

5. Organic Molecules: Electronic Structure and Chemical Reactions5.1 Brief reminder: LCAO approximation

We describe the molecular wave functions as a Linear Combination of Atomic Orbitals (LCAO)

$$\psi_k = \sum_i c_{ik} \phi_i$$

and use this ansatz in the Schrödinger equation:

$$\hat{H}\psi - E\psi = 0$$

and obtain

$$\sum_i c_{ik} (H - E_k) \phi_i = 0$$

Multiplication by ϕ_j from left and integration:

$$\sum_i c_{ik} \langle j | \hat{H} - E_k | i \rangle = \sum_i c_{ik} (\langle j | \hat{H} | i \rangle - E_k \langle j | i \rangle) = \sum_i c_{ik} (H_{ji} - E_k S_{ji}) = 0$$

with the Hamilton matrix $H_{ji} = \langle j | \hat{H} | i \rangle$

and the overlap matrix $S_{ji} = \langle j | i \rangle$.

Secular equations:

$$\boxed{\sum_i c_{ik} (H_{ji} - E_k S_{ji}) = 0 \quad \text{or} \quad (\underline{H} - E_k \underline{S}) \underline{c}_k = 0}$$

Solution: Secular determinant: $|\underline{H} - E \underline{S}| = 0 \Rightarrow$ eigenvectors \underline{c}_k , eigenvalues E_k .

(5.1 Example: secular equation for butadien, C-2p orbitals only).

5.2 Brief: reminder: Hückel molecular orbital model (HMO)

We consider only the π -system of a conjugated hydrocarbon using the approximations:

$$H_{ji} = \begin{cases} \alpha; & \text{for } i = j \\ \beta; & \text{for } i, j \text{ next neighbors} \\ 0; & \text{else} \end{cases}$$

$$S_{ji} = \begin{cases} 1; i = j \\ 0; \text{else} \end{cases}$$

(5.2 Comments to HMO theory, example: butadiene).

5.3 The connection to symmetry

The LCAO ansatz in a basis set of n orbitals leads in general to a coupled set of n secular equations. With increasing number of basis function the numerical effort to solve the system becomes becomes large quite rapidly. Even if some of the matrix elements of the H or S matrix are zero, this does not necessarily simplify the problem.

The only way to drastically reduce the (numerical) effort for solving the system is to find a basis transformation which blockdiagonalizes the H , S matrices. A basis of symmetry adapted fulfils this requirement:

We assume a set of $\sum_i l_i$ basis functions ϕ_j which can be transformed to a i sets of l_i functions,

i.e. $\chi_{k=1..l_i}^{j=1..i}$ is the k -th function belonging to irrep j . As $S_{jj'} = 0$ for $j \neq j'$ and $H_{jj'} = 0$ for $j \neq j'$,

the $H_{kk'}$ and $S_{kk'}$ matrices are blockdiagonal:

$$\left(\begin{array}{cccccc} H_{1,1}^{1,1} & \dots & H_{1,l_1}^{1,1} & & & \\ \vdots & \ddots & \vdots & & 0 & 0 \\ H_{l_1,1}^{1,1} & \dots & H_{l_1,l_1}^{1,1} & & & \\ & & & H_{1,1}^{2,2} & \dots & H_{1,l_1}^{2,2} \\ & 0 & & \vdots & \ddots & \vdots \\ & & & H_{l_1,1}^{2,2} & \dots & H_{l_1,l_1}^{2,2} \\ & 0 & & & & \ddots \end{array} \right) - E \left(\begin{array}{cccccc} S_{1,1}^{1,1} & \dots & S_{1,l_1}^{1,1} & & & \\ \vdots & \ddots & \vdots & & 0 & 0 \\ S_{l_1,1}^{1,1} & \dots & S_{l_1,l_1}^{1,1} & & & \\ & & & S_{1,1}^{2,2} & \dots & S_{1,l_1}^{2,2} \\ & 0 & & \vdots & \ddots & \vdots \\ & & & S_{l_1,1}^{2,2} & \dots & S_{l_1,l_1}^{2,2} \\ & 0 & & & & \ddots \end{array} \right) \left. \vphantom{\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \end{array}} \right\} \mathcal{E} = 0$$

Recipe:

1. The AO basis is a n dimensional reducible representation of the symmetry group.

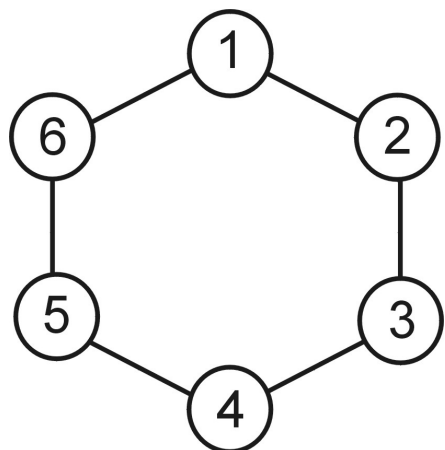
Determine the number and symmetry type of contained irreps (section 3.13).

2. Construction of a set of orthonormal SALC using projection operators (section 4.6).
3. Reformulate secular equation in SALC basis.

(5.3 Example: butadiene).

5.4 Cyclic electron systems and cyclic groups

As an example we investigate the electronic structure of the π -system of benzene:



The symmetry group of the molecules is

$$D_{6h}: \quad E \quad 2C_6 \quad 2C_3 \quad C_2 \quad 3C_2' \quad 3C_2'' \quad i \quad 2S_3 \quad 2S_6 \quad \sigma_h \quad 3\sigma_d \quad 3\sigma_{vT}$$

The characters can be determined by applying the operations and counting the number of unaffected (+1) and inverted (-1) AOs (only those AOs which are moved in space contribute to the character):

$$\Gamma_{\pi}: \quad 6 \quad 0 \quad 0 \quad 0 \quad -2 \quad 0 \quad 0 \quad 0 \quad 0 \quad -6 \quad 2 \quad 0$$

The representation can be analysed according to section 3.13, yielding:

$$\Gamma_{\pi} = A_{2u} + B_{2g} + E_{1g} + E_{2u}$$

Now the SALCs can be constructed applying the projection operators. However, there is a simpler procedure using the properties of cyclic groups.

We do not necessarily have to take into account all symmetry elements of the group, but can choose any subgroup as well (accepting only partial symmetry adaptation if the choice of

subgroup is bad). A good choice for cyclic electron systems is the corresponding pure rotational group (C_6 in this case).

The uniaxial rotational groups are cyclic groups (section 3.4). All cyclic groups are Abelian (section 3.4). In an Abelian group each element belongs to its own class ($AB=BA$, $A=B^{-1}AB$, i.e. all elements are only self-conjugated). Therefore, the order of the group is equal to the number of classes and all representations must be one-dimensional (section 3.12).

There is a general formulation for the j -th irrep of a cyclic group:

Cyclic group C_n : $C_n^1, C_n^2, \dots, C_n^n = E$

j -th irreducible representation: $\Gamma^j(C_n^m) = \varepsilon^{jm}$ with $\varepsilon = e^{\frac{2\pi i}{n}}$

For the benzene case we obtain the character table:

C_6	C_6	C_6^2	C_6^3	C_6^4	C_6^5	$E=C_6^6$
Γ_1	ε^1	ε^2	ε^3	ε^4	ε^5	ε^6
Γ_2	ε^2	ε^4	ε^6	ε^8	ε^{10}	ε^{12}
Γ_3	ε^3	ε^6	ε^9	ε^{12}	ε^{15}	ε^{18}
Γ_4	ε^4	ε^8	ε^{12}	ε^{16}	ε^{20}	ε^{24}
Γ_5	ε^5	ε^{10}	ε^{15}	ε^{20}	ε^{25}	ε^{30}
Γ_6	ε^6	ε^{12}	ε^{18}	ε^{24}	ε^{30}	ε^{36}

It can be shown that the representations fulfil the orthogonality requirements in section 3.12.

The character table can be rearranged as follows:

C_6		E	C_6	C_3	C_2	C_3^2	C_6^5
A	Γ_6	1	1	1	1	1	1
B	Γ_3	1	-1	1	-1	1	-1
E_1	Γ_1	1	ϵ	$-\epsilon^*$	-1	$-\epsilon$	ϵ^*
	Γ_5	1	ϵ^*	$-\epsilon$	-1	$-\epsilon^*$	ϵ
E_2	Γ_2	1	$-\epsilon^*$	$-\epsilon$	-1	$-\epsilon^*$	$-\epsilon$
	Γ_4	1	$-\epsilon$	$-\epsilon^*$	-1	$-\epsilon$	$-\epsilon^*$

There are 6 1-dimensional irreps. Γ_1 and Γ_5 (Γ_2 and Γ_4) can be combined to form two dimensional reducible representations with non-complex characters. If some additional symmetry is introduced such as e.g. mirror planes, which makes C_6 / C_6^5 and C_3 / C_3^2 conjugate, Γ_1 / Γ_5 and Γ_2 / Γ_4 merge to two 2-dimensional irreps E_1 and E_2 .

An analysis of the benzene AO's in terms of the group C_6 yields:

$$\Gamma_\pi = \Gamma_6 + \Gamma_3 + \Gamma_1 + \Gamma_5 + \Gamma_2 + \Gamma_4$$

Application of the projection operators of C_6 to φ_1 yields automatically the orthogonal set of SALCs. After normalization:

$$\chi_{\Gamma_6} = 1/\sqrt{6} (+1 \varphi_1 \quad +1 \varphi_2 \quad +1 \varphi_3 \quad +1 \varphi_4 \quad +1 \varphi_5 \quad +1 \varphi_6)$$

$$\chi_{\Gamma_3} = 1/\sqrt{6} (+1 \varphi_1 \quad -1 \varphi_2 \quad +1 \varphi_3 \quad -1 \varphi_4 \quad +1 \varphi_5 \quad -1 \varphi_6)$$

$$\chi_{\Gamma_1} = 1/\sqrt{6} (+1 \varphi_1 \quad +\epsilon \varphi_2 \quad -\epsilon^* \varphi_3 \quad -1 \varphi_4 \quad -\epsilon \varphi_5 \quad +\epsilon^* \varphi_6)$$

$$\chi_{\Gamma_5} = 1/\sqrt{6} (+1 \varphi_1 \quad +\epsilon^* \varphi_2 \quad -\epsilon \varphi_3 \quad -1 \varphi_4 \quad -\epsilon^* \varphi_5 \quad +\epsilon \varphi_6)$$

$$\chi_{\Gamma_2} = 1/\sqrt{6} (+1 \varphi_1 \quad -\epsilon^* \varphi_2 \quad -\epsilon \varphi_3 \quad -1 \varphi_4 \quad -\epsilon^* \varphi_5 \quad -\epsilon \varphi_6)$$

$$\chi_{\Gamma_4} = 1/\sqrt{6} (+1 \varphi_1 \quad -\epsilon \varphi_2 \quad -\epsilon^* \varphi_3 \quad -1 \varphi_4 \quad -\epsilon \varphi_5 \quad -\epsilon^* \varphi_6)$$

If real coefficients are preferred, one may choose suitable linear combinations (although this is not necessary in principal):

$$\chi_A = \chi_{\Gamma_6}; \chi_B = \chi_{\Gamma_3}; \chi_{E_{1,1}} = \chi_{\Gamma_1} + \chi_{\Gamma_5}; \chi_{E_{1,2}} = i(\chi_{\Gamma_1} - \chi_{\Gamma_5}); \chi_{E_{2,1}} = \chi_{\Gamma_2} + \chi_{\Gamma_4}; \chi_{E_{2,2}} = i(\chi_{\Gamma_2} - \chi_{\Gamma_4})$$

$$\chi_A = 1/\sqrt{6} (+1 \varphi_1 \quad +1 \varphi_2 \quad +1 \varphi_3 \quad +1 \varphi_4 \quad +1 \varphi_5 \quad +1 \varphi_6)$$

$$\chi_B = 1/\sqrt{6} (+1 \varphi_1 \quad -1 \varphi_2 \quad +1 \varphi_3 \quad -1 \varphi_4 \quad +1 \varphi_5 \quad -1 \varphi_6)$$

$$\chi_{E_{1,1}} = 1/\sqrt{12} (+2 \varphi_1 \quad +1 \varphi_2 \quad -1 \varphi_3 \quad -2 \varphi_4 \quad -1 \varphi_5 \quad +1 \varphi_6)$$

$$\chi_{E_{1,2}} = 1/2 (\quad +1 \varphi_2 \quad +1 \varphi_3 \quad -1 \varphi_4 \quad -1 \varphi_5 \quad)$$

$$\chi_{E_{2,1}} = 1/\sqrt{12} (+2 \varphi_1 \quad -1 \varphi_2 \quad -1 \varphi_3 \quad +2 \varphi_4 \quad -1 \varphi_5 \quad -1 \varphi_6)$$

$$\chi_{E_{2,2}} = 1/2 (\quad +1 \varphi_2 \quad -1 \varphi_3 \quad +1 \varphi_4 \quad -1 \varphi_5 \quad)$$

(5.4 Energy levels of benzene in HMO model)

(5.5 Energy levels of cyclic unsaturated hydrocarbons in HMO model, geometric construction)

(5.6 Example: naphthalene, C_{60})

5.5 Symmetry of many electron states

How can we derive the symmetry of many electron states from the symmetry of the single electron wave functions discussed so far? In the simplest approximation we assume that the Hamiltonian is the sum of single electron Hamiltonians:

$$\hat{H} = \sum_i \hat{h}_i$$

yielding wave functions which are the product of the single electron wave functions:

$$\Psi = \prod_i \varphi_i.$$

The permutation symmetry for fermions can be taken into account by generating the product wavefunction of N electrons in N spin orbitals in the form of the Slater determinant:

$$\Psi(1,2,\dots,N) = \sqrt{\frac{1}{N!}} \begin{vmatrix} \varphi_1(1) & \dots & \varphi_N(1) \\ \vdots & \ddots & \vdots \\ \varphi_1(N) & \dots & \varphi_N(N) \end{vmatrix} = \|\varphi_1 \dots \varphi_n\|$$

We consider the spatial symmetry of the many electron wave function. In general the symmetry is obtained as the direct product of the irreps of the participating one electron functions. There may however arise limitations from the Pauli principle, excluding multi-occupation of spin orbitals. This will be further discussed in chapter 6.

Example: Naphthalene ground state

3b_{3g}

2a_u

3b_{1u}

2b_{3g}

2b_{2g}

1a_u ||

2b_{1u} ||

1b_{3g} ||

1b_{2g} ||

1b_{1u} ||

ground state: $\underbrace{\underbrace{1b_{1u}^2}_{A_{1g}} \underbrace{1b_{2g}^2}_{A_{1g}} \underbrace{1b_{3g}^2}_{A_{1g}} \underbrace{2b_{1u}^2}_{A_{1g}} \underbrace{1a_u^2}_{A_{1g}}}_{A_{1g}}$

Important: A fully occupied set of space orbitals belonging to one arbitrary irrep of the group belongs to the totally symmetric irrep (easy to see for 1-dim. irreps., more complicated to prove for more-dimensional irreps.)

5.5 Symmetry of excited states and dipole selection rules

Example: Lowest excited states in naphthalene

$$\Psi_0 = 1b_{1u}^2 1b_{2g}^2 1b_{3g}^2 2b_{1u}^2 1a_u^2 \quad \text{Symmetry: } A_{1g}$$

$$\Psi_1 = 1b_{1u}^2 1b_{2g}^2 1b_{3g}^2 2b_{1u}^2 1a_u 2b_{2g} \quad B_{2u}$$

$$\Psi_2 = 1b_{1u}^2 1b_{2g}^2 1b_{3g}^2 2b_{1u}^2 1a_u 2b_{3g} \quad B_{3u}$$

$$\Psi_3 = 1b_{1u}^2 1b_{2g}^2 1b_{3g}^2 2b_{1u} 1a_u^2 2b_{2g} \quad B_{3u}$$

$$\Psi_4 = 1b_{1u}^2 1b_{2g}^2 1b_{3g}^2 2b_{1u} 1a_u^2 2b_{3g} \quad B_{2u}$$

D_{2h}	E	C _{2x}	C _{2y}	C _{2z}	i	σ_{xy}	σ_{xz}	σ_{yz}	
a _u	1	1	1	1	-1	-1	-1	-1	
b _{2g}	1	-1	1	-1	1	-1	1	-1	
a _u × b _{2g}	1	-1	1	-1	-1	1	-1	1	= B _{2u}
b _{3g}	1	-1	-1	1	1	-1	-1	1	
a _u × b _{3g}	1	-1	-1	1	-1	1	1	-1	= B _{3u}
b _{1u}	1	1	-1	-1	-1	-1	1	1	
b _{1u} × b _{2g}	1	-1	-1	1	-1	1	1	-1	= B _{3u}
b _{1u} × b _{3g}	1	-1	1	-1	-1	1	-1	1	= B _{2u}

Dipole activity of transitions:

$$\langle \Psi_0 | \vec{\mu} | \Psi_1 \rangle : A_{1g} \otimes \begin{Bmatrix} B_{3u} \\ B_{2u} \\ B_{1u} \end{Bmatrix} \otimes B_{2u} \begin{Bmatrix} \neq \\ = \\ \neq \end{Bmatrix} A_{1g} \Rightarrow \text{el. dipole active, y-polarisation}$$

$$\langle \Psi_0 | \vec{\mu} | \Psi_2 \rangle : A_{1g} \otimes \begin{Bmatrix} B_{3u} \\ B_{2u} \\ B_{1u} \end{Bmatrix} \otimes B_{3u} \begin{Bmatrix} = \\ \neq \\ \neq \end{Bmatrix} A_{1g} \Rightarrow \text{el. dipole active, x-polarisation}$$

$$\langle \Psi_0 | \bar{\mu} | \Psi_3 \rangle : A_{1g} \otimes \begin{Bmatrix} B_{3u} \\ B_{2u} \\ B_{1u} \end{Bmatrix} \otimes B_{3u} \begin{Bmatrix} = \\ \neq \\ \neq \end{Bmatrix} A_{1g} \Rightarrow \text{el. dipole active, x-polarisation}$$

$$\langle \Psi_0 | \bar{\mu} | \Psi_4 \rangle : A_{1g} \otimes \begin{Bmatrix} B_{3u} \\ B_{2u} \\ B_{1u} \end{Bmatrix} \otimes B_{2u} \begin{Bmatrix} \neq \\ = \\ \neq \end{Bmatrix} A_{1g} \Rightarrow \text{el. dipole active, y-polarisation}$$

5.6 Symmetry and configuration interaction

We consider a set of many electron states Ψ_i . Beyond the simple one electron picture considered so far, there might be electron correlations, which lead to deviations from these states. In order to describe this effect, we start with an configuration interaction (CI) ansatz, describing the many electron wave function as a linear combination of the many electron wave functions over the ground and excited states

$$\Psi_k = \sum_i a_{ik} \Psi_i$$

which again leads to a set of secular equations

$$\boxed{\sum_i a_{ik} (H_{ji} - E_k S_{ji}) = 0 \quad \text{or} \quad (\underline{H} - E_k \underline{S}) \underline{a}_k = 0.}$$

Here, H_{ji} and S_{ji} are matrix elements over the many electron functions $\Psi_{i,j}$. Again $H_{ji} \neq 0$ for $\Gamma_i = \Gamma_j$ and $H_{ji} = 0$ for $\Gamma_i \neq \Gamma_j$, i.e. a configuration interaction (mixing of states) is only expected for states which belong to the same irrep of the group.

(5.7 Example: CI for excited states in naphthalene)

5.7 Symmetry and chemical reactions

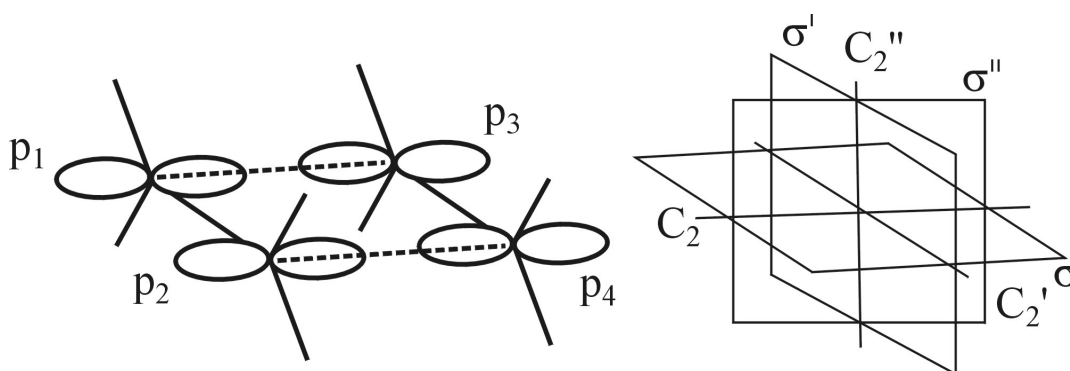
A well known example are the “Woodward-Hoffmann” for cyclisation reactions. We consider processes

- for which the considered step is rate-determining
- for which symmetry elements are preserved during the reaction

Example: [2+2] cycloaddition



1. Determination of preserved symmetry elements:



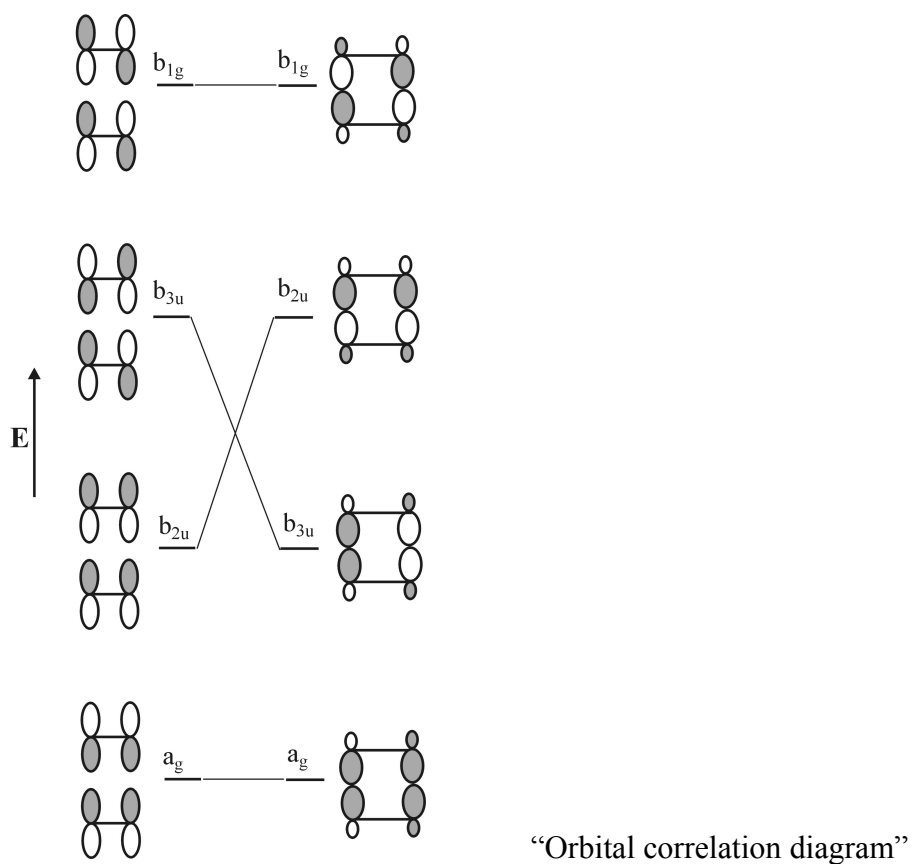
The symmetry group D_{2h} . For the determination of the irreps it is sufficient to consider a set of generating elements of the group, e.g. σ , σ' , σ'' .

2. We identify the orbital basis involved in the reaction:

$p_1 - p_4$ in case of 2 C_2H_4 ,

$sp_1 - sp_4$ (hybrid) in case of C_4H_8

3. Classification of SALCs according to (1) symmetry and (2) energy

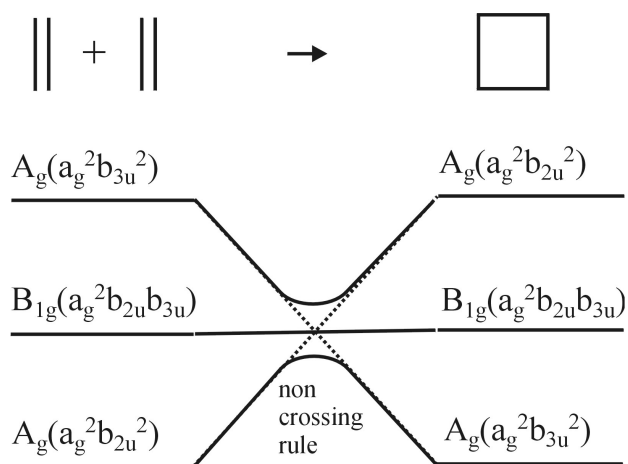


Construction of ground state and lowest excited states:

$$\Psi_0 = a_g^2 b_{2u}^2 \quad \text{Symmetry: } A_{1g}$$

$$\Psi_1 = a_g^2 b_{2u}^1 b_{3u}^1 \quad B_{1g}$$

$$\Psi_2 = a_g^2 b_{3u}^2 \quad A_g$$



High activation barrier for [2+2] cycloaddition for molecules in ground state:

thermal activation forbidden.

Low activation barrier for [2+2] cycloaddition for molecules in 1st excited state:

photochemical activation allowed.

Similar models for other cycloaddition and cyclisation reactions.