Solutions, Problem Set 9, CHM 3411, Spring 2009

1. Atkins Problem 12.3

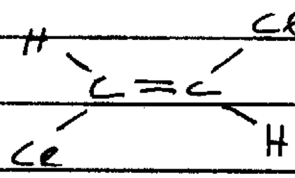
C_{2h}	E	C_2	σ_h	i
E	E	C_2	σ_h	i
C_2	C_2	E	i	σ_h
σ_h	σ_h	i	E	C_2
i	i	σ_h	C_2	E

Note $C_2(z)$: $(x,y,z) \rightarrow (-x,-y,z)$

$\sigma_h(xy)$: $(x,y,z) \rightarrow (x,y,-z)$

i : $(x,y,z) \rightarrow (-x,-y,-z)$

Example:

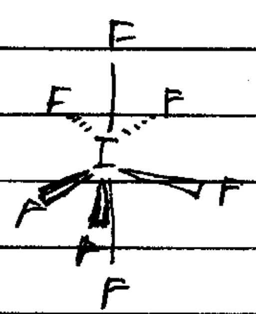


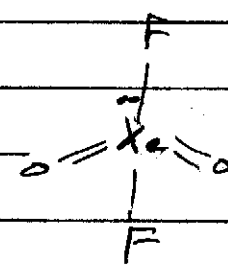
C_2 axis is perpendicular to plane of paper, through center of mass

σ_h is the plane of the paper

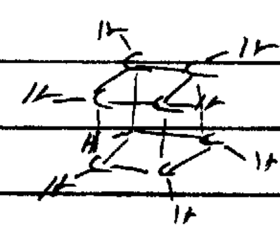
2. Atkins Exercise 12.10b

a) HF $C_{\infty v}$ b) IF_7 D_{5h} c) XeO_2F_2 C_{2v}

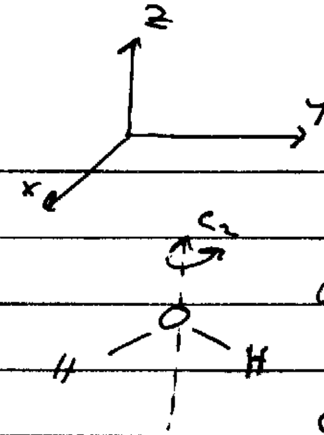




d) $Fe(CO)_9$ D_{3h} e) cubane O_h f) $C_8H_4F_4$ (see Atkins)



T_d



3. Atkins Problem 12.4

Refer to Fig 12.3 in text:

σ_v': plane through O, H, H

σ_v: plane through O, containing C_2, perpendicular to σ_v'

Place orbitals h_1 and h_2 on H atoms and s, p_x, p_y, p_z on O atom.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1		xy
B_1	1	-1	1	-1	x	xz
B_2	1	-1	-1	1	y	yz

	E	C_2	σ_v	σ_v'
h_1	h_1	h_2	h_2	h_1
h_2	h_2	h_1	h_1	h_2
s	s	s	s	s
p_x	p_x	$-p_x$	p_x	$-p_x$
p_y	p_y	$-p_y$	$-p_y$	p_y
p_z	p_z	p_z	p_z	p_z

$$D(E) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad D(C_2) = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$D(\sigma_v) = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad D(\sigma_v') = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

a) $D(C_2)\,D(\sigma_v) = D(\sigma_v')$ (multiply matrices shown to confirm)

b) $D(\sigma_v)\,D(\sigma_v') = D(C_2)$ " " " "

Trace is sum of diagonal elements.

$Tr(D(E)) = 6 \quad Tr(D(C_2)) = 0 \quad Tr(D(\sigma_v)) = 2 \quad Tr(D(\sigma_v')) = 4$

All belong to different classes, and all have different traces, as expected.

The traces above are not the characters of any one irreducible representation (compare to ~~[illegible]~~ character tables), so the representation is reducible

From the character table, we find

	E	C_2	σ_v	σ_v'
$3A_1$	3	3	3	3
B_1	1	-1	1	-1
$2B_2$	2	-2	-2	2
Sum	6	0	2	4

Then the matrices $D(E)$, $D(C_2)$, $D(\sigma_v)$, $D(\sigma_v')$ constitute a representation that is $3A_1 + B_1 + 2B_2$; thus $D(E)$, $D(C_2)$, $D(\sigma_v)$, $D(\sigma_v')$ span $3A_1 + B_1 + 2B_2$

4 Atkins Exercise 12.46

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	1	−1	−1	1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1		
B_{2g}	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1		
E_{1g}	2	1	−1	−2	0	0	2	1	−1	−2	0	0	(R_x, R_y)	(xz, yz)
E_{2g}	2	−1	−1	2	0	0	2	−1	−1	2	0	0		(x^2-y^2, xy)
A_{1u}	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1		
B_{2u}	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1		
E_{1u}	2	1	−1	−2	0	0	−2	−1	1	2	0	0	(x, y)	
E_{2u}	2	−1	−1	2	0	0	−2	1	1	−2	0	0		

$h = 24$

We need to evaluate whether $\mu_{fi} = \int f_1 \vec{\mu} f_2 \, d\tau = 0$ when f_1 has symmetry species E_{2u} and f_2 has symmetry species A_{1g}.

This will be the case only if all three of the following integrals are zero:

$$\underbrace{\int_{-\infty}^{\infty} f_1 x f_2 \, dx \quad \int_{-\infty}^{\infty} f_1 y f_2 \, dy}$$

These two must be considered together

$$\int_{-\infty}^{\infty} f_1 z f_2 \, dz$$

The integral is non zero only if the decomposition of the direct product includes A_{1g}

for x,y	E_{2u}	2	−1	−1	2	0	0	−2	1	1	−2	0	0
	A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
	E_{1u} (x,y)	2	1	−1	−2	0	0	−2	−1	1	2	0	0
		4	−1	1	−4	0	0	4	−1	1	−4	0	0

Contain A_{1g}?	A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
		4	−1	1	−4	0	0	4	−1	1	−4	0	0

Sum = 0 NO

Multiply each value by the number of operations in the class (from character table) and sum:

$$1(4)+2(-1)+2(1)+1(-4)+0+0+1(4)+2(-1)+2(1)+1(-4)+0+0=0$$

$\therefore$ A_{1g} <u>not</u> included in direct product

for z												
E_{2u}	2	−1	−1	2	0	0	−2	1	1	−2	0	0
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
$A_{2u} \leftarrow z$	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1
	2	−1	−1	2	0	0	2	−1	−1	2	0	0

Contain A_{1g}?												
	1	1	1	1	1	1	1	1	1	1	1	1
	2	−1	−1	2	0	0	2	−1	−1	2	0	0

$$1(2)+2(-1)+2(-1)+1(2)+0+0+1(2)+2(-1)+2(-1)+1(2)+0+0=0$$

$\therefore$ A_{1g} not included in direct product.

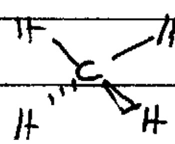
$\therefore$ Transition is $\boxed{\text{forbidden}}$.

5. Atkins Problem 12.8

Point group of CH_4 is T_d:

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	$h = 24$	
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	−1	1	−1		
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

Consider each class of operation. Each orbital unchanged by operation contributes 1; each that changes sign contributes −1; all others contribute 0 to the character.



E	4
C_3	1
C_2	0
S_4	0
σ_d	2

This spans $A_1 + T_2$

$$\begin{array}{ccccc} 1 & 1 & 1 & 1 & 1 \\ 3 & 0 & -1 & -1 & 1 \\ \hline 4 & 1 & 0 & 0 & 2 \end{array} \checkmark$$

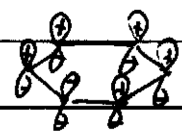
Inspection of the character table of T_d shows that
S spans A_1 and p_x, p_y, p_z on the C atom span T_2.
Thus the s and p orbitals of the C atom may
form Molecular orbitals with the four H1s orbitals.

The d orbitals span $E + T_2$, with T_2 corresponding
to (xy, yz, xz). Thus on C (d_{xy}, d_{yz}, d_{zx}) may
contribute to a molecular orbital with the H_{1s} orbitals.

6. Atkins Problem 12.16

Before beginning this problem note that though benzene belongs to the D_{6h} point group, when one adds the six Cp_z orbitals, the resulting object has lower symmetry, C_{6v}.

D_{6h}

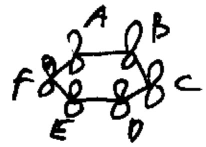


C_{6v}

Thus we will only need to consider the operations of the C_{6v} point group, which are a subset of those of the D_{6h} point group. This will simplify our work.

C_{6v}	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$	$h=12$	
A_1	1	1	1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	1	1	-1	-1		
B_1	1	-1	1	-1	1	-1		
B_2	1	-1	1	-1	-1	1		
E_1	2	1	-1	-2	0	0	(x,y)	(xz, yz)
E_2	2	-1	-1	2	0	0		(x^2-y^2, xy)

The two C_6 operations are rotation about C_6 axis by $\pm 60°$.
" " C_3 " " " " " C_6 axis by $\pm 120°$.
" one C_2 " is " " C_6 axis by $180°$.
Let the σ_v operations are planes through C atoms
" " σ_d " " " " bisecting C–C bonds



Label p_z orbitals A through F

		Original basis					
		A	B	C	D	E	F
	E	A	B	C	D	E	F
	C_6^+	B	C	D	E	F	A
	C_6^-	F	A	B	C	D	E
	C_3^+	C	D	E	F	A	B
	C_3^-	E	F	A	B	C	D
	C_2	D	E	F	A	B	C
through A, D	σ_v	A	F	E	D	C	B
.. B, E	σ_v'	C	B	A	F	E	D
.. C, F	σ_v''	E	D	C	B	A	F
bisecting A–B	σ_d	B	A	F	E	D	C
– B–C	σ_d'	D	C	B	A	F	E
.. C–D	σ_d''	F	E	D	C	B	A

using column A

$$a_1 = \frac{1}{12}(A+B+F+C+E+D+A+C+E+B+D+F)$$
$$= \frac{1}{6}(A+B+C+D+E+F)$$

This is not normalized, but normalization yields:

$$a_1 = \frac{1}{\sqrt{6}}(A+B+C+D+E+F)$$

using column B

$$b_1 = \frac{1}{12}(A-B-F+C+E-D+A+C+E-B-D-F)$$
$$= \frac{1}{6}(A-B+C-D+E-F)$$

Normalization:

$$b_1 = \frac{1}{\sqrt{6}}(A-B+C-D+E-F)$$

For e_1, we can expect to have an linearly dependent set if we use all the columns. In fact, we will use the first three columns, and take a linear combination of the results from the second step.

From column A: $\frac{1}{\sqrt{12}}(2A+B+F-C-E-2D)$

$= \frac{1}{\sqrt{12}}(2A+B-C-2D-E+F)$

From column B: $\frac{1}{\sqrt{12}}(2B+C+A-D-F-2E)$

$= \frac{1}{\sqrt{12}}(A+2B+C-D-2E-F) \quad (1)$

From column C: $\frac{1}{\sqrt{12}}(2C+D+B-E-A-2F)$

$= \frac{1}{\sqrt{12}}(-A+B+2C+D-E-2F) \quad (2)$

Adding (1) + (2): $\frac{1}{\sqrt{12}}(3B+3C-3E-3F)$

$= \frac{1}{4}(B+C-E-F)$

Thus for e_1, after normalizing, we get:

$$e_1 = \begin{cases} \frac{1}{\sqrt{12}}(2A+B-C-2D-E+F) \\ \frac{1}{2}(B+C-E-F \end{cases}$$

Same idea for e_2

From column A: $\frac{1}{\sqrt{12}}(2A-B-F-C-E+2D)$

$$\Downarrow$$

$$\frac{1}{\sqrt{12}}(2A-B-C+2D-E-F)$$

From column B: $\frac{1}{2}(2B-C-A-D-F+2E)$

$$= \frac{1}{2}(-A+2B-C-D+2E-F) \quad (1)$$

From column C: $\frac{1}{2}(2C-D-B-E-A+2F)$

$$= \frac{1}{2}(-A-B+2C-D-E+2F) \quad (2)$$

Subtracting: $(1)-(2)$: $\frac{1}{2}(3B-3C+3E-3F)$

$$= \frac{1}{2}(B-C+E-F)$$

$$\Downarrow$$

$$\frac{1}{2}(B-C+E-F)$$

Thus for e_2 we got:

$$e_2 = \begin{cases} \frac{1}{\sqrt{12}}(2A-B-C+2D-E-F) \\ \frac{1}{2}(B-C+E-F) \end{cases}$$