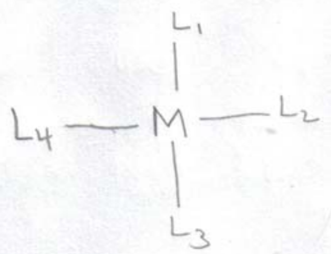
C734b 2008

Solutions Problem Set 4.

① ML_4 Square planar complex: D_{4h} symmetry

use 4σ orbitals on ligands as a basis



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

$h = 16$

$a_{1g} = \frac{1}{16}[(1)(4)(1) + (2)(2)(1) + (1)(4)(1) + (2)(2)(1)] = 1$

$a_{2g} = \frac{1}{16}[(1)(4)(1) + (2)(2)(-1) + (1)(4)(1) + (2)(2)(-1)] = 0$

$b_{1g} = \frac{1}{16}[(1)(4)(1) + (2)(2)(1) + (1)(4)(1) + (2)(2)(1)] = 1$

$b_{2g} = \frac{1}{16}[(1)(4)(1) + (2)(2)(-1) + (1)(4)(1) + (2)(2)(-1)] = 0$

$e_g = \frac{1}{16}[(1)(4)(2) + 0 + (1)(4)(-2) + 0] = 0$

$a_{1u} = \frac{1}{16}[(1)(4)(1) + (2)(2)(1) + (1)(4)(-1) + (2)(2)(-1)] = 0$

$a_{2u} = \frac{1}{16}[(1)(4)(1) + (2)(2)(-1) + (1)(4)(-1) + (2)(2)(1)] = 0$

$b_{1u} = \frac{1}{16}[(1)(4)(1) + (2)(2)(1) + (1)(4)(-1) + (2)(2)(-1)] = 0$

$b_{2u} = \frac{1}{16}[(1)(4)(1) + (2)(2)(-1) + (1)(4)(-1) + (2)(2)(1)] = 0$

$e_u = \frac{1}{16}[(1)(4)(2) + 0 + (1)(4)(2) + 0] = 1$

$\therefore \Gamma_\sigma = a_{1g} \oplus b_{1g} \oplus e_u$

on M s orbital transforms as a_{1g} (as does d_{z^2})

$d_{x^2-y^2}$ orbital transforms as b_{1g}

(p_x, p_y) transform as e_u.

$\therefore dsp^2$ bonding $\Rightarrow d_{x^2-y^2}\ s\ p_x p_y$.

Use projection operators to find ligand combinations for the IRs in Γ_σ.

use σ_1

$$a_{1g} = N(a_{1g})\,[\underset{E}{(1)(\sigma_1)} + \underset{2C_4}{(1)[\sigma_2+\sigma_4]} + \underset{C_2}{(1)(\sigma_3)} + \underset{2C_2'}{(1)[\sigma_1+\sigma_3]} + \underset{2C_2''}{(1)[\sigma_2+\sigma_4]}$$

$$+ \underset{i}{(1)(\sigma_3)} + \underset{2S_4}{(1)[\sigma_2+\sigma_4)} + \underset{\sigma_h}{(1)\,\sigma_1)} + \underset{2\sigma_v}{(1)(\sigma_1+\sigma_3)} + \underset{2\sigma_d}{(1)(\sigma_2+\sigma_4)}]$$

$$= N(a_{1g})[4\sigma_1 + 4\sigma_2 + 4\sigma_3 + 4\sigma_4] = N'(a_{1g})[\sigma_1+\sigma_2+\sigma_3+\sigma_4]$$

in ZOA $\quad \langle a_{1g}|a_{1g}\rangle = N^2\cdot 4 = 1 = \quad N=\frac{1}{2}$

$$\therefore \boxed{a_{1g} = \frac{1}{2}(\sigma_1+\sigma_2+\sigma_3+\sigma_4)}$$

Next $\quad b_{1g} = N(b_{1g})[(1)(\sigma_1) - (\sigma_2+\sigma_4) + \sigma_3 + (\sigma_1+\sigma_3) - (\sigma_2+\sigma_4)$

$$+ \sigma_3 - (\sigma_2+\sigma_4) + \sigma_1 + \sigma_1+\sigma_3 - (\sigma_2+\sigma_4)]$$

$$= N(b_{1g})[4\sigma_1 - 4\sigma_2 + 4\sigma_3 - 4\sigma_4]$$

$$= N'(b_{1g})[\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4]$$

in ZOA $\quad \boxed{b_{1g} = \frac{1}{2}(\sigma_1-\sigma_2+\sigma_3-\sigma_4)}$

Next: $e_u(1) =$ (using σ_1) $= N(e_u(1))[2\sigma_1 + 0 - 2\sigma_3 + 0 + 0 - 2\sigma_3 + 0$

$$+ 2\sigma_1 + 0 + 0]$$

$$= N(e_u(1))[4\sigma_1 - 4\sigma_3] = N'(e_u(1))(\sigma_1 - \sigma_3)$$

in ZOA $\quad \boxed{e_u(1) = \frac{1}{\sqrt{2}}(\sigma_1 - \sigma_3)}$

using $e_2 \Rightarrow \boxed{e_u(2) = \frac{1}{\sqrt{2}}(\sigma_2 - \sigma_4)}$

$$\Psi_1 = s + b_1 a_{1g}$$

$$\Psi_2 = d_{x^2-y^2} + b_2 b_{1g}$$

$$\Psi_3 = p_y + b_3 e_u(1)$$

$$\Psi_4 = p_x + b_4 e_u(2)$$

$$\langle \Psi_1\ \Psi_2\ \Psi_3\ \Psi_4 | = \langle s, d_{x^2-y^2}, p_y, p_x | + \langle a_{1g}, b_{1g}, e_u(1), e_u(2) | \tilde{B}$$

$$\langle a_{1g}, b_{1g}, e_u(1), e_u(2) | = \langle \sigma_1\ \sigma_2\ \sigma_3\ \sigma_4 | \tilde{M}$$

$$\tilde{M} = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{\sqrt{2}} & 0 \\ \frac{1}{2} & -\frac{1}{2} & 0 & \frac{1}{\sqrt{2}} \\ \frac{1}{2} & \frac{1}{2} & -\frac{1}{\sqrt{2}} & 0 \\ \frac{1}{2} & -\frac{1}{2} & 0 & -\frac{1}{\sqrt{2}} \end{pmatrix}$$

$$\tilde{M}^{-1} = \tilde{M}^T = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \end{pmatrix}$$

$$\therefore \langle h_1\ h_2\ h_3\ h_4 | = \langle s\ d_{x^2-y^2}\ p_y\ p_x | \tilde{M}^T$$

$$\therefore \boxed{\begin{aligned} h_1 &= \frac{s}{2} + \frac{1}{2} d_{x^2-y^2} + \frac{1}{\sqrt{2}} p_y \\ h_2 &= \frac{s}{2} - \frac{1}{2} d_{x^2-y^2} + \frac{1}{\sqrt{2}} p_x \\ h_3 &= \frac{s}{2} + \frac{1}{2} d_{x^2-y^2} - \frac{1}{\sqrt{2}} p_y \\ h_4 &= \frac{s}{2} - \frac{1}{2} d_{x^2-y^2} - \frac{1}{\sqrt{2}} p_x \end{aligned}}$$

② Benzene belongs to D_{6h} point group $h = 24$.

a) Use projection operation using ϕ_1 as the starting p_z orbital on carbon 1.

$$b_{2g} = N(b_{2g})[(1)\phi_1 + (-1)(\phi_2+\phi_6) + (1)(\phi_3+\phi_5) + (-1)\phi_4 + (-1)(-\phi_1-\phi_5-\phi_3)$$
$$+ (1)[-\phi_6-\phi_2-\phi_4] + (1)(-\phi_4) + (-1)(-\phi_3-\phi_5) + (1)(-\phi_2-\phi_6)$$
$$+ (-1)[-\phi_1] + (-1)(\phi_6+\phi_2+\phi_4) + (1)(\phi_1+\phi_3+\phi_5)$$

$$= N(b_{2g})[4\phi_1 - 4\phi_2 + 4\phi_3 - 4\phi_4 + 4\phi_5 - 4\phi_6]$$
$$= N'(b_{2g})[\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6]$$

$\because \langle b_{2g}|b_{2g}\rangle = 1 \Rightarrow N(b_{2g}) = 1/\sqrt{6}$ in ZOA

$$\therefore \boxed{b_{2g} = \frac{1}{\sqrt{6}}(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)}$$

Next: $e_{1g}(1)$ (using ϕ_1) $= N(e_{1g}(1))[(2)\phi_1 + (1)(\phi_2+\phi_6) + (-1)(\phi_3+\phi_5) + (-2)\phi_4$
$+ 0 + 0 + (2)(-\phi_4) + (1)(-\phi_3-\phi_5) + (-1)(-\phi_2-\phi_6)$
$+ (-2)(-\phi_1) + 0 + 0]$

$$= N(e_{1g}(1))\cdot[4\phi_1 + 2\phi_2 - 2\phi_3 - 4\phi_4 - 2\phi_5 + \phi_6]$$
$$= N'(e_{1g}(1))[2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6]$$

$\because \langle e_{1g}(1)|e_{1g}(1)\rangle = 1 \Rightarrow N(e_{1g}(1)) = 1/\sqrt{12}$ in ZOA

$$\therefore e_{1g}(1) = \frac{1}{\sqrt{12}}[2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6]$$

$e_{1g}(2)$ (using ϕ_2) $= N(e_{1g}(2))[(2)(\phi_2) + (1)(\phi_1+\phi_3) + (-1)(\phi_4+\phi_6) + (-2)\phi_5 + (2)(-\phi_5)$
$+ (1)(-\phi_4-\phi_6) + (-1)(-\phi_1-\phi_3) + (-2)(-\phi_2)]$

$$= N(e_{g}(2))[2\phi_1 + 4\phi_2 + 2\phi_3 - 2\phi_4 - 4\phi_5 - 2\phi_6]$$
$$= N'(e_{g}(2))[\phi_1 + 2\phi_2 + \phi_3 - \phi_4 - 2\phi_5 - \phi_6]$$

$\because \langle e_{1g}(2)|e_{1g}(2)\rangle = 1 \Rightarrow N(e_{1g}(2)) = 1/\sqrt{12}$ in ZOA

$$\therefore \boxed{e_{1g}(2) = \frac{1}{\sqrt{12}}[\phi_1 + 2\phi_2 + \phi_3 - \phi_4 - 2\phi_5 - \phi_6]}$$

$e_{2u}(1)$ (using ϕ_1) $= N(e_{2u}(1))[2\phi_1 + (-1)(\phi_2+\phi_6) + (-1)(\phi_3+\phi_5) + 2\phi_4 + 0 + 0$
$- (2)(-\phi_4) + (1)(-\phi_3-\phi_5) + (1)(-\phi_2-\phi_6)$
$+ (-2)(-\phi_1) + 0 + 0\ ]$

$= N(e_{2u}(1))[4\phi_1 - 2\phi_2 - 2\phi_3 + 4\phi_4 - 2\phi_5 - 2\phi_6]$

$= N(e_{2u}(1))[2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6]$

$\because \langle e_{2u}(1) | e_{2u}(1) \rangle = 1 \Rightarrow N(e_{2u}(1)) = 1/\sqrt{12}$ in ZOA,

$\therefore \boxed{e_{2u}(1) = \frac{1}{\sqrt{12}}[2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6]}$

$e_{2u}(2)$ (using ϕ_2) $= N(e_{2u}(2))[2\phi_2 + (-1)(\phi_1+\phi_3) + (-1)(\phi_4+\phi_6) + 2\phi_5 - (2)(-\phi_5)$
$+ (1)(-\phi_4-\phi_6) + (1)(-\phi_1-\phi_3) + (-2)(-\phi_2)\ ]$

$= N(e_{2u}(2))[\phi_1 - 2\phi_2 + \phi_3 + \phi_4 - 2\phi_5 + \phi_6]$

$\because \langle e_{2u}(2) | e_{2u}(2) \rangle = 1 \Rightarrow N(e_{2u}(2)) = 1/\sqrt{12}$ in ZOA

$\therefore \boxed{e_{2u}(2) = \frac{1}{\sqrt{12}}(\phi_1 - 2\phi_2 + \phi_3 + \phi_4 - 2\phi_5 + \phi_6)}$

b) $e_{1g}() = \frac{1}{\sqrt{3}}[e_{1g}(1) + e_{1g}(2)]$

$= \frac{1}{\sqrt{3}}\left[\frac{1}{\sqrt{12}}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6) + \frac{1}{\sqrt{12}}(\phi_1 - 2\phi_2 + \phi_3 - \phi_4 - 2\phi_5 - \phi_6)\right]$

$= \frac{1}{\sqrt{3}\sqrt{12}}[3\phi_1 + 3\phi_2 - 3\phi_4 - 3\phi_5] = \frac{3}{\sqrt{3}\sqrt{12}}[\phi_1 + \phi_2 - \phi_4 - \phi_5]$

$= \boxed{\frac{1}{2}(\phi_1 + \phi_2 - \phi_4 - \phi_5)}$

$e_{1g}(2) = e_{1g}(1) - e_{1g}(2) = \frac{1}{\sqrt{12}}[(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6) - (\phi_1 + 2\phi_2 + \phi_3 - \phi_4 - 2\phi_5 - \phi_6)]$

$= \boxed{\frac{1}{\sqrt{12}}[\phi_1 - \phi_2 - 2\phi_3 - \phi_4 + \phi_5 + 2\phi_6]}$

$f^{n}s$ are normalized if $\langle e_{1g}(1) | e_{1g}(1) \rangle = 1 = \langle e_{1g}(2) | e_{1g}(2) \rangle$
① ②

and orthogonal if $\langle e_{1g}(1) | e_{1g}(2) \rangle = 0 \quad (= \langle e_{1g}(2) | e_{1g}(1) \rangle)$
③

① $\langle e_{1g}(1) | e_{1g}(1) \rangle = \frac{1}{4} \int (\phi_1^2 + \phi_2^2 + \phi_4^2 + \phi_5^2)\, d\tau = \frac{4}{4} = 1$

② $\langle e_{1g}(2) | e_{1g}(2) \rangle = \frac{1}{12} \int \phi_1^2 + \phi_2^2 + 4\phi_3^2 + \phi_4^2 + \phi_5^2 + 4\phi_6^2 \,]\, d\tau$

$$= \frac{1}{12} [1 + 1 + 4 + 1 + 1 + 4] = \frac{12}{12} = 1$$

③ $\langle e_{1g}(1) | e_{1g}(2) \rangle = \frac{1}{2\sqrt{12}} \int (\phi_1 + \phi_2 - \phi_4 - \phi_5)(\phi_1 - \phi_2 - 2\phi_3 - \phi_4 + \phi_5 + 2\phi_6)\, d\tau$

$$= \frac{1}{2\sqrt{12}} \int (\phi_1^2 - \phi_2^2 + \phi_4^2 - \phi_5^2)\, d\tau = \frac{1}{2\sqrt{12}} [1 - 1 + 1 - 1] = 0$$

Similarly: $e_{2u}(1) = \frac{1}{\sqrt{3}} (e_{2u}(1) + e_{2u}(2))$

$$= \frac{1}{\sqrt{3}} \frac{1}{\sqrt{12}} [(2\phi_1 - \phi_2 - \phi_2 + 2\phi_4 - \phi_5 - \phi_6) + (\phi_1 - 2\phi_2 + \phi_3 + \phi_4 - 2\phi_5 + \phi_6)]$$

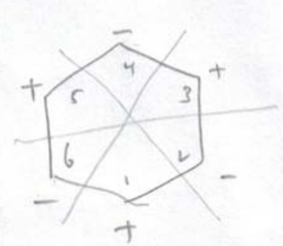
$$= \frac{1}{\sqrt{3}} \frac{1}{\sqrt{12}} [3\phi_1 - 3\phi_2 + 3\phi_4 - 3\phi_5] = \boxed{\frac{1}{2}(\phi_1 - \phi_2 + \phi_4 - \phi_5)}$$

$$e_{2u}(2) = (e_{2u}(1) - e_{2u}(2)) = \frac{1}{\sqrt{12}} [(2\phi_1 - \phi_2 - \phi_3 + 2\phi_4 - \phi_5 - \phi_6) - (\phi_1 - 2\phi_2 + \phi_3 + \phi_4 - 2\phi_5 + \phi_6)]$$

$$= \boxed{\frac{1}{\sqrt{12}} (\phi_1 + \phi_2 - 2\phi_3 + \phi_4 + \phi_5 - 2\phi_6)}$$

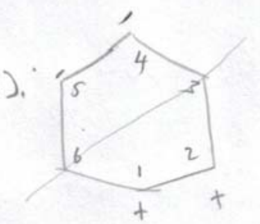
These $f^{n}s$ are also normalized and orthogonal.

c) b_{2g}:



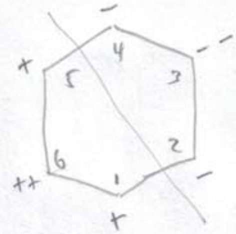
3 nodal planes.

$e_{1g}(1)$:



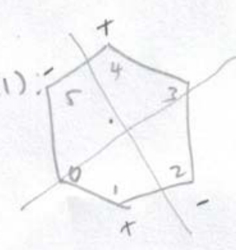
1 nodal plane.

$e_{1g}(2)$



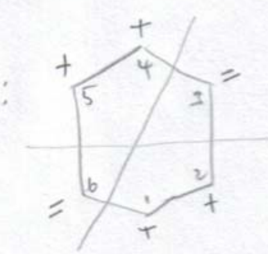
1 nodal plane

$e_{2u}(1)$:



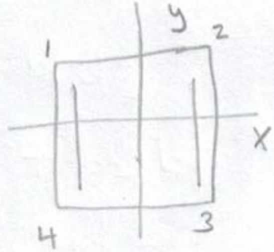
2 nodal planes

$e_{2u}(2)$:



2 nodal planes

③

a) 

Point group is D_{2h}
numbering refers to specific carbons

Use 4 p_z orbitals as basis set. for π-orbitals

D_{2h}	E	C_{2z}	C_{2y}	C_{2x}	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ_π	4	0	0	0	0	−4	0	0

$h = 8$

$$a_g = \frac{1}{8}[(1)(4)(1) + (1)(-4)(1)] = 0$$
$$b_{1g} = \frac{1}{8}[(1)(4)(1) + (1)(-4)(1)] = 0$$
$$b_{2g} = \frac{1}{8}[(1)(4)(1) + (1)(-4)(-1)] = 1$$
$$b_{3g} = \frac{1}{8}[(1)(4)(1) + (1)(-4)(-1)] = 1$$
$$a_u = \frac{1}{8}[(1)(4)(1) + (1)(-4)(-1)] = 1$$
$$b_{1u} = \frac{1}{8}[(1)(4)(1) + (1)(-4)(-1)] = 1$$
$$b_{2u} = \frac{1}{8}[(1)(4)(1) + (1)(-4)(1)] = 0$$
$$b_{3u} = \frac{1}{8}[(1)(4)(1) + (1)(-4)(1)] = 0$$

$$\therefore \Gamma_\pi = B_{2g} \oplus B_{3g} \oplus A_u \oplus B_{1u}.$$

Use projection operator and start with ϕ_1

$$\underline{b_{2g}} = N(b_{2g})\big[\underset{E}{(1)(\phi_1)} + \underset{C_{2z}}{(-1)(\phi_3)} + \underset{C_{2y}}{(1)(-\phi_2)} + \underset{C_{2x}}{(-1)(-\phi_4)} + \underset{i}{(1)(-\phi_3)} + \underset{\sigma(xy)}{(-1)(-\phi_1)}$$
$$+ \underset{\sigma(xz)}{(1)(\phi_4)} + \underset{\sigma(yz)}{(-1)(\phi_2)}\big]$$

$$= N(b_{2g})[2\phi_1 - 2\phi_2 - 2\phi_3 + 2\phi_4] = N'(b_{2g})[\phi_1 - \phi_2 - \phi_3 + \phi_4]$$

$$\langle b_{2g} | b_{2g}\rangle = 1 \Rightarrow N'(b_{2g}) = \frac{1}{2} \text{ in ZOA}.$$

$$\therefore \boxed{b_{2g} = \frac{1}{2}(\phi_1 - \phi_2 - \phi_3 + \phi_4)}$$

$$\underline{b_{3g}} = N(b_{3g})[(1)(\phi_1) + (-1)(\phi_3) + (-1)(-\phi_2) + (1)(-\phi_3) + (-1)(-\phi_1) + (-1)(\phi_4) + (1)(\phi_2)] = N'(b_{3g})[\phi_1 + \phi_2 - \phi_3 - \phi_4]$$
$$= N(b_{3g})[2\phi_1 + 2\phi_2 - 2\phi_3 - 2\phi_4]$$
$$\langle b_{3g} | b_{3g}\rangle = 1 = N'(b_{3g}) = \frac{1}{2} \text{ in ZOA} \Rightarrow \boxed{b_{3g} = \frac{1}{2}(\phi_1 + \phi_2 - \phi_3 - \phi_4)}$$

$a_u = N(a_u)[(1)(\phi_1) + (1)(\phi_3) + (1)(-\phi_2) + (1)(-\phi_4) + (-1)(-\phi_3) + (-1)(-\phi_1) + (-1)(\phi_4) + (-1)(\phi_2)]$

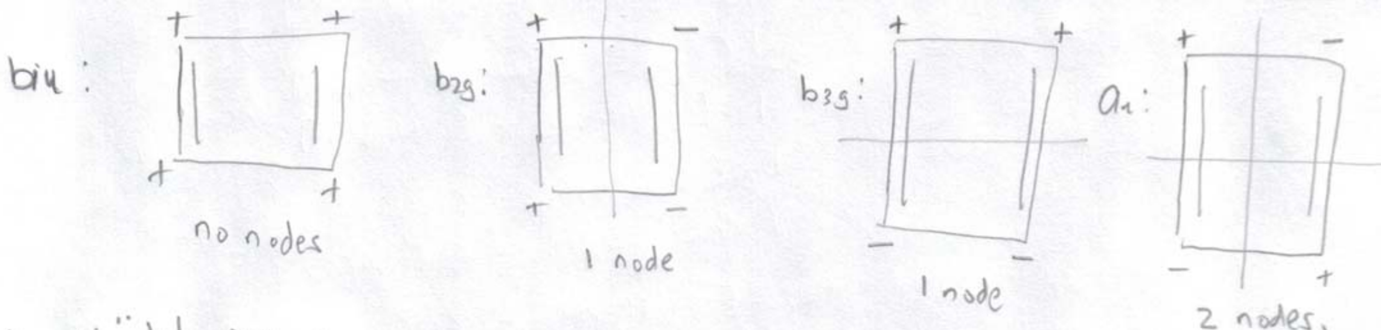
$= N(a_u)[2\phi_1 - 2\phi_2 + 2\phi_3 - 2\phi_4] = N'(a_u)(\phi_1 - \phi_2 + \phi_3 - \phi_4)$

$\because \langle a_u | a_u \rangle = 1 \Rightarrow N'(a_u) = \frac{1}{2} \Rightarrow \boxed{a_u = \frac{1}{2}(\phi_1 - \phi_2 + \phi_3 - \phi_4)}$

$b_{1u} = N(b_{1u})[(1)(\phi_1) + (1)(\phi_3) + (-1)(-\phi_2) + (-1)(-\phi_4) + (-1)(-\phi_3) + (-1)(-\phi_1) + (1)(\phi_4) + (1)(\phi_2)]$

$= N(b_{1u})[2\phi_1 + 2\phi_2 + 2\phi_3 + 2\phi_4] = N'(b_{1u})(\phi_1 + \phi_2 + \phi_3 + \phi_4)$

$\langle b_{1u} | b_{1u} \rangle = 1 \Rightarrow N'(b_{1u}) = \frac{1}{2}$ in ZOA $\Rightarrow \boxed{b_{1u} = \frac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4)}$



b) Hückel energies.

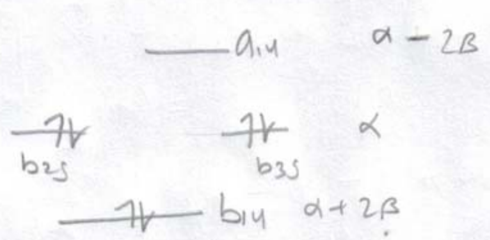
from class: $E^j = |N_j|^2 \left[\sum_r |c_{rj}|^2 \alpha + \sum_r \sum_s c_{rj}^* c_{sj} \beta \right]$

b_{1u}: $E_{b_{1u}} = \frac{1}{4}[4\alpha + 2[c_1c_2 + c_2 + c_3c_4 + c_4c_1]\beta = \frac{1}{4}[4\alpha + 8\beta] = \alpha + 2\beta$

b_{2g}: $E_{b_{2g}} = \frac{1}{4}[4\alpha + 2(-1+1-1+1)\beta] = \alpha$

b_{3g}: $E_{b_{3g}} = \frac{1}{4}[4\alpha + 2(1-1+1-1)\beta] = \alpha$

a_u: $E_{a_u} = \frac{1}{4}[4\alpha + 2(-1-1-1-1)\beta] = \alpha - 2\beta$



Remember $\alpha, \beta < 0$: total energy $C_4H_4^{2-} = 2(\alpha + 2\beta) + 4\alpha = 6\alpha + 4\beta$

from class total energy $C_6H_6 = 2(\alpha + 2\beta) + 4(\alpha + \beta) = 6\alpha + 8\beta$

$8\beta < 4\beta \Rightarrow E_{C_6H_6} < E_{C_4H_4^{2-}}$

(4)

a) C_{2z} axis, i σ_h S_2 $\Rightarrow$ C_{2h} point group.

b)

C_{2h}	E	C_2	i	σ_h
Γ_π	4	0	0	−4

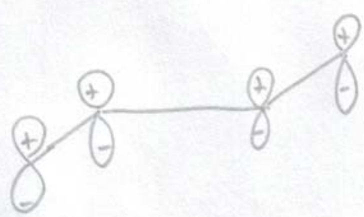
using 4 p_z orbitals as a basis.

$$a_g = \frac{1}{4}[(1)(4)(1) + (1)(-4)(1)] = 0$$
$$b_g = \frac{1}{4}[(1)(4)(1) + (1)(-4)(-1)] = 2$$
$$a_u = \frac{1}{4}[(1)(4)(1) + (1)(-4)(-1)] = 2$$
$$b_u = \frac{1}{4}[(1)(4)(1) + (1)(-4)(1)] = 0$$

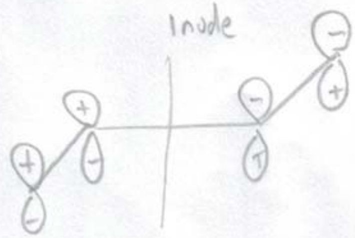
$$\therefore \Gamma_\pi = 2b_g \oplus 2a_u.$$

c)

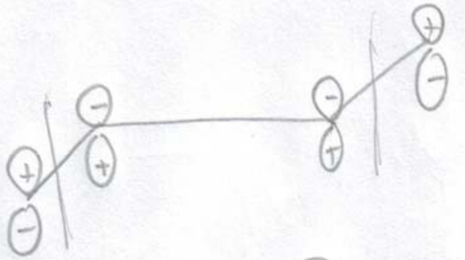
"looking" at entire MO



$\chi(E) = +1$
$\chi(C_2) = +1$ $\Rightarrow a_u(1)$ no nodes.
$\chi(i) = -1$
$\chi(\sigma_h) = -1$

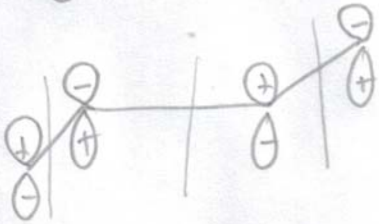


$\chi(E) = +1$
$\chi(C_2) = -1$ $\Rightarrow b_g(1)$ 1 node.
$\chi(i) = +1$
$\chi(\sigma_h) = -1$



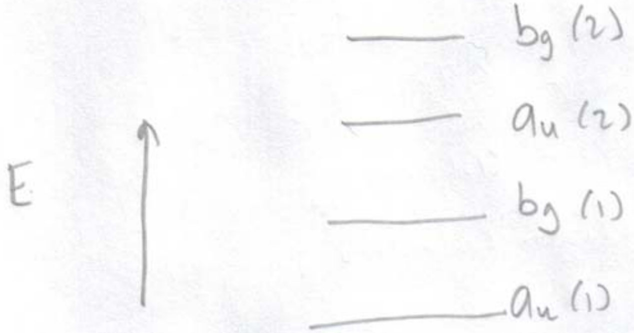
$\chi(E) = +1$
$\chi(C_2) = +1$
$\chi(i) = -1$
$\chi(\sigma_h) = -1$

$\Rightarrow a_u(2)$ 2 nodes



$\chi(E) = +1$
$\chi(C_2) = -1$
$\chi(i) = +1$
$\chi(\sigma_h) = -1$

$\Rightarrow b_g(2)$ 3 nodes.



d) 4 π electrons. Pauli Principle $\Rightarrow$ 2 spin-paired e^-'s / orbital

$\therefore$ ground state $= a_u(1)^2\, b_g(1)^2$

IR given by $\underbrace{a_u(1) \otimes a_u(1)}_{A_g} \otimes \underbrace{b_g(1) \otimes b_g(1)}_{A_g} = A_g$

S total $= 0 \Rightarrow 2S+1 = 1 \Rightarrow {}^1A_g \equiv$ HOMO

LUMO : $a_u(1)^2\, b_g(1)\, a_u(2)^2$

IR $= \underbrace{a_u(1) \otimes a_u(1)}_{A_g} \otimes \underbrace{b_g(1) \otimes a_u(2)}_{B_u} = B_u$ by inspection.

invoking a $\Delta S = 0$ selection rule LUMO $\equiv {}^1B_u$

e) transition is allowed if $\Gamma_{LUMO} \otimes \Gamma_{HOMO} \subset \Gamma_{x,y,z}$

$B_u \otimes A_g = B_u \subset \Gamma_x, \Gamma_y$ $\therefore$ it is allowed.

Alternatively $\Gamma_{x,y,z} = 2B_u \oplus A_u$.

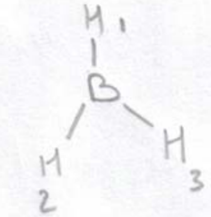
$\therefore A_g \otimes B_u \otimes (2B_u \oplus A_u) = \{1\ -1\ -1\ 1\} \otimes \{3\ -1\ -3\ 1\}$

$= \{3\ 1\ 3\ 1\}$.

reduce $a_g = \frac{1}{4}[(1)(3)(1) + (1)(1)(1) + (1)(3)(1) + (1)(1)(1)] = 2$

$\therefore \Gamma_{LUMO} \otimes \Gamma_{HOMO} \otimes \Gamma_{x,y,z} \subset \Gamma_1 \equiv A_g$ $\therefore$ allowed.

(5.)



- use s-orbitals on 3 H's as a basis for the ligands.
- point group is D_{3h}.

∴

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

$h = 12$

$$a_1' = \frac{1}{12}\left[(1)(3)(1) + (3)(1)(1) + (1)(3)(1) + (3)(1)(1)\right] = 1$$

$$a_2' = \frac{1}{12}\left[(1)(3)(1) + (3)(1)(-1) + (1)(3)(1) + (3)(1)(-1)\right] = 0$$

$$e' = \frac{1}{12}\left[(1)(3)(2) + 0 + (1)(3)(2) + 0\right] = 1$$

can stop here ∴ $\Gamma_s = a_1' \oplus e'$ is 3×3.

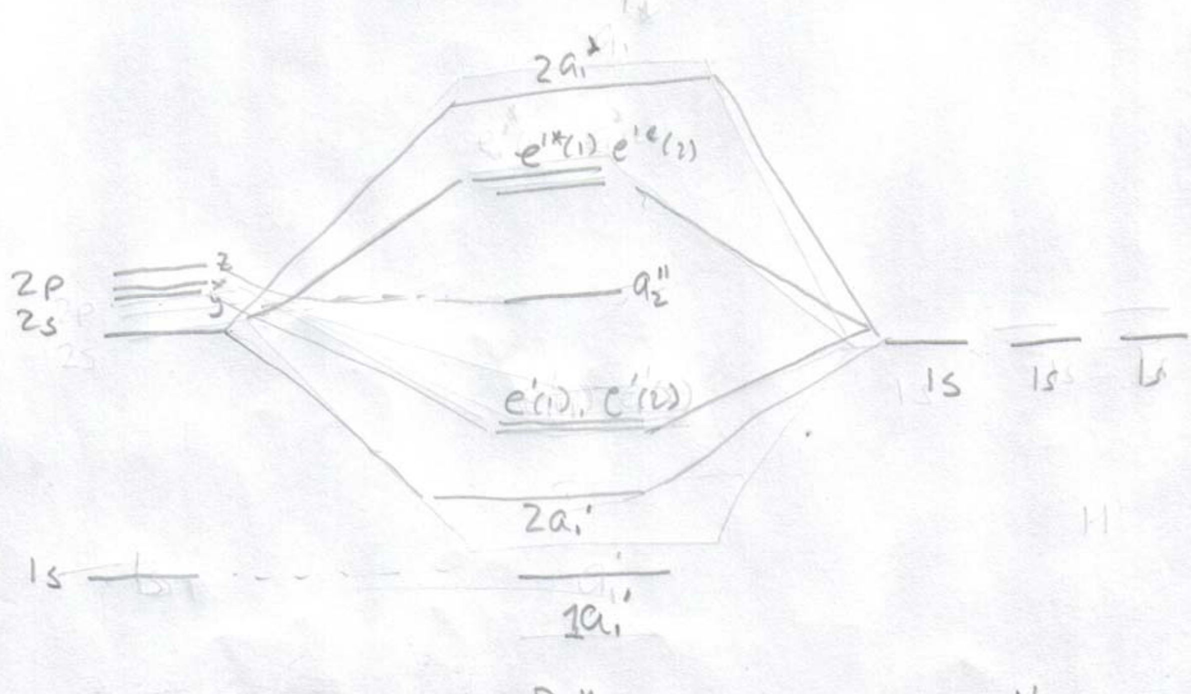
B atom: s orbital transforms as a_1'

p_x, p_y orbitals transform as e'

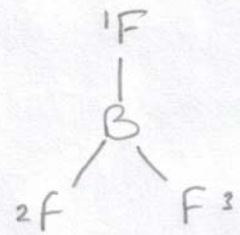
∴ $\psi_1 = 2s + b_1 a_1' \equiv a_1', a_1^*$ b_i + ⇒ bonding

$\psi_2(1) = 2p_x + b_2 e' \equiv e'(1), e'^*(1)$ b_i − ⇒ antibonding

$\psi_2(2) = 2p_y + b_3 e' \equiv e'(2), e'^*(2)$



⑥



D_{3h}

use 3 p_z orbitals on F as a basis.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_π	3	0	-1	-3	0	1

$h = 12$

$$a_1' = \frac{1}{12}\left[(1)(3)(1) + (3)(-1)(1) + (1)(-3)(1) + (3)(1)(1)\right] = 0$$

$$a_2' = \frac{1}{12}\left[(1)(3)(1) + (3)(-1)(-1) + (1)(-3)(1) + (3)(1)(-1)\right] = 0$$

$$e' = \frac{1}{12}\left[(1)(3)(2) + 0 + (1)(-3)(2) + 0\right] = 0$$

$$a_1'' = \frac{1}{12}\left[(1)(3)(1) + (3)(-1)(1) + (1)(-3)(-1) + (3)(1)(-1)\right] = 0$$

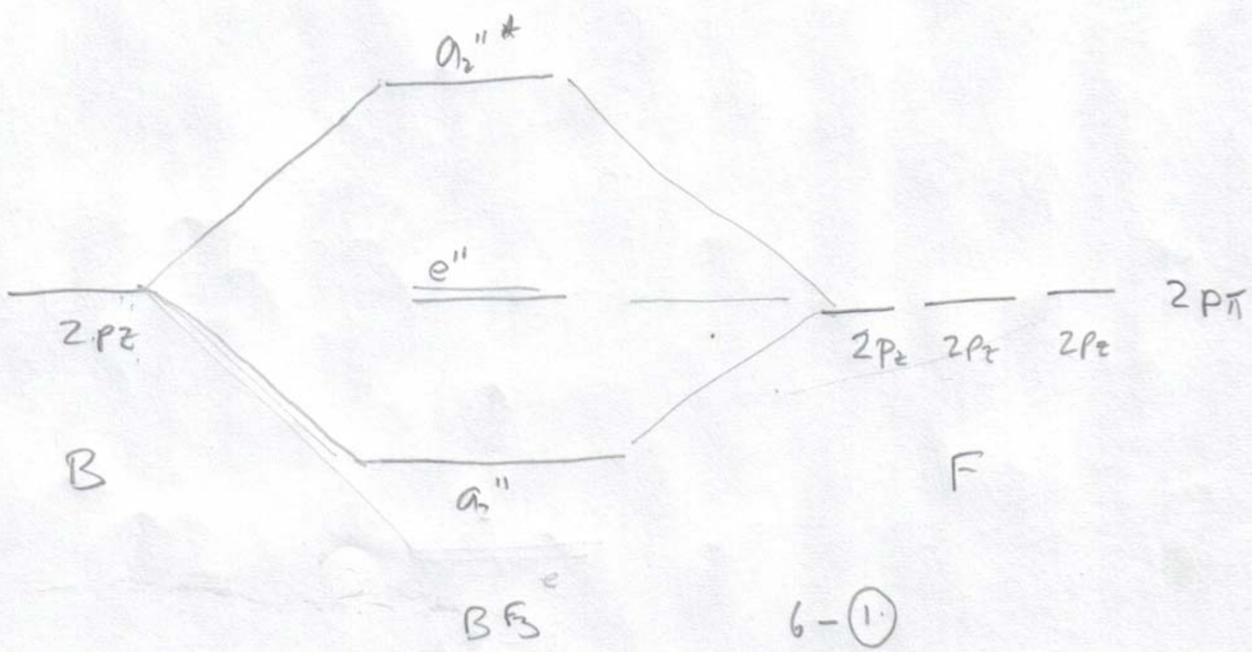
$$a_2'' = \frac{1}{12}\left[(1)(3)(1) + (3)(-1)(-1) + (1)(-3)(-1) + (3)(1)(1)\right] = 1$$

$$e'' = \frac{1}{12}\left[(1)(3)(2) + 0 + (1)(-3)(-2) + 0\right] = 1$$

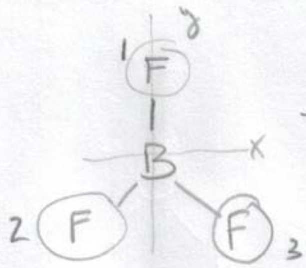
$\therefore \quad \Gamma_\pi = a_2'' \oplus e''$

p_z on B transforms as a_2'' $\Rightarrow$ e'' ligand orbitals are non-bonding

$\therefore$ MO scheme for $p\pi$-MOs of BF_3



b)



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

$\therefore a_1' = \frac{1}{12}[(1)(3)(1) + (3)(1)(1) + (1)(3)(1) + (3)(1)(1)] = 1$

$a_2' = \frac{1}{12}[(1)(3)(1) + (3)(1)(-1) + (1)(3)(1) + (3)(1)(-1)] = 0$

$e' = \frac{1}{12}[(1)(3)(2) + 0 + (1)(3)(2) + 0] = 1$

$a_1'' = \frac{1}{12}[(1)(3)(1) + (3)(1)(1) + (1)(3)(-1) + (3)(1)(-1)] = 0$

$a_2'' = \frac{1}{12}[(1)(3)(1) + (3)(1)(-1) + (1)(3)(-1) + (3)(1)(1)] = 0$

$e'' = \frac{1}{12}[(1)(3)(2) + 0 + (1)(3)(-2) + 0] = 0$

$\therefore \Gamma_s = a_1' \oplus e'$

use projection operator

a_1' (using s_1) $= N(a_1')[\underset{E}{(1)s_1} + \underset{2C_3}{(1)(s_2+s_3)} + \underset{3C_2}{(1)(s_1+s_2+s_3)} + \underset{\sigma_h}{(1)(s_1)} + (1)(s_2+s_3) + \underset{\sigma_v}{(1)(s_1+s_2+s_3)}]$

$= N(a_1')[4s_1 + 4s_2 + 4s_3] = N'(a_1')(s_1+s_2+s_3)$

$\langle a_1' | a_1' \rangle = 1 \Rightarrow N'(a_1') = \frac{1}{\sqrt{3}}$ in ZOA $\Rightarrow \boxed{a_1' = \frac{1}{\sqrt{3}}(s_1+s_2+s_3)}$

$e'(1)$ (using s_1) $= N(e'(1))[(2)(s_1) + (-1)(s_2+s_3) + 0 + (2)(s_1) + (-1)(s_2+s_3) + 0]$

$= N(e'(1))[4s_1 - 2s_2 - 2s_3] = N'(e'(1))[2s_1 - s_2 - s_3]$

$\langle e'(1) | e'(1) \rangle = 1 \Rightarrow N'(e'(1)) = \frac{1}{\sqrt{6}}$ in ZOA

$\Rightarrow \boxed{e'(1) = \frac{1}{\sqrt{6}}(2s_1 - s_2 - s_3)}$

$$\therefore\ e'(2)(\text{using } s_2) = N(e'(2))\left[(2)(s_2) + (-1)(s_1+s_3) + (2)(s_2) + (-1)(s_1+s_3)\right]$$

$$= N(e'(2))\left[4s_2 - 2s_1 - 2s_3\right]$$

$$\Rightarrow\ e'(2) = \frac{1}{\sqrt{6}}\left[2s_2 - s_1 - s_3\right]$$

$$e'(3)(\text{using } s_3) = N(e'(3))\left[(2)(s_3) + (-1)(s_1+s_2) + (2)(s_3) + (-1)(s_1+s_2)\right]$$

$$= N(e'(3))\left[4s_3 - 2s_1 - 2s_2\right]$$

$$\Rightarrow\ e'(3) = \frac{1}{\sqrt{6}}\left[2s_3 - s_1 - s_2\right]$$

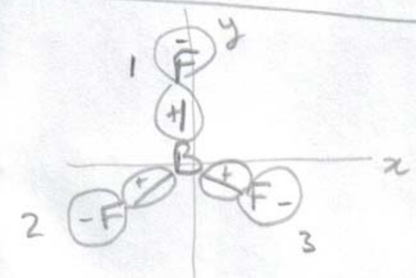
As drawn s_1 points along y-axis $\therefore$ $e'(1)$ is OK.

eliminate s_1 from $e'(2)$ / $e'(3)$ by taking $e'(2) - e'(3)$ and normalizing

$$e'(2) - e'(3) \propto \cancel{\tfrac{1}{\sqrt{6}}}\left[2s_2 - 2s_3 \cancel{- s_1 + s_1} - s_3 + s_2\right] = 3s_2 - 3s_3$$

$$\therefore\ \boxed{e'(2) = \frac{1}{\sqrt{2}}(s_2 - s_3)}$$

c)

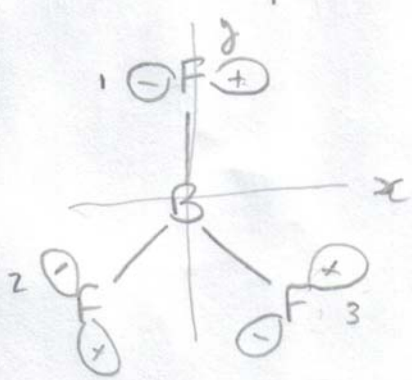


D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{p\sigma}$	3	0	1	3	0	1

Same character set as Γ_s

$$\Rightarrow\ \Gamma_{p\sigma} = a_1' \oplus e' \qquad \text{on B} \quad s \sim a_1' \quad (p_x, p_y) \sim e'$$

d)



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{p_{nb}}$	3	0	-1	3	0	-1

$$a_1' = \frac{1}{12}[(1)(3)(1) + (3)(-1)(1) + (1)(3)(1) + (3)(-1)(1)] = 0$$

$$a_2' = \frac{1}{12}[(1)(3)(1) + (3)(-1)(-1) + (1)(3)(1) + (3)(-1)(-1)] = 1$$

$$e' = \frac{1}{12}[(1)(3)(2) + 0 + (1)(3)(2) + 0] = 1$$

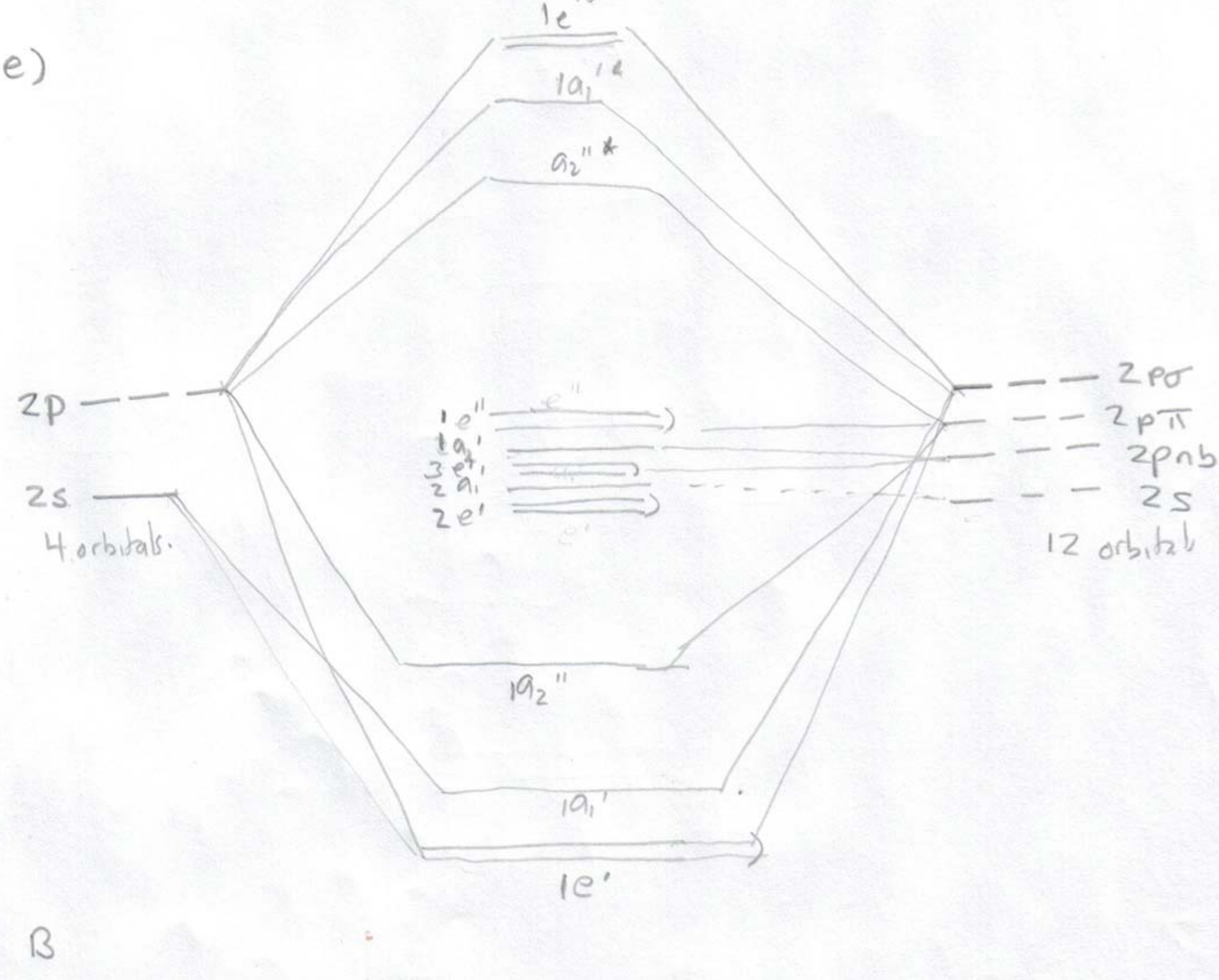
$$a_1'' = \frac{1}{12}[(1)(3)(1) + (3)(-1)(1) + (1)(3)(-1) + (3)(-1)(-1)] = 0$$

$$a_2'' = \frac{1}{12}[(1)(3)(1) + (3)(-1)(-1) + (1)(3)(-1) + (3)(-1)(1)] = 0$$

$$e'' = \frac{1}{12}[(1)(3)(2) + 0 + (1)(3)(-2) + 0] = 0.$$

$$\Gamma_{pnb} = a_2' \oplus e'$$

e)

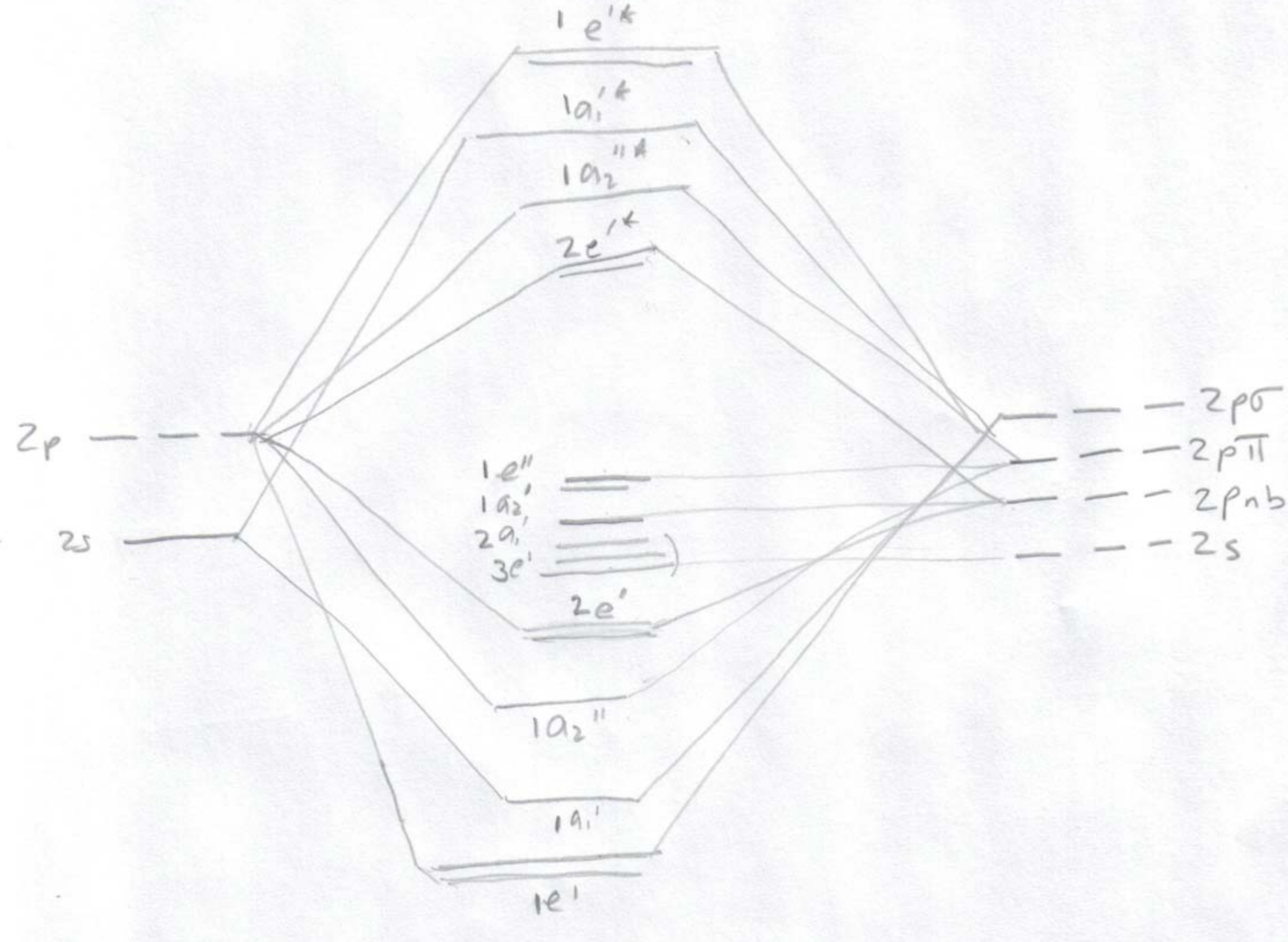


6-4

f) Examine $\Gamma_{pnb} = a_2' \oplus e'$

From character table (p_x, p_y) transform as e'; therefore there will be a weak interaction with the e' combination on the F's.

new MO



might also expect some bonding with 2s orbital combination on Fs with 2s orbital on B.

Note: in all MO diagrams the orbital ordering will be affected by the relative energies of the B & F levels and the 2p-2s energy splittings. The diagrams here are "qualitative".