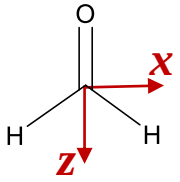
Symmetry & Bonding

Answers to the Questions 8, 11, 12ab

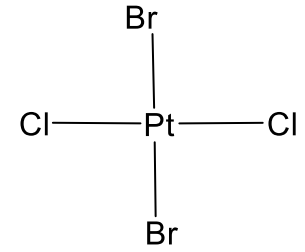
8. (a) In formaldehyde (methanal) determine the irreducible representation which each of the following AOs on the carbon transforms as: the 2*s*, the three 2*p* AOs and the five 3*d*. Repeat the process for the corresponding AOs on the oxygen.
(b) The species $[PtCl_2Br_2]^{2-}$ has square planar coordination about the platinum atom with the two chlorine ligands being placed at opposite corners of the square. Determine the point group and hence the irreducible representation for each of the five 5*d* AOs on the platinum.



(a) C_{2v};

	2s	$2p_x$	$2p_y$	$2p_z$	d_{z^2}	d_{xz}	d_{yz}	d_{xy}	$d_{x^2-y^2}$
C	A_1	B_1	B_2	A_1	A_1	B_1	B_2	A_2	A_1
O	A_1	B_1	B_2	A_1	A_1	B_1	B_2	A_2	A_1

I.R.



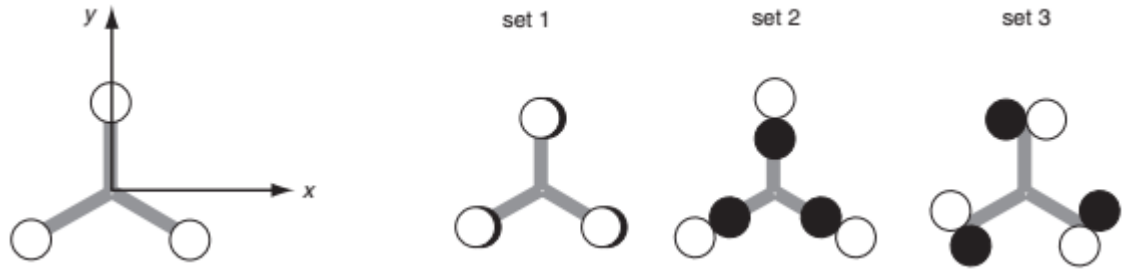
C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2;y^2;z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

(b) D_{2h}; d_{z^2} $d_{x^2-y^2}$ A_g

d_{xz} B_{2g} d_{yz} B_{3g} d_{xy} B_{1g}

$\mathcal{D}_{2h}$	E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{xz}	σ^{yz}		
A_g	1	1	1	1	1	1	1	1		$x^2;y^2;z^2$
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

11. (a) State the point group of BF_3.
(b) Using the 'counting method' determine the characters of the representation generated by the three fluorine $2p_z$ AOs, set 1. *Using the reduction formula* determine the corresponding irreducible representations.
(c) Do the same for the three fluorine $2p$ AOs forming set 2.
(d) Do the same for the three fluorine $2p$ AOs forming set 3.



$\mathcal{D}_{3h}$	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$			
A_1'	1	1	1	1	1	1			$x^2+y^2;z^2$
A_2'	1	1	−1	1	1	−1		R_z	
E'	2	−1	0	2	−1	0	(x,y)		$(x^2-y^2,2xy)$
A_1''	1	1	1	−1	−1	−1			
A_2''	1	1	−1	−1	−1	1	z		
E''	2	−1	0	−2	1	0		(R_x,R_y)	(xz,yz)

Set 1	3	0	-1	-3	0	1	$A_2''\oplus E''$
Set 2	3	0	1	3	0	1	$A_1'\oplus E'$
Set 3	3	0	-1	3	0	-1	$A_2'\oplus E'$

12. (a) Determine the characters of the representation generated by the six out-of-plane carbon 2*p* AOs in benzene. Reduce the representation.
(b) Determine the characters of the representation generated by the four hydrogen 1*s* AOs in methane. Reduce the representation.

(a) C_6H_6, D_{6h}

$\mathcal{D}_{6h}$	E	$2C_6$	$2C_6^2$	C_6^3	$3C_2$	$3C_2'$	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		$(x^2-y^2,2xy)$
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		

$\Gamma(6xp_z)$	6	0	0	0	-2	0	0	0	0	-6	0	2	$B_{2g}\oplus A_{2u}\oplus E_{1g}\oplus E_{2u}$
$\chi(c)\times g(c)$	6	0	0	0	-6	0	0	0	0	-6	0	6	

12. (a) Determine the characters of the representation generated by the six out-of-plane carbon 2*p* AOs in benzene. Reduce the representation.
(b) Determine the characters of the representation generated by the four hydrogen 1*s* AOs in methane. Reduce the representation.

(b) CH_4, T_d

$\mathcal{T}_d$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$			
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			$((2z^2-x^2-y^2),\sqrt{3}(x^2-y^2))$
T_1	3	0	−1	1	−1		(R_x,R_y,R_z)	
T_2	3	0	−1	−1	1	(x,y,z)		(yz,xz,xy)

Γ(4xs)	4	1	0	0	2	$A_1 \oplus T_2$

C_5H_5,D_{5h}

$\mathcal{D}_{5h}$	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^3$	$5\sigma_v$	$\eta_\pm = \frac{1}{2}(\sqrt{5}\pm 1)$
A_1'	1	1	1	1	1	1	1	1	$x^2+y^2;z^2$
A_2'	1	1	1	−1	1	1	1	−1	R_z
E_1'	2	η_-	$-\eta_+$	0	2	η_-	$-\eta_+$	0	(x,y)
E_2'	2	$-\eta_+$	η_-	0	2	$-\eta_+$	η_-	0	$(x^2-y^2,2xy)$
A_1''	1	1	1	1	−1	−1	−1	−1	
A_2''	1	1	1	−1	−1	−1	−1	1	z
E_1''	2	η_-	$-\eta_+$	0	−2	$-\eta_-$	η_+	0	(R_x,R_y) (xz,yz)
E_2''	2	$-\eta_+$	η_-	0	−2	η_+	$-\eta_-$	0	

Γ(5xp$_z$)	5	0	0	-1	-5	0	0	1	$A_2'' \oplus E_1'' \oplus E_2''$
χ(c)xg(c)	5	0	0	-5	-5	0	0	5	