primitive symmetry label for a given electron be the same from both $\Psi_R$ and $\Psi_P$. Thus, eq 12 for $\theta_2$ has nonzero contributions only if $\Psi_R$ and $\Psi_P$ have either lists of identical primitive symmetry labels or these lists differ by exactly two labels.

The preceding discussion can now be summarized for the matrix elements of the $K$-particle operator $\theta_K$

$$\langle \theta_K \rangle = \langle \Psi_R[N_1^{\mathrm{R}} N_2^{\mathrm{R}} \ldots] | \theta_K | \Psi_P[N_1^{\mathrm{P}} N_2^{\mathrm{P}} \ldots] \rangle \tag{17}$$

where the number of primitive symbols of type $i$ appearing in the primitive symmetry classification of wave function $\Psi_R$ is given by $N_i^{\mathrm{R}}$. Defining $\Delta_{RP}$ to be the discordance in primitive symmetry between the two wave functions

$$\Delta_{RP} = \tfrac{1}{2} \sum_i |N_i^{\mathrm{R}} - N_i^{\mathrm{P}}| \tag{18}$$

the following relationships exist by virtue of the construction of the symmetry adapted geminal structures.

$$\langle \theta_0 \rangle = 0 \text{ unless } \Delta_{RP} = 0 \tag{19}$$

$$\langle \theta_1 \rangle = 0 \text{ unless } \Delta_{RP} = 0 \tag{20}$$

$$\langle \theta_2 \rangle = 0 \text{ unless } \Delta_{RP} = 0 \text{ or } 2 \tag{21}$$

These results are general and hold for all irreducible representations of each point group, including multidimensional representations. In the latter case, each component (e.g., $E_x$ and $E_y$) of a multidimensional representation is a distinct entity and must be separately considered in the determination of $\Delta_{RP}$ for use in eq 19-21.

**B. Interaction Energy Along Symmetry Conserving Paths.** We assume that the wave function corresponding to a representative reaction can be expressed as

$$\Psi_{VB} = C_R \Psi_R + C_P \Psi_P \tag{22}$$

where both contributing structures, $\Psi_R$ valid for reactants and $\Psi_P$ valid for products, are fully antisymmetrized, $n$-electron wave functions constructed from symmetry-adapted geminals as described in eq 1-11, and $C_R$ and $C_P$ are linear coefficients determined by the variation principle: the values of the coefficients vary as a function of the distance along the appropriate chosen "reaction coordinate". In Figure 1, we show a schematic diagram representing the energies corresponding to $\Psi_R$ and $\Psi_P$ along the reaction coordinate; that is

$$\alpha = E_R = \langle \Psi_R | \mathcal{H} | \Psi_R \rangle / \langle \Psi_R | \Psi_R \rangle \tag{23}$$

$$\gamma = E_P = \langle \Psi_P | \mathcal{H} | \Psi_P \rangle / \langle \Psi_P | \Psi_P \rangle \tag{24}$$

where $\mathcal{H}$ is the Hamiltonian for the system. Solution of the eigenvalue equation associated with $\Psi_{VB}$ in eq 22 gives the total energy of the system as

$$E_{VB} = \{\tfrac{1}{2}(\alpha + \gamma) - \beta S \pm [\alpha\gamma S^2 - \beta S(\alpha + \gamma) + \beta^2 + \tfrac{1}{4}(\alpha - \gamma)^2]^{1/2}\}(1 - S^2)^{-1} \tag{25}$$

where the interaction or "exchange" energy, $\beta$. is defined as

$$\beta = \langle \Psi_R | \mathcal{H} | \Psi_P \rangle [\langle \Psi_R | \Psi_R \rangle \langle \Psi_P | \Psi_P \rangle]^{-1/2} \tag{26}$$

and the overlap integral $S$ has the form

$$S = \langle \Psi_R | \Psi_P \rangle [\langle \Psi_R | \Psi_R \rangle \langle \Psi_P | \Psi_P \rangle]^{-1/2} \tag{27}$$

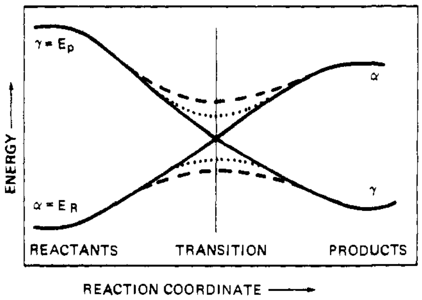


**Figure 1.** Potential energy as a function of reaction coordinate for a hypothetical system. See text for an explanation of the various curves.

The values of the quantities $\alpha$, $\gamma$, $\beta$, and $S$ vary as a function of position along the chosen reaction path.

In the case that $\Psi_R$ and $\Psi_P$ do not have the same composite symmetry, the overlap integral vanishes identically on symmetry grounds. Correspondingly, since the Hamiltonian is a totally symmetric operator, the interaction integral $\beta$ vanishes when $\Psi_R$ and $\Psi_P$ belong to different irreducible representations of the molecular symmetry group. Thus, for wave functions having different composite symmetry, there is no configurational mixing and no concomitant energy lowering along the reaction path. In this case, eq 25 reduces to the expression

$$E_{VB} = \alpha \tag{28}$$

along the entire reaction path, which in terms of Figure 1 implies an endothermic path toward an excited state. Of course, deviations from the symmetry preserving path can occur and result in "crossings" from the surface with energy $\alpha$, corresponding to $\Psi_R$, to the surface with energy $\gamma$, corresponding to $\Psi_P$.

In order to achieve configurational mixing and energy lowering along a symmetry preserving reaction path, the product function $\Psi_P$ must have composite symmetry that is the same as that of the reactant function $\Psi_R$. If one has two alternative paths, both corresponding to component structures of matching composite symmetries, it is necessary to determine along which of the two the lower energy barrier will be encountered. The most frequently considered examples are those in which one path preserves a mirror plane and the other path a twofold axis of symmetry. The symmetry conservation rules permit one to determine which is the lower energy path on the basis of the concordance of the primitive symmetry labels, summarized in eq 19–21.

For a situation where the primitive symmetry is not conserved and $\Delta_{RP} = 2$, the overlap integral $S$ vanishes by eq 19. The interaction energy $\beta$ contains no contributions from the one-electron operators in the Hamiltonian because of eq 20 and consists only of contributions from the two-electron repulsion terms. In this case, eq 25 reduces to

$$E_{VB} = \tfrac{1}{2}(\alpha + \gamma) \pm [\tfrac{1}{4}(\alpha - \gamma)^2 + \beta^2]^{1/2} \tag{29}$$

which yields an energy lowering along the reaction path, as shown schematically by the dotted curves in Figure 1.

When the primitive symmetry is conserved, $\Delta_{RP} = 0$, the overlap integral $S$ is nonzero and the interaction energy consists of both one-electron and two-electron terms. The energy lowering is given by eq 25 and is seen to be made up of two contributions. It arises both from the strength of the interaction energy term $\beta$ as well as the influence of overlap $S$. The dashed curves in Figure 1 represent this case.

It is convenient to choose a particular point along the reaction paths where the energy expressions simplify in order to gain a better understanding of these relationships. In particular, there is always some point along the reaction coordinate where $\alpha = \gamma$, that is, where the energies corresponding to $\Psi_R$ and $\Psi_P$ are equal. If the composite symmetry is conserved but the primitive symmetry is not, eq 29 is applicable and reduces at this point to

$$E|_{\alpha=\gamma} = \alpha \pm \beta' \tag{30}$$

where the prime on $\beta$ denotes contributions to the interaction energy arising only from the two-electron operators. When both composite and primitive symmetries are conserved, the full energy expression given in eq 25 is appropriate; at the equivalence point on the reaction path, the energy becomes

$$E|_{\alpha=\gamma} = (\alpha \pm \beta)/(1 \pm S) \tag{31}$$

In a case where both $\beta$ and $S$ are positive, the positive signs in eq 30 and 31 give the higher energy curves in Figure 1 while the negative signs give the lower energy curves. For a nominal value for $S$ of 0.2, the influence of overlap in eq 31, relative to eq 30, is on the order of 20% of the total energy.

The customary but perhaps too restrictive terminology, "allowed" and "forbidden", applied to two alternative reactive modes of a system, implies only that in the "allowed" case the energy barrier encountered along the reaction coordinate is expected to be significantly lower than in the "forbidden" case.[23,24] As we have shown, the lower barrier is a result of the greater interaction energy that can occur when the principal reactant and product structures have concordant primitive symmetry classifications. Thus, for example, if a path along which a twofold axis was preserved led to concordance for the primitive symmetry labels while that involving a mirror symmetry plane did not, the former would be expected to have a lower barrier than the latter.

**C. Further Energy Considerations.** The energy profile along a reaction path has been discussed in relation to the concordance or discordance of the primitive symmetry classification of the reactant and the product wave functions. The discussion pertained specifically to the case where the reactant and product system could both be described by a single symmetry-adapted electron-pair wave function. In particular, eq 19–21 were derived on the assumption that the component pair functions were strict symmetry eigenfunctions. For certain systems, electron-pair functions corresponding to several resonance structures might be required to provide an adequate description of the reactant or the product state. Moreover, as we show in the following section, pure covalent valence-bond wave functions may not by themselves satisfy the symmetry requirements, so that correction terms may have to be added to the wave function to obtain exact symmetry eigenfunctions. The present section presents an analysis of these more complex situations.

The $n$-electron reactant wave function, $\Psi_R$, is written as

$$\Psi_R = A_1\Phi_1 + A_2\Phi_2 + \ldots \tag{32}$$

where each of the contributing structures, $\Phi_i$, is taken to be a fully-antisymmetrized, $n$-electron symmetry-adapted electron-pair wave function and the $A$'s are linear coefficients. We limit the expansion in eq 32 to two terms since the generalization required for additional terms is straightforward.

From eq 23 and 32, a set of secular equations is derived. If the coefficients in eq 32 are determined by a variational procedure, the energy $\alpha$ of the reactant function $\Psi_R$ (eq 23) is given by

$$\alpha = \{\tfrac{1}{2}(E_{11} + E_{22}) - E_{12}S_{12} \pm [E_{11}E_{22}S_{12}^2 - E_{12}S_{12}(E_{11} + E_{22}) + E_{12}^2 + \tfrac{1}{4}(E_{11} - E_{22})^2]^{1/2}\} \times (1 - S_{12}^2)^{-1} \quad (33)$$

where

$$E_{ij} = \langle\Phi_i|\mathcal{H}|\Phi_j\rangle[\langle\Phi_i|\Phi_i\rangle\langle\Phi_j|\Phi_j\rangle]^{-1/2} \quad (34)$$

$$S_{ij} = \langle\Phi_i|\Phi_j\rangle[\langle\Phi_i|\Phi_i\rangle\langle\Phi_j|\Phi_j\rangle]^{-1/2} \quad (35)$$

The coefficients $A_1$ and $A_2$ have the relative values ($|A_2| < |A_1|$)

$$A_2 = rA_1(\langle\Phi_1|\Phi_1\rangle/\langle\Phi_2|\Phi_2\rangle)^{1/2} \quad (36)$$

with

$$r = (\alpha S_{12} - E_{12})/(E_{22} - \alpha S_{22}) \quad (37)$$

Evaluation of the resonance interaction $E_{12}$ and the overlap $S_{12}$ proceeds by use of eq 17–21. Since $\Phi_1$ and $\Phi_2$ generally have the same composite symmetry, only the primitive symmetry classifications can be different; in that case, we have $\Delta_{12} = 2$, and $S_{12}$ vanishes while $E_{12}$ consists only of two-electron repulsion terms. If $\Phi_1$ and $\Phi_2$ have the same primitive classification, $\Delta_{12} = 0$, $S_{12}$ is nonvanishing, and $E_{12}$ contains both one-electron and two-electron contributions.

In similar fashion, the $n$-electron product wave function, $\Psi_P$, is written

$$\Psi_P = B_1\Phi_3 + B_2\Phi_4 \quad (38)$$

where $\Phi_3$ and $\Phi_4$ are appropriate structures for the product state. Solution of the secular equations arising from eq 24 and 38 gives the eigenvalues $\gamma$

$$\gamma = \{\tfrac{1}{2}(E_{33} + E_{44}) - E_{34}S_{34} \pm [E_{33}E_{44}S_{34}^2 - E_{34}S_{34}(E_{33} + E_{44}) + E_{34}^2 + \tfrac{1}{4}(E_{33} - E_{44})^2]^{1/2}\} \times (1 - S_{34}^2)^{-1} \quad (39)$$

and relative coefficients ($|B_2| < |B_1|$)

$$B_2 = pB_1(\langle\Phi_3|\Phi_3\rangle/\langle\Phi_4|\Phi_4\rangle)^{1/2} \quad (40)$$

with

$$p = (\gamma S_{34} - E_{34})/(E_{44} - \gamma S_{44}) \quad (41)$$

and eq 34 and 35 defining the remaining quantities.

The reactant and product wave functions described by eq 32 and 38, respectively, must be combined as indicated in eq 22 to form the total wave function, $\Psi_{VB}$, corresponding to the total reaction system. The total energy, $E_{VB}$, along the reaction coordinate, is still given by eq 25 but with $\alpha$ and $\gamma$ now defined by eq 33 and 39, respectively. Moreover, the interaction energy $\beta$, defined in eq 26, is now given by

$$\beta = (E_{13} + rE_{23} + pE_{14} + rpE_{24})/D \quad (42)$$

where

$$D = (1 + 2rS_{12} + r^2)^{1/2}(1 + 2pS_{34} + p^2)^{1/2} \quad (43)$$

The overlap integral $S$, defined in eq 27, is

$$S = (S_{13} + rS_{23} + pS_{14} + rpS_{24})/D \quad (44)$$

Again, evaluation of the individual terms, $E_{ij}$ and $S_{ij}$, is performed through use of eq 17–21.

As in the simpler case considered in section IIB, both $\beta$ and $S$ can be responsible for energy lowerings along a reaction path, with eq 42 and 44 specifying the manner in which the secondary structures $\Phi_2$ and $\Phi_4$ enter the energy expressions. However, when $r$ and $p$ are very small, the symmetry properties of the principal structures $\Phi_1$ and $\Phi_3$ determine the behavior of $\beta$ and $S$ through the terms $E_{13}$ and $S_{13}$. In the case where the secondary structures are more heavily weighted, the concordance or discordance of symmetry classifications must be assessed for principal-principal, principal-secondary and secondary-secondary interactions in order to determine the nature of $\beta$ and $S$. *It* is evident that for such reactions the symmetry rules may not have the simple form assumed in most qualitative discussions.

### III. Simple Valence-Bond Formulation

In this and the following sections, we wish to utilize the general arguments developed for electron-pair functions to formulate primitive symmetry labels and a symmetry conservation postulate for a simple valence-bond representation of the reacting system. We construct the valence-bond wave function from an antisymmetrized product of two-electron functions, each describing a pair of electrons in the system. These valence-bond pairs are taken to be spin eigenfunctions and therefore have singlet or triplet spin functions associated with them. In addition, the bond pairs are constructed so as to be adapted in an approximate way to the symmetry element under consideration.

As pointed out in the introduction, the symmetry labels for the electron-pair functions are chosen by examination of the molecular orbital two-electron wave function that makes the dominant contribution. The singlet valence-bond function, ${}^1\sigma_{AB}$, is assumed to be composed predominantly of the molecular orbital function $(a + b)^2$, where $a$ and $b$ represent functions located at centers A and B, respectively, and to a lesser extent of the function $(a - b)^2$. The symmetry label used for the ${}^1\sigma_{AB}$ function is, thus, that associated with $(a + b)^2$. The triplet pair is exactly equivalent to the molecular orbital description in which one electron occupies $(a + b)$ and the other $(a - b)$. The same molecular orbital arrangement but with a singlet spin function describes the ionic pair $a^2 - b^2$. The remaining singlet pair, which is primarily ionic, has a dominant contribution from the doubly occupied $(a - b)$ molecular orbital. This device of combining molecular orbital and valence bond concepts to generate the required two-electron symmetry labels enables the latter to be classified even with respect to higher symmetry groups such as $C_{nv}$, $D_{nh}$, etc. The resulting prescriptions for the symmetry classification of bond pairs are given in Figures 2–4. In the case of the bond type designated ${}^1\pi_{AB\pm CD}$ and ${}^1\sigma_{AB\pm CD}$, neither the AB nor CD bonds are individually symmetry adapted to the symmetry elements of the system. Thus, the appropriate linear combinations are formed and serve as the symmetry adapted bond functions. The triplet pair function in Figure 3 has the two electrons with parallel spins located on different atoms. The ionic structures in Figure 4 have the two electrons with paired spins located on the same atom.

The symmetry classification for an $n$-electron valence-bond structure consists of $n$ symbols which form a primitive representation of the total wave function under the symmetry operation in question. The $n$-term label is formed from each of the two-term primitive symmetry classifications labeling each of the pairs in the system. The order of the symbols within the label is immaterial: AASA is equivalent to SAAA. A composite symmetry label can be obtained through repeated use of the multiplication rules, SS = AA = S and SA = AS = A. As already discussed in section II, structures belonging to different composite irreducible symmetry classes have vanishing matrix elements with respect to the Hamiltonian. Those in the same composite irreducible class interact with one another even if they have differ-

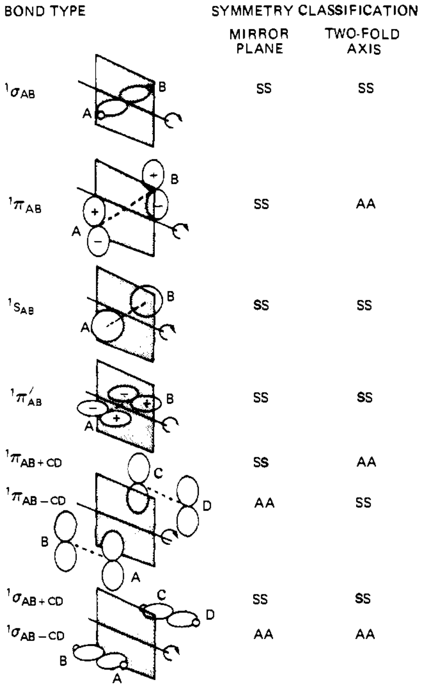


**Figure 2.** Symmetry classifications of singlet covalent bonds.

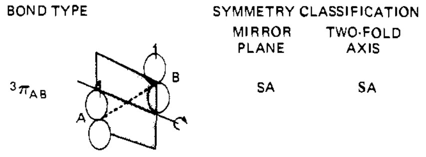


**Figure 3.** Symmetry classification of triplet pair.

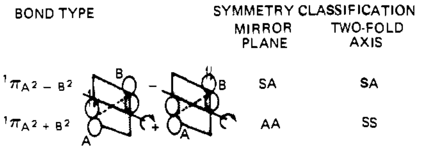


**Figure 4.** Symmetry classification of singlet ionic pairs.

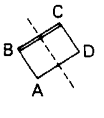
ent primitive classifications.

To generalize the relation between the valence-bond and the molecular-orbital formulation, we can view a valence-bond structure as a constrained type of configuration interaction wave function where the linear coefficients of the molecular orbital determinants are fixed by the values of certain overlap integrals.[17,18] This procedure allows for convenient comparisons between valence-bond and molecular-orbital descriptions of a given state and between valence-bond wave functions corresponding to different states. As an example, we examine the excited triplet and singlet valence-bond wave functions of cyclobutene

$$\mathrm{VB(triplet)} = [{}^1\sigma_{\mathrm{AD}}][{}^3\pi_{\mathrm{BC}}] \qquad (45)$$

$$\mathrm{VB(singlet)} = [{}^1\sigma_{\mathrm{AD}}][{}^1\pi_{\mathrm{B^2-C^2}}] \qquad (46)$$

where the labeling of the bond functions corresponds to I.



(I)

The primitive symmetry classification of these principal valence-bond structures is SSAS with respect to either a twofold axis or a mirror plane, as can be seen from Figures 2–4. Only four electrons are explicitly considered in eq 45 and 46 since the remaining electrons of the cyclobutene system are assumed not to be direct participants in the ring-open chain isomerization.

The unnormalized molecular orbitals $\chi$ for cyclobutene are

$$\begin{aligned}\chi_1(2\mathrm{f},\mathrm{S};\ \mathrm{m},\mathrm{S}) &= \sigma_{\mathrm{A}} + \sigma_{\mathrm{D}}\\ \chi_2(2\mathrm{f},\mathrm{A};\ \mathrm{m},\mathrm{S}) &= \pi_{\mathrm{B}} + \pi_{\mathrm{C}}\\ \chi_3(2\mathrm{f},\mathrm{S};\ \mathrm{m},\mathrm{A}) &= \pi_{\mathrm{B}} - \pi_{\mathrm{C}}\\ \chi_4(2\mathrm{f},\mathrm{A};\ \mathrm{m},\mathrm{A}) &= \sigma_{\mathrm{A}} - \sigma_{\mathrm{D}}\end{aligned} \qquad (47)$$

where the molecular orbital symmetries with respect to a twofold axis (2f) and mirror plane (m) are given in parentheses, and the letter subscripts indicate the atomic center on which the respective $\sigma$ or $\pi$ orbital is located. By substituting these relations into eq 45 and 46, the valence-bond structures can be expressed in terms of four-electron molecular orbital determinants

$$\mathrm{VB(triplet)} = (1 + S_\sigma)|1\bar{1}23| - (1 - S_\sigma)|4\bar{4}23| \qquad (48)$$

$$\mathrm{VB(singlet)} = (1 + S_\sigma)(|1\bar{1}2\bar{3}| - |1\bar{1}\bar{2}3|) - (1 - S_\sigma)(|4\bar{4}2\bar{3}| - |4\bar{4}\bar{2}3|) \qquad (49)$$

where $S_\sigma$ is the overlap integral between the $\sigma$ orbitals on centers A and D, the bar represents $\beta$ spin, and normalization constants have been suppressed. Thus, the two valence-bond structures in eq 45 and 46 are composed of the same two determinantal configurations, 1123 and 4423, but differ in the coupling of the electron spins.

With respect to either a twofold axis or mirror plane, the molecular orbital state symmetry[4] corresponding to 1123 and 4423 is SSAS and AASA, respectively. Since $S_\sigma$ is positive in eq 48 and 49, the leading term of the valence bond series is 1123. The primitive symmetry label of SSAS assigned to the valence-bond pair functions of eq 45 and 46 is therefore an "approximate" valence-bond symmetry because it corresponds only to the symmetry of the leading term of the valence-bond expression of eq 48 and 49. The "exact" valence bond symmetry consists predominantly of SSAS and secondarily of AASA, with the relative importance of these two symmetries being governed by the coefficients 1 ± $S_\sigma$ in eq 48 and 49. Alternatively, additional structures could be added to the canonical covalent structures of eq 45 and 46 so as to obtain an augmented valence-bond wave function with SSAS as the "exact" symmetry.

If, instead of the canonical valence-bond scheme, the more general electron-pair wave functions described in section IIA were used, then the basis set of eq 47 could be expanded to include additional orbitals. This would allow further determinants of both SSAS and AASA symmetries to be employed in a configuration interaction series of the form of eq 48 and 49; only now the coefficients would not be fixed by the values of an overlap integral but would be determined variationally as described in section IIC. The leading term of such a more general scheme would still be the 1123 determinant, and the SSAS symmetry of the latter might still be expected to exert a dominant influence on symmetry-related energy considerations.

In the Woodward–Hoffmann molecular orbital scheme, the photochemical isomerization of cyclobutene to butadiene is analyzed by means of the configuration 1123 without considering spin multiplicity. For both the triplet and singlet states of interest here, the molecular orbital single determinant 1123 is the leading term of the valence bond series, which in turn is expected to be a good approximation to a variationally determined configuration interaction wave function. The success of the Woodward–Hoffmann rules can be ascribed in part to this relation of the simple molecular orbital description of a system to more exact wave functions and to the decisive role played by the primitive symmetry properties of the principal component of a wave function.

## IV. Symmetry Conservation Postulate

As we have seen in section II, if the primitive symmetry classification of the principal structure of a molecular system is conserved throughout the course of a concerted reaction, the energy barrier is expected to be lower than if it is not. We, therefore, make the following symmetry conservation postulate: a concerted reaction is "allowed" if the primitive symmetry classification of the principal reactant structure $\Psi_R$ is the same as that of the principal product structure $\Psi_P$; it is "forbidden" if the primitive symmetry classifications of these two structures are not the same and differ by exactly two labels.

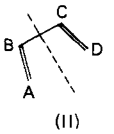
The symmetry conservation postulate applies to concerted reactions in which the symmetry operator of interest bisects the bonds which are formed or those which are broken during the process. The terms "allowed" and "forbidden" are to be interpreted[23-24] as indicating that a fairly low or a fairly high activation barrier exists. Consequently, an allowed reaction is much more likely to proceed under ordinary thermal conditions than a forbidden one.

It is evident that to apply the symmetry postulates appropriate wave functions must be chosen as the principal structures for the reactant and product molecular species. In the case of thermal reactions, the ground state species are to be described. For photochemical processes, one must be careful to distinguish which excited states are involved. At any point along the reaction path, the total wave function for the reacting system consists of a linear combination of a principal structure and possibly several other lesser important contributing structures, all having the same composite symmetry. However, it will be assumed that usually only the principal structures need to be considered. As the reaction proceeds, the principal reactant structure, which dominates the wave function at the beginning of the process, diminishes in importance in accord with the variation principle while the principal product structure gains in importance until it dominates the total wave function at the end of the process. It is the primitive symmetry classification of these principal structures, derived from the approximate primitive pair function symmetries, indicated in Figures 2-4, that must be conserved for allowed processes. In certain situations, secondary energy effects must be considered, as discussed in sections IIC and III.

## V. Examples

To illustrate the symmetry conservation rules, we give some examples in this section.

**A. Cyclobutene–Butadiene Isomerization.**[2-10,14,15] The cyclobutene-butadiene isomerization[25-41] provides a classic system for the application of the symmetry conservation rule. The principal valence-bond structure of the ground state of cyclobutene consists of a $\sigma$ bond between AD and a $\pi$ bond between BC, as already indicated in I; the wave function for the other electron pairs in the molecule is assumed to remain unchanged during the reaction and can therefore be ignored. The principal valence-bond structure of the butadiene ground state consists of $\pi$ bonds between AB and CD, indicated in II.



(II)

The question to be answered is whether a symmetry conserving path preserving a twofold axis of symmetry or a mirror plane of symmetry, both of which are present in reactant and product species, leads to a lower energy barrier for the ring-opening isomerization. (The trace of the symmetry operators in the plane of the molecules is indicated by the dotted lines in I and II.) To answer the question, the valence-bond structures must be classified according to the two symmetry elements. The cyclobutene structure is written

$$\Psi_{\text{cyclobutene}} = [{}^1\sigma_{AD}][{}^1\pi_{BC}] \tag{50}$$

and from Figure 2, it has the primitive symmetry classifications

$$\text{twofold axis—SSAA} \tag{51}$$

$$\text{mirror plane—SSSS} \tag{52}$$

As the reaction proceeds, the $\sigma$ orbitals on centers A and D are regarded as rotating in either a conrotatory or disrotatory fashion such that the symmetry of the twofold axis or mirror plane is conserved, respectively. Changes in orbital hybridization would also be expected to occur. Since the theory in its present form does not impose any orthogonality constraints on the form of the orbitals making up the bond pairs, the wave function in eq 50 remains a bona fide structure throughout.

The butadiene structure is written in terms of the symmetry adapted pair functions as

$$\Psi_{\text{butadiene}} = [{}^1\pi_{AB+CD}][{}^1\pi_{AB-CD}] \tag{53}$$

and has the primitive symmetry classifications

$$\text{twofold axis—AASS} \tag{54}$$

$$\text{mirror plane—SSAA} \tag{55}$$

Here again, the orbitals on centers A and D are assumed to rotate and distort in the appropriate conrotatory or disrotatory fashion as the reaction proceeds but the structure and its symmetry classification remain valid.

With the twofold axis, the symmetry, SSAA, of the principal structure is conserved during the reaction from reactants to products and this conrotatory process is termed "allowed". With the mirror plane, the symmetry classification is not conserved and thus the disrotatory mode of reaction is termed "forbidden". This prediction of a conrotatory isomerization is valid for thermal reactions and photochemical processes involving electronic excitations that are quenched to vibrational levels of the electronic ground state before isomerization since in each case the electronic ground state wave function behavior would be appropriate. This conrotatory ring opening has been observed experimentally[41] and agrees with the conclusions of the molecular orbital schemes.[2-10,14,15]

The usual photochemical reaction proceeds along a reaction path lying on a potential energy surface corresponding to excited state species. The lowest energy excited state of cyclobutene is expected to have the triplet structure

$$\Psi_{\text{cyclobutene}} = [{}^1\sigma_{AD}][{}^3\pi_{BC}] \tag{56}$$

which has the symmetry classification SSSA with respect to either the twofold axis or mirror plane. Though the exact energy is not known, this state has been estimated to lie 87 kcal/mol above ground state cyclobutene,[42a] and hence about 100-105 kcal/mol above the ground state butadiene energy. The corresponding localized description of the triplet excited state wave function of butadiene is

$$\Psi_{\text{butadiene}} = [{}^1\pi_{BC}][{}^3\pi_{AD}] \tag{57}$$

and has the primitive symmetry classifications

twofold axis—AASA (58)

mirror plane—SSSA (59)

Its energy lies about 60 kcal/mol above the ground state butadiene singlet.[43,44] In order to conserve the symmetry classification SSSA, a disrotatory opening has to be followed.

A further excited state of butadiene is known[44] to lie *107–124* kcal/mol above the ground state singlet. This corresponds to the ionic singlet structure

$$\Psi_{\text{butadiene}} = [{}^1\pi_{\mathrm{BC}}][{}^1\pi_{\mathrm{A2-D2}}] \tag{60}$$

having the primitive classifications

twofold axis—AASA (61)

mirror plane—SSSA (62)

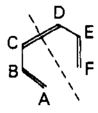
Since this structure has an antisymmetric composite representation, it would be noninteracting with the ground state. A corresponding excited singlet state for cyclobutene is represented by the structure

$$\Psi_{\text{cyclobutene}} = [{}^1\sigma_{\mathrm{AD}}][{}^1\pi_{\mathrm{B2-C2}}] \tag{63}$$

which has the primitive classification SSSA for both symmetry operators. Therefore, these excited singlet states would be correlated in a disrotatory fashion.

The predictions regarding the thermal conrotatory and photochemical disrotatory nature of these reactions appear to be in agreement with the work of Srinivasan[41] on the isomerization of *cis*-3,4-dimethylcyclobutene. The fact that the butadiene triplet lies 45 kcal/mol lower than the cyclobutene triplet[42-44] is consistent with the observation[45] that the photochemical ring closure does not proceed via triplet state intermediates. The present analysis would indicate that the ring closure could proceed through excited singlet states with conservation of symmetry, spin angular momentum, and energy if the excited singlet of cyclobutene is assumed to lie only slightly higher than the excited cyclobutene triplet. However, if the excited cyclobutene singlet does lie considerably higher,[41] the ring closure would probably involve a crossing from the singlet butadiene to triplet cyclobutene during the course of reaction.

**B. Other Ring-Chain Isomerizations.**[2,9,10] As a second example, we consider the hexatriene-cyclohexadiene isomerization.[46-58] There are six electrons to account for, in this case, since all the remaining electrons keep their pairing relationships, and thus, their symmetry characteristics remain invariant throughout the process.



(III)

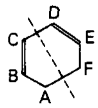
The reactant hexatriene is labelled as in III. The principal ground state structure can be written with reference to Figure 2 as

$$\Psi_{\text{hexatriene}} = [{}^1\pi_{\mathrm{AB+EF}}][{}^1\pi_{\mathrm{AB-EF}}][{}^1\pi_{\mathrm{CD}}] \tag{64}$$

and has the primitive symmetry classifications

twofold axis—AASSAA (65)

mirror plane—SSAASS (66)



(IV)

The product molecule contains the new $\sigma$ bond between atoms A and F, indicated in IV. The corresponding principal ground state wave function

$$\Psi_{\text{cyclohexadiene}} = [{}^1\sigma_{\mathrm{AF}}][{}^1\pi_{\mathrm{BC+DE}}][{}^1\pi_{\mathrm{BC-DE}}] \tag{67}$$

has the primitive symmetry classifications

twofold axis—SSAASS (68)

mirror plane—SSSSAA (69)

Symmetry can be conserved only through preservation of the mirror plane, and the reaction path is termed disrotatory.

The first excited triplet state, which could be involved in certain photolytic isomerizations, has the structure

$$\Psi_{\text{hexatriene}} = [{}^1\pi_{\mathrm{BC+DE}}][{}^1\pi_{\mathrm{BC-DE}}][{}^3\pi_{\mathrm{AF}}] \tag{70}$$

and has the symmetry classification SSSAAA with respect to both a twofold axis and a mirror plane of symmetry. The product molecule has the description

$$\Psi_{\text{cyclohexadiene}} = [{}^1\sigma_{\mathrm{AF}}][{}^3\pi_{\mathrm{BE}}][{}^1\pi_{\mathrm{CD}}] \tag{71}$$

with the primitive symmetry classifications

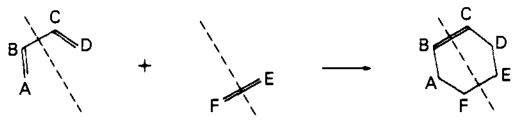
twofold axis—SSSAAA (72)

mirror plane—SSSASS (73)

The excited state reaction from triplet hexatriene to triplet cyclohexadiene would have an "allowed" path that conserves a twofold axis of symmetry. The next lowest singlet excited state also exhibits this conrotatory behavior.

The octatetraene to cyclooctatriene isomerization[59,60] and higher ring-chain homologs can each be treated in the same general fashion as above. Correlation of these results leads to the $4n$ and $4n + 2$ rules:[2,5,6] namely, (a) if the related ring and chain molecules have $4n$ and $4n + 2$ $\pi$ electrons, respectively, the thermal isomerization proceeds in a disrotatory fashion and photochemical isomerization proceeds in a conrotatory manner, and (b) if the ring and chain isomers have respectively $4n - 2$ and $4n$ $\pi$ electrons, thermal conrotatory and photolytic disrotatory reactions are expected.

**C. Diels-Alder Reaction.**[2,6,8,11] The Diels-Alder [4 + 2] cycloaddition of butadiene to ethylene giving cyclohexene, which is shown in V, is an example of a symmetry allowed process.



(V)

The principal structures of the reactants are

$$\Psi_{\text{reactants}} = [{}^1\pi_{\mathrm{AB+CD}}][{}^1\pi_{\mathrm{AB-CD}}]\cdot[{}^1\pi_{\mathrm{EF}}] \tag{74}$$

with the primitive symmetry classifications

twofold axis—AASSAA (75)

mirror plane—SSAASS (76)

The product wave function is of the form

$$\Psi_{\text{product}} = [{}^1\sigma_{\mathrm{AF+DE}}][{}^1\sigma_{\mathrm{AF-DE}}][{}^1\pi_{\mathrm{BC}}] \tag{77}$$

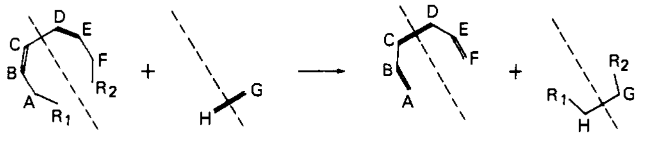
and has the primitive symmetry classifications

twofold axis—SSAAAA (78)

mirror plane—SSAASS (79)

The reaction is seen to be symmetry allowed with respect to both of the symmetry elements present.

**D. Allowed Group Transfer Reaction.**[2] A more complex example is provided by the group transfer reaction depicted in VI with $R_1 = R_2$. The reactant structure and its symmetry classifications are written as



(VI)

$$\Psi_{\text{reactant}} = [{}^1\sigma_{\text{AR}_1+\text{FR}_2}][{}^1\sigma_{\text{AR}_1-\text{FR}_2}][{}^1\pi_{\text{BC+DE}}] \times [{}^1\pi_{\text{BC-DE}}]\cdot[{}^1\pi_{\text{GH}}] \quad (80)$$

twofold axis—SSAAAASSAA (81)
mirror plane—SSAASSAASS (82)

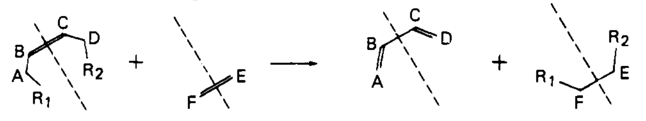
The product species have the wave function and symmetry characteristics

$$\Psi_{\text{product}} = [{}^1\pi_{\text{AB+EF}}][{}^1\pi_{\text{AB-EF}}][{}^1\pi_{\text{CD}}]\cdot[{}^1\sigma_{\text{HR}_1+\text{GR}_2}] \times [{}^1\sigma_{\text{HR}_1-\text{GR}_2}] \quad (83)$$

twofold axis—AASSAASSAA (84)
mirror plane—SSAASSSSAA (85)

Thus, the transfer is a symmetry allowed process.

**E. Forbidden Group Transfer Reaction.**[2] An example of a symmetry forbidden reaction is provided by the group transfer reaction given in VII. The reactant molecules have the description



(VII)

$$\Psi_{\text{reactant}} = [{}^1\sigma_{\text{AR}_1} + {}_{\text{DR}_2}][{}^1\sigma_{\text{AR}_1-\text{DR}_2}][{}^1\pi_{\text{BC}}]\cdot[{}^1\pi_{\text{EF}}] \quad (86)$$

and the primitive symmetry classifications

twofold axis—SSAAAAAA (87)
mirror plane—SSAASSSS (88)

The product molecules have the structure and primitive symmetry classifications

$$\Psi_{\text{product}} = [{}^1\pi_{\text{AB+CD}}][{}^1\pi_{\text{AB-CD}}]\cdot[{}^1\sigma_{\text{FR}_1+\text{ER}_2}][{}^1\sigma_{\text{FR}_1-\text{ER}_2}] \quad (89)$$

twofold axis—AASSSSAA (90)
mirror plane—SSAASSAA (91)

Neither symmetry classification is conserved during this process and a high thermal activation barrier is expected.

## VI. Limitations of Symmetry Rules

The principal concern in the present work has been the discussion of symmetry conservation of concerted reactions in the framework of generalized electron pair functions. The salient feature of the development has been the introduction of a primitive symmetry classification which permits one to compare the barrier heights expected for two possible symmetry-preserving paths along which a reaction might proceed. Symmetry conservation rules are then obtained by assuming that the path corresponding to the lower energy barrier is the more probable one. In such a qualitative comparison the assessment of barrier heights is a *relative* assessment; a numerical evaluation of the expression in eq 25 for the transition state species would be necessary to obtain an *absolute* value of a given barrier height.

Although the symmetry rules have had a remarkable success, there are certain situations where a breakdown could occur in the simple arguments based on the conservation of primitive symmetry between principal valence-bond structures.[61-65] In particular, if a multistructure wave function is required to achieve an adequate description of the reacting system as described in section IIC, as assessment of relative barrier heights would have to include the effects of interactions arising from secondary valence-bond structures. Further, if there exist nonsymmetry preserving paths having low enough potential energy barriers to make them important to the reaction system, these paths would need to be considered. Finally, if dynamical effects are important or if the system encounters strained geometries or hindered rotation along a reaction path, these could also lead to a breakdown of the rules. For such situations, the rules could be refined or supplemented by calculations within the present general framework by including the relevant interactions in the Hamiltonian or by considering secondary symmetry components of the canonical valence-bond wave function as discussed in section III and evaluating their effect on the energy expressions given in section II.

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# Oxidation–Reduction Photochemistry. Intramolecular Electron Transfer in Cobalt(III)–Copper(I) Bridged Binuclear Ions

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**Abstract:** Photolytic oxidation–reduction reactions of $(NH_3)_5Co^{III}LCu^{I}$ bridged binuclear ions, where L = alkenoic acids or primary aminoalkenes, are described. Excitation of Cu(d) → L(π*) charge transfer bands causes intramolecular electron transfer between metal centers, $\Phi_{Co(II)} = 0.24–0.65$, according to the equation $(NH_3)_5Co^{III}LCu^{I} + 6H^+ \rightarrow Co(II) + Cu(II) + 5NH_4^+ + HL$. The first excited *singlet* charge transfer state is tentatively identified as photoreactive from studies on analogous intermolecular reactions. Results are rationalized in terms of electron transfer mediated by π-delocalized orbitals of the bridging ligands; for nonconjugated ligands, the pathway is provided by direct overlap of olefin π-antibonding orbitals with metal donor and acceptor orbitals. Irradiation in the wavelength region of the low-energy cobalt(III) ligand field bands ($L_1$) also causes photoredox decomposition in the binuclear ions, $\Phi_{Co(II)} \leq 1.3 \times 10^{-3}$.

Recent investigations of luminescence quenching of excited state organic[1] and inorganic[2] molecules, and of photosensitized redox decompositions,[3] have led to the realization that electron transfer mechanisms can play a dominant role in these photochemical processes. In this report we present evidence for excited state electron transfer in bridged binuclear ions of the type $RoLCu^{I}$ ($Ro \equiv (NH_3)_5Co^{III}$ moiety, L = $^{-}O_2C(CH_2)_nCH{=}CHR$ or $NH_2(CH_2)_nCH{=}CH_2$),[4] arising from irradiation of either charge-transfer or metal-centered chromophores. Whereas photoredox decomposition of bridged binuclear ions has generally involved oxidation–reduction of ligands in addition to metal centers,[5,6] reaction in the present systems comprises net electron transfer between metal centers.

Our interest in these reactions derives principally from our conviction that study of intramolecular redox processes[7] offers the prospect of direct analysis for significant factors controlling the electron-transfer event, ambiguities associated with uncertainties in stabilities and structures of interacting partners inherent in intermolecular redox reactions being minimized. Electron transfer in the cobalt(III)–copper(I) binuclear ions at thermal energies is extremely slow (generally, $t_{1/2} \geq 5$ years) despite a favorable reaction free energy;[4] we have therefore examined their reactivity in electronically excited states. Comparison of rate data for various bridging ligands has provided evidence favoring electron transfer attending charge-transfer excitation which is mediated by olefin π-antibonding orbitals; the pathway is unique in that formal conjugation through the bridging ligand is not required.[8,9] Limitations imposed by our studies upon mechanistic alternatives for photoredox reactions initiated by excitation in the cobalt(III) ligand field region are also discussed.

## Experimental Section

**Reagents.** Carboxylatopentaamminecobalt(III) complexes were synthesized and characterized as previously described.[4] The cobalt(III) complexes containing aminoalkene ligands were prepared by equilibrating dry dimethylformamide (DMF) solutions of Ro–DMF perchlorate at ca. 60° for 1.5 hr with an excess of the amine; in these instances, the reaction was carried out under a blanket of nitrogen to minimize air oxidation of the organic ligand and molecular sieve (4A) was added to maintain anhydrous conditions. The complexes were isolated as their perchlorate salts after concentration on a rotary evaporator and recrystallized from hot dilute