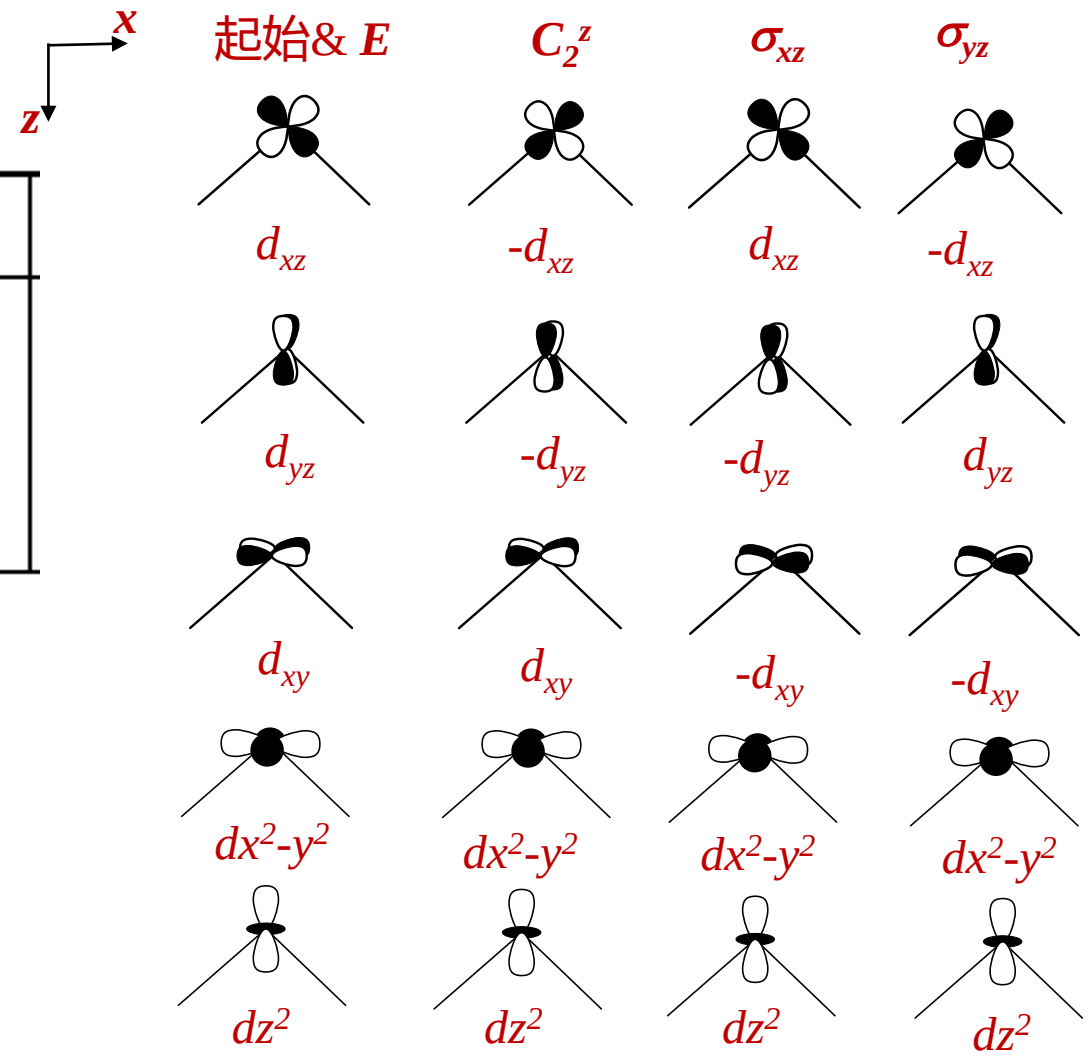
Symmetry & Bonding

Answers to the Questions 5-7

5. For H_2O, determine the effect of each symmetry operation on each of the five oxygen 3*d* orbitals by using a similar approach to that shown in Fig. 3.1 on page 20. Hence determine the representation generated by each orbital, and then by inspection of the character table determine to which irreducible representation this corresponds. (Of course you can read the answers straight off the table, but this is not what you are being asked to do.)

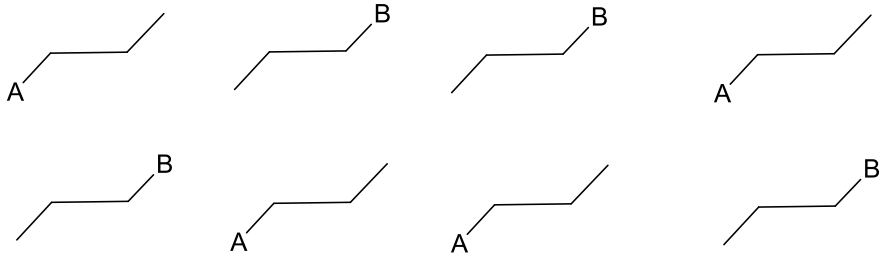
C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}	
A_1	1	1	1	1	
A_2	1	1	−1	−1	
B_1	1	−1	1	−1	
B_2	1	−1	−1	1	



E	C_2^z	σ_{xz}	σ_{yz}	
+1	-1	+1	-1	B_1
+1	-1	-1	+1	B_2
+1	+1	-1	-1	A_2
+1	+1	+1	+1	A_1
+1	+1	+1	+1	A_1

6. (a) Determine the point group of *trans* F-N=N-F.
(b) Using a similar approach to that in section 3.1.2 on page 21, determine the two-by-two representative matrix for each operation of the group using the two fluorine 2*s* AOs A and B as the basis.
(c) Hence find the corresponding characters of the representation and, by inspection of the character table, to which irreducible representations this can be reduced.
(d) For the same basis determine the characters using the 'counting method'.

(b) E C_2 i σ_h

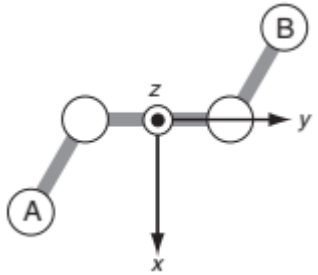


$$E\begin{pmatrix}A\\B\end{pmatrix}=\begin{pmatrix}A\\B\end{pmatrix} \quad C_2\begin{pmatrix}A\\B\end{pmatrix}=\begin{pmatrix}B\\A\end{pmatrix} \quad i\begin{pmatrix}A\\B\end{pmatrix}=\begin{pmatrix}B\\A\end{pmatrix} \quad \sigma_h\begin{pmatrix}A\\B\end{pmatrix}=\begin{pmatrix}A\\B\end{pmatrix}$$

$$E=\begin{pmatrix}1&0\\0&1\end{pmatrix} \quad C_2=\begin{pmatrix}0&1\\1&0\end{pmatrix} \quad i=\begin{pmatrix}0&1\\1&0\end{pmatrix} \quad \sigma_h=\begin{pmatrix}1&0\\0&1\end{pmatrix}$$

(c) $\chi(E)=2 \quad \chi(C_2)=0 \quad \chi(i)=0 \quad \chi(\sigma_h)=2$

(d)

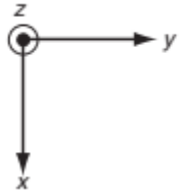


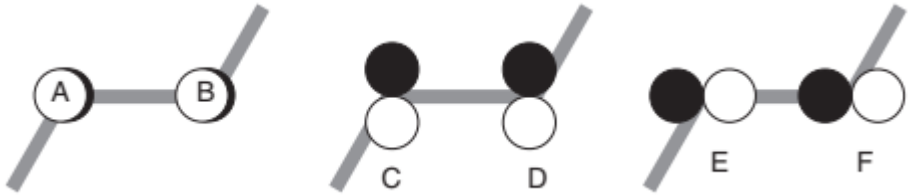
(a) C_{2h}

E	Neither move, 1+1= 2
C_2	Both move, 0+0= 0
i	Both move, 0+0= 0
σ_h	Neither move, 1+1= 2

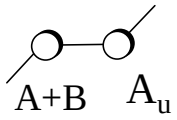
C_{2h}	E	C_2^z	i	σ^{xy}		
A_g	1	1	1	1	R_z	$x^2;y^2;z^2;xy$
B_g	1	−1	1	−1	$R_x;R_y$	$xz;yz$
A_u	1	1	−1	−1	z	
B_u	1	−1	−1	1	$x;y$	

7. (a) Using the 'counting method' determine the characters of the representations generated by: (i) the two nitrogen 2*pz* AOs A and B; (ii) the two nitrogen 2*px* AOs C and D; (iii) the two nitrogen 2*py* AOs E and F. In each case determine, by inspection of the relevant character table, the corresponding irreducible representations.
(b) In each case (i)–(iii) sketch the form of the two symmetry orbitals arising from each pair of orbitals and identify to which irreducible representation each belongs.

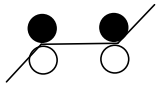




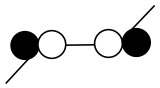
E	2	2	2
C_2	0	0	0
i	0	0	0
σ_h	-2	2	2
	$B_g \oplus A_u$	$A_g \oplus B_u$	$A_g \oplus B_u$



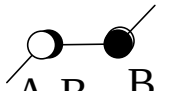
A_u



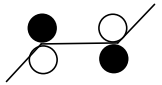
B_u



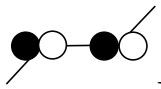
A_g



B_g



A_g



B_u

C_{2h}	E	C_2^z	i	σ^{xy}		
A_g	1	1	1	1	R_z	$x^2;y^2;z^2;xy$
B_g	1	−1	1	−1	$R_x;R_y$	$xz;yz$
A_u	1	1	−1	−1	z	
B_u	1	−1	−1	1	$x;y$	