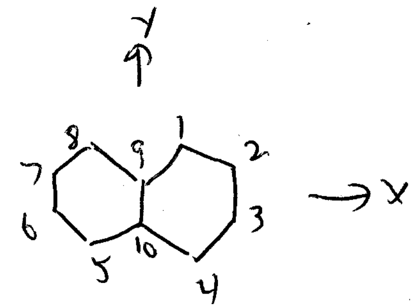
INORGANIC STRUCTURE AND BONDING - PROBLEM Set 2

10/30/00

6.1.

a) symmetry subsets



A) p_1, p_4, p_5, p_8

B) p_2, p_3, p_6, p_7

C) p_9, p_{10}

b)

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ_A	4	0	0	0	0	-4	0	0
Γ_B	4	0	0	0	0	-4	0	0
Γ_C	2	0	-2	0	0	-2	0	2

$$\Gamma_A = \Gamma_B = B_{2g} + B_{3g} + A_u + B_{1u}$$

$$\Gamma_C = B_{3g} + B_{1u}$$

c)
$$\hat{P}^{A_u}(p_1) \cong (1)p_1 + (1)p_5 + (1)(-p_8) + (1)(-p_4)$$
$$+(-1)(-p_5) + (-1)(-p_1) + (-1)p_4 + (-1)p_8$$
$$\cong 2p_1 - 2p_4 + 2p_5 - 2p_8$$
$$\cong p_1 + p_5 - p_4 - p_8$$
$$= \frac{1}{2}(p_1 + p_5 - p_4 - p_8)$$

$$\hat{P}^{B_{2g}}_{(P_1)} \cong (1)P_1 + (-1)P_5 + (1)(-P_8) + (-1)(-P_4)$$
$$+ (1)(-P_5) + (-1)(-P_1) + (1)(P_4) + (-1)P_8$$
$$\cong 2P_1 - 2P_5 + 2P_4 - 2P_8$$
$$\cong P_1 + P_4 - P_5 - P_8$$
$$= \underline{\tfrac{1}{2}(P_1 + P_4 - P_5 - P_8)}$$

$$\hat{P}^{B_{3g}}_{(P_1)} \cong (1)P_1 + (-1)P_5 + (-1)(-P_8) + (1)(-P_4)$$
$$(1)(-P_5) + (-1)(-P_1) + (-1)(P_4) + (1)P_8$$
$$\cong 2P_1 - 2P_5 + 2P_8 - 2P_4$$
$$\cong P_1 + P_8 - P_5 - P_4$$
$$= \underline{\tfrac{1}{2}(P_1 + P_8 - P_5 - P_4)}$$

$$\hat{P}^{B_{1u}}_{(P_1)} \cong (1)P_1 + (1)P_5 + (-1)(-P_8) + (-1)(-P_4)$$
$$+ (-1)(-P_5) + (-1)(-P_1) + (1)(P_4) + (1)P_8$$
$$\cong 2P_1 + 2P_5 + 2P_8 + 2P_4$$
$$\cong P_1 + P_5 + P_8 + P_4$$
$$= \underline{\tfrac{1}{2}(P_1 + P_5 + P_8 + P_4)}$$

Similarly, using P_2 as a basis function, the following SALCS are obtained.

A_u: $\frac{1}{2}(P_2 + P_6 - P_3 - P_7)$ $\quad$ B_{3g}: $\frac{1}{2}(P_2 + P_7 - P_3 - P_6)$

B_{2g}: $\frac{1}{2}(P_2 + P_3 - P_6 - P_7)$ $\quad$ B_{1u}: $\frac{1}{2}(P_2 + P_3 + P_6 + P_7)$

$$\hat{P}^{B_{3g}}_{(\rho_9)} \cong (1)\rho_9 + (-1)\rho_{10} + (-1)(-\rho_9) + (1)(-\rho_{10})$$

$$+ (1)(-\rho_{10}) + (-1)(-\rho_9) + (-1)(\rho_{10}) + (1)(\rho_9)$$

$$\cong 2\rho_9 - 2\rho_{10} \cong \rho_9 - \rho_{10}$$

$$= \underline{\frac{1}{\sqrt{2}}(\rho_9 - \rho_{10})}$$

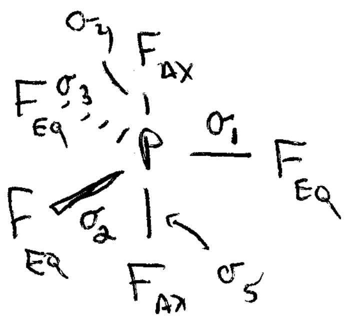
$$\hat{P}^{B_{1u}}_{(\rho_9)} \cong (1)\rho_9 + (1)\rho_{10} + (-1)(-\rho_9) + (-1)(-\rho_{10})$$

$$+ (-1)(-\rho_{10}) + (-1)(-\rho_9) + (1)(\rho_{10}) + (1)(\rho_9)$$

$$\cong 4\rho_9 + 4\rho_{10} \cong \rho_9 + \rho_{10}$$

$$= \underline{\frac{1}{\sqrt{2}}(\rho_9 + \rho_{10})}$$

6.4



$\underline{\underline{D_{3h}}}$

EQUATORIAL: $\sigma_1, \sigma_2, \sigma_3$
AXIAL: σ_4, σ_5

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{eq}	3	0	1	3	0	1
Γ_{AX}	2	2	0	0	0	2

$\Gamma_{eq} = A_1' + E'$ $\qquad$ $\Gamma_{AX} = A_1' + A_2''$

$$\hat{P}^{A_1'}(\sigma_1) \cong (1)\sigma_1 + (1)\sigma_2 + (1)\sigma_3 + (1)\sigma_1 + (1)\sigma_2 + (1)\sigma_3$$
$$+ (1)\sigma_1 + (1)\sigma_2 + (1)\sigma_3 + (1)\sigma_1 + (1)\sigma_2 + (1)\sigma_3$$
$$\cong 4\sigma_1 + 4\sigma_2 + 4\sigma_3 \cong \sigma_1 + \sigma_2 + \sigma_3$$
$$= \frac{1}{\sqrt{3}}(\sigma_1 + \sigma_2 + \sigma_3)$$

For E representation, let's use the character table for the pure rotational subgroup C_3.

C_3	E	C_3	C_3^2
A	1	1	1
E	$\left\{\begin{matrix} 1 \\ 1 \end{matrix}\right.$	$\begin{matrix} \varepsilon \\ \varepsilon^* \end{matrix}$	$\left.\begin{matrix} \varepsilon^* \\ \varepsilon \end{matrix}\right\}$

$\varepsilon = \exp(2\pi i/3)$

$$\hat{P}^{E_1}(\sigma_1) \cong (1)\sigma_1 + (\varepsilon)\sigma_2 + (\varepsilon^*)\sigma_3$$

$$\hat{P}^{E_2}(\sigma_1) \cong (1)\sigma_1 + \varepsilon^*(\sigma_2) + \varepsilon\sigma_3$$

Additive combination:

$$\cong 2\sigma_1 + (\varepsilon + \varepsilon^*)\sigma_2 + (\varepsilon + \varepsilon^*)\sigma_3$$
$$\cong 2\sigma_1 - \sigma_2 - \sigma_3$$
$$= \frac{1}{\sqrt{6}}(2\sigma_1 - \sigma_2 - \sigma_3)$$

$\varepsilon + \varepsilon^* = 2\cos\frac{2\pi}{3}$
$= -1$

Subtractive combination:

$$\cong (\varepsilon - \varepsilon^*)\sigma_2 + (\varepsilon^* - \varepsilon)\sigma_3$$
$$\cong -i\sqrt{3}\,\sigma_2 + i\sqrt{3}\,\sigma_3$$
$$\cong \sigma_2 - \sigma_3$$
$$= \frac{1}{\sqrt{2}}(\sigma_2 - \sigma_3)$$

$\varepsilon - \varepsilon^* = i2\sin\frac{2\pi}{3}$
$= -i\sqrt{3}$

Axial

$$\hat{P}^{A_1'}_{(\sigma_4)} \cong (1)\sigma_4 + (1)\sigma_4 + (1)\sigma_4 + (1)\sigma_5 + (1)\sigma_5 + (1)\sigma_5$$

$$+ (1)\sigma_5 + (1)\sigma_5 + (1)\sigma_5 + (1)\sigma_4 + (1)\sigma_4 + (1)\sigma_4$$

$$\cong 6\sigma_4 + 6\sigma_5 \cong \sigma_4 + \sigma_5$$

$$= \frac{1}{\sqrt{2}}(\sigma_4 + \sigma_5)$$

$$\hat{P}^{A_2''}_{(\sigma_4)} \cong (1)\sigma_4 + (1)\sigma_4 + (1)\sigma_4 \; (-1)\sigma_5 + (-1)\sigma_5 + (-1)\sigma_5$$

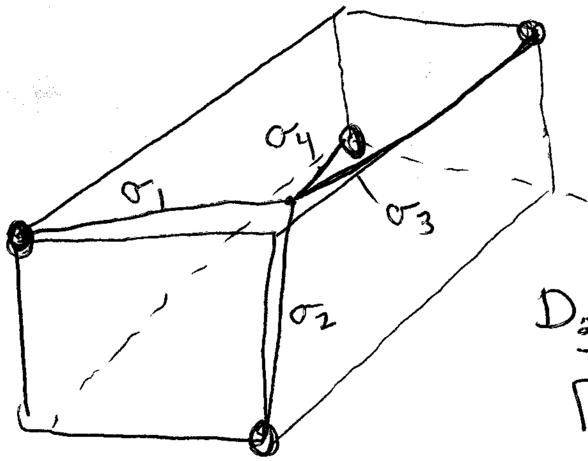
$$+ (-1)\sigma_5 + (-1)\sigma_5 + (-1)\sigma_5 \; + (1)\sigma_4 + (1)\sigma_4 + (1)\sigma_4$$

$$\cong 6\sigma_4 - 6\sigma_5 \cong \sigma_4 - \sigma_5$$

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

8.2

MX_4 (D_{2d})



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

$$a(A_1) = \frac{1}{8}\left((1)(4) + 2(2)\right) = \frac{1}{8}(8) = 1$$
$$a(A_2) = \frac{1}{8}\left((1)(4) + (-2)(2) = \frac{1}{8}(0) = 0\right.$$
$$a(B_1) = \frac{1}{8}\left((1)(4) + (-2)(2) = \frac{1}{8}(0) = 0\right.$$
$$a(B_2) = \frac{1}{8}\left((1)(4) + (2)(2)\right) = \frac{1}{8}(8) = 1$$
$$a(E) = \frac{1}{8}\left(2(4) + 0(2)\right) = \frac{1}{8}(8) = 1$$

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

<u>SALC's</u>

$$\hat{P}^{A_1}_{(\sigma_1)} \cong (1)\sigma_1 + (1)\sigma_3 + (1)\sigma_4 + (1)\sigma_2 + (1)\sigma_3 + (1)\sigma_4 + (1)\sigma_1 + (1)\sigma_2$$
$$\cong 2\sigma_1 + 2\sigma_2 + 2\sigma_3 + 2\sigma_4 \cong \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4$$
$$= \frac{1}{2}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$$

⑦

$$\hat{P}^{B_2}_{(\sigma_1)} \cong (1)\sigma_1 + (-1)\sigma_3 + (-1)\sigma_4 + (1)\sigma_2 + (-1)\sigma_3 + (-1)\sigma_4 + (1)\sigma_1 + (1)\sigma_2$$

$$\cong 2\sigma_1 + 2\sigma_2 - 2\sigma_3 - 2\sigma_4 \cong \sigma_1 + \sigma_2 - \sigma_3 - \sigma_4$$

$$= \frac{1}{2}(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4)$$

$$\hat{P}^{E}_{(\sigma_1)} \cong (2)\sigma_1 \cancel{(0)} + (-2)\sigma_2 \cong \sigma_1 - \sigma_2$$

$$= \frac{1}{\sqrt{2}}(\sigma_1 - \sigma_2)$$

This is just one solution; there must be a partner

let's apply a $\hat{S}_4^1$ operation on this solution →

3 possibilities → partner

± original function

linear combination

$$\hat{S}_4^1(\sigma_1 - \sigma_2) = \underline{\sigma_4 - \sigma_3}$$

partner (orthonormal to first solution)

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

SALC's on X atoms

$\psi^s_{A_1} = \frac{1}{2}(s_1 + s_2 + s_3 + s_4)$

$\psi^s_{B_2} = \frac{1}{2}(s_1 + s_2 - s_3 - s_4)$

$\psi^s_{E_1} = \frac{1}{\sqrt{2}}(s_1 - s_2)$

$\psi^s_{E_2} = \frac{1}{\sqrt{2}}(s_3 - s_4)$

also for p_σ orbitals

$\psi^p_{A_1} = \frac{1}{2}(p_1 + p_2 + p_3 + p_4)$

$\psi^p_{B_1} = \frac{1}{2}(p_1 + p_2 - p_3 - p_4)$

$\psi^p_{E_1} = \frac{1}{\sqrt{2}}(p_1 - p_2)$

$\psi^p_{E_2} = \frac{1}{\sqrt{2}}(p_3 - p_4)$

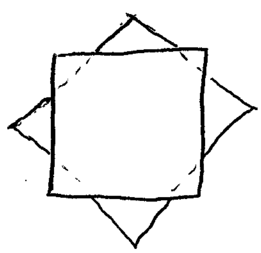
ORBITALS ON ATOM M WHICH CAN INTERACT WITH X by σ bonding - inspection of D_{2d} character table

A_1: s, d_{z^2}

B_2: p_z, d_{xy}

E : (p_x, p_y), (d_{xz}, d_{yz})

8.4



Bird's Eye View of Square Anti-Prism

point group - D_{4d}

1) Determine σ SALC's

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	2

$a(A_1) = \frac{1}{16}((1)(1)(8) + (4)(2)(1)) = \frac{1}{16}(16) = 1$

$a(A_2) = \frac{1}{16}((1)(1)(8) + (4)(2)(-1)) = 0$

$a(B_1) = \frac{1}{16}((1)(1)(8) + (4)(2)(-1)) = 0$

$a(B_2) = \frac{1}{16}((1)(1)(8) + (4)(2)(1)) = \frac{1}{16}(16) = 1$

$a(E_1) = \frac{1}{16}((1)(2)(8) + (4)(2)(0)) = \frac{1}{16}(16) = 1$

$a(E_2) = \frac{1}{16}(1(2)(8) + (4)(2)(0)) = \frac{1}{16}(16) = 1$

$a(E_3)$ $\frac{1}{16}(1(2)(8) + 4(2)(0)) = \frac{1}{16}(16) = 1$

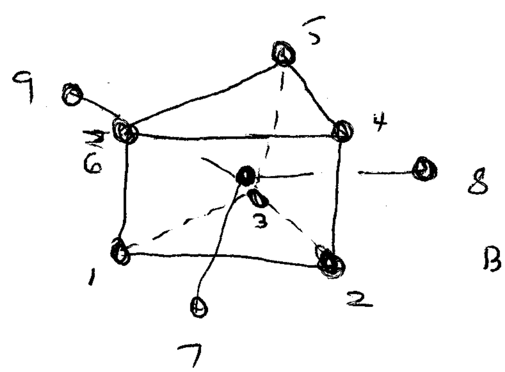
$$\Gamma_\sigma = A_1 + B_2 + E_1 + E_2 + E_3$$

Central metal orbitals which may hybridize:

$s(A_1) + p_z(B_2) + (p_x, p_y)(E_1) + (d_{x^2-y^2}, d_{xy})(E_2) + (d_{xz}, d_{yz})(E_3)$

$+ d_{z^2}(A_1)$

Capped Trigonal Bipyramid (D_{3h})



2 symmetry subsets

BIPYRAMID $\sigma_1, \sigma_2, \sigma_3, \sigma_4, \sigma_5, \sigma_6$

and

CAPPING $\sigma_7, \sigma_8, \sigma_9$

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{BIPYR}	6	0	0	0	0	2
Γ_{CAPS}	3	0	1	3	0	1

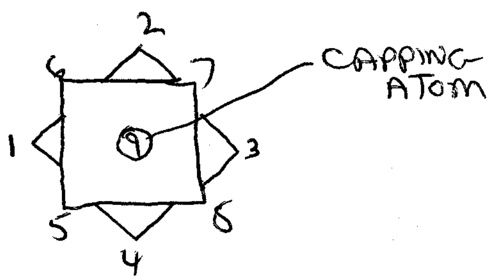
$$\Gamma_{\sigma(BIPYR)} = A_1' + A_2'' + E' + E''$$

$$\Gamma_{\sigma}(CAPS) = A_1' + E'$$

Metal Orbitals

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}

Capped Anti Prism (C_{4v})



3 symmetry subsets
$(\sigma_1, \sigma_2, \sigma_3, \sigma_4) \rightarrow A$
$(\sigma_5, \sigma_6, \sigma_7, \sigma_8) \rightarrow B$
$\sigma_9 \rightarrow C$

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
Γ_σ^A	4	0	0	2	0
Γ_σ^B	4	0	0	0	2
Γ_σ^C	1	1	1	1	1

$\Gamma_\sigma^A = A_1 + B_1 + E$
$\Gamma_\sigma^B = A_1 + B_2 + E$
$\Gamma_\sigma^C = A_1$

Metal ORBITALS

A_1 : s, p_z, d_{z^2}

B_2 : d_{xy}

E : $(p_x, p_y)\ (d_{xz}, d_{yz})$