

## Solution Exercise 5

### Exercise 1: Molecular oxygen from a group theoretical point of view

a) The symmetry elements and operations of  $O_2$  are:

- identity  $E$  with operation  $E$
- $C_\infty$  axis coinciding with an  $S_\infty$  axis, which correspond to infinitely many  $C_\infty$  and  $S_\infty$  operations
- infinitely many  $C_n$  axes with any  $n$ , which each correspond to  $n - 1$  symmetry operations  $C_n^m$  with  $m = 1, \dots, n - 1$
- infinitely many  $\sigma_v$ -planes with  $\infty\sigma_v$  reflection operations
- a  $\sigma_h = S_1$  plane with reflection operation  $\sigma_h$
- an inversion center  $i$  with inversion operation  $i$
- and infinitely many  $C'_2$  axes with  $\infty C'_2$  rotation operations.

These symmetry elements form the point group  $D_{\infty h}$ . Note that  $\sigma_h = S_1$  is implicitly included in the character table Ref.[1].

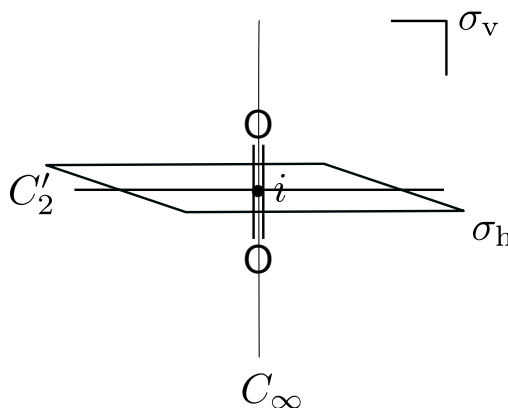


Figure 1-1: Symmetry elements of  $O_2$ .

b) A vector representation of the p-orbitals of  $O_2$  can look like Figure 1-2 (one possibility).

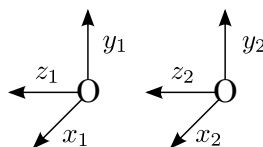


Figure 1-2: Vectors representing p-orbitals for  $O_2$ .

We now set up matrices which represent the symmetry operations of the group on our vector basis  $\{x_1, y_1, z_1, x_2, y_2, z_2\}$  and determine the characters  $\chi$  of the matrices.

- The matrix representation of  $E$  is

$$\begin{pmatrix} x_1 & y_1 & z_1 & x_2 & y_2 & z_2 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \rightarrow \chi(E) = 6.$$

- $C_\infty$ : For these symmetry operations we have to take into account that a rotation of any angle  $\varphi$  around  $C_\infty$  in one of the two directions leaves the molecule unchanged. The  $z$  vectors are not changed during rotation, resulting in the value one for the diagonal elements. For the  $x$  and  $y$  vectors, we can look at a two dimensional rotation of unit vectors in the  $xy$  plane which is performed by the following matrix:  $\begin{pmatrix} \cos \varphi & -\sin \varphi \\ \sin \varphi & \cos \varphi \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$ . Consequently, we end up with the full rotation matrix

$$\begin{pmatrix} \cos \varphi & -\sin \varphi & 0 & 0 & 0 & 0 \\ \sin \varphi & \cos \varphi & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & \cos \varphi & -\sin \varphi & 0 \\ 0 & 0 & 0 & \sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \rightarrow \chi(C_\infty) = 2 + 4 \cos \varphi.$$

- $i$ :

$$\begin{pmatrix} 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \end{pmatrix} \rightarrow \chi(i) = 0.$$

- $\sigma_v$ : Here the question arises which plane to pick to derive the character of the class. In group theory equivalent symmetry operations are grouped in classes by means of a similarity transform: Let  $\hat{P}, \hat{Q}$  be two symmetry operations of a group. Then

$$\hat{R} = \hat{Q}^{-1} \hat{P} \hat{Q} \quad (1.1)$$

is also a member of the group (the equation reads: Apply  $\hat{Q}$ , then apply  $\hat{P}$ , then apply the inverse of  $\hat{Q}$ ).<sup>1</sup> The two operations  $\hat{P}$  and  $\hat{R}$  are called “conjugate” and all conjugate operations form a class. From (1.1) follows immediately that all conjugate operations have the same character, as a similarity transformation preserves the trace of a matrix. Therefore we can pick an arbitrary  $\sigma_v$  plane to determine the character of the operation. For simplicity we pick the  $xz$  plane:

$$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \rightarrow \chi(\sigma_v) = 2.$$

<sup>1</sup>Example: For  $\text{NCl}_3$ , apply  $\sigma_v$  for any plane, rotate by  $2\pi/3$  around the  $C_3$  axis, apply  $\sigma_v^{-1} = \sigma_v$  for the previously chosen plane; you get rotation by  $4\pi/3$  around the  $C_3$ , which is thus conjugate to the  $2\pi/3$ -rotation.

- $S_\infty$ : We can look at  $C_\infty$  and first rotate (same matrix as for  $C_\infty$ ) and then we mirror at the  $\sigma_h$  plane, which exchanges the non-zero and the zero blocks:

$$\begin{pmatrix} 0 & 0 & 0 & \cos \varphi & -\sin \varphi & 0 \\ 0 & 0 & 0 & \sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ \cos \varphi & -\sin \varphi & 0 & 0 & 0 & 0 \\ \sin \varphi & \cos \varphi & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \end{pmatrix} \rightarrow \chi(\hat{S}_\infty) = 0.$$

- $C'_2$ : We consider the  $C'_2$  axis to be parallel to the  $y$  axis for instance, which gives the following rotation matrix:

$$\begin{pmatrix} 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \end{pmatrix} \rightarrow \chi(C'_2) = 0.$$

To summarize we obtain the following representation:

$D_{\infty h}$	$E$	$2C_\infty$	$\infty\sigma_v$	$i$	$2S_\infty$	$\infty C'_2$
$\Gamma_{\text{red}}$	6	$2 + 4 \cos \varphi$	2	0	0	0

- c) Infinite point groups cannot be treated with the reduction formula because there is an infinite number of symmetry elements. One way to solve this problem is to reduce the representation “by inspection” of the character table of the  $D_{\infty h}$  point group: One guesses the right combination of irreducible representations. This is possible because there is only one way to decompose the reducible representation. The reducible representation of the p orbitals  $\Gamma_{\text{red}}$  can be reduced as follows:  $\Gamma_{\text{red}} = \Pi_g \oplus \Pi_u \oplus \Sigma_g^+ \oplus \Sigma_u^+$ . Note that the  $\Pi_g$  and  $\Pi_u$  irreps are of dimension two, so we obtain the required total dimension of 6. Mathematical methods to treat infinite point groups can be found for example in Refs. [2, 3]. When we compare these results to Fig. 1-1 of the solution to Exercise 4 we find that the irreducible representations we have found match the labels given to the orbitals.
- d) For comparison we use the orbital diagram of Exercise 4. The partially occupied molecular orbitals have  $\pi_g$  symmetry. To find the term symbols, we multiply the corresponding characters of this irrep under the  $D_{\infty h}$  point group:

$D_{\infty h}$	$E$	$2C_\infty$	$\infty\sigma_v$	$i$	$2S_\infty$	$\infty C'_2$
$\Gamma_{\pi_g \otimes \pi_g}$	4	$4 \cos^2(\phi)$	0	4	$4 \cos^2(\phi)$	0

Recognizing that  $\cos^2(\phi) = \frac{1}{2}[1 - \cos(2\phi)]$ , the  $\Gamma_{\pi_g \otimes \pi_g}$  representation can be reduced to  $\Gamma_{\pi_g \otimes \pi_g} = \Delta_g + \Sigma_g^+ + \Sigma_g^-$ . Alternatively, this could have been deduced from the direct product table, which gives the following result:  $\Pi_g \otimes \Pi_g = \Sigma_g^+ \oplus [\Sigma_g^-] \oplus \Delta_g$ . The square brackets indicate that this direct product has an antisymmetric spatial part and thus a symmetric (triplet) spin part. This yields the following molecular terms:  $^1\Sigma_g^+, ^3\Sigma_g^-, ^1\Delta_g$ .

- e) The irreducible representations of the dipole operator are the same as those of the linear functions. From the character table we read that those are  $\Pi_u$  and  $\Sigma_u^+$ . To determine all possible final states we must thus take the product of the ground state irreducible representation  $\Sigma_g^-$  with  $\Pi_u$  and  $\Sigma_u^+$ , which gives  $\Sigma_g^- \otimes \Pi_u = \Pi_u$  and  $\Sigma_g^- \otimes \Sigma_u^+ = \Sigma_u^-$ . From the product table, we see that the totally symmetric representation is only obtained if the irreducible representation is multiplied with itself. Consequently, only states that can be excited from the ground state are  ${}^3\Sigma_u^-$  and  ${}^3\Pi_u$  states; only those result in the totally symmetric representation (and do not change the spin). The likelihood of these transitions can be obtained from electronic structure calculations. Group theory only allows us to determine which integrals are guaranteed to be zero due to symmetry.

## Exercise 2: Vibrations of $\text{BrF}_5$

- a) The symmetry elements of  $\text{BrF}_5$  (Figure 2-1) are  $E$ ,  $C_4$ ,  $C_2$ ,  $2\sigma_v$ ,  $2\sigma_d$ .

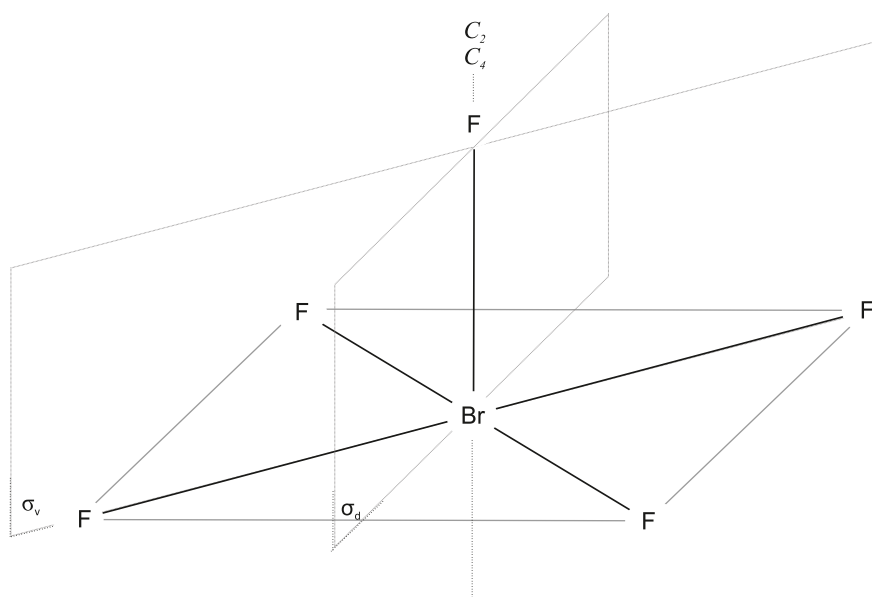


Figure 2-1: Symmetry elements of  $\text{BrF}_5$ .

- b)  $\text{BrF}_5$  belongs to the  $C_{4v}$  point group.  
 Additional information: There is another notation, which also specifies the symmetry of molecules. The so called Hermann-Mauguin symbols give only the generating elements from which all other symmetry elements can be derived. In this case it is  $4mm$ . 4 represents the 4-fold axis and mm represents two mirror planes ( $\sigma_v$  and  $\sigma_d$ ).
- c) The molecule has  $3N$  degrees of freedom where  $N$  is the number of nuclei. Among these 18 degrees of freedom, three are rotations and three are translations leaving twelve vibrational degrees of freedom.
- d) Two equivalent approaches can be taken to derive  $\Gamma_{\text{tot}}$ :
- To derive the matrix representation of all displacement coordinates we define three displacement vectors on each nucleus, as depicted in Figure 2-2. For a given symmetry operation, a vector  $\vec{v}$  only contributes to the character of the matrix if it is either unchanged (+1) or if it is inverted  $-\vec{v}$  (-1).
- In the following, a detailed explanation is given for a few symmetry operations. For the remaining ones the reasoning is similar and can be adapted from problem 1:

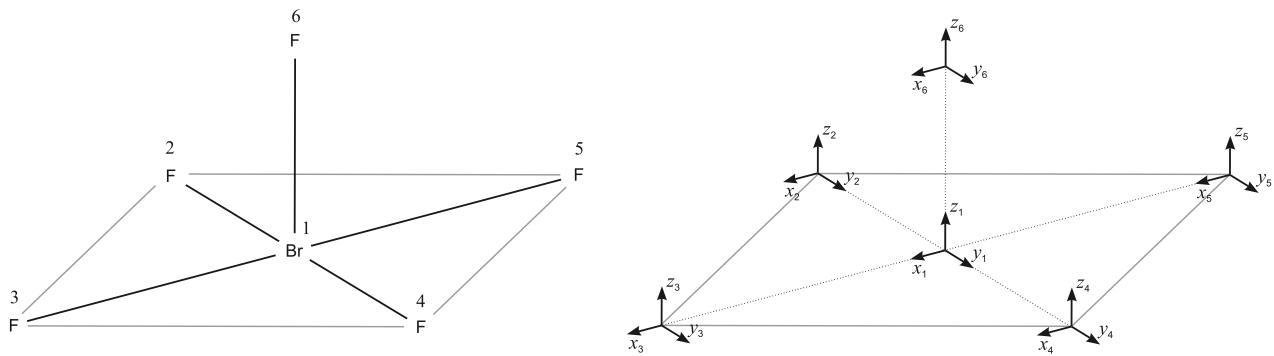


Figure 2-2: Displacement vectors for  $\text{BrF}_5$ . The  $z$  axis is along the 4-fold rotation axis. The  $y$  and  $x$  axis were chosen to coincide with the intramolecular bonds.

- $E$ : The identity operation leaves all vectors unchanged:  $\chi(E) = 18$ .
- $C_4$ : The vectors of the F nuclei all change their places and, therefore, do not contribute to the character. At the central Br nucleus and at the fluorine nucleus located on the principal axis, only the  $z$  vector is left in place and keeps its direction. This yields:  $\chi(C_4) = 2$  and  $\chi(C_2) = -2$ .
- $\sigma_v$ : At each of the Br nucleus and the three fluorine nuclei in the reflection plane, the two vectors in the plane stay the same but the vector perpendicular to the plane changes sign. We thus have  $2 - 1 = 1$  for each of the four nuclei, hence  $\chi(\sigma_v) = 4$ .
- $\sigma_d$ : F nuclei number 2-5 changes their places and do not contribute to the value of character. At the Br atom and at the F atom (number 6), the  $x$  and  $y$  vectors are exchanges, and, therefore the  $z$  vectors contribute with 1:  $\chi(\sigma_d) = 2$ .

In the end, one obtains for the displacement vectors of all nuclei the following reducible representation:

$C_{4v}$	$E$	$2C_4$	$C_2$	$2\sigma_v$	$2\sigma_d$
$\Gamma_{\text{tot}}$	18	2	-2	4	2

- Alternatively, we can construct the total representation as

$$\Gamma_{\text{tot}} = \Gamma_{x,y,z} \otimes \Gamma_{\text{nuclei}} \quad (2.1)$$

where  $\Gamma_{x,y,z}$  is the sum of all different irreducible representations of the unit vectors.  $\Gamma_{\text{nuclei}}$  is the reducible representation in the basis of atomic cores  $\{r_1, r_2, r_3, r_4, r_5\}$ . The characters of the symmetry elements in this representation are given by the number of unmoved nuclei.

We obtain the reducible representation ( $\Gamma_{\text{tot}}$ ) for the displacement vectors of all nuclei given in table 2.1.

$C_{4v}$	$E$	$2C_4$	$C_2$	$2\sigma_v$	$2\sigma_d$
$\Gamma_{x,y,z} (A_1 + E)$	3	1	-1	1	1
$\Gamma_{\text{nuclei}}$	6	2	2	4	2
$\Gamma_{\text{tot}}$	18	2	-2	4	2

Table 2.1

- e) Translations transform like the vectors  $x, y, z$ , giving the irreducible representations  $\Gamma_{\text{trans}} = A_1 \oplus E$ . Rotations transform like  $R_x, R_y, R_z$ , giving the irreducible representations  $\Gamma_{\text{rot}} = A_2 \oplus E$  (as can be seen from the point group table). Note that E has the dimension two, giving three degrees of freedom for the rotation and the translation.
- f) Subtraction of the translational and rotational irreducible representations gives:

$C_{4v}$	E	$2 C_4$	$C_2$	$2 \sigma_v$	$2 \sigma_d$
$\Gamma_{\text{tot}}$	18	2	-2	4	2
$-\Gamma_{\text{trans}}$	-3	-1	1	-1	-1
$-\Gamma_{\text{rot}}$	-3	-1	1	1	1
$\Gamma_{\text{vib}}$	12	0	0	4	2

*i.e.* twelve degrees of freedom for the vibrations.

Application of the reduction formula to  $\Gamma_{\text{vib}}$  gives the decomposition into irreducible representations:

$$\begin{aligned}
 n(A_1) &= \frac{1}{8}(12 + 0 - 0 + 8 + 4) = 3 \\
 n(A_2) &= \frac{1}{8}(12 + 0 - 0 - 8 - 4) = 0 \\
 n(B_1) &= \frac{1}{8}(12 - 0 - 0 + 8 - 4) = 2 \\
 n(B_2) &= \frac{1}{8}(12 - 0 - 0 - 8 + 4) = 1 \\
 n(E) &= \frac{1}{8}(12 \times 2 + 0 + 0 + 0 + 0) = 3
 \end{aligned}$$

Thus, the irreducible representations for the vibrational degrees of freedom are:

$$\Gamma_{\text{vib}} = 3 A_1 \oplus 2 B_1 \oplus B_2 \oplus 3 E.$$

- g) Infrared spectra result from the absorption of light by a molecule, while Raman spectroscopy is based on inelastic scattering. Let us assume that infrared light, which excites the molecule, is polarized along the  $x$ -axis of the coordinate system in which the position of the molecule is defined. Since the absorption intensity is proportional to the matrix element of the dipole moment component  $\hat{\mu}_x$  ( $I \propto \int \psi_0 \hat{\mu}_x \psi_1 d\vec{r}$ ), the selection rules establish non-zero integrals for symmetry reasons. At room temperature, most molecules are present in their ground vibrational state ( $\nu_0$ ), which has a totally symmetric vibrational wavefunction. Hence, as  $\psi_0$  is totally symmetric,  $\psi_1$  has to belong to the same representation as  $\hat{\mu}_x$  for the integral to be non-zero and therefore the same representation as  $x$ . For a mode to be Raman active, the corresponding integral  $\int \psi_0 \hat{\alpha}_{qq'} \psi_1 d\vec{r}$  must be non-zero. Here,  $\hat{\alpha}_{qq'}$  ( $q, q' = x, y, z$ ) is a component of the polarizability tensor ( $qq' = x^2, y^2, z^2, xy, xz, yz$  and their linear combinations). One can easily recognize absorption and Raman active modes by regarding the character table:

- absorption active modes have the same symmetry as translational vectors, *i.e.* in our case  $\{A_1, E\}$ .
- Raman-active modes have the same symmetry as the quadratic functions, which for the  $C_{4v}$  point group are  $\{A_1, B_1, B_2, E\}$ .

Thus, in the vibrational spectrum of the  $\text{BrF}_5$  molecule, one can expect six absorption active modes, three of which will have a two-fold degeneracy and nine Raman-active modes, six of which will coincide with absorption peaks.

### Exercise 3: Hückel MO treatment of cyclobutadiene

- a) The principal axis of a square-shaped cyclobutadiene is a  $C_4$  rotation axis. It has a  $C_2$  axis along the principal axis, as well as two  $C'_2$  axes, two  $C''_2$  axes, one  $\sigma_h$  mirror plane, two  $S_4$  axes, two  $\sigma_v$  mirror planes, two  $\sigma_d$  mirror planes, a center of inversion  $i$ , and the identity  $E$ , giving the point group  $D_{4h}$ . The symmetry elements are sketched in Figure 3-1.

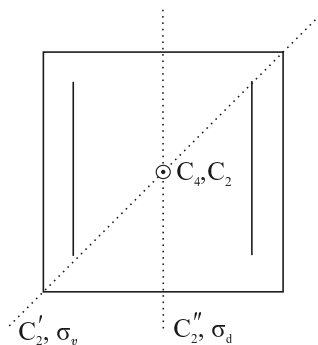


Figure 3-1: Some of the symmetry elements of the cyclobutadiene molecule.

- b) The orbitals contributing to the  $\pi$ -system are all carbon  $p_z$  orbitals as it is depicted in Figure 3-2 in a schematic way.

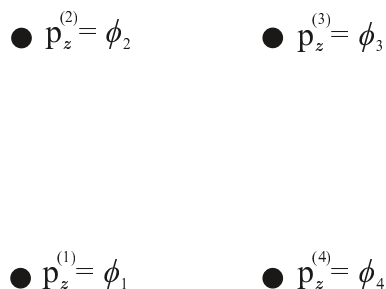


Figure 3-2: Carbon  $p$  orbitals of the cyclobutadiene viewed from above the molecular plane.

- c) Operating with the symmetry elements of the group on the  $p_z$  orbitals as sketched in Figure 3-1 gives the following characters for the reducible representation:

$D_{4h}$	$E$	$2C_4$	$C_2$	$2C'_2$	$2C''_2$	$i$	$2S_4$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$
$\Gamma_{\text{tot}}$	4	0	0	-2	0	0	0	-4	2	0

Application of the reduction formula yields:

$$\begin{aligned}
 n_{A_{1g}} &= \frac{1}{16}(4 - 2 \cdot 2 - 4 + 2 \cdot 2) = 0 \\
 n_{A_{2g}} &= \frac{1}{16}(4 + 2 \cdot 2 - 4 - 2 \cdot 2) = 0 \\
 n_{B_{1g}} &= \frac{1}{16}(4 - 2 \cdot 2 - 4 + 2 \cdot 2) = 0 \\
 n_{B_{2g}} &= \frac{1}{16}(4 + 2 \cdot 2 - 4 - 2 \cdot 2) = 0 \\
 n_{E_g} &= \frac{1}{16}(2 \cdot 4 + 0 - 2 \cdot (-4) + 0) = 1 \\
 n_{A_{1u}} &= \frac{1}{16}(4 - 2 \cdot 2 + 4 - 2 \cdot 2) = 0 \\
 n_{A_{2u}} &= \frac{1}{16}(4 + 2 \cdot 2 + 4 + 2 \cdot 2) = 1 \\
 n_{B_{1u}} &= \frac{1}{16}(4 - 2 \cdot 2 + 4 - 2 \cdot 2) = 0 \\
 n_{B_{2u}} &= \frac{1}{16}(4 + 2 \cdot 2 + 4 + 2 \cdot 2) = 1 \\
 n_{E_u} &= \frac{1}{16}(2 \cdot 4 + 0 + 2 \cdot (-4) + 0) = 0
 \end{aligned}$$

The four  $p_z$  orbitals can be decomposed into the representations  $\Gamma = E_g \oplus A_{2u} \oplus B_{2u}$ .

d) The projection operators for the three irreducible representations are:

$$\begin{aligned}
 P^{A_{2u}} &= (E + C_4 + C_4^3 + C_2 - \sum_{i=1}^2 C_2^i - \sum_{i=1}^2 C_2^{i3} - i - S_4 - S_4^3 - \sigma_h + \sum_{i=1}^2 \sigma_v^i + \sum_{i=1}^2 \sigma_d^i), \\
 P^{E_g} &= (2E - 2C_2 + 2i - 2\sigma_h), \\
 P^{B_{2u}} &= (E - C_4 - C_4^3 + C_2 - \sum_{i=1}^2 C_2^i + \sum_{i=1}^2 C_2^{i3} - i + S_4 + S_4^3 - \sigma_h + \sum_{i=1}^2 \sigma_v^i - \sum_{i=1}^2 \sigma_d^i)
 \end{aligned}$$

With these operators the new set of symmetry-adapted basis functions can be generated. Prefactors from the projection operators are combined in the normalization factor  $1/16$  for non-degenerate states and  $2/16$  for two-fold degenerate states:

$$\begin{aligned}
 \psi_{A_{2u}} &= P^{A_{2u}} \phi_1 = \frac{1}{16}(4\phi_1 + 4\phi_2 + 4\phi_3 + 4\phi_4) \\
 \psi_{E_g,1} &= P^{E_g} \phi_1 = \frac{2}{16}(4\phi_1 - 4\phi_3) \\
 \psi_{B_{2u}} &= P^{B_{2u}} \phi_1 = \frac{1}{16}(2\phi_1 - 2\phi_2 + 2\phi_3 - 2\phi_4)
 \end{aligned}$$

Since the irreducible representation  $E_g$  is two-fold degenerate, two orthogonal basis functions exist. There are several possibilities to derive the second basis function. Here we use the fact that each symmetry operation on a basis function for a doubly-degenerate representation needs to give  $\pm$  itself or the other member or a linear combination of both.

Therefore we apply a  $C_4$  rotation to  $\psi_{E_g,1}$  (neglecting any normalization for the moment):

$$\psi_{E_g,2} \equiv C_4 \psi_{E_g,1} = \frac{1}{2}(\phi_2 - \phi_4)$$



Thus, after normalization one obtains the following four orthonormal and symmetry adapted basis functions:

$$\begin{aligned}\psi_1 &= \psi_{A_{2u}} = \frac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4) \\ \psi_2 &= \psi_{B_{2u}} = \frac{1}{2}(\phi_1 - \phi_2 + \phi_3 - \phi_4) \\ \psi_3 &= \psi_{E_g,1} = \frac{1}{\sqrt{2}}(\phi_1 - \phi_3) \\ \psi_4 &= \psi_{E_g,2} = \frac{1}{\sqrt{2}}(\phi_2 - \phi_4)\end{aligned}$$

- e) With the new, symmetry-adapted basis functions, the Hückel Hamiltonian matrix can be constructed by evaluating the integrals  $H'_{rs} = \int \psi_r^* \hat{H}^{\text{eff}} \psi_s d\vec{r}$ .

Because all off-diagonal elements  $\int \phi_i H^{\text{eff}} \phi_j d\vec{r}$  ( $i \neq j$ ) of the original Hückel Hamiltonian matrix  $H$  are equal to zero unless  $i$  and  $j$  are neighboring (in which case  $H_{ij}^{\text{eff}} = \beta$ ) and its diagonal elements  $\int \phi_i H^{\text{eff}} \phi_j d\vec{r} = \alpha$  (for  $i = j$ ), one gets for the diagonal elements of the new Hückel Hamiltonian matrix:

$$\begin{aligned}H'_{11} &= \int \psi_1^* \hat{H}^{\text{eff}} \psi_1 d\vec{r} = \frac{1}{4} \int (\phi_1^* + \phi_2^* + \phi_3^* + \phi_4^*) \hat{H}^{\text{eff}} (\phi_1 + \phi_2 + \phi_3 + \phi_4) d\vec{r} \\ &= \frac{1}{4}(\alpha + \beta + \beta + \beta + \alpha + \beta + \beta + \alpha + \beta + \beta + \beta + \alpha) = \alpha + 2\beta \\ H'_{22} &= \int \psi_2^* \hat{H}^{\text{eff}} \psi_2 d\vec{r} = \frac{1}{4} \int (\phi_1^* - \phi_2^* + \phi_3^* - \phi_4^*) \hat{H}^{\text{eff}} (\phi_1 - \phi_2 + \phi_3 - \phi_4) d\vec{r} = \alpha - 2\beta \\ H'_{33} &= \int \psi_3^* \hat{H}^{\text{eff}} \psi_3 d\vec{r} = \frac{1}{2} \int (\phi_1^* - \phi_3^*) \hat{H}^{\text{eff}} (\phi_1 - \phi_3) d\vec{r} = \alpha \\ H'_{44} &= \int \psi_4^* \hat{H}^{\text{eff}} \psi_4 d\vec{r} = \frac{1}{2} \int (\phi_2^* - \phi_4^*) \hat{H}^{\text{eff}} (\phi_2 - \phi_4) d\vec{r} = \alpha\end{aligned}$$

In a similar manner one obtains for the off-diagonal elements:<sup>2</sup>

$$H'_{12} = H'_{13} = H'_{14} = H'_{23} = H'_{24} = H'_{34} = 0$$

After evaluating all matrix elements, the Hückel Hamiltonian matrix in the new basis set can be set up:

$$\mathbf{H}' = \begin{pmatrix} \alpha + 2\beta & 0 & 0 & 0 \\ 0 & \alpha - 2\beta & 0 & 0 \\ 0 & 0 & \alpha & 0 \\ 0 & 0 & 0 & \alpha \end{pmatrix}$$

Since the basis set is still orthonormal, the overlap matrix  $\mathbf{S}'$  remains the identity matrix.

As opposed to the original Hückel Hamiltonian matrix, the Hückel matrix in the new basis is diagonal. In general, the symmetry-adapted Hückel-determinant will have a block-diagonal form, each  $n \times n$  block belonging to the  $n$  basis functions displaying the same symmetry. In the present case,  $H'_{11}$  and  $H'_{22}$  belong to the non-degenerate irreducible representations  $A_{2u}$  and  $B_{2u}$ , respectively. The remaining diagonal block belongs to the two-fold degenerate representation  $E_g$ .

<sup>2</sup>Note that this is only true for the particular functions that we have chosen.

f) The Hückel determinant is given by

$$\det(\mathbf{H}' - \epsilon \mathbf{S}') = \begin{vmatrix} \alpha + 2\beta - \epsilon & 0 & 0 & 0 \\ 0 & \alpha - 2\beta - \epsilon & 0 & 0 \\ 0 & 0 & \alpha - \epsilon & 0 \\ 0 & 0 & 0 & \alpha - \epsilon \end{vmatrix}$$

A block diagonal structure simplifies the calculation of the energy levels. In fact, for each subblock the problem can be solved separately, since

$$\det \begin{pmatrix} \mathbf{A} & 0 \\ 0 & \mathbf{B} \end{pmatrix} = \det(\mathbf{A}) \cdot \det(\mathbf{B})$$

where  $\mathbf{A}$  and  $\mathbf{B}$  are symmetric matrices of any size.

In our case the Hückel determinant is diagonal. Due to this fact, one can straightforwardly obtain the energy values:

$$\begin{aligned} \epsilon_1 &= \alpha + 2\beta \\ \epsilon_2 &= \alpha - 2\beta \\ \epsilon_3 &= \alpha \text{ (two-fold degenerate)} \end{aligned}$$

Note that the  $E_g$  block is diagonal, even though this is not required by symmetry. Thus, diagonal elements of the block are the eigenvalues themselves. This is not generally true and eigenvalues have to be calculated by diagonalization.

The parameter  $\beta$  describes the interaction energy due to the chemical bond and is negative. Therefore the lowest lying orbital is  $a_{2u}$  orbital followed by the degenerate  $e_g$  orbitals. The  $b_{2u}$  is the antibonding orbital. Figure 3-3 shows the energy level diagram. According to standard notation, molecular orbitals are labelled with the lower-case Mulliken symbols of their irreducible representations.

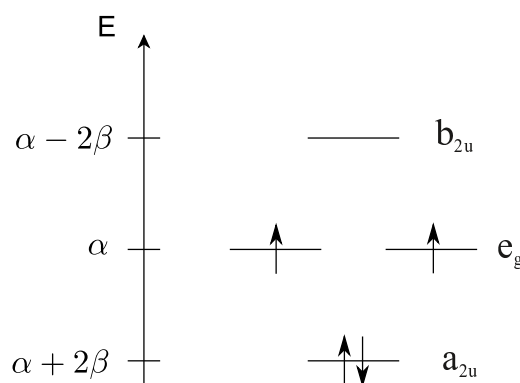


Figure 3-3: The energy levels for the cyclobutadiene from a HMO treatment.

g) In the ground state, the energetically lowest-lying orbital is completely filled, leading to the totally symmetric irreducible representation  $A_{1g}$ . The doubly degenerate state of  $e_g$  symmetry is occupied by two electrons. Therefore:

$$\Gamma_1 \otimes \Gamma_2 \equiv e_g \otimes e_g = a_{1g} \oplus a_{2g} \oplus b_{1g} \oplus b_{2g}$$

Thus, these two electrons give rise to the states:  $A_{1g}$ ,  $A_{2g}$ ,  $B_{1g}$  and  $B_{2g}$ . The states could be singlet or triplet. For the overall wavefunctions of the singlet states to be antisymmetric, the

spatial part of the wavefunction needs to be symmetric (as the spin wavefunction is antisymmetric in this case). For the triplet state, the spatial wavefunction has to be antisymmetric. The only antisymmetric representation for the above direct product is  $A_{2g}$ . Therefore, the term symbol for the triplet state is  ${}^3A_{2g}$ . The possible term symbols for the singlet states are  ${}^1A_{1g}$ ,  ${}^1B_{1g}$  and  ${}^1B_{2g}$ . In accordance with Hund's rule the ground state (state with the lowest energy) is that with the highest multiplicity, namely  ${}^3A_{2g}$ .

- h) A rectangular cyclobutadiene molecule belongs to the  $D_{2h}$  symmetry group. Because of that, the molecule does not have a  $C'_2$  axis or a symmetry plane  $\sigma_v$  anymore.

$D_{2h}$	$E$	$C_2(x)$	$C_2(y)$	$C_2(z)$	$i$	$\sigma_{xy}$	$\sigma_{xz}$	$\sigma_{yz}$
$\Gamma_{\text{tot}}$	4	0	0	0	0	-4	0	0

For the four  $p_z$  orbitals, localized on the carbon nuclei, the representation is given by:  $\Gamma = B_{2g} \oplus B_{3g} \oplus A_u \oplus B_{1u}$ . Applying the projection operator on the  $\phi_1$  orbital, one obtains the following normalized basis functions:

$$\begin{aligned}\psi_1 &= \psi_{B_{1u}} = \frac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4) \\ \psi_2 &= \psi_{A_u} = \frac{1}{2}(\phi_1 - \phi_2 + \phi_3 - \phi_4) \\ \psi_3 &= \psi_{B_{2g}} = \frac{1}{2}(\phi_1 + \phi_2 - \phi_3 - \phi_4) \\ \psi_4 &= \psi_{B_{3g}} = \frac{1}{2}(\phi_1 - \phi_2 - \phi_3 + \phi_4)\end{aligned}$$

The functions are schematically depicted in Figure 3-4 together with their nodal planes. As one can see, the basis functions look similar to those obtained for the square structure of cyclobutadiene. Decreasing the symmetry leads to splitting of the doubly degenerate energy level of  $e_g$  symmetry into two non-degenerate levels of  $b_{2g}$  and  $b_{3g}$  symmetry.

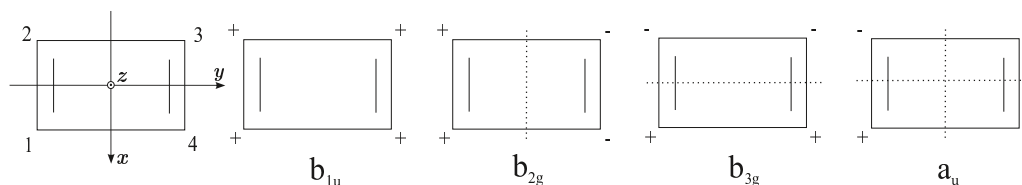


Figure 3-4: Molecular orbitals of cyclobutadiene in rectangular structure.

The interaction between neighbouring atoms, that we called  $\beta$  before, now differ depending on whether the neighbours are along the elongated or shortened bonds. This means that by the symmetry arguments alone, it is not possible to say what the energetic ordering of the  $b_{2g}$  and  $b_{3g}$  states will be. However, chemical reasoning tells us that the  $b_{2g}$  state will be lower in energy because here the two  $p_z$  orbitals that have a binding overlap are along the double bond, where the distance between them is shorter than for  $b_{3g}$  state. The most stable configuration is  $(b_{1u})^2(b_{2g})^2$ , corresponding to two doubly occupied orbitals. The ground state term symbol for this configuration is  ${}^1A_g$ .

For the excited state configuration  $(b_{1u})^2(b_{2g})^1(b_{3g})^1$ , the direct product of the irreducible representations of the two singly occupied orbitals is:  $B_{2g} \otimes B_{3g} = B_{1g}$ . The resulting molecular term symbols are:  ${}^1B_{1g}$ ,  ${}^3B_{1g}$ . Note that here both terms exist with singlet and triplet spin multiplicity because there is no Pauli restriction due to the two different spatial orbitals. However, one expects that the triplet state is slightly lower in energy due to exchange interaction.

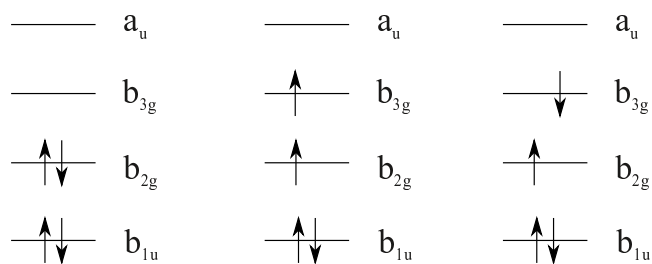


Figure 3-5: Left panel: most stable configuration of the rectangular cyclobutadiene. Middle panel: excited triplet configuration of the rectangular cyclobutadiene. Right panel: excited singlet configuration of the rectangular cyclobutadiene.

## References

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