

CHEMICAL APPLICATIONS OF GROUP THEORY

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Answers to Problems and Exercises

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Chapter 2

1. Any similarity transform we set up, say $A^{-1}BA$, may be rearranged because of the commutative property of Abelian groups to $A^{-1}AB$ which equals B . In other words every possible similarity transform on every element converts that element into itself.
2. If in a group of order h any element, X , has a cycle (i.e., $X, X^2 \dots X^n = E$) such that $n < h$, it must give rise to a cyclic subgroup of order n . However, orders of subgroups must be integral divisors of the group order h . If h is prime it has no divisors. Hence the only possible cycle for any group element is h itself. Thus, only one group of order h is possible if h is a prime number, namely, the cyclic group of order h .
3. The cyclic group has the following multiplication table.

	E	A	B	C	D
E	E	A	B	C	D
A	A	B	C	D	E
B	B	C	D	E	A
C	C	D	E	A	B
D	D	E	A	B	C

The only way we can change this table (in a real way, not just by shuffling letters) would be to allow some more elements to be their own inverses. In so doing we shall always have to leave pairs that are inverses to each other. Thus, we can try to go from two such pairs (B,C and A,D) to only one or to none. Let us first make B and C their own inverses, leaving just one pair (A,D) that are inverse to each other. This will give us the following start on the multiplication table:

	E	A	B	C	D
E	E	A	B	C	D
A	A				E
B	B		E		
C	C			E	
D	D	E			

Suppose we now say that either $BC = D$ or $BC = F$. It makes no real difference. Now, invoking the assumed inverse relationships we can obtain the following results:

$$\begin{array}{ll}
 BC = D & BC = D \\
 BBC = BD & BCC = DC \\
 C = BD & B = DC
 \end{array}$$

If we now enter these results into the table we have:

	E	A	B	C	D
E	E	A	B	C	D
A	A				E
B	B		E		
C	C		D	E	B
D	D	E	C		

Now, to complete the C row we have to put in an A. But we cannot do that because there is already an A in column 2. It is impossible to complete the table.

Similarly, if we attempt to make every element its own inverse and then let $BC = D$, etc., we get as far as

	E	A	B	C	D
E	E	A	B	C	D
A	A	E			
B	B		E		
C	C		D	E	B
D	D		C		E

Again we are at the same impasse.

4. Because if $A^2 = B^2 \neq E$, then $A = B$, which violates the rule that all elements of a group are distinct.
5. Since G_3 is a group, it will have to be a subgroup of whatever larger group we make. The smallest such group of which 3 is an integral divisor (a requirement of a subgroup) is of order 6. In other words it is not possible to simply add one more element and make a group of order 4. Instead, we are required to postulate that $CA = D$ and $CB = F$. We may now use the multiplication table for G_3 to show:

$$\begin{array}{ll} CA = D & CB = F \\ CAB = DB & CBA = FA \\ C = DB & C = FA \end{array}$$

We thus have the following partial table:

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	B	E	D		C
B	B	E	A	F	C	
C	C					
D	D					
F	F					

The three added elements C, D and F must give rise to three subgroups of order 2 (since a single new subgroup of order 4 is not possible). This means that C, D and F are each inverse to themselves (and require E's along the diagonal). Moreover, the only way to complete rows 2 and 3 is to put F in row 2 and D in row 3. After making these additions to the partial table above we have

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	B	E	D	F	C
B	B	E	A	F	C	D
C	C			E		
D	D				E	
F	F					E

The rest of the table is now actually fixed for us, as the following representative relationships, all based on the $CC = E$, $DD = E$ and $FF = E$ relationships, show.

$$\begin{array}{ll} FA = C & CD = A \\ FFA = FC & CDD = A \\ A = FC & C = AD \\ \text{etc.} & \text{etc.} \end{array}$$

The final result is:

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	B	E	D	F	C
B	B	E	A	F	C	D
C	C	F	D	E	B	A
D	D	C	F	A	E	B
F	F	D	C	B	A	E

The reader can verify that this is actually the group $G_6^{(2)}$ given in the text. It differs only in that the assignment of letters has changed, with the present ones corresponding to the previous ones, in parentheses, as follows: $E(E)$, $A(C)$, $B(D)$, $C(F)$, $D(A)$, $F(A)$.

6. In the complete group $X, X^2, \dots X^n, \dots X^h$, let n be a divisor of h .

Thus $mn = h$, where m and n are both integral divisors of h , and $(X^n)^m = X^{mn} = X^h$. It then follows that $X^n, X^{2n}, \dots X^{mn}$ is a subgroup of order m . There will be just one subgroup for each value of m or n .

As an example, take the cyclic group of order 8. For each divisor of 8, namely, 2 and 4, there is one subgroup, viz.,

$$E, X^2, X^4, X^6$$

$$E, X^4$$

7. There are four groups of order eight. The cyclic group, $G_8^{(1)}$, must have two E's on the diagonal of its multiplication table, resulting from $EE = E$ and $X^4X^4 = E$. This leaves three pairs of elements that are inverse to each other. The remaining three groups are those in which there are only 2 such pairs (4E's on the diagonal), one such pair (6 E's on the diagonal) and no such pair (8 E's on the diagonal). Their multiplication tables are as follows.

$G_8^{(2)}$	E	A	B	C	D	F	G	H
E	E	A	B	C	D	F	G	H
A	A	B	C	E	F	G	H	D
B	B	C	E	A	G	H	D	F
C	C	E	A	B	H	D	F	G
D	D	F	G	H	E	A	B	C
F	F	G	H	D	A	B	C	E
G	G	H	D	F	B	C	E	A
H	H	D	F	G	C	E	A	B

$G_8^{(4)}$	E	A	B	C	D	F	G	H
E	E	A	B	C	D	F	G	H
A	A	E	C	B	F	D	H	G
B	B	C	E	A	G	H	D	F
C	C	B	A	E	H	G	F	D
D	D	F	G	H	E	A	B	C
F	F	D	H	G	A	E	C	B
G	G	H	D	F	B	C	E	A
H	H	G	F	D	C	B	A	E

$G_8^{(3)}$	E	A	B	C	D	F	G	H
E	E	A	B	C	D	F	G	H
A	A	C	E	B	H	G	D	F
B	B	E	C	A	G	H	F	D
C	C	B	A	E	F	D	H	G
D	D	G	H	F	E	C	A	B
F	F	H	G	D	C	E	B	A
G	G	F	D	H	B	A	E	C
H	H	D	F	G	A	B	C	E

8. For $G_8^{(2)}$ each element is in a class by itself. Subgroups are:

$(E, B), (E, D), (E, G)$

(E, A, B, C)

For $G_8^{(3)}$ the classes are $E; A, B; C; D, F; G, H$. The subgroups are

(E, C)

$(E, A, B, C), (E, A, D, F), (E, C, G, H)$

For $G_8^{(4)}$ each element is in a class by itself because the group is Abelian (symmetrical about the diagonal - all multiplications therefore commute). Subgroups of orders 2 and 4 are possible and several of each exist:

$(E, A), (E, B), (E, C), \dots$ and (E, H)

$(E, A, B, C), (E, A, D, F), (E, B, D, G)$ and (E, C, D, H)

9. We may proceed as we did for the groups of order 8. Begin with the cyclic group, $G_6^{(1)}$, whose multiplication table can be written straightforwardly:

$G_6^{(1)}$	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	B	C	D	F	E
B	B	C	D	F	E	A
C	C	D	F	E	A	B
D	D	F	E	A	B	C
F	F	E	A	B	C	D

This group has two E's on the diagonal. The remaining possibilities to consider are those with four and six E's on the diagonal. We already have the multiplication table for $G_6^{(2)}$, the one with four diagonal E's. We now turn to the task of working out the multiplication table for the one with six, a task we shall find to be impossible.

We begin with the following partial multiplication table, which incorporates the assumption:

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E				
B	B		E			
C	C			E		
D	D				E	
F	F					E

We may now assume that $BA = C$. Since the elements B, C, D and F are still arbitrary we can make this assumption arbitrarily. We could equally well have assumed $BA = D$ or F. All we are saying is that the product BA is not, B, A or E. We then proceed by left-multiplying or right-multiplying both sides of this and subsequent equations and making use of the fact that each element is its own inverse.

$$\begin{aligned}
 BA &= C & BA &= C \\
 BBA &= BC & BAA &= CA \\
 A &= BC & B &= CA
 \end{aligned}$$

With these results included, the table is now:

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	C	B		
B	B		E			
C	C		A	E		
D	D				E	
F	F					E

Now, the only way to complete row 2 is to accept that $DA = F$ and $FA = D$. From these equalities we derive some others:

$$\begin{aligned}
 DA &= F & FA &= D \\
 DDA &= DF & FFA &= FD \\
 A &= DF & A &= FD
 \end{aligned}$$

In a similar way, the remaining places in column 3 must be filled by $BD = F$ and $BF = D$. Adding all these new results we have:

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	C	B	F	D
B	B		E			
C	C		A	E		
D	D		F		E	A
F	F		D		A	E

We now find that it is impossible to go further without violating the rules of group theory. The product CD cannot be C , D or E ; it must therefore be A or F . But we cannot put A or F into the D row because both are already there.

10. For group $G_4^{(1)}$ the multiplication table is symmetrical about the diagonal and is thus Abelian. Therefore, each element is in a class by itself. There is one subgroup of order 2, namely, (E, B) .

For group $G_4^{(2)}$ the table is again symmetrical and each element is in a class by itself. There are three subgroups, (E, A) , (E, B) , and (E, C) .

For $G_6^{(1)}$, the cyclic subgroup of order 6, as for all cyclic groups, is Abelian and each element is in a class by itself. There are two subgroups, based on the concept that the group is the cycle of some generating element X , namely

$$X, X^2, X^3, X^4, X^5, X^6$$

Clearly, $X^6 = E$, hence (E, X^3) is a subgroup, and $X^2X^2 = X^4$ and $X^4X^2 = X^6$, hence (E, X^2, X^4) form a subgroup. In the table as worked out in exercise 9, we would write these as (E, C) and (E, B, D) .

Chapter 3

Set A

A3.1 C_{8h} (C_8); D_{2d} (D_2); C_{5v} (C_5)

A3.2 (a) S_6 (b) D_{3d} (c) D_{5h} (d) C_3 (e) O_h
(f) S_6 (g) C_{3v} (h) C_{4h} (i) C_3

A3.3 C_{nh}

A3.4 S_5 - see C_{5h}

S_8 - S_8 , S_8^2 (C_4), S_8^3 , S_8^4 (C_2), S_8^5 , S_8^6 (C_4^3), S_8^7 , S_8^8 (E)

Set B

B3.1

B3.2 D_{2d} and O_h

B3.3 D_{2d}

B3.4 T_d

B3.5 T_h

B3.6 T and T_d

B3.7 T

B3.8 If $\theta = 30^\circ$, O_h ; Otherwise 0

B3.9 D_{2h} . The pentagons are not regular

B3.10 D_{3d}

B3.11 D_{2d}

Set C

- (1) C_{4v} (2) C_{2v} (3) C_{2v} (4) C_{2v} (5) D_{2h} (6) D_{3h} (7) C_{2v} (8) C_s
 (9) D_{4h} (10) C_{2h} (11) C_{3v} (12) D_{2h} (13) C_{2v} (14) C_s (15) a, C_5
 b, C_{2v} ; c, C_5 ; d, C_2 ; e, C_{2v} ; f, C_{2h} ; g, C_s ; h, C_{4v} ; i, D_{2h} ; j, C_{2h} ;
 k, C_{2h} ; l, D_{2d} ; m, C_1 .

Set D

- (1) C_{3v} (2) C_{2h} (3) C_{2h} (4) D_{2d} (5) D_{4h} (6) C_{2h} (7) C_{3h}
 (8) C_2 (9) D_{2h} (10) D_{3d} (11) D_{2d} (12) C_2

Set E

- | | |
|--------------|---------------|
| (1) D_{3d} | (7) S_6 |
| (2) C_1 | (8) D_4 |
| (3) D_{6h} | (9) D_3 |
| (4) D_{6d} | (10) D_{4d} |
| (5) D_6 | (11) S_8 |
| (6) D_2 | (12) C_{2h} |
| | (13) C_1 |

Chapter 4

1. (1) Two rotations about the same axis. Choose the z axis. A rotation by an angle α or β is given by the matrices

$$\begin{bmatrix} \cos\alpha & -\sin\alpha & \cos\beta & -\sin\beta \\ \sin\alpha & \cos\alpha & \sin\beta & \cos\beta \end{bmatrix}$$

Their product, multiplied in the order given is

$$\begin{bmatrix} \cos\alpha\cos\beta - \sin\alpha\sin\beta & -\cos\alpha\sin\beta - \sin\alpha\cos\beta \\ \sin\alpha\cos\beta + \cos\alpha\sin\beta & -\sin\alpha\sin\beta + \cos\alpha\cos\beta \end{bmatrix}$$

and when multiplied in reverse order is

$$\begin{bmatrix} \cos\alpha\cos\beta - \sin\alpha\sin\beta & -\sin\alpha\cos\beta - \cos\alpha\sin\beta \\ \cos\alpha\sin\beta + \sin\alpha\cos\beta & -\sin\alpha\sin\beta + \cos\alpha\cos\beta \end{bmatrix}$$

Except for trivial rearrangement these are identical.

(2) Reflections through planes \perp to each other. Take xz and yz planes

$$\begin{matrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} & \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} & - & \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} & - & \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} & \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \\ \text{xz} & \text{yz} & & \text{yz} & & \text{xz} \end{matrix}$$

(3) Inversion and any reflection or rotation. The inversion matrix is a unit matrix with a minus sign:

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

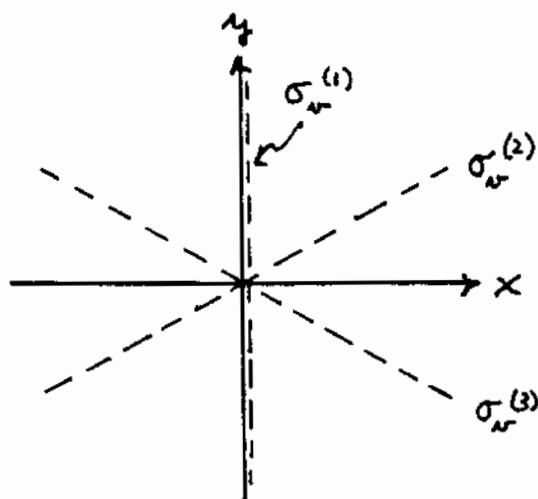
A unit matrix commutes with all other matrices.

(4) Two C_2 rotations about \perp axes. Such rotations are described by diagonal matrices. All pairs of diagonal matrices commute.

(5) Rotation and a \perp reflection. Take rotation about z by α and reflection in the xy plane. The following matrices clearly commute.

$$\begin{bmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \\ 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & -1 \end{bmatrix}$$

2. The operations are E , C_3 , C_3^2 , $\sigma_v^{(1)}$, $\sigma_v^{(2)}$, $\sigma_v^{(3)}$, as shown below.



For the two one-dimensional representations, the characters themselves are the complete matrices. For a general point, 3-dimensional matrices will be generated, but all of them will be of the form:

$$\begin{bmatrix} M_{11} & M_{12} & 0 \\ M_{21} & M_{22} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

since no operation changes the z coordinate. We may therefore consider only the x and y coordinates. For C_3 , C_3^2 and $\sigma_v^{(1)}$ we can write down by inspection:

$$\begin{bmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{bmatrix}, \begin{bmatrix} \cos 2\alpha & -\sin 2\alpha \\ \sin 2\alpha & \cos 2\alpha \end{bmatrix}, \text{ and } \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$$

$C_3 \qquad C_3^2 \qquad \sigma_v^{(1)}$

where $\alpha = 2\pi/3$. The simplest way to get the matrices for $\sigma_v^{(2)}$ and $\sigma_v^{(3)}$ is to use the multiplication properties of the group, i.e., $\sigma_v^{(2)} = C_3 \sigma_v^{(1)}$ and $\sigma_v^{(3)} = C_3^2 \sigma_v^{(1)}$. When the corresponding matrices are multiplied we get:

$$\begin{bmatrix} -\cos\alpha & \sin\alpha \\ \sin\alpha & \cos\alpha \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} -\cos 2\alpha & \sin 2\alpha \\ \sin 2\alpha & \cos 2\alpha \end{bmatrix}$$

$\sigma_v^{(2)} \qquad \qquad \sigma_v^{(3)}$

Note that these matrices have characters of 0. Of course, they must since the one for $\sigma_v^{(1)}$ has $\chi = 0$. All operations in the same class are required to have the same characters. If all we want is the character for a class,

we can just choose the easiest one to work with and forget the others.

3. All the necessary matrices are given in the text or are obvious. One simply has to recognize which are inverse to which (e.g., C_3 and C_3^2 are inverses) and grind through all the similarity transforms. Note first that only one operation in each class needs to be used to get the character for that class.

4. The matrices for the various C_2 , C_3 and C_4 rotations as they affect a general point, x, y, z , which have been discussed in the text will give the representations and hence the characters for T_1 directly.

For the more complex functions we proceed as follows:

A $C_4(z)$ operation applied to the set of functions xz, yz, xy will give the set $-yz, xz, -xy$. To express this in a matrix equation, we clearly require:

$$\begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} xz \\ yz \\ xy \end{bmatrix} = \begin{bmatrix} -yz \\ xz \\ -xy \end{bmatrix}$$

The character is -1.

For a C_3 operation (the one which permutes x, y, z to z, x, y) we can see that the set xz, yz, xy becomes $yx(-xy), zx(-xz), yz$. Again the pertinent matrix equation is written and the character (0) determined.

$$\begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} xz \\ yz \\ xy \end{bmatrix} = \begin{bmatrix} xy \\ xz \\ yz \end{bmatrix}$$

For the two kinds of C_2 operations (i.e., $C_2 = C_4^2$ and the class of six) we have:

$C_2(z)$ applied to xz, yz, xy gives $-xz, -yz, xy$. The matrix will clearly be diagonal with elements $-1, -1, 1$ and $\chi = -1$.

For the C_2 axis that lies between the $+x$ and $+y$ axes in the xy plane the set xz, yz, xy becomes $-yz, -xz, xy$. The matrix equation is

$$\begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} xz \\ yz \\ xy \end{bmatrix} = \begin{bmatrix} -yz \\ -xz \\ xy \end{bmatrix}$$

and the character is 1.

5. Because of the commutative property of an Abelian group, each operation is in a class by itself. Thus, for an Abelian group of order h there are h irreducible representations (rule 5). The only set of h integers whose squares add up to h^2 is a set of 1's.

6. The group C_4 is a cyclic group. Its representations must consist of the ϵ^p where $\epsilon = \exp(2\pi i p/4) = \cos 2\pi p/4 + i \sin 2\pi p/4$. Since a cyclic (hence Abelian) group of order 4 must have 4 one-dimensional representations, we have

	C_4	C_4^2	C_4^3	$C_4^4(-\epsilon)$
Γ_1	ϵ	ϵ^2	ϵ^3	ϵ^4
Γ_2	ϵ^2	ϵ^4	ϵ^6	ϵ^8
Γ_3	ϵ^3	ϵ^6	ϵ^9	ϵ^{12}
Γ_4	ϵ^4	ϵ^8	ϵ^{12}	ϵ^{16}

From the trigonometric functions, all ϵ^p with $p = 4n$ are equal to 1 and those with $p = 2n$ are equal to -1. Those with $p = 4n + 1$ and $4n + 3$ will be i or $-i$, respectively. We thus obtain:

	C_4	C_4^2	C_4^3	$C_4^4(-\epsilon)$
Γ_1	1	-1	-i	1
Γ_2	-1	1	-1	1
Γ_3	-i	-1	i	1
Γ_4	1	1	1	1

When regrouped and relabeled in conventional fashion, this becomes:

C_4	E	C_4	C_4^2	C_4^3
A	1	1	1	1
B	1	-1	1	-1
E	$\begin{pmatrix} 1 & i & -1 & -i \\ 1 & -i & -1 & i \end{pmatrix}$			

7. The approach here is to write down the matrices for C_3 , C_3^2 and $C_2(x)$ by inspection, using a general point x, y, z . Obtain those for the other C_2 operations by matrix multiplication. It will be found that these will factor into a set of two-dimensional representations that form the E representation. Since the other two representations are one-dimensional, their matrices consist entirely of ± 1 and can be written down by inspection.

Note. If you are really alert, you will observe that all three C_2 operations are in the same class and therefore have the same characters. You can thus work only with the "obvious" matrices for C_3 , C_3^2 and $C_2(x)$.

8. For the two dihedral planes, the results are

$$\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 1 \end{bmatrix} \text{ and } \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

For reflection in the xy plane the matrix is

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

This matrix commutes with each of the others and thus we need examine only two products, e.g.,

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} - \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

This matrix must describe the two-fold rotation about an axis along the line of intersection of the two planes, and it can be seen that it does.

Chapter 5

1. The characters of the direct products are:

D_{6h}	E	$2C_6$	$3C_2$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
$A_{1g} \times B_{1g}$	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
$A_{1u} \times A_{1u}$	1	1	1	1	1	1	1	1	1	1	1	1
$B_{2u} \times E_{1g}$	2	-1	-1	2	0	0	-2	1	1	-2	0	0
$E_{1g} \times E_{2u}$	4	-1	1	-4	0	0	-4	1	-1	4	0	0
$E_{1g} \times B_{2g}$	4	-1	1	-4	0	0	4	-1	1	-4	0	0
$\times A_{2u} \times E_{1u}$												

and they reduce as follows:

$$A_{1g} \times B_{1g} = B_{1g}$$

$$A_{1u} \times A_{1u} = A_{1g}$$

$$B_{2u} \times E_{1g} = E_{2u}$$

$$E_{1g} \times E_{2u} = B_{1u} + B_{2u} + E_{1u}$$

$$E_{1g} \times B_{2g} \times A_{2u} \times E_{1u} = B_{1g} + B_{2g} + E_g$$

The important points to note here are:

- (1) when any representation is taken in direct product with the totally symmetric one, it goes into itself.
- (2) any one-dimensional representation times itself is the totally symmetric representation.
- (3) the products of $u \times g$ or $g \times u$ must be u .
- (4) more generally, any direct product containing an odd number of u 's will be u ; otherwise it will be g .

2. Since ψ_v° belongs to A_1 or A_{1g} (for C_{4v} or D_{3d}) we need only examine the various binary direct products for the representations to which the algebraic functions belong and the representations to which ψ_v^1 may belong.

and see if they are or contain A_1 or A_{1g} . This is really a trivial task. From the character table one finds the representation to which the function belongs and then ψ^1_v must belong to the same one. Thus z requires A_1 , (x,y) require E , $(x^2 + y^2)$ requires A_1 , and so on in C_{4v} .

3. In T_d the character table shows that the set, (R_x, R_y, R_z) belongs to the T_1 representation. Therefore, the direct product of the representations of the upper and lower states for an allowed transition must be or contain the T_1 representation. Only those direct products of dimension ≥ 3 need be examined. The results are tabulated below. It is seen that there are 7 possible pairs of states that could participate in magnetically allowed transitions in a tetrahedral molecule.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	irred. components
$A_1 \times T_1$	3	0	-1	1	-1	T_1
$A_1 \times T_2$	3	0	-1	-1	1	T_2
$A_2 \times T_1$	3	0	-1	-1	1	T_2
$A_2 \times T_2$	3	0	-1	1	-1	T_1
$E \times E$	4	1	4	0	0	$A_1 + A_2 + E$
$E \times T_1$	6	0	-2	0	0	$T_1 + T_2$
$E \times T_2$	6	0	-2	0	0	$T_1 + T_2$
$T_1 \times T_1$	9	0	1	1	1	$A_1 + E + T_1 + T_2$
$T_1 \times T_2$	9	0	1	-1	-1	$A_2 + E + T_1 + T_2$
$T_2 \times T_2$	9	0	1	1	1	$A_1 + E + T_1 + T_2$

Chapter 6

1. (a) It should be obvious by inspection that there are four sets of orbitals, members of which can be exchanged only among themselves by the symmetry operations of D_{2h} . These are (1,4,5,8), (2,3,6,7), (9,10)

(b) Each of these sets must be used as the basis of a reducible representation of D_{2h} , and then each of these representations must be reduced. We must refer to the indicated coordinate system so we know which plane and axis is which. We shall go through the first set of orbitals, (1,4,5,8) in detail.

For E, each orbital goes into itself $\chi = 4$.

For all C_2 rotations, i , $\sigma(xy)$ and $\sigma(yz)$, each orbital goes somewhere else. Therefore, the character for each of these operations is 0.

Reflection in the xy plane changes each p_x orbital into the negative of itself, thus giving a matrix with -1 at each diagonal position and $\chi = -4$.

The results for all three sets are as follows:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_{1,4,5,8}$	4	0	0	0	0	-4	0	0
$\Gamma_{2,3,6,7}$	4	0	0	0	0	-4	0	0
$\Gamma_{9,10}$	2	0	-2	0	0	-2	0	2

$$\Gamma_{1,4,5,8} = \Gamma_{2,3,6,7} = B_{2g} + B_{3g} + A_u + B_{1u}$$

$$\Gamma_{9,10} = B_{3g} + B_{1u}$$

(c) The ten normalized SALCSs can be written down by inspection of the character table since all representations are one-dimensional. For a B_{2g} combination of functions 1,4,5 and 8 we require a linear combination that

will change sign by application of $C_2(z)$ and also on application of $\sigma(yz)$. This clearly requires the following set of signs:

$$\phi_1 + \phi_4 - \phi_5 - \phi_8$$

Similarly, a B_{3g} combination must be antisymmetric to $C_2(z)$ but symmetric to $\sigma(yz)$. This requires:

$$\phi_1 - \phi_4 - \phi_5 + \phi_8$$

It is quite easy to do this for all ten SALCs.

We may, of course, crank through the entire projection operator procedure. For the above B_{2g} orbital

$$\begin{array}{cccccccc} E & C_2(z) & C_2(y) & C_2(x) & i & \sigma(xy) & \sigma(xz) & \sigma(yz) \\ \hline \hat{P}^{B_{2g}} (\phi_1) & = 1\phi_1 + (-1)\phi_5 - (1)\phi_8 - (-1)\phi_4 - (1)\phi_5 - (-1)\phi_1 + (1)\phi_4 + (-1)\phi_8 \\ & = 2\phi_1 + 2\phi_4 - 2\phi_5 - 2\phi_8 \approx \phi_1 + \phi_4 - \phi_5 - \phi_8 \end{array}$$

Either way, the entire set of normalized results is as follows:

$$\begin{array}{l} B_{2g}: \quad \frac{1}{2} (\phi_1 + \phi_4 - \phi_5 - \phi_8) \\ \quad \quad \frac{1}{2} (\phi_2 + \phi_3 - \phi_6 - \phi_7) \\ B_{3g}: \quad \frac{1}{2} (\phi_1 - \phi_4 - \phi_5 + \phi_8) \\ \quad \quad \frac{1}{2} (\phi_2 - \phi_3 - \phi_6 + \phi_7) \\ \quad \quad \frac{1}{\sqrt{2}} (\phi_9 - \phi_{10}) \end{array}$$

$$A_u : \frac{1}{2} (\phi_1 - \phi_4 + \phi_5 - \phi_8)$$

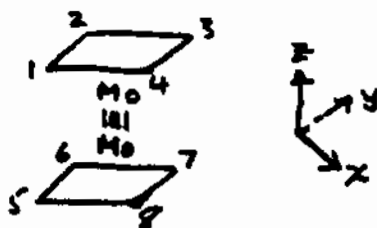
$$a \quad \frac{1}{2} (\phi_2 - \phi_3 + \phi_6 - \phi_7)$$

$$B_{1u} : \frac{1}{2} (\phi_1 + \phi_4 + \phi_5 + \phi_8)$$

$$\frac{1}{2} (\phi_2 + \phi_3 + \phi_6 + \phi_7)$$

$$\frac{1}{\sqrt{2}} (\phi_9 + \phi_{10})$$

2. The $\text{Mo}_2\text{X}_8^{4-}$ ion has the form of a square parallelipiped with the Mo-Mo unit along the z axis. The point group is D_{4h} . We shall use the following numbering scheme and coordinate system:



The eight σ orbitals form the basis for a reducible representation:

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ	8	0	0	0	0	0	0	0	4	0

$$\Gamma = A_{1g} + B_{1g} + E_g + A_{2u} + B_{2u} + E_u$$

The expressions for the SALCs can be obtained by the systematic application of the projection operators. However, with the results for PtCl_4^{2-} in hand, they can be written down more easily.

If we take two functions, one on each end of the molecule, that are totally symmetric to C_4 , C_2 , σ_v and σ_d they must belong to A_{1g} or A_{2u}

representations. If we combine them first with a plus sign and then with a minus sign, we must have an A_{1g} function in the first case, and an A_{2u} function in the second, since this will give the proper behavior under all the operations that move basis functions from one end to the other (i.e., i , C_2' , C_2'' , S_4 and σ_h):

$$\psi_{A_{1g}} = \frac{1}{\sqrt{8}} [(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) + (\sigma_5 + \sigma_6 + \sigma_7 + \sigma_8)]$$

$$\psi_{A_{2u}} = \frac{1}{\sqrt{8}} [(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) - (\sigma_5 + \sigma_6 + \sigma_7 + \sigma_8)]$$

Similarly, we take the B_{1g} function from $PtCl_4^{2-}$, write one of that type for each end of the molecule and combine them with a + sign or a - sign to get the B_{1g} and B_{2u} SALCs, respectively.

$$\psi_{B_{1g}} = \frac{1}{\sqrt{8}} [(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4) + (\sigma_5 - \sigma_6 + \sigma_7 - \sigma_8)]$$

$$\psi_{B_{2u}} = \frac{1}{\sqrt{8}} [(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4) - (\sigma_5 - \sigma_6 + \sigma_7 - \sigma_8)]$$

Finally, we proceed the same way with pairs of E orbitals, obtaining:

$$\psi_{E_g} = \frac{1}{2} [(\sigma_1 - \sigma_3) + (\sigma_5 - \sigma_7)] \text{ and}$$

$$\frac{1}{2} [\sigma_2 - \sigma_4) + (\sigma_6 - \sigma_8)]$$

$$\psi_{E_u} = \frac{1}{2} [(\sigma_1 - \sigma_3) - (\sigma_5 - \sigma_7)] \text{ and}$$

$$\frac{1}{2} [\sigma_2 - \sigma_4) - (\sigma_6 - \sigma_8)].$$

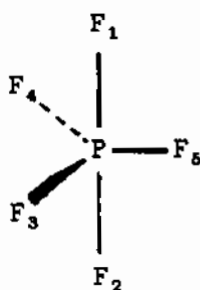
3. The representations and their breakdown into irreducible representations are as follows:

Γ_h	E	$12C_6$	$12C_6^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^3$	$20S_6$	15σ
Γ_{CH}	20	0	0	2	0	0	0	0	0	4
Γ_{CC}	30	0	0	0	2	0	0	0	0	4

$$\Gamma_{CH} = A_g + G_g + H_g + T_{1u} + T_{2u} + G_u$$

$$\Gamma_{CC} = A_g + G_g + 2H_g + T_{1u} + T_{2u} + G_u + H_u$$

4. The set of F atom σ orbitals, numbered as shown below, gives rise to the following representations in the group D_{3h} .



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_6$	$3\sigma_v$
Γ_{12}	2	2	0	0	0	2
Γ_{3-5}	3	0	1	3	0	1

$$\Gamma_{12} = A_1' + A_2''$$

$$\Gamma_{3-5} = A_1' + E'$$

The application of the projection operators is as follows:

$$\begin{aligned} \hat{P}^{A_1'}(\sigma_1) &= (1)\sigma_1 + (2)(1)\sigma_1 + 3(1)\sigma_2 + (1)\sigma_2 + 2(1)\sigma_2 + 3(1)\sigma_1 \\ &= 6\sigma_1 + 6\sigma_2 \approx \frac{1}{\sqrt{2}} (\sigma_1 + \sigma_2) \end{aligned}$$

$$\begin{aligned} \hat{P}^{A_2''}(\sigma_1) &= (1)\sigma_1 + (2)(1)\sigma_1 + 3(-1)\sigma_2 + (-1)\sigma_2 + 2(-1)\sigma_2 + 3(1)\sigma_1 \\ &= 6\sigma_1 - 6\sigma_2 \approx \frac{1}{\sqrt{2}} (\sigma_1 - \sigma_2) \end{aligned}$$

$$\begin{aligned}
\hat{P}^{A_1'}(\sigma_3) &= (1)\sigma_3 + (1)\sigma_4 + (1)\sigma_5 + (1)\sigma_3 + (1)\sigma_4 + (1)\sigma_5 \\
&\quad + (1)\sigma_3 + (1)\sigma_4 + (1)\sigma_5 + (1)\sigma_3 + (1)\sigma_4 + (1)\sigma_5 \\
&= 4\sigma_3 + 4\sigma_4 + 4\sigma_5 \approx \frac{1}{\sqrt{3}} (\sigma_3 + \sigma_4 + \sigma_5)
\end{aligned}$$

$$\begin{aligned}
\hat{P}^{E'}(\sigma_3) &= (2)\sigma_3 + (-1)\sigma_4 + (-1)\sigma_5 + (2)\sigma_3 + (-1)\sigma_4 + (-1)\sigma_5 \\
&= 4\sigma_3 - 2\sigma_4 - 2\sigma_5 \approx \frac{1}{\sqrt{6}} (2\sigma_3 - \sigma_4 - \sigma_5)
\end{aligned}$$

We now proceed as we did for the $E^* \pi$ orbitals of the cyclopropenyl groups, where a C_3 rotation converts this to

$$\frac{1}{\sqrt{6}} (2\sigma_4 - \sigma_5 - \sigma_3)$$

which then is made into a linear combination with the first one to yield

$$\frac{1}{\sqrt{6}} (\sigma_4 - \sigma_5)$$

5. A SALC for the A_{1g} representation must go into itself under every symmetry operation. It is obvious that it must be, in normalized form

$$= \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

To obtain a pair of E_g SALCs, we proceed as follows, employing the same coordinate system and numbering scheme used for the T_{1u} SALCs. We may also save unnecessary algebra by working with the characters for the E representation of group O and making sure later that our functions are symmetric to the operation i . Again, we must be sure to look at the action of every operation (not just every class) that has a non-zero character.

$$\hat{P}^E(\sigma_1) = (2)\sigma_1 + \underbrace{(2)(\sigma_1 + \sigma_2 + \sigma_2)}_{3C_2} + \underbrace{(-1)(\sigma_3 + \sigma_6 + \sigma_6 + \sigma_4 + \sigma_4 + \sigma_5 + \sigma_5 + \sigma_3)}_{8C_3}$$

E 3C₂ 8C₃

$$= 4\sigma_1 + 4\sigma_2 - 2\sigma_3 - 2\sigma_4 - 2\sigma_5 - 2\sigma_6 = 2\psi_1$$

$$\hat{P}^E(\sigma_3) = 4\sigma_3 + 4\sigma_4 - 2\sigma_1 - 2\sigma_2 - 2\sigma_5 - 2\sigma_6 = 2\psi_2$$

$$\hat{P}^E(\sigma_6) = 4\sigma_6 + 4\sigma_5 - 2\sigma_1 - 2\sigma_2 - 2\sigma_3 - 2\sigma_4 = 2\psi_3$$

These three functions can be combined into three simpler ones by three independent subtractions, i.e., $\psi_1 - \psi_2$ (ψ_{12}), $\psi_2 - \psi_3$ (ψ_{23}) and $\psi_3 - \psi_1$ (ψ_{31}):

$$\psi_{12} = \sigma_1 + \sigma_2 - \sigma_3 - \sigma_4$$

$$\psi_{23} = \sigma_3 + \sigma_4 - \sigma_5 - \sigma_6$$

$$\psi_{31} = \sigma_5 + \sigma_6 - \sigma_1 - \sigma_2$$

Now we have two problems. (a) There are three functions rather than two. (b) No two are orthogonal. Both of these problems are solved by combining any two, e.g.,

$$\psi_{12} - \psi_{31} = 2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6$$

This function is orthogonal to ψ_{23} . This pair of functions will give rise to the correct matrices for the E representation.

In normalized form, these functions are:

$$\frac{1}{\sqrt{12}} (2\sigma_1 + 2\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5 - \sigma_6)$$

$$\frac{1}{2} (\sigma_3 + \sigma_4 - \sigma_5 - \sigma_6)$$

One may also note that according to the character tables for O and O_h , the two d orbitals commonly labeled d_{z^2} and $d_{x^2-y^2}$ form a basis for the E (or E_g) representation. We could have obtained the SALCs by simply requiring a match to these d orbitals.

Chapter 7 - Answers

1. For C_4H_4 :

C_4	E	C_4	C_2	C_4^3
Γ_π	4	0	0	0

$$\Gamma_\pi = A + B + E$$

$$\left. \begin{aligned} \psi(A) &= \frac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4) \\ \psi(B) &= \frac{1}{2}(\phi_1 - \phi_2 + \phi_3 - \phi_4) \end{aligned} \right\} \begin{array}{l} \text{directly from} \\ \text{character table} \end{array}$$

For $\psi(E)$'s we get two functions directly, but to obtain real coefficients, we take the sum, and the difference divided by 1

$$\psi(E_a) \approx 2\phi_1 + (1-1)\phi_2 - 2\phi_3 + (-1+1)\phi_4$$

$$= \frac{1}{\sqrt{2}} (\phi_1 - \phi_3)$$

$$\psi(E_b) \approx [0\phi_1 + 2i\phi_2 + 0\phi_3 - 2i\phi_4]/1$$

$$= \frac{1}{\sqrt{2}} (\phi_2 - \phi_4)$$

To find the energies:

$$A: \int \psi(A) H \psi(A) d\tau = \frac{1}{4} (\int \phi_1 H \phi_1 d\tau + \int \phi_1 H \phi_2 d\tau + \text{etc.})$$

$$= \frac{1}{4} (4\alpha + 8\beta) = \alpha + 2\beta$$

$$B: \int \psi(B) H \psi(B) d\tau = \frac{1}{4} (\int \phi_1 H \phi_1 d\tau - \int \phi_1 H \phi_2 d\tau + \dots)$$

$$= \frac{1}{4} (4\alpha - 8\beta) = \alpha - 2\beta$$

$$\begin{aligned}
 E: \int \psi(E_a) H \psi(E_b) d\tau &= \frac{1}{2} (\int \phi_1 H \phi_1 d\tau - \int \phi_1 H \phi_3 d\tau \\
 &\quad - \int \phi_3 H \phi_1 d\tau + \int \phi_3 H \phi_3 d\tau) \\
 &= \frac{1}{2} (2\alpha) = \alpha
 \end{aligned}$$

For C_8H_8 , the procedure is analogous but requires the manipulation of the quantities

$$\begin{aligned}
 \epsilon &= \exp(2\pi i/8) = \cos 2\pi/8 + i \sin 2\pi/8 \\
 \epsilon^* &= \exp(-2\pi i/8) = \cos 2\pi/8 - i \sin 2\pi/8
 \end{aligned}$$

In doing the required additions and subtractions of coefficients required to obtain real coefficients for the E_1 , E_2 and E_3 orbitals, the quantities $\epsilon + \epsilon^*$ and $(\epsilon - \epsilon^*)/i$ will be obtained. These reduce to trigonometric functions and then to numerical values in the following way.

$$\begin{aligned}
 \epsilon + \epsilon^* &= 2\cos 2\pi/8 = 2\cos 45^\circ = 2/\sqrt{2} = \sqrt{2} \\
 (\epsilon - \epsilon^*)/i &= 2\sin 2\pi/8 = 2\sin 45^\circ = 2/\sqrt{2} = \sqrt{2}
 \end{aligned}$$

The derivation of the E_1 orbitals with real coefficients can be summarized as follows:

ϕ_1	ϕ_2	ϕ_3	ϕ_4	ϕ_5	ϕ_6	ϕ_7	ϕ_8
1	ϵ	1	$-\epsilon^*$	-1	$-\epsilon$	-i	ϵ^*
± 1	ϵ^*	-i	$-\epsilon$	-1	$-\epsilon^*$	i	ϵ
+ 2	$(\epsilon + \epsilon^*)$	0	$-(\epsilon + \epsilon^*)$	-2	$-(\epsilon + \epsilon^*)$	0	$\epsilon + \epsilon^*$
- 0	$(\epsilon - \epsilon^*)$	2i	$(\epsilon - \epsilon^*)$	0	$-(\epsilon - \epsilon^*)$	-2i	$-(\epsilon - \epsilon^*)$

For the + combination we substitute for $(\epsilon + \epsilon^*)$ and obtain

$$2 \quad \sqrt{2} \quad 0 \quad -\sqrt{2} \quad -2 \quad -\sqrt{2} \quad 0 \quad \sqrt{2}$$

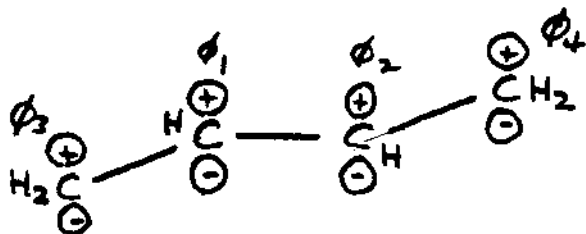
while for the - combination we substitute for $(\epsilon - \epsilon^*)$ and divide by i to obtain

$$0 \quad \sqrt{2} \quad 2 \quad \sqrt{2} \quad 0 \quad -\sqrt{2} \quad -2 \quad -\sqrt{2}$$

We then divide each of these sets by $\sqrt{2}$ and normalize to obtain the results in Table 7.1.

The energies are obtained straightforwardly.

2. trans-Butadiene:



Since the pairs (ϕ_1, ϕ_2) and (ϕ_3, ϕ_4) are not equivalent they must be used separately to form representations of C_{2h}

C_{2h}	E	C_2	i	h
Γ_{12}	2	0	0	-2
Γ_{34}	2	0	0	-2

$$\Gamma_{12} = \Gamma_{34} = B_g + A_u$$

$$\psi(B)^{12} = \frac{1}{\sqrt{2}} (\phi_1 - \phi_2)$$

$$\psi(B)^{24} = \frac{1}{\sqrt{2}} (\phi_3 - \phi_4)$$

$$\psi(A)^{12} = \frac{1}{\sqrt{2}} (\phi_1 + \phi_2)$$

$$\psi(A)^{34} = \frac{1}{\sqrt{2}} (\phi_3 + \phi_4)$$

To obtain the energies, two 2-dimensional secular equations must be set up:

$$\begin{vmatrix} H_{12}-E & H_{12,34} \\ H_{12,34} & H_{34}-E \end{vmatrix} = 0$$

For the B orbitals:

$$\begin{aligned} H_{12} &= \int \psi(B)^{12} H \psi(B)^{12} d\tau \\ &= \frac{1}{2} (\int \phi_1 H \phi_1 d\tau - 2 \int \phi_1 H \phi_2 d\tau + \int \phi_2 H \phi_2 d\tau) \\ &= \frac{1}{2} (2\alpha - 2\beta) = \alpha - \beta \end{aligned}$$

$$\begin{aligned} H_{34} &= \int \psi(B)^{34} H \psi(B)^{34} d\tau \\ &= \frac{1}{2} (\int \phi_3 H \phi_3 d\tau - 2 \int \phi_3 H \phi_4 d\tau + \int \phi_4 H \phi_4 d\tau) \\ &= \frac{1}{2} (2\alpha - 0) = \alpha \end{aligned}$$

[$\int \phi_3 H \phi_4 d\tau = 0$ because ϕ_3 and ϕ_4 are not on adjacent atoms.]

$$\begin{aligned} H_{12,34} &= \int \psi(B)^{12} H \psi(B)^{34} d\tau \\ &= \frac{1}{2} (\int \phi_1 H \phi_3 d\tau - \int \phi_1 H \phi_4 d\tau - \int \phi_2 H \phi_3 d\tau + \int \phi_2 H \phi_4 d\tau) \\ &= \frac{1}{2} (\beta - 0 - 0 + \beta) \\ &= \beta \end{aligned}$$

Substituting into the secular equation (with $\alpha = 0$ and β as the unit of energy):

$$\begin{vmatrix} -1 - E & 1 \\ 1 & -E \end{vmatrix} = 0$$

This gives the quadratic equation

$$E^2 + E - 1 = 0$$

In a similar way, we obtain the following secular equation for the A orbitals:

$$\begin{vmatrix} 1 - E & 1 \\ 1 & -E \end{vmatrix} = 0$$

$$E^2 - E - 1 = 0$$

The roots of these equations from the standard algebraic formula^{*} are

$$E_B = \frac{-1 \pm \sqrt{5}}{2}$$

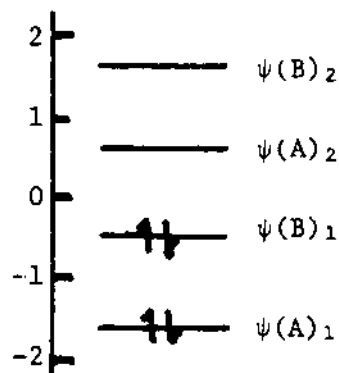
$$-1.62, 0.62$$

$$E_A = \frac{1 \pm \sqrt{5}}{2}$$

$$+1.62, -0.62$$

^{*}For $ax^2 + bx + c = 0$ $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

These results may be summarized
in an energy level diagram,
shown at right



The two most stable orbitals will each be doubly occupied giving a total energy of $2(1.62 + 0.62) = 4.48$. Since two localized bonding pairs of electrons would have an energy of 4.00, the delocalization energy is $4.48 - 4.00 = 0.48$.

To find the bond orders we must find the expressions for the occupied MO's, which are normalized combinations of the SALCs. The procedure has been illustrated in the text for tetramethylenecyclobutane and we give below a summary of the same steps as they apply to butadiene. For the occupied B_g orbitals:

$$c_{12}(H_{12} - E) + c_{34}H_{12,34} = 0 = c_{12}(-1-E) + c_{34}$$

$$c_{12}H_{12,34} + c_{34}(H_{34} - E) = 0 = c_{12} - c_{34}E$$

$$\frac{c_{12}}{c_{34}} = \frac{1}{E + 1} \quad \text{or } E$$

For the occupied B_g orbital the energy (remembering that β is intrinsically negative) is 0.62, which gives, either way

$$\frac{c_{12}}{c_{34}} = 0.62$$

If we solve this equation simultaneously with the normalization equation,

$$c_{12}^2 + c_{34}^2 = 1$$

we get

$$c_{12} = 0.52 \text{ and } c_{34} = 0.85$$

For the occupied A_u orbital

$$c_{12}(H_{12} - E) + c_{34}H_{12,34} = 0 = c_{12}(1-E) + c_{34}$$

$$c_{12}H_{12,34} + c_{34}(H_{34} - E) = 0 = c_{12} - c_{34}E$$

$$\frac{c_{12}}{c_{34}} = \frac{1}{E-1} \quad \text{or } E$$

$$= 1.62$$

$$c_{12} = 0.85 \text{ and } c_{34} = 0.52$$

For the wave functions of the two occupied MOs, we have finally:

$$\begin{aligned} \psi(B)_1 &= 0.52 \psi(B)^{12} + 0.85\psi(B)^{34} \\ &= 0.36 (\phi_1 - \phi_2) + 0.60 (\phi_3 - \phi_4) \end{aligned}$$

$$\begin{aligned} \psi(A)_1 &= 0.85 \psi(A)^{12} + 0.52\psi(A)^{34} \\ &= 0.60 (\phi_1 + \phi_2) + 0.36 (\phi_3 + \phi_4) \end{aligned}$$

We come now to our final task, the calculation of the bond orders.

Since those for $C_1 - C_3$ and $C_2 - C_4$ are the same, we compute only the former.

$C_1 - C_3$ Bond order:

$$\psi(A)_1: 2 \times (0.60)(0.36) = 0.44$$

$$\psi(B)_1: 2 \times (0.36)(0.60) = \frac{0.44}{0.88}$$

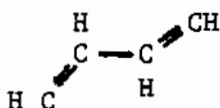
$C_1 - C_2$ Bond order:

$$\psi(A)_1: 2 \times (0.60)(0.60) = 0.72$$

$$\psi(B)_1: 2 \times (0.36)(-0.36) = \underline{-0.26}$$

$$0.46$$

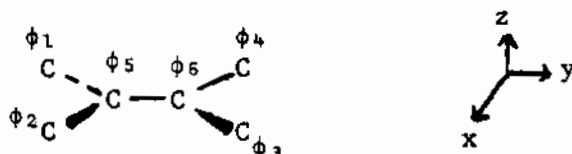
Thus, we see that the simplest way of representing butadiene,



neglects the delocalization of π electrons into the region between the two inner atoms.

3. Each of the molecules shown must be treated in the same way as was butadiene. There are 2 or more sets of non-equivalent atoms, and the SALCs must be constructed for each set. Then, the secular equations must be set up and solved to obtain the total π -electron energy, from which the delocalization energy is obtained. Finally, the coefficients required to combine the SALCs into actual MOs must be found so that the bond orders can be calculated.

4. Again we have two non-equivalent sets of orbitals, as shown



The symmetry is D_{2h} and the representations are:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	1	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ_{1234}	4	0	0	0	0	-4	0	0
Γ_{56}	2	0	-2	0	0	-2	0	2

$$\Gamma_{1234} = B_{2g} + B_{3g} + A_u + B_{1u}$$

$$\Gamma_{56} = B_{3g} + B_{1u}$$

$$B_{2g}: \psi_{B_{2g}} = \frac{1}{2}(\phi_1 - \phi_2 - \phi_3 - \phi_4)$$

$$B_{3g}: \psi_{B_{3g}}^o = \frac{1}{2}(\phi_1 + \phi_2 - \phi_3 - \phi_4)$$

$$\psi_{B_{3g}}^1 = \frac{1}{\sqrt{2}}(\phi_5 - \phi_6)$$

$$A_u: \psi_{A_u} = \frac{1}{2}(\phi_1 - \phi_2 + \phi_3 - \phi_4)$$

$$B_{1u}: \psi_{B_{1u}}^o = \frac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4)$$

$$\psi_{B_{1u}}^1 = \frac{1}{\sqrt{2}}(\phi_5 + \phi_6)$$

To find the energies we set up the secular equations. For the unique B_{2g} and A_u orbitals, these are simple linear equations:

$$E_{B_{2g}} = \frac{1}{4} \int (\phi_1 - \phi_2 - \phi_3 + \phi_4) H (\phi_1 - \phi_2 - \phi_3 + \phi_4) d\tau$$

$$= \alpha$$

$$E_{A_u} = \alpha$$

For the B_{3g} and B_{1u} cases we have quadratic secular equations of the general form

$$\begin{vmatrix} H_{oo} - E & H_{oi} \\ H_{oi} & H_{ii} - E \end{vmatrix} = 0$$

The various matrix elements are:

	B_{3g}	B_{1u}
H_{oo}	α	α
H_{ii}	$\alpha - \beta$	$\alpha + \beta$
H_{oi}	$\sqrt{2}\beta$	$\sqrt{2}\beta$

When we set $\alpha = 0$ and make β the unit of energy, the two secular equations and their roots are:

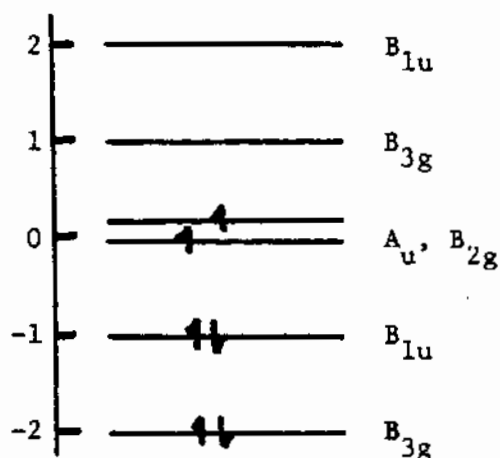
$$B_{3g}: E^2 + E - 2$$

$$E = +1, -2$$

$$B_{1u}: E^2 - E - 2$$

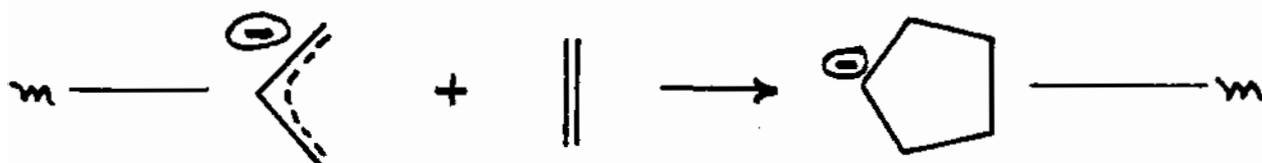
$$E = -1, +2$$

All of these results may be presented in the form of an energy level diagram:

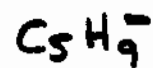
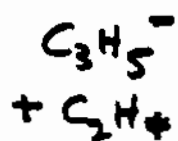
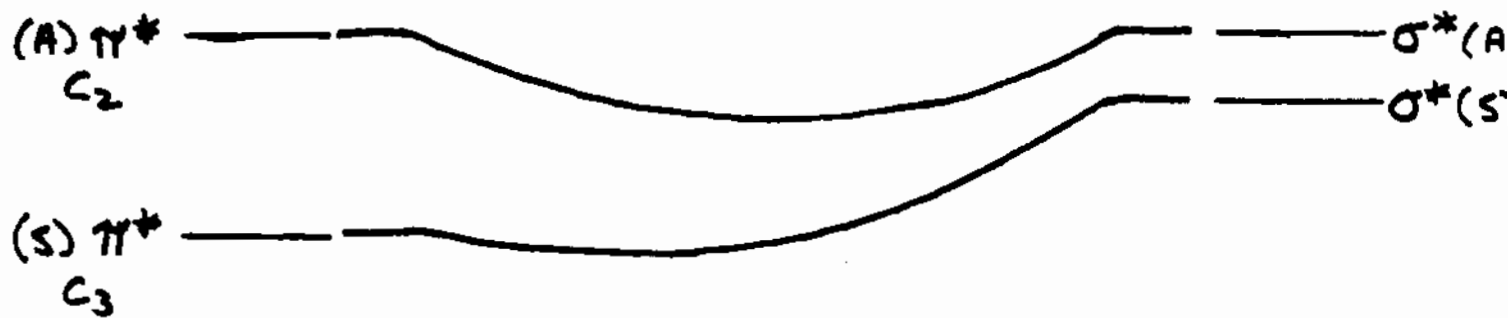


Clearly, in the Huckel approximation, accidental degeneracy of the A_u and B_{2g} orbitals leads to the prediction that the molecule is a diradical with the unpaired electrons delocalized on the outer carbon atoms only. The delocalization energy is found to be $6\beta - 6\beta = 0$. To see how accurate these predictions are, the student should consult the reference cited.

5. For this reaction we can draw the diagrams below, showing the orbitals as being either S (symmetric) or A (antisymmetric) with respect to the mirror plane. Note that we

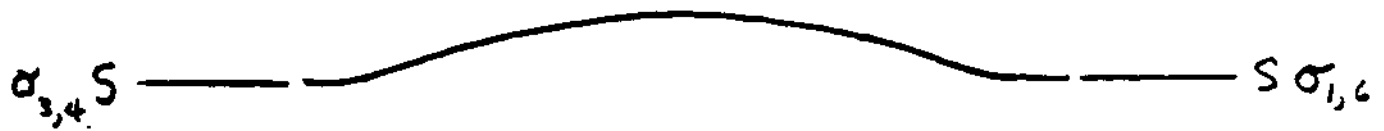
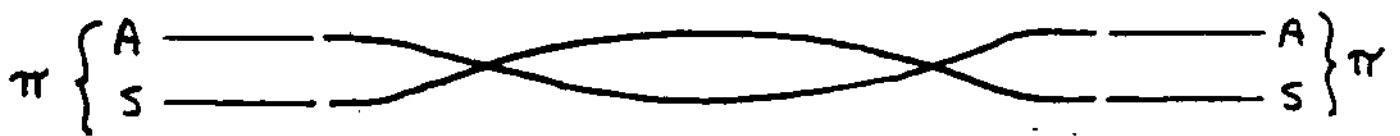
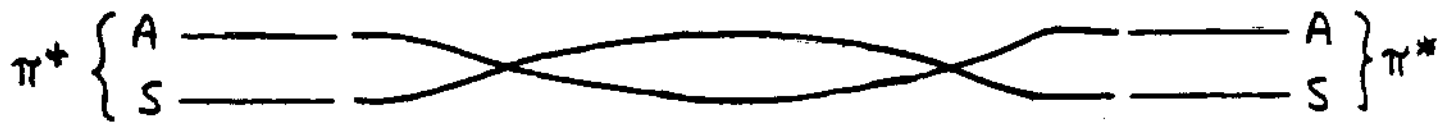


put the σ orbitals well below π and σ^* well above π^* . The lone pair orbital of the product and the non-bonding π orbital of the allyl anion are placed at ~ 0 in energy.



6. For the Cope rearrangement we draw the energy level diagrams shown below. At the left is the set of levels for the starting molecule. The most stable orbital of interest is the σ bonding orbital, σ_{34} , and the next two of interest are the two π bonding orbitals. All these are filled. Further up we have the π^* and σ^* orbitals, which are vacant. The members of the pairs of π and π^* orbitals do not interact with each other very strongly, but still, they will form symmetric (S) and antisymmetric (A) combinations. The σ bonding orbital is, of course symmetric with respect to the mirror plane, while the σ^* orbital is antisymmetric. For the product molecule the energy level diagram is the same, except for the numbering of atoms.

It can be seen that the two diagrams can be connected, ground state to ground state, without mixing any bonding and antibonding orbitals. Hence, the Cope rearrangement is thermally allowed.



Chapter 8

1. The answers are given in the book.
2. The solution begins with the representation given by the four sigma orbitals, σ_1 , σ_2 , σ_3 and σ_4 .



D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$
Γ_σ	4	0	0	0	2

$$\Gamma_\sigma = A_1 + B_2 + E$$

Since the properties of the SALCs are essentially dependent on the main rotational symmetry about the z axis, we can use the representations of the group S_4 to write them by inspection. We can take linear combinations of the two components of the E representation to eliminate the imaginary coefficients.

$$\psi(Ea) \approx \sigma_1 + i\sigma_2 - \sigma_3 - i\sigma_4$$

$$\psi(Eb) \approx \sigma_1 - i\sigma_2 - \sigma_3 + i\sigma_4$$

$$\psi(Ea) + \psi(Eb) = 2\sigma_1 - 2\sigma_3$$

$$[\psi(Ea) - \psi(Eb)]/i = 2\sigma_2 - 2\sigma_4$$

The final results are:

Irred.	At. Orbs.	SALCs on B atoms
Reps.	on M	
A_1	s, d_{z^2}	$\frac{1}{2} (\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$
B_2	p_z , d_{xy}	$\frac{1}{2} (\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$
E	(p_x, p_y) , (d_{xz}, d_{yz})	$\frac{1}{2} (\sigma_1 - \sigma_3)$ and $\frac{1}{2} (\sigma_2 - \sigma_4)$

3. The left side of the diagram (page 45) shows the metal orbitals according to their relative energies, $d < s < p$. The ligand orbitals may be assumed to have an energy comparable to the energies of the metal d and s orbitals.

The A_1 SALC may interact with both the s and the d_{z^2} orbitals, giving three MOs. Since the molecule is nearly flat, the B_2 SALC may be expected to interact strongly with d_{xy} and only weakly with p_z . The interaction with p_z is also disfavored by the large energy difference.

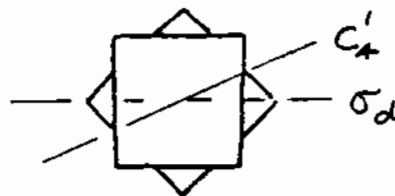
The E SALC will overlap best with p_x, p_y but the energy difference is large. On the other hand, the d_{xz} and d_{yz} orbitals, while close in energy are not as well directed unless the ligands are well out of the median xy plane. Probably both sets of metal E type orbitals will make some contribution to M-X σ bonding.

Finally, the $d_{x^2-y^2}$ orbital has the wrong symmetry to participate in any σ interaction. The diagram will therefore be approximately as shown on page 45.

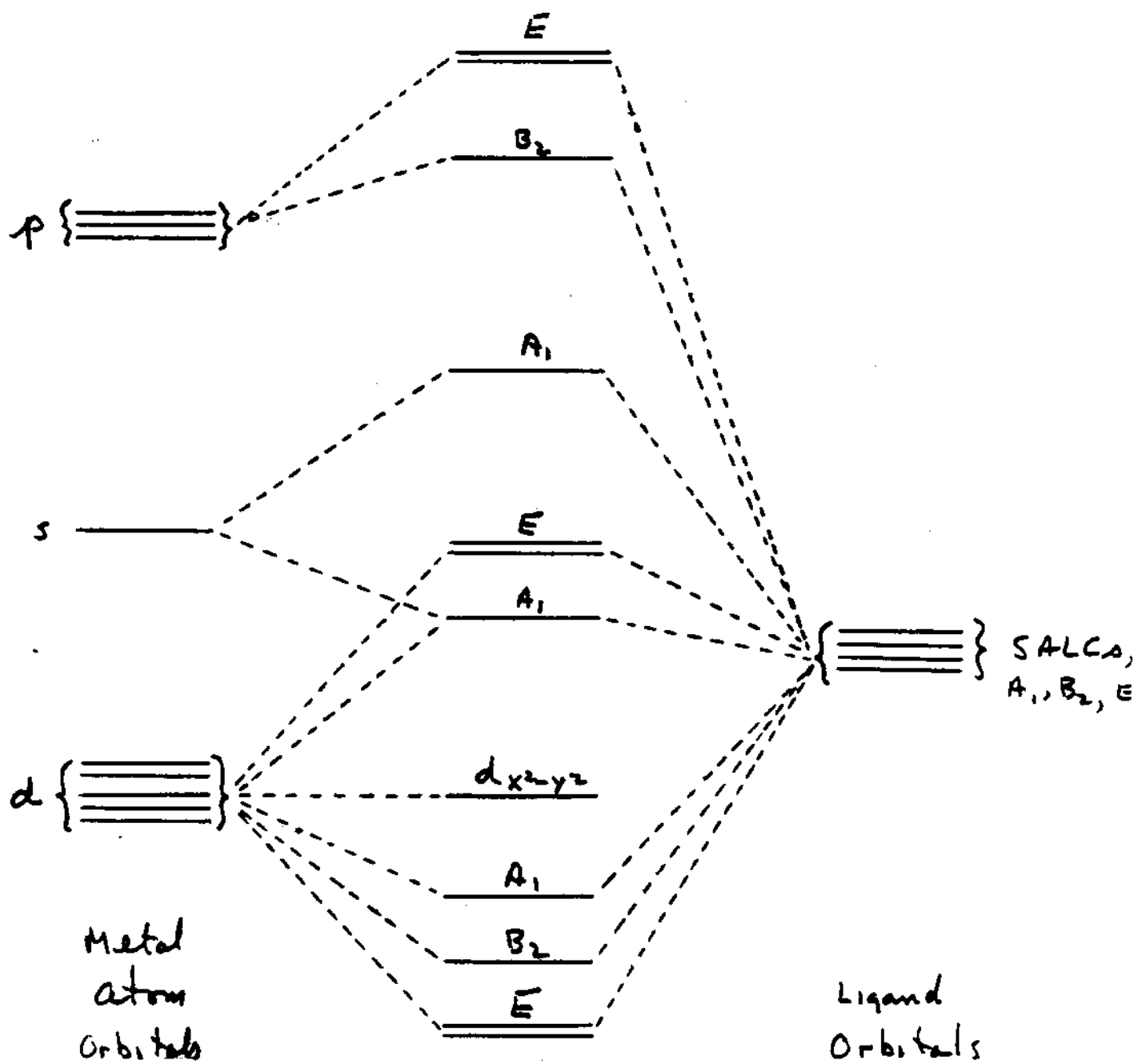
4. The square antiprism has D_{4d} symmetry, as shown in the sketch below. The view is down the z axis and the locations of one C_2 and one σ_d are indicated

D_{4d}	E	$2S_8$	$2C_4$	$2S_8^3$	C_2	$4C_2'$	$4\sigma_d$
Γ_σ	8	0	0	0	0	0	0

$$\Gamma_\sigma = A_1 + B_2 + E_1 + E_2 + E_3$$



The information given at the right of the D_{4d} character table shows that there are atomic orbitals belonging to each of the required

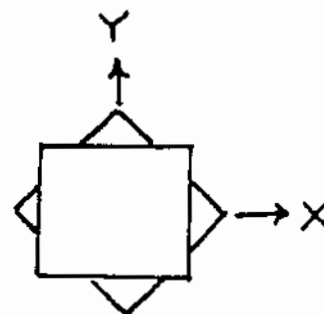


representations. For A_1 there are, actually, two atomic orbitals, \underline{s} and d_{z^2} . The shape of the \underline{s} orbital is better suited to reach the vertices of the square antiprism, so the best hybridization would be sp^3d^4 (with d_{z^2} absent) although p^3d^5 is compatible with symmetry restrictions.

5. For the capped square antiprism the answer is immediately obvious from the result already obtained in problem 3 for the square antiprism itself. If we use the sp^3d^4 hybrids to reach the eight atoms at the vertices of the distorted square antiprism, the d_{z^2} orbital is well suited to bind the additional atom along the z axis.

Of course, one could treat the problem ab initio, by employing the C_{4v} symmetry of the capped square antiprism, with the following results:

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
$\Gamma_{\sigma}^{\text{total}}$	9	1	1	3	3
$\Gamma_{\sigma}^{\text{ax}}$	1	1	1	1	1
$\Gamma_{\sigma}^{\text{upper}}$	4	0	0	0	2
$\Gamma_{\sigma}^{\text{lower}}$	4	0	0	2	0



Note that there are now three non-equivalent sets of bonds and that the location of the X and Y axes must be consistent with that implied by the character table, namely, to have the σ_v 's coincide with the axes.

$$\Gamma_{\sigma}^{\text{ax}} = A_1$$

$$\Gamma_{\sigma}^{\text{upper}} = A_1 + B_2 + E$$

$$\Gamma_{\sigma}^{\text{lower}} = A_1 + B_1 + E$$

Inspection of the C_{4v} character table shows that there are three A_1 orbitals (\underline{s} , \underline{p}_z , \underline{d}_{z^2}), a B_1 orbital ($\underline{d}_{x^2-y^2}$), a B_2 orbital (\underline{d}_{xy}) and two

sets of E orbitals ($p_x, p_y; d_{xz}, d_{yz}$). The end result is thus entirely consistent with that obtained by considering the capped figure to be a "perturbation" of the uncapped one.

For the tricapped trigonal prism, we turn to group D_{3h} . The nine bonds clearly belong to two subsets, namely those to prism vertices (p) and those to capping vertices (c)

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{\sigma}^{\text{total}}$	9	0	1	3	0	3
$\Gamma_{\sigma}^{\text{P}}$	6	0	0	0	0	2
$\Gamma_{\sigma}^{\text{C}}$	3	0	1	3	0	1

$$\Gamma_{\sigma}^{\text{P}} = A_1' + A_2'' + E' + E''$$

$$\Gamma_{\sigma}^{\text{C}} = A_1' + E'$$

Inspection of the character table shows that the available orbitals are as follows:

$$A_1': s, d_{z^2}$$

$$A_2'': p_z$$

$$E': (p_x, p_y), (d_{x^2-y^2}, d_{xy})$$

$$E'': (d_{xz}, d_{yz})$$

Again, a full set of bonds can be formed by using sp^3d^5 hybrids.

6. We first work out the π MOs on the planar C_4H_6 group. Its full symmetry is D_{3h} , but this will be reduced to no more than C_{3v} in $C_4H_6Fe(CO)_3$. For practical purposes, we can work with C_3 to get the desired information. From the outer three $p\pi$ orbitals we get A and E MOs

of the familiar form (Cf. cyclopropenyl radical)

$$\psi_A^0 = \frac{1}{\sqrt{3}} (\phi_1 + \phi_2 + \phi_3) \quad E = 0$$

$$\psi_E^0 = \left\{ \begin{array}{l} \frac{1}{\sqrt{6}} (2\phi_1 - \phi_2 - \phi_3) \\ \frac{1}{\sqrt{2}} (\phi_2 - \phi_3) \end{array} \right\} \quad E = 0$$

The energies are set equal to zero since there is no direct bonding between any pair of these orbitals (or so it is assumed). The $p\pi$ orbital of the inner carbon atom has A symmetry, with an energy of 0. The secular equation for the A MOs of the complete C_4H_8 unit is

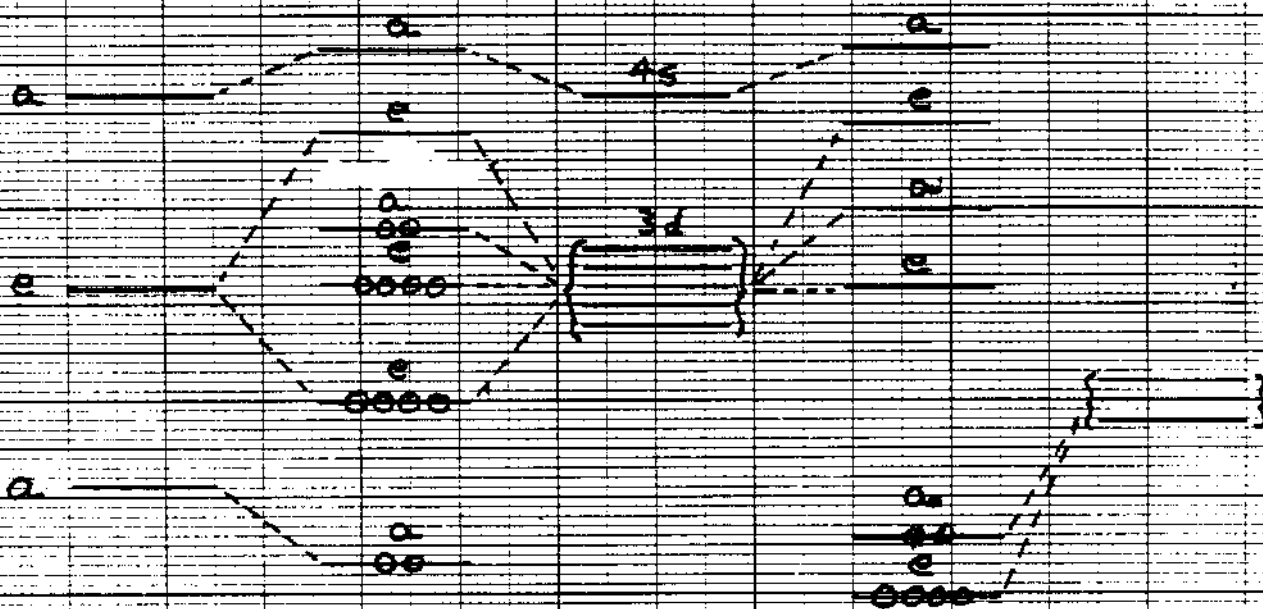
$$\begin{vmatrix} -E & \sqrt{3}\beta \\ \sqrt{3}\beta & -E \end{vmatrix} = 0$$

$$E^2 - 3\beta^2 = 0$$

$$E = \pm \sqrt{3}\beta$$

We now proceed in the same way as we did with $(C_6H_6)Cr(CO)_3$ (although here the symmetry arguments can be rigorous. This results in the qualitative diagram given on page 49. Note that the same qualitative diagram will be obtained regardless of the rotational relationship of the C_4H_8 group to the $Fe(CO)_3$ group. In the gas phase, electron diffraction showed a staggered relationship (Cf. A. Almendinger, A. Haaland and K. Wahl, Acta Chem. Scand., 1969, 23, 1145).

4p



C_4H_6

Fe

CO or
 $Sulfur$

Chapter 9

1. We first take the direct product $t_{2g} \times t_{2g}$ and list the resulting states and their possible multiplicities. We then list below the breakdown of each of these states in O_h into their states when the symmetry is lowered to C_{2v}

A_{1g}	E_g	T_{1g}	T_{2g}
1	1	1	3
1	1	3	1
3	3	1	1
A_1	A_1	A_2	A_1
	A_2	B_1	B_1
		B_2	B_2

Since t_{2g} goes over to $a_1 + b_1 + b_2$ in C_{2v} , we next take six direct products of these:

$$a_1 \times a_1 = A_1$$

$$a_1 \times b_1 = B_1$$

$$a_1 \times b_2 = B_2$$

$$b_1 \times b_1 = A_1$$

$$b_1 \times b_2 = A_2$$

$$b_2 \times b_2 = A_1$$

All the A_1 states must be 1A_1 because they all arise by placing two electrons in the same orbital. This completely solves the problem by requiring that we have $^1A_{1g}$, 1E_g and $^1T_{2g}$ states in O_h and thus a $^3T_{1g}$ state.

2. For T_d we again have two problems of spin multiplicity assignment to make. For the e^2 configuration we have the following alternatives:

A_1	A_2	E	
3	1	1	} possible spin multiplicities
1	3	1	
A_1	A_2	A_1	
		A_2	

We may choose C_{2v} as our lower symmetry and this leads to the states shown below each of the T_d symmetries. The direct product representations for the individual orbitals in C_{2v} are:

$$a_1 \times a_1 = A_1$$

$$a_1 \times a_2 = A_2$$

$$a_2 \times a_2 = A_1$$

Since both A_1 states must be 1A_1 because they arise from doubly occupied orbitals, the solution to the spin multiplicity problem for the states arising from e^2 is 1A_1 , 3A_2 , 1E .

For the t_2^2 problem, the critical considerations are summarized compactly as follows:

States from $t_2 \times t_2$	A_1	E	T_1	T_2
possible spin multiplicity assignments	1	1	1	3
	1	1	3	1
	3	3	1	1
Corresponding representations in C_{2v}	A_1	A_1	A_2	A_1
		A_2	B_1	B_1
			B_2	B_2

Clearly the solution follows here exactly as it did in problem 1 discussed above.

3. We can idealize the symmetry of trans- $[\text{Coen}_2\text{Cl}_2]^+$ as D_{4h} . The character table tells us that R_z belongs to the A_{2g} representation and (R_x, R_y) to the E_g representation. We have to see whether any of the three types of electronic transition, namely, from the $^1A_{1g}$ ground state to excited states of symmetries A_{2g} , B_{2g} and E_g are active as a result of the magnetic dipole mechanism. We are, in effect, asking if any of the appropriate integrals, i.e., $\int \psi'_e R_z \psi_e dr$ and $\int \psi'_e R_{x,y} \psi_e dr$ are non-vanishing. This means that the direct products of the symmetry species of the integrands must be, or contain, the A_{1g} representation.

Since the ground state is of A_{1g} symmetry, we ask whether any of the excited state symmetries gives a suitable direct product with either R_z or (R_x, R_y) . The results are as follows:

For R_z :

$$A_{2g} \times A_{2g} = A_{1g}$$

$$A_{2g} \times B_{2g} = B_{1g}$$

$$A_{2g} \times E_g = E_g$$

For (R_x, R_y) :

$$E_g \times A_{2g} = E_g$$

$$E_g \times B_{2g} = E_g$$

$$E_g \times E_g = A_{1g} + A_{2g} + B_{1g} + B_{2g}$$

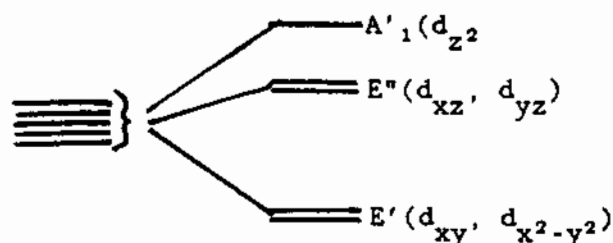
Thus, we see that the selection rules are as summarized in the following table:

Transition	Magnetic Polarization		Observed Polarization	
	Z	X,Y	Z	X,Y
$A_{1g} \rightarrow A_{2g}$	allowed	forbidden	absent	present
$A_{1g} \rightarrow B_{2g}$	forbidden	forbidden	present	present
$A_{1g} \rightarrow E_g$	forbidden	allowed	present	present

If the reader will refer to the discussion in Sec. 9.6 of the assignments of the observed bands, it will be clear that these predictions are in almost total disagreement with the observations (in particular, for the $A_{1g} \rightarrow A_{2g}$ transition, exactly reversed), and this leaves only the vibronic mechanism as acceptable.

4. As the D_{3h} character table shows, the d orbitals span the following representations: $d_{z^2}(A'_1)$, d_{xy} , $d_{x^2-y^2}(E')$, and d_{xz} , $d_{yz}(E'')$.

On the basis of a pure crystal field model, the d_{z^2} orbital must be highest since it has amplitude in both the z and x,y directions. The d_{xz} and d_{yz} orbitals do not point directly at any ligands and thus lie lowest. The splitting diagram will thus have the following qualitative character:



5. The extreme left side of the diagram will start with the same arrangement of free ion states shown in Figs. 9.3 and 9.4. They will split into states that can be identified by taking those given in Fig. 9.3 for O_h and using the Correlation Table, Appendix IIB.

At the extreme right, in the strong field limit we will have a set of configurations based on the various ways the electrons may occupy the $(d_{xy}, d_{x^2-y^2})$ orbitals ($1e_g$) the d_{z^2} orbital (a_{1g}) and the (d_{xz}, d_{yz}) orbitals ($2e_g$). In view of the assumed energy differences the order of the energies of the possible configurations is unambiguous. Moreover, the direct products allow us to obtain the following results:

Relative Energy

0	$1e_g \times 1e_g = {}^3A_{1g} + {}^1A_{2g} + {}^1E_g$ or ${}^1A_{1g} + {}^3A_{2g} + {}^1E_g$
E_2	$1e_g \times a_{1g} = {}^1E_g + {}^3E_g$
$2E_2$	$a_{1g} + a_{1g} = {}^1A_{1g}$
$4E_2$	$1e_g \times 2e_g = {}^1A_{1g} + {}^3A_{1g} + {}^1A_{2g} + {}^3A_{2g} + {}^1E_g + {}^3E_g$
$5E_2$	$a_{1g} \times 2e_g = {}^1E_g + {}^3E_g$
$6E_2$	$2e_g \times 2e_g = {}^3A_{1g} + {}^1A_{2g} + {}^1E_g$ or ${}^1A_{1g} + {}^3A_{1g} + {}^1E_g$

We have only one type of spin multiplicity ambiguity to resolve, although it occurs twice. We may use the method of descending symmetry by turning to C_{2v} as a subgroup of D_{3d} . following the usual layout, we have

$$e_g \times e_g = A_{1g} + A_{2g} + E_g$$

possible	{	3	1	1
spins		1	3	1

$$C_{2v} \left\{ \begin{array}{lll} A_1 & A_2 & A_1 \\ & & A_2 \end{array} \right.$$

representations

with the direct products in C_{2v} being

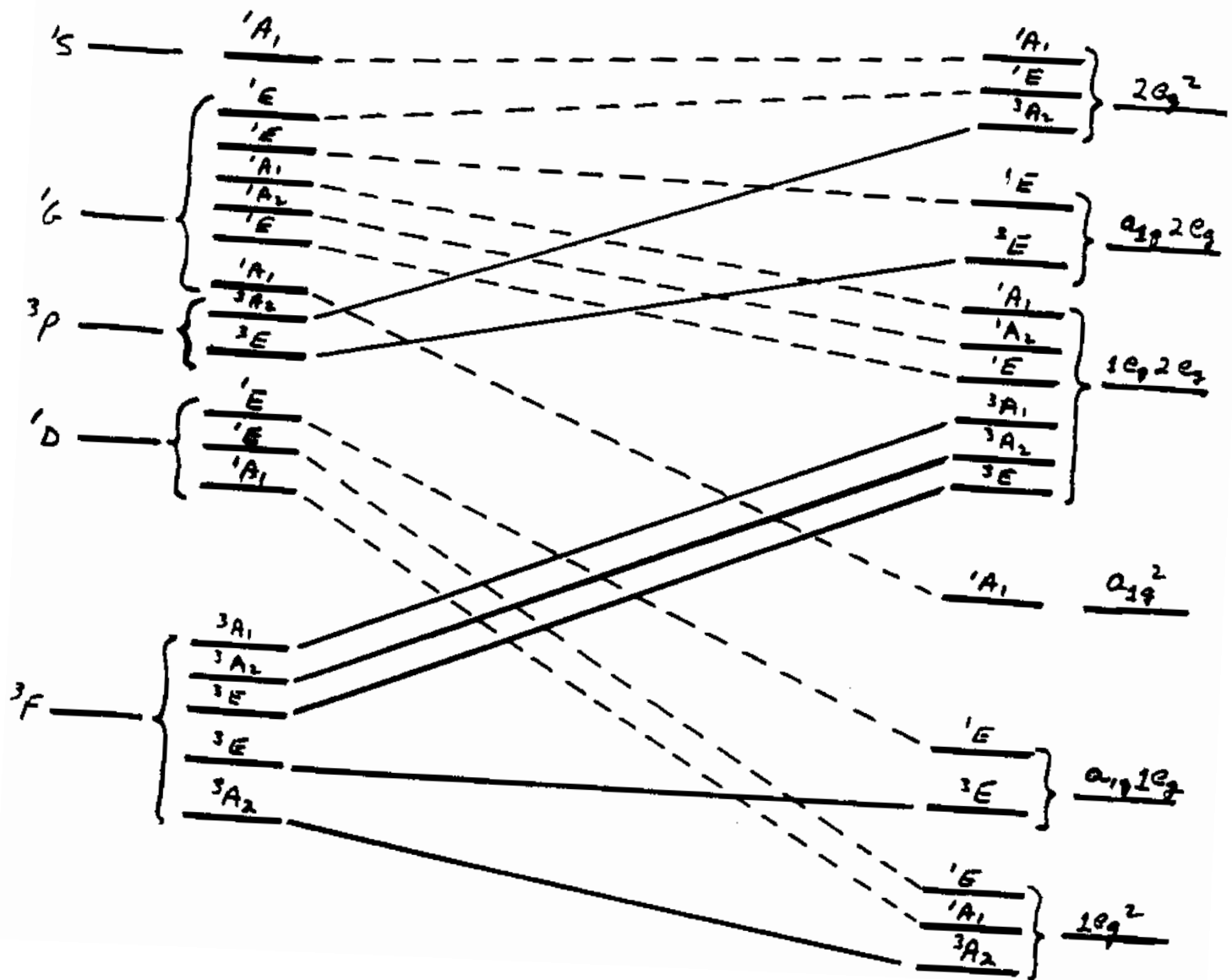
$$a_1 \times a_1 = {}^1A_1$$

$$a_2 \times a_2 = {}^1A_1$$

$$a_1 \times a_2 = {}^1A_2 + {}^3A_2$$

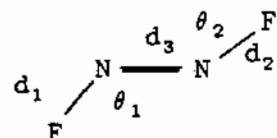
which shows us that the correct assignment in D_{3d} is ${}^1A_{1g} + {}^3A_{2g} + {}^1E_g$.

We are now able to draw connecting lines and thus obtain the diagram on the next page.



Chapter 10

1. The internal coordinates that come into play for the in-plane vibrations are the three bond lengths and two angles:



The molecule belongs to point group C_{2h} , with the z axis perpendicular to the molecular plane.

The symmetry types of the vibrations may be determined as follows:

C_{2h}	E	C_2	i	σ_h	
$\Delta d_1, \Delta d_2$	2	0	0	2	$= A_g + B_u$
$\Delta \theta_1, \Delta \theta_2$	2	0	0	2	$= A_g + B_u$
Δd_3	1	1	1	1	$= A_g$

It is obvious by inspection that the symmetry coordinates are:

$$A_g: S_1 = \frac{1}{\sqrt{2}}(\Delta d_1 + \Delta d_2)$$

$$S_2 = \frac{1}{\sqrt{2}}(\Delta \theta_1 + \Delta \theta_2)$$

$$S_3 = \Delta d_3$$

$$B_u: S_4 = \frac{1}{\sqrt{2}}(\Delta d_1 - \Delta d_2)$$

$$S_5 = \frac{1}{\sqrt{2}}(\Delta \theta_1 - \Delta \theta_2)$$

We therefore will have 3 x 3 matrices for the A_g modes and 2 x 2 matrices for the B_u modes. We shall use the following f matrix, where we include interaction constants for Δd_1 with Δd_2 , for Δd_1 and Δd_2 with Δd_3 , and $\Delta \theta_1$ with $\Delta \theta_2$.

	Δd_1	Δd_2	Δd_3	$\Delta \theta_1$	$\Delta \theta_2$
Δd_1	f_{NF}	$f_{NF,NF}$	$f_{NF,NN}$	0	0
Δd_2	$f_{NF,NF}$	f_{NF}	$f_{NF,NN}$	0	0
Δd_3	$f_{NF,NN}$	$f_{NF,NN}$	f_{NN}	0	0
$\Delta \theta_1$	0	0	0	f_θ	$f_{\theta\theta'}$
$\Delta \theta_2$	0	0	0	$f_{\theta\theta'}$	f_θ

The U matrix, based on the above symmetry coordinates is:

	d_1	d_2	d_3	θ_1	θ_2
S_1	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0	0	0
S_2	0	0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$
S_4	0	0	1	0	0
S_4	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	0	0	0
S_5	0	0	0	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$

To obtain the F matrix the transform UfU' must be carried out. Let us begin with fU' , where

$$U' = \begin{bmatrix} \frac{1}{\sqrt{2}} & 0 & 0 & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & 0 & 0 & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & 0 & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{2}} & 0 & 0 & -\frac{1}{\sqrt{2}} \end{bmatrix}$$

$$f_{U'} = \begin{bmatrix} \frac{1}{\sqrt{2}}f_{NF} + \frac{1}{\sqrt{2}}f_{NF,NF} & 0 & f_{NF,NN} \\ \frac{1}{\sqrt{2}}f_{NF,NF} + \frac{1}{\sqrt{2}}f_{NF} & 0 & f_{NF,NN} \\ \frac{1}{\sqrt{2}}f_{NF,NN} + \frac{1}{\sqrt{2}}f_{NF,NN} & 0 & f_{NN} \\ 0 & \frac{1}{\sqrt{2}}f_{\theta} + \frac{1}{\sqrt{2}}f_{\theta\theta'} & 0 \\ 0 & \frac{1}{\sqrt{2}}f_{\theta} + \frac{1}{\sqrt{2}}f_{\theta\theta'} & 0 \end{bmatrix}$$

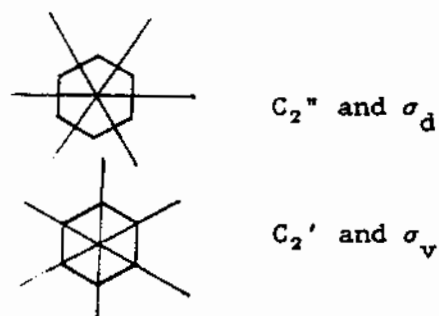
$$\begin{bmatrix} \frac{1}{\sqrt{2}}f_{NF} - \frac{1}{\sqrt{2}}f_{NF,NF} & 0 \\ \frac{1}{\sqrt{2}}f_{NF,NF} - \frac{1}{\sqrt{2}}f_{NF} & 0 \\ \frac{1}{\sqrt{2}}f_{NF,NN} - \frac{1}{\sqrt{2}}f_{NF,NN} & 0 \\ 0 & \frac{1}{\sqrt{2}}f_{\theta} - \frac{1}{\sqrt{2}}f_{\theta\theta'} \\ 0 & \frac{1}{\sqrt{2}}f_{\theta\theta'} - \frac{1}{\sqrt{2}}f_{\theta} \end{bmatrix}$$

$$U f_{U'} = \begin{bmatrix} f_{NF} + f_{NF,NF} & 0 & \frac{2}{\sqrt{2}}f_{NF,NN} & 0 & 0 \\ 0 & f_{\theta} + f_{\theta\theta'} & 0 & 0 & 0 \\ \frac{2}{\sqrt{2}}f_{NF,NN} & 0 & f_{NN} & 0 & 0 \\ 0 & 0 & 0 & f_{NF} - f_{NF,NF} & 0 \\ 0 & 0 & 0 & 0 & f_{\theta} - f_{\theta\theta'} \end{bmatrix}$$

2. (a) The symmetry types for all genuine vibrations are obtained by first employing a set of x, y, z displacement vectors on each atom (36 altogether) to give a representation, as shown for Γ_T :

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
Γ_T	36	0	0	0	-1	0	0	0	0	12	0	4
Γ_{CH}	6	0	0	0	2	0	0	0	0	6	0	2
Γ_{CC}	6	0	0	0	0	2	0	0	0	6	2	0
T_g	6	0	0	0	-2	0	0	0	0	-6	0	2

It is to be noted that we have chosen the C_2' , C_2'' , σ_v and σ_d operations as follows:



When Γ_T is reduced we get

$$\Gamma_T = 2A_{1g} + 2A_{2g} + 2B_{2g} + 2E_{1g} + 4E_{2g} + 2A_{2u} + 2B_{1u} + 2B_{2u} + 4E_{1u} + 2E_{2u}$$

Inspection of the character table shows that the translations and rotations account for $A_{2g} + E_{1g} + A_{2u} + E_{1u}$, so these must be struck from the list to get the genuine vibrations.

(b) The activities of the genuine vibrations are obtained simply by looking at the character table. Those representations to which z, or (x,y) belong are infrared-active and those to which the quadratic functions belong are Raman-active. The rest are inactive. The results for benzene

are:

$$\text{Ir-active: } A_{2u} + 3E_{1u}$$

$$\text{Raman-active: } 2A_{1g} + E_{1g} + 4E_{2g}$$

$$\text{Inactive: } A_{2g} + 2B_{2g} + 2B_{1u} + 2B_{2u} + 2E_{2u}$$

(c) In-plane vibrations can belong only to those representations that are symmetrical to σ_h , viz., A_{1g} , A_{2g} , E_{2g} , B_{1u} , B_{2u} and E_{1u} . To find which ones can involve C-H stretching, we find the representation for which the six C-H bonds form a basis. This is shown in the table above as Γ_{CH} . It can be reduced to:

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

Similarly, for C-C stretching, from the representation given we have

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

The remaining in-plane modes, namely $A_{2g} + 2E_{2g} + 2B_u$ must correspond to in-plane angle bending. Note that although there are eighteen in-plane angles, there are not eighteen independent internal vibrational coordinates, because the sizes of many angles are fixed once the sizes of others are chosen. This is a case of redundant coordinates which occurs often in cyclic systems. We shall not, however, treat it in any further detail here.

(d) Taking an upward bend of each C-H bond out of the plane as a basis for a 6-dimensional representation, we get the result given above for Γ_6 and this reduces to:

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

(e) We may use projection operators to arrange the six C-H bond stretches, $r_{C-H}^{(1)}$ to $r_{C-H}^{(6)}$, into the proper symmetry coordinates (SALCs). For the two non-degenerate ones it is easy to write them down by inspection. The A_{1g} SALC must be symmetric to every operation and this can only be satisfied by

$$S_{CH}^{A_{1g}} = \frac{1}{\sqrt{6}} (r_1 + r_2 + r_3 + r_4 + r_5 + r_6)$$

It is about as easy to see that the B_{1u} SALC must be:

$$S_{CH}^{B_{1u}} = \frac{1}{\sqrt{6}} (r_1 - r_2 + r_3 - r_4 + r_5 - r_6)$$

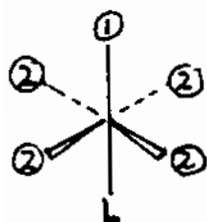
To find the E_{2g} and E_{1u} pairs, we can save time by using only the symmetry of the group C_6 to find E_1 and E_2 representations. This will work out to exactly the expressions as we had (page) for the E_1 and E_2 π MOs of benzene.

3. In each case the first step is to use the molecular symmetry to determine the symmetry types for the vibrations. The set of C-O bonds is used as a basis for a representation. After the representation is reduced, the activity of each type (IR, R, ia) is obtainable directly from the character table. These results are given below. In cases where all CO's are not equivalent, the two types are designated 1 and 2.

$M(CO)_6:$	O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	1	$6S_4$	$8S_6$	$3\sigma_h$	$3\sigma_d$
Γ_{CO}		6	0	0	2	2	0	0	0	4	2

$$\Gamma_{CO} = A_{1g}(R) + E_g(R) + \Gamma_{1u}(IR)$$

$ML(CO)_6:$

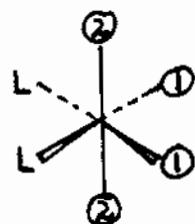


C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
Γ_1	1	1	1	1	1
Γ_2	4	0	0	2	0

$$\Gamma_1 = A_1(R, IR)$$

$$\Gamma_2 = A_1(R, IR) + B_1(R) + E(R, IR)$$

cis- $ML_2(CO)_4:$

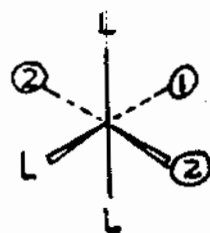


C_{2v}	E	C_2	σ	σ'
Γ_1	2	0	2	0
Γ_2	2	0	0	2

$$\Gamma_1 = A_1(R, IR) + B_1(R, IR)$$

$$\Gamma_2 = A_1(R, IR) + B_2(R, IR)$$

mer- $ML_3(CO)_3:$



C_{2v}	E	C_2	σ	σ'
Γ_1	1	1	1	1
Γ_2	2	0	2	0

$$\Gamma_1 = A_1(R, IR)$$

$$\Gamma_2 = A_1(R, IR) + B_1(R, IR)$$

fac- $ML_3(CO)_3:$

C_{3v}	E	$2C_2$	$3\sigma_v$
Γ	3	0	1

$$\Gamma = A_1(R, IR) + E(R, IR)$$

We shall work out the secular equations for the $\text{ML}(\text{CO})_5$ case. We call the unique C-O bond r_1 and the others r_2 - r_5 .

The symmetry coordinates are the appropriate SALCs that employ r_1 , r_2 , r_3 , r_4 , r_5 as a basis set. By the methods of chapters 6 and 10 these are found to be those represented in the following U matrix, from which the U' matrix is immediately obtainable:

	r_1	r_2	r_3	r_4	r_5
S_1	1	0	0	0	0
S_2	0	1/2	1/2	1/2	1/2
S_3	0	1/2	-1/2	1/2	-1/2
S_4	0	$1/\sqrt{2}$	0	$-1/\sqrt{2}$	0
S_5	0	0	$1/\sqrt{2}$	0	$-1/\sqrt{2}$

We then write the f and g matrices and carry out the necessary similarity transforms to get the F and G matrices

$$f \text{ matrix: } \begin{bmatrix} k_1 & k_1 & k_1 & k_1 & k_1 \\ k_1 & k_2 & k_1 & 2k_1 & k_1 \\ k_1 & k_1 & k_2 & k_1 & 2k_1 \\ k_1 & 2k_1 & k_1 & k_2 & k_1 \\ k_1 & k_1 & 2k_1 & k_1 & k_2 \end{bmatrix}$$

$$g \text{ matrix: } \begin{bmatrix} \mu & 0 & 0 & 0 & 0 \\ 0 & \mu & 0 & 0 & 0 \\ 0 & 0 & \mu & 0 & 0 \\ 0 & 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & \mu \end{bmatrix}$$

$$\text{where } = \frac{M_c + M_o}{M_c M_o} = \frac{1}{M_c} + \frac{1}{M_o}$$

$$UfU' = \begin{bmatrix} k_1 & 2k_1 & 0 & 0 & 0 \\ 2k_1 & k_2+4k_1 & 0 & 0 & 0 \\ 0 & 0 & k_2 & 0 & 0 \\ 0 & 0 & 0 & k_2-2k_1 & 0 \\ 0 & 0 & 0 & 0 & k_2-2k_1 \end{bmatrix}$$

$$UgU' = \begin{bmatrix} \mu & 0 & 0 & 0 & 0 \\ 0 & \mu & 0 & 0 & 0 \\ 0 & 0 & \mu & 0 & 0 \\ 0 & 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & \mu \end{bmatrix}$$

Now, for each symmetry type we write out the appropriate secular equation:

$$A_1: \begin{bmatrix} k_1 & 2k_1 \\ 2k_1 & k_2+4k_1 \end{bmatrix} \begin{bmatrix} \mu & 0 \\ 0 & \mu \end{bmatrix} - \begin{bmatrix} \lambda & 0 \\ 0 & \lambda \end{bmatrix} =$$

$$\begin{vmatrix} \mu k_1 - \lambda & 2\mu k_1 \\ 2\mu k_1 & \mu(k_2 + 4k_1) - \lambda \end{vmatrix} = 0$$

$$B_2: \mu k_2 - \lambda = 0$$

$$E: \mu(k_2 - 2k_1) - \lambda = 0$$

The secular equations for the other cases are obtained in the same way and are as follows:

$$\text{M(CO)}_6 \quad A_{1g}: \mu(k + 6k_1) - \lambda = 0$$

$$E_g: \mu k - \lambda = 0$$

$$T_{1u}: \mu(k - 2k_1) - \lambda = 0$$

$$\underline{\text{cis-ML}_2(\text{CO})}_4 \quad A_1: \begin{vmatrix} \mu(k_2 + 2k_1) - \lambda & 2\mu k_1 \\ 2\mu k_1 & \mu(k_1 + k_1) - \lambda \end{vmatrix} = 0$$

$$B_1: \mu(k_2 - 2k_1) - \lambda = 0$$

$$B_2: \mu(k_1 - k_1) - \lambda = 0$$

$$\underline{\text{mer-ML}_3(\text{CO})}_3 \quad A_1: \begin{vmatrix} \mu k_1 - \lambda & \sqrt{2}\mu k_1 \\ \sqrt{2}\mu k_1 & \mu(k_2 + 2k_1) - \lambda \end{vmatrix} = 0$$

$$B_1: \mu(k_2 - 2k_1) - \lambda = 0$$

$$\underline{\text{fac-ML}_3(\text{CO})}_3 \quad A_1: \mu(k + 2k_1) - \lambda = 0$$

$$E: \mu(k - k_1) - \lambda = 0$$

4. The SO_4^{2-} ion, having T_d symmetry, has a set of S-O stretches corresponding to the C-H stretches of methane, viz., of A_1 and T_2 symmetries. The A_1 stretch is active in the Raman only while the T_2 mode is both IR and Raman active.

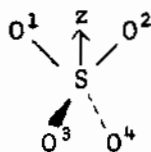
Attaching one O atom to a metal atom lowers the symmetry to C_{3v} . Actually, if the M-O-S angle is not 180° , the true symmetry is even lower, but effectively, it is C_{3v} . Similarly, when the SO_4^{2-} ion coordinates through three oxygen atoms, the symmetry is C_{3v} . In each case there is a

unique S-O bond (1) and a set of three equivalent ones (2, 3, 4). They form representations as follows:

C_{3v}	E	$2C_3$	$3\sigma_v$	
Γ_1	1	1	1	A_1
$\Gamma_{2,3,4}$	3	0	1	$A_1 + E$

The A_1 and E vibrations are all active in both IR and Raman.

The remaining two cases involve reduction of the T_d symmetry to C_{2v} and divide the four S-O bonds into two sets of two. Since the two sets are in perpendicular planes they do not lead to the same representations as shown below, where we



C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$
Γ_{12}	2	0	0	2
Γ_{34}	2	0	2	0

take the plane of the paper to be $\sigma(xz)$

$$\Gamma_{12} = A_1 + B_2 \quad (\text{both R, IR})$$

$$\Gamma_{34} = A_1 + B_1 \quad (\text{both R, IR})$$

Chapter 11

1. See text, pages
2. See text, page
3. (a) Cmm, (b) pg, (c) p4, (d) p3lm,
(e) pmg, (f) p4g, (g) cm, (h) pgg, (i) p4m
4. See page
5. At the vertices, centers of all edges, centers of all faces, and center of cell. There are 8 distinct ones (i.e., unrelated to one another by lattice translations).
6. The matrix should leave the coordinates (z) along the unique axis (c) unchanged and replace x and y by (x + y)/2 and (x - y)/2. Hence, the matrix equation is:

$$\begin{bmatrix} 1/2 & 1/2 & 0 \\ 1/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} (x + y)/2 \\ (x - y)/2 \\ z \end{bmatrix}$$

7. If the hint is followed it will be found that the distribution of points is the same in the upper half of the cell as in the lower half, this meaning that the true unit cell is only half as high and would belong to the space group Pba2
8. In Cmm2 the centering is on the face (C) to which the mirror planes and 2-fold axes are perpendicular, whereas in Amm2 the centering is on one of the faces that is parallel to these symmetry elements.
9. Pn $\bar{3}$ n (isometric); P3₂21 (trigonal-hexagonal); P $\bar{4}$ 2₁m (tetragonal); Ccca (orthorhombic); P2/n (monoclinic); Pcmb (orthorhombic); I4/mmm (tetragonal); Amam (orthorhombic).

10. Pbc2₁ and Pbcm: indistinguishable. The absences due to the b- and c-glides are $Ok\ell$, $k = 2n + 1$ and $h0\ell$, $\ell = 2n + 1$. The screw absences, 00ℓ , $\ell = 2n + 1$ are covered up by the c-glide absences.

Pcca: $Ok\ell$, $\ell = 2n + 1$; $h0\ell$, $\ell = 2n + 1$; $hk0$, $h = 2n + 1$

Cmca and C2cb: Indistinguishable. The use of an a- or b-glide \perp to the c axis is not a real difference, but only one of axis labeling. Hence we can compare Cmca and C2ca. Since the only difference is substitution of 2 for m, the absences must be the same. The C-centering causes the absences hkl , $h + k = 2n + 1$. The two glides alone would require $h0\ell$, $\ell = 2n + 1$ and $hk0$, $h = 2n + 1$. However, because of the centering condition, the restrictions are a bit more severe. For $h0\ell$, h must also be even (since k is even) and we therefore have $h0\ell$, h , $\ell = 2n + 1$. Similarly, instead of merely $hk0$, $h = 2n + 1$ we have h , $k = 2n + 1$.

Pbcm: $Ok\ell$, $k = 2n + 1$; $h0\ell$, $\ell = 2n + 1$.

I4/mcm: $h + k + \ell = 2n + 1$. For the c-glide alone we expect $h0\ell$, $\ell = 2n + 1$ but because of the centering absence this becomes $h0\ell$, h , $\ell = 2n + 1$.

F222: From the face centering we have $h + k$, $h + \ell$, $k + \ell = 2n + 1$. This subsumes all lesser classes that include zeros because zero is an even number, e.g., $Ok\ell$, k , $\ell = 2n + 1$, $h00$, $h + 2n + 1$, etc.