

An Improved Interpretation of the Woodward–Hoffmann Rules

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One of the basic questions that still surround the Woodward–Hoffmann (W-H) rules is just how these rules are connected to the more conventional theories of chemical reactions¹ and reactivity. Because this conceptual gap has not been closed, these “rules” are treated as if they are some fortuitous application of group theory or the orbital correlations are misrepresented because the information actually provided by such correlations is misunderstood. Thus one is left with a set of graphically derived rules that seem to have only a remote connection to more quantitative discussions of chemical reactivity.

Why Is Symmetry a Superior Diagnostic Tool for Reaction Pathways?

Usually these more quantitative discussions (1–5) of possible reaction pathways focus on properties like the conservation of total electronic angular momentum between reactant (R) and product (P) states² (G). Such discussions have implied that evaluation of electronic angular momentum (I) is a more rigorous approach to the characterization of an electronic state than a graphical representation of state symmetry. However, this misrepresents the relationship between the symmetry properties of a state and a directly observable property such as electronic angular momentum. Total electronic angular momentum as well as state symmetry depends on both the electronic configuration of the state and molecular geometry. Unlike symmetry properties, the value measured for electronic angular momentum will be physically meaningful (quantized) only for electronic configurations within special molecular geometries (7).³ This restricts the application of electronic angular momentum conservation as a tool for sorting out possible reaction pathways (2). However, when it is possible to evaluate conservation of both electronic angular momentum and the corresponding symmetry properties for a state, one can establish an important relation between these two properties (Fig. 1). If total electronic angular momentum is conserved during reaction, then it necessarily follows that the symmetry of that given electronic state will also be conserved. One will never see a situation where, say, a state has $\Lambda = 0$ and P-type symmetry. Only if the state has $\Lambda = 1$ will it have P-type symmetry. Thus both properties will be conserved simultaneously or not at all. It follows that not discussing electronic angular momentum does not degrade, limit, or impinge the application of the conservation of symmetry for electronic states as a diagnostic tool for evaluating possible reaction pathways.

As a corollary to previous observations on conservation, it is also true that if a reaction pathway changes or disrupts the occupied orbital nodal geometries of a reactant state during reaction, then this disruption *may* result in a failure to conserve state symmetry. Within this covering point group G for a reaction pathway, the reactant state is usually a reducible representation: $\Gamma_R(G) = \prod \Gamma_i(G)$; likewise, for products, $\Gamma_P(G) = \prod \Gamma_j(G)$ where $\Gamma_i(G)$ and $\Gamma_j(G)$ are irreducible representa-

tions within G . State symmetry is conserved for this reaction when $\prod \Gamma_j(G) = \prod \Gamma_i(G)$. As it will be shown later, state symmetry can be conserved even if symmetry is not conserved by two or more of a state's irreducible “orbital” components (2).

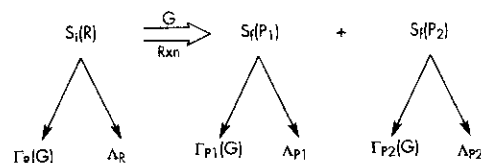


Figure 1. Suppose reactant R is in an initial state i and it undergoes a single-step reaction within a certain geometry or covering point group G to yield two products (P_1 and P_2) in some final states f . Each of the R and P states possesses both symmetry properties (Γ) and a certain value of angular momentum (Λ). Angular momentum is conserved if $\Lambda_R = \Lambda_{P_1} + \Lambda_{P_2}$. State symmetry is conserved for this reaction if $\Gamma_R(G) = \Gamma_P(G)$. Furthermore, the representation of the overall product state P can be factored: $\Gamma_P(G) = \Gamma_{P_1}(G) \otimes \Gamma_{P_2}(G)$.

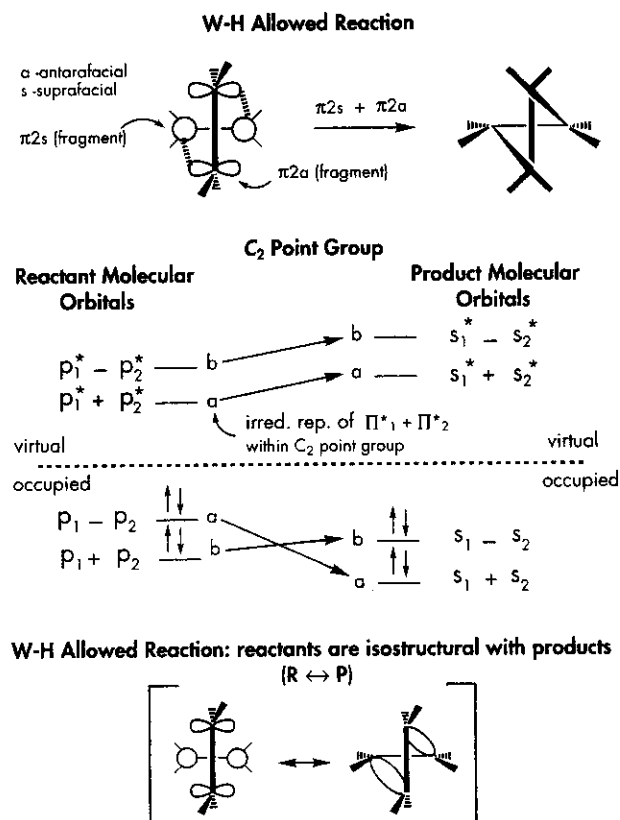


Figure 2. Reaction pathway geometry for a W-H “allowed” reaction.

What Information Is Provided by a Correlation Diagram?

The approach described by W-H is based on a graphical representation of occupied reactant and product molecular orbital nodal geometries (i.e., the in-phase out-of-phase relationships within each MO), which are then characterized in terms of their respective symmetry properties. These nodal geometries of the occupied orbitals can be conserved between reactants R and products P only when a reaction pathway possesses a geometry sufficient to force an isostructural relationship among the critical bonds (i.e., bonds undergoing connectivity changes during the conversion of R to P). Along a W-H "allowed" reaction pathway, the transforming bonds of the reactants and products become indistinguishable (i.e., resonance) structures of each other, analogous to Wheland structures that are used for the valence bond representation of benzene. Thus a correlation diagram is used to establish, graphically, whether the reactants and products can become structurally identical within a particular reaction path geometry. As an example, consider the W-H allowed $\pi 2s + \pi 2a$ reaction pathway⁴ for two ethylene molecules to yield cyclobutane (Fig. 2). Within this proposed $\pi 2s + \pi 2a$ allowed reaction pathway geometry there are no distinct reactants or product entities, only a super molecule representing a reaction pathway whose *structural form* consists of reactants and products as its *principle structural extremes*. This type of isostructural relationship between reactants and products cannot exist for a $\pi 2s + \pi 2s$ reaction pathway because for a "forbidden" geometry, not all the occupied reactant nodal geometries correlate to all the occupied product nodal geometries.

What Is the Relationship between Orbital Symmetry and Energy?

Conservation of total electronic angular momentum, in addition to conserving orbital symmetry for simple elementary reactions (atom-atom, diatomic molecules with atoms or other diatomic molecules), also affects the total electronic energy of a reacting system. Reformulation of this transformation in terms of total electronic energy provides a more finely calibrated evaluation of symmetry effects on the interaction of the reactant and product potential energy curves or surfaces (8). Instead of focusing on angular momentum or symmetry labels for states and orbitals, attention is shifted

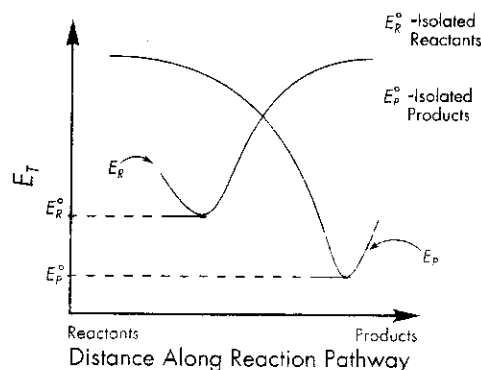


Figure 3. Plot of energy of products and reactants as a function of distance traveled along a proposed reaction pathway.

to the consequences that these symmetry properties have on the interaction energy⁵ (9) between the reactant and product potential energy surfaces (2, 4, 8, 10).

Following the notation used by Flurry (8), a reacting system wave function, Ψ_r , is designated as a linear combination of the total (i.e., state) wave functions of the reactants Ψ_R^c and products Ψ_P^c :

$$\Psi_r = C_R \Psi_R^c + C_P \Psi_P^c$$

The coefficients C_R and C_P are adjusted as a function of distance traveled along a proposed reaction pathway (Fig. 3). For isolated systems (i.e., undistorted reactants or products), Ψ_r converges to Ψ_R^c for the reactants and Ψ_P^c for the products and E converges to E_R^0 and E_P^0 for the isolated reactants and products, respectively. The Hamiltonian operator is totally symmetric (i.e., invariant with respect to any symmetry operation). As for the wave functions, it is assumed that both Ψ_R^c and Ψ_P^c are adequately described within the limits imposed by the Born-Oppenheimer approximation.

If one moves along either of the potential energy curves toward a proposed intersection of R and P, then E_R and E_P will increase (i.e., become less stabilizing) as the reactants and products are distorted toward the intersection of these two PE curves. If the matrix elements or integrals H_{RP} and S_{RP} are zero, then R and P do not interact (10, 11) and as a result there is a crossing but no pathway by which reactants can be adiabatically interconverted with products (12).⁶ If this conversion of reactants to products is to be allowed then it must be determined where on the potential energy surfaces of the reactants and products the integrals H_{RP} and S_{RP} are nonvanishing (9, 10):⁵

\mathcal{H} Hamiltonian operator for reaction.

E_r Total electronic energy for reactants and products at some distance r along the reaction pathway.

$\Psi_r = C_R \Psi_R^c + C_P \Psi_P^c$ Wave function describing the reaction potential energy surface in terms of isolated reactant, Ψ_R^c , and product, Ψ_P^c , state wave functions.

Schrödinger equation: $\langle \Psi_r | \mathcal{H} - E_r | \Psi_r \rangle = 0$

Secular determinant:
$$\begin{vmatrix} (H_{RR} - E_r) & (H_{RP} - E_r S_{RP}) \\ (H_{RP} - E_r S_{RP}) & (H_{PP} - E_r) \end{vmatrix} = 0$$

$H_{RP} = \langle \Psi_R^c | \mathcal{H} | \Psi_P^c \rangle = H_{PR}$; $S_{RP} = \langle \Psi_R^c | \Psi_P^c \rangle = S_{PR}$

Use group theory to decide whether H_{RP} and $S_{RP} = 0$.

An analysis of H_{RP} and S_{RP} integrals can be accomplished (8, 10) using the geometry at the intersection to determine a point group G and then representations of Ψ_R^c and Ψ_P^c within this point group. If H_{RP} and S_{RP} are not forced to be zero by symmetry, then these reducible representations of H_{RP} and S_{RP} must contain the totally symmetric representation $\Gamma_1(G)$. A reducible representation of the integral H_{RP} is determined by taking the direct product of its three component representations:

$$H_{RP} = \langle \Psi_R^c | \mathcal{H} | \Psi_P^c \rangle = H_{PR}; \quad S_{PP} = \langle \Psi_R^c | \Psi_P^c \rangle$$

$$\Gamma_{H_{RP}} = \Gamma_R \otimes \Gamma_H \otimes \Gamma_P$$

** $\Gamma_H = \Gamma_1(G)$ (this is the totally symmetric representation of group G)

$$\Gamma_{H_{RP}} = \Gamma_R \otimes \Gamma_1(G) \otimes \Gamma_P$$

$$\Gamma_{H_{RP}} = \Gamma_R \otimes \Gamma_P \otimes \Gamma_1(G)$$

** $\Gamma_{H_{RP}} = \Gamma_R \otimes \Gamma_P$; this result also means that $\Gamma_{H_{RP}} = \Gamma_{S_{RP}}$

The representation of the Hamiltonian operator is $\Gamma_1(G)$, a result of the requirement that the Hamiltonian operator describing this reaction pathway be totally symmetric with respect to all symmetry operations. This symmetry invariance of the Hamiltonian requires that the reducible representation of the direct product $\Gamma(\Psi_R^o) \otimes \Gamma(\Psi_P^o)$ contain at least one component of the totally symmetric representation $\Gamma_1(G)$ if both these integrals (H_{RP} and S_{RP}) are to have an opportunity to be nonzero:

$$** \quad \Gamma_R \otimes \Gamma_P = \sum_{\text{Rep}} \Gamma_i(G)$$

If the direct product of $\Gamma_R \otimes \Gamma_P$ contains the totally symmetric representation of the group G , $\Gamma_1(G)$ then H_{RP} and S_{RP} need not be equal to zero.

Two results are possible for the reducible representations of H_{RP} and S_{RP} when these R and P states intersect (4). For case 1 (i.e., state forbidden), the reducible representations Γ_{RP} for H_{RP} and S_{RP} do not contain the totally symmetric representation $\Gamma_1(G)$. This means that H_{RP} and S_{RP} must vanish (must be equal to zero) and there is no net interaction between R and P states. As a result, these R and P potential energy curves or surfaces merely cross each other because there is no adiabatic pathway for the interconversion of R and P (12).⁶

Case 1: State forbidden

$$\Gamma_R \otimes \Gamma_P = \sum_{\text{Rep}} \Gamma_i(G) \not\supset \Gamma_1(G)$$

$$\Rightarrow H_{RP} \text{ and } S_{RP} = 0$$

In case 2 (state allowed), the reducible representation for Γ_{RP} contains a totally symmetric representation $\Gamma_1(G)$. Since H_{RP} and S_{RP} are not required to vanish, there can be a net interaction between the reactant and product potential energy surfaces. As a result, there now is an adiabatic pathway within this geometry that permits interconversion of R and P. Such a state allowed interaction between R and P states will always occur when both reactants and products are closed-shell molecules (all molecular orbitals are doubly occupied). The resulting Γ_{RP} representations between closed shell electronic states always contain a totally symmetric representation, since the ground states (Ψ_R and Ψ_P) are themselves totally symmetric:

Case 2: State allowed

$$\Gamma_R \otimes \Gamma_P = \sum_{\text{Rep}} \Gamma_i(G) \supset \Gamma_1(G)$$

$$* \Rightarrow H_{RP} \text{ and } S_{RP} \neq 0, \text{ need not be zero}$$

However, within this general requirement for state allowed interactions is a subset of interactions for which $\Gamma_R \otimes \Gamma_P = \Gamma_1(G)$

However, within case 2 there is a subset of allowed interactions that generates two situations of particular interest. In case 2a, there is only a partial correlation among the occupied reactant (ϕ_R) and occupied product (ϕ_P) molecular orbitals:

** \Rightarrow If it happens that $\Gamma_R \otimes \Gamma_P = \Gamma_1(G)$ then $\Gamma_R = \Gamma_P$ and because the symmetry of a state is a product of the irreducible representations of its occupied MO,

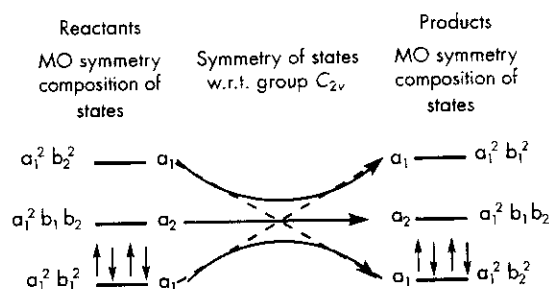
$$\prod_i \Gamma_{\phi_R}(i) = \prod_i \Gamma_{\phi_P}(i)$$

but, case 2a:
 $\Gamma_{\phi_R} \neq \Gamma_{\phi_P} \forall \phi_R$ and ϕ_P in Ψ_R^o and Ψ_P^o , respectively

W-H forbidden

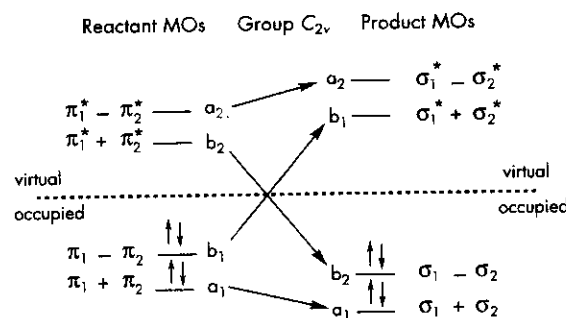
As an example of a case 2a reaction, consider the state correlation diagram for the C_{2v} or $\pi 2s + \pi 2s$ dimerization of ethylene to form cyclobutane. This reaction is one for which the reaction pathway is state allowed but W-H forbidden. In this geometry, the ground state of the ethylene reactants possesses a₁ symmetry (i.e., total symmetry within the C_{2v} group) and correlates with the ground state of cyclobutane, which also possesses a₁ symmetry and so is a state allowed process:

State Correlation Diagram for $\pi 2s + \pi 2s$



This C_{2v} or $\pi 2s + \pi 2s$ dimerization of ethylene is W-H forbidden because the occupied reactant orbital ($\pi_1 - \pi_2$) correlates with a vacant product orbital ($\sigma_1^* + \sigma_2^*$) rather than with the other occupied ($\sigma_1 - \sigma_2$) product orbital:

W-H Orbital Correlation Diagram for $\pi 2s + \pi 2s$



Since the ground states of these reactants and products both transform as a₁, it follows that

$$\Gamma_R = a_1 \otimes a_1 \otimes b_1 \otimes b_1 = a_1 \text{ and } \Gamma_P = a_1 \otimes a_1 \otimes b_2 \otimes b_2 = a_1$$

$$\text{and } \Gamma_R \otimes \Gamma_P = \Gamma_1(G) = a_1$$

but not all the orbitals correlate:

$$a_1 = a_1 \text{ but } b_1 \neq b_2$$

which means that

$$\Gamma_{\phi_R} \neq \Gamma_{\phi_P} \forall \phi_R \text{ and } \phi_P \text{ in } \Psi_R^o \text{ and } \Psi_P^o, \text{ respectively}$$

Although this reaction geometry is allowed by the state-to-state correlation, this same reaction geometry is orbitally forbidden according to the W-H correlation diagram.⁷ This lack of complete correlation at the orbital level results in less than the maximum possible amount of interaction (4) or "resonance" between reactants and products.

The next scenario of interest is case 2b, in which correlation occurs simultaneously between R and P states with complete orbital correlations between R and P:

** \Rightarrow Once again, $\Gamma_R \otimes \Gamma_P = \Gamma_1(G)$; then $\Gamma_R = \Gamma_P$ and

$$\prod_i \Gamma_{\phi_R}(i) = \prod_i \Gamma_{\phi_P}(i), \text{ but now}$$

Case 2b:

$$\Gamma\phi_R = \Gamma\phi_P \quad \forall \phi_R \text{ and } \phi_P \text{ in } \Psi_R^0 \text{ and } \Psi_P^0, \text{ respectively}$$

W-H allowed

Here too, the reducible representation of Γ_{RP} for the R and P states also contains a totally symmetric representation (i.e., a) but now these correlations between reactant and product ground states occur along with complete correlations among the occupied reactant and product orbitals undergoing reaction. For example, consider the $\pi 2s + \pi 2a$ dimerization of ethylene to give cyclobutane:

State Correlation Diagram for $\pi 2s + \pi 2a$

Reactants MO symmetry composition of states	Symmetry of states w.r.t. group C_{2v}	Products MO symmetry composition of states
b^2b^2	a	a^2a^2
b^2ab	b	a^2bo
b^2a^2	a	a^2b^2

W-H Orbital Correlation Diagram for $\pi 2s + \pi 2a$

Reactant MOs	Group C_2	Product MOs
$\pi_1^* - \pi_2^*$	b	$\sigma_1^* - \sigma_2^*$
$\pi_1^* + \pi_2^*$	b	$\sigma_1^* + \sigma_2^*$
$\pi_1^* - \pi_2^*$	a	$\sigma_1 - \sigma_2$
$\pi_1^* + \pi_2^*$	b	$\sigma_1 + \sigma_2$

virtual occupied virtual occupied

This time not only does the ground state of these reactants correlate with the ground state of the products, but within this C_2 reaction geometry, symmetries of the occupied molecular orbitals of the reactant and products also correlate with each other. The significance of this combined state and orbital correlation is that these R and P structures are one and the same structure within this particular reaction geometry. In terms of energy, case 2b provides the maximum possible stabilizing interaction (4, 8) between the reactant and product potential energy surfaces:

$$\Gamma_R = a \otimes a \otimes b \otimes b = a \quad \text{and} \quad \Gamma_P = a \otimes a \otimes b \otimes b = a$$

$$\text{and } \Gamma_R \otimes \Gamma_P = \Gamma_1(G) = a$$

but this time the occupied orbitals correlate: for each occupied a-orbital in R there is a corresponding occupied a-orbital in P, and for each occupied b-orbital in R there is a corresponding b-orbital in P; and

$$\Gamma\phi_R = \Gamma\phi_P \quad \forall \phi_R \text{ and } \phi_P \text{ in } \Psi_R^0 \text{ and } \Psi_P^0, \text{ respectively}$$

The advantage of recasting this problem in terms of symmetry effects on electronic energy is that such an approach offers a global view of orbital correlation effects on total electronic energy. It is now obvious that there is a continuum of orbital correlations within state allowed reaction pathways. At one extreme is a state allowed reaction that has no orbital correlations between R and P states and at the other extreme

are those reactions with complete orbital correlations among R and P states (i.e., W-H allowed).

According to Silver (4), state allowed reactions (case 2) obey the Wigner–Witmer rules, which require conservation of the total electronic orbital angular momentum (Λ) and/or symmetry (Γ) between reactant and product states. This requirement for state symmetry correlation is global and represents the minimum amount of interaction (4, 8) necessary for an adiabatic interconversion of reactants and products. Case 2b describes reactions that obey the W-H rules and in addition to conserving total electronic symmetry between states (case 2) also conserve individual electronic orbital symmetry between the R and P occupied molecular orbitals. Conservation of both orbital and state symmetry between R and P provides the maximum amount of stabilizing interaction between R and P because critical reactant and product orbitals are not only “in phase” but also become identical along the pathway for reaction.

Discussion

Conservation of orbital symmetry does not mean that there is no activation energy for a W-H allowed reaction, nor is it proper to infer that the W-H allowed process has the lowest activation energy of all possible pathways connecting R to P. Indeed, the major contributors to an activation energy such as the distortion of bond lengths and bond angles from their equilibrium values cannot be evaluated by the W-H correlation diagrams. Disregarding the distortion energy of nonreacting bonds can be justified in part because such bonds do not undergo any connectivity changes (breakage and reformation). Thus the nodal geometry (i.e., the in-phase–out-of-phase relationships within each MO) of nonreacting bonds remains unchanged.

Another assumption in the application of these symmetry rules is that if a given reaction geometry is “allowed” then a thermal pathway should exist for this interconversion of R and P. Although this assumption is reasonable, there is no requirement that such a pathway exist.

A W-H allowed reaction pathway conserves R (reactant) and P (product) nodal geometries, which in turn guarantees continuous covalent bonding along an adiabatic reaction pathway (12)⁶ that takes the reactants through a transition state and on into products. A W-H forbidden pathway can either maintain this continuous bonding (interaction energy between R and P) along an adiabatic pathway and generate products in excited electronic states, or disrupt reactant nodal geometry or bonding to reach diabatically (or nonadiabatically) a lower-energy pathway to products (12).⁶ Based on the idea that continuous bonding is energetically more favorable than either nonbonding or antibonding interactions, a W-H forbidden reaction is not impossible; rather it is just less probable than an W-H allowed reaction pathway. One should consider these W-H rules as a kinetic equivalent to the more familiar spectroscopic selection rules. It is also worth emphasizing that it is not necessary that intermediates intervene for a W-H forbidden reaction pathway to be realized. In other words, it is also possible for a W-H forbidden pathway to occur as a single-step reaction (13) (case 2a) and one cannot argue, a priori, that the difference between a W-H allowed and a W-H forbidden pathway is that the latter must pass through an intermediate on the way to products. As a result of the

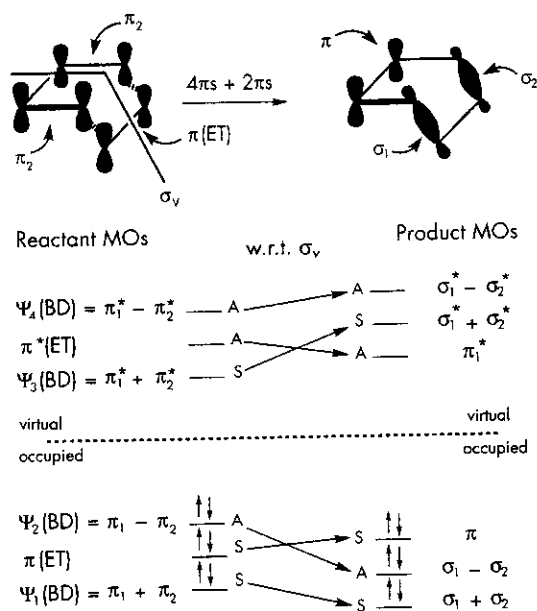


Figure 4. W-H orbital correlation diagram for $\pi 4s + \pi 2s$ reaction.

description provided here, these W-H allowed reactions are best conceptualized as special types of molecular distortions that are more physically analogous, for example, to the inversion of ammonia than to a dissociative-recombination reaction like that between methoxide and *tert*-butylchloride (e.g. an S_N1 substitution).

Since reaction and product bonds in an allowed reaction are distorted but not broken to form a transition state, it was stated that an allowed reaction permits an uninterrupted bonding between reactants, which extends through a transition state and on into the products. Although true, this idea often leads to erroneous physical interpretations of W-H correlation diagrams. For example, it is incorrect to interpret orbital correlations as a physical mapping or connection of specific reactant orbitals to particular product orbitals. Such a positional correlation is not necessary, nor is it required by group theory.⁸ Consider, for example, the correlation diagram for the allowed $\pi 4s + \pi 2s$ reaction of butadiene with ethylene (Fig. 4). In the correlation diagram for this Diels-Alder reaction, the π ethylene is correlated to the π double bond of cyclohexene. It is not required nor does it make any physical sense to argue that the ethylene π orbitals have moved from ethylene (14) onto the butadiene fragment to become a cyclohexene double bond. Although examples of such positional correlations may exist for other molecular orbitals in this reaction or even in other reaction diagrams, these types of "natural" correlations (15) are extraneous. From a group theoretical perspective a correlation diagram indicates whether the reactant and product structures, as defined by their respective nodal geometries, can become electronically identical within a

proposed reaction geometry, but not whether this reactant orbital becomes that product orbital.

If one desires to map a specific ebb and flow of reactant orbital interactions as they interact to form product orbitals, then an orbital interaction diagram⁹ should be constructed using some other quantum mechanical technique. However, one should not expect the results (orbital coefficients and energies) from such a resolution to be invariant with respect to the choice of basis set. On the contrary, one should expect that such orbital interaction diagrams might possess some dependence upon the type of basis set utilized for the computation, as well as upon the computational technique used for calculation.

Far from being an interesting diversion, the W-H rules have a solid fundamental basis within the theory of chemical reactions. These W-H diagrams of occupied R and P nodal geometries and their symmetry properties are a part of the same theory of electronic structure that make applications like Hund-Mulliken diagrams (16) possible. The very fact that the W-H selection rules can be derived from a variety of theoretical perspectives (1, 17) is an indication of just how fundamental molecular orbital nodal geometries are to covalent bonding and the application of bonding principles to chemical reactions and reactivity.

Acknowledgments

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Notes

1. Typically a chemical reaction is defined as a transformation of reactant molecules into one or more new substances. Such a transformation will necessarily involve changes in bonding of the reactant molecules as well as possible changes in the number and type of molecules produced as R evolves into P. However, for this article, these bonding transformations must result from an intersection of at least two PE surfaces (one for R and another for P) as a function of atom

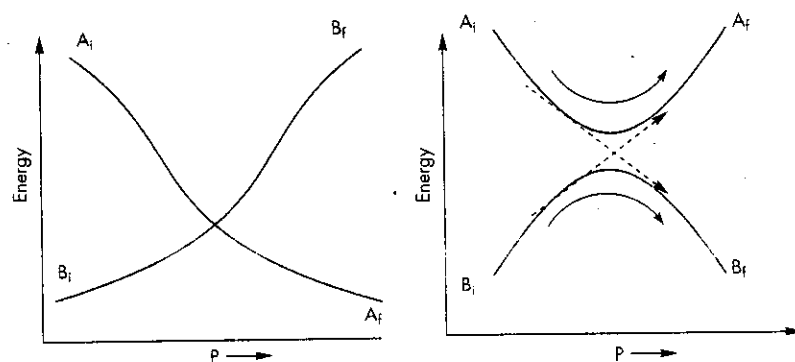


Figure 5. The adiabatic pathway starts at B_i and ends at B_f , or starts at A_i and ends at A_f . The diabatic pathway starts at B_i and ends at A_f , or starts at A_i and ends at B_f . Left: Case 1. A_i and B_i are of different symmetries (i.e., states do not mix or interact). In reality, case 1 doesn't exist. Two states can never cross each other—they will always interact (mix) at the intended point of intersection. For a diabatic pathway there is a finite probability at this crossing point that the final state will be on either A_f or B_f after the states cross. This probability depends upon the rate at which P changes and it is independent of the starting point (A_i or B_i) (18). Right: Case 2. A_i and B_i are of the same symmetry (i.e., states mix or interact). The arrow with the solid line indicates the adiabatic pathway, and the arrow with the broken line indicates the diabatic pathway.

reorganization. Since a photoexcitation results in a change of state for a molecule and thus a change in bonding, one might be tempted to view this process as a type of reaction. A phototransition is a transition between molecular states (vertical); subsequent atom rearrangement to a minimum energy conformation occurs after the transition and before any "reaction". In a chemical reaction, the transition between R and P states is adiabatic (12)⁶ and bonding changes occur simultaneously with atom reorganization.

2. It is assumed in this presentation¹ as well as in the presentations in refs 2–5 that each of the angular momentum components (nuclear and electronic [i.e., orbital and electron spin]) of the reacting system is separately conserved. Although spin multiplicity is not considered in this discussion, it remains a meaningful property for all symmetry groups (6).

3. The projection of this total electronic momentum vector onto an axis of rotation symmetry is a good quantum number for point groups containing at least one doubly degenerate representation (i.e., C_3-C_{3v} ; D_3-D_{3h} ; $C_{3v}-C_{3h}$; $C_{3h}-C_{nh}$; $D_{3h}-D_{nh}$; $D_{2d}-D_{nd}$; $S_{2n,n/2+2}$; T ; T_h ; T_d ; O ; O_h). For diatomic molecules (with geometries of $C_{\infty v}$ or $D_{\infty h}$) projection of this total electronic orbital angular momentum onto the internuclear axis is given the designation Λ . This projection of total electronic orbital angular momentum for the molecular state Λ analogous to the many-electron atomic vector M_Z :

$$\Lambda = |\Sigma_j \lambda(j)|; \quad M_Z(j) = \Sigma_j m_j i(j)$$

where $m_j i(j)$ is the azimuthal quantum number for the i th valence electron of atom j .

4. $\pi 2s + \pi 2a$: This notation tells the reader that this pericyclic reaction involves π bonding orbitals. These two sets of π bonds are orientated in such a way that the (s) π bond reacts in a suprafacial (same side, cis or syn fashion) with another π bond. The second ethylene (a) π bond reacts in an antarafacial (opposite side, trans or anti fashion) with the first π bond. The number 2 tells the reader the number of atoms involved in the fragment of the pericyclic reaction: $2 + 2 = 4$ total atoms involved in this cyclization reaction. Theoretically, one should use the point group for a reaction geometry and its irreducible representations for the various R and P molecular orbitals in order to obtain the maximum symmetry information possible about the nodal geometries of these wave functions and electronic states within that particular geometry.

5. Interaction energy refers to intermolecular interaction energy, which contains both stabilizing and destabilizing components. Based on Fukui's version of frontier molecular orbital theory (9), the interaction energy can be partitioned into some of its more familiar components:

$$E_{\text{int}} \approx E_{\text{electrostatic}} + E_{\text{polarization}} + E_{\text{charge transfer}} + \Delta E(2e^-)_{\text{covalent}} + \Delta E(4e^-)_{\text{closed shell}}$$

6. Adiabatic and diabatic (or nonadiabatic): To avoid confusion, one should distinguish two types of potential energy curve crossings and then define adiabatic and diabatic with respect to these curve crossings (Fig. 5). For both cases, if perturbation of a molecular system changes the state in a continuous fashion along some classical pathway (i.e., electron density adjusting to position of nuclei), then the electronic state will also change in a continuous fashion and the transition from i to f will be associated with a single potential energy surface (12a).

Ehrenfest's adiabatic law states that for a virtual, infinitely slow alteration of coupling conditions, the quantum numbers of the system do not change (12b). The confusion arises when an initial state is expanded in terms of its zeroth or unperturbed wave functions. For example, let the unperturbed state A be characterized by $\Psi^0(U)$ and for state B by $\Psi^0(L)$. Once a perturbation (P) is applied and A and B are of the same symmetry (case 2) then let:

$$A(P) = a \Psi^0(U) + b \Psi^0(L) \quad \text{and} \quad B(P) = a \Psi^0(U) + b \Psi^0(L); \quad \text{with the normalization condition that } a^2 + b^2 = 1$$

At the start of the perturbation, if at A_1 , $a \approx 1$, $b \approx 0$ and at B_1 , $a \approx 0$, $b \approx 1$. then at the end of the perturbation, at A_2 , $a \approx 0$, $b \approx 1$ and at B_2 , $a \approx 1$, $b \approx 0$. The transition of state A_1 to A_2 is still adiabatic even though the wave function describing this state evolved from $\Psi^0(U)$ at A_1 to $\Psi^0(L)$ at A_2 .

7. An adiabatic correlation among the orbitals is still possible in this example because the doubly excited reactant state of ($a_1^2 b_2^2$) symmetry can mix into the ground reactant state to force the necessary orbital correlations between R and P. However, mixing in an excited

state will provide much less stabilizing interaction energy than a direct orbital correlation among the occupied orbitals.

8. Strictly speaking, such a group theoretical argument is not dependent upon a particular type of basis set; any proper basis set that spans the group in question will lead to the same conclusion.

9. One needs to be aware that cavalier interpretation of an interaction diagram can lead to conclusions that are basis-set dependent. For example, one can talk about bonding and antibonding interactions among a set of molecular orbitals, but a line is crossed when one resolves these interactions into percentage contributions from the various molecular orbitals. At this point, one has moved into territory that might be basis-set dependent.

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