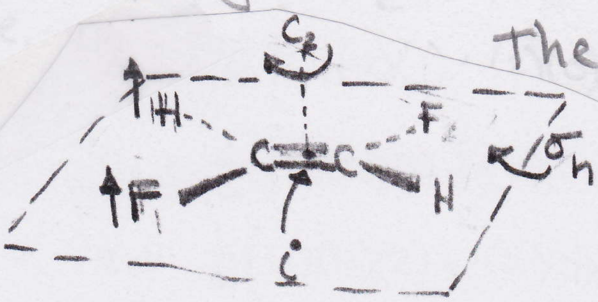
Answers - chapter 4

1. a) C_{3h} b) D_{4h} c) D_{3h} d) D_{2h} e) D_{2d}
f) T_d g) O_h h) C_{4v} i) D_{7h} j) D_{3d}
k) C_2 l) C_{3v} m) eclipsed $= D_{5h}$; staggered $= D_{5d}$
n) T_h o) C_s p) C_2 q) D_{2d} r) D_{3h} s) I_h

<u>note</u> - if you have gotten more than one incorrect answer (n) is tricky!), then get one or two inorganic texts and work more problems like this. It is absolutely vital that the point group is selected correctly or else everything after will be wrong!

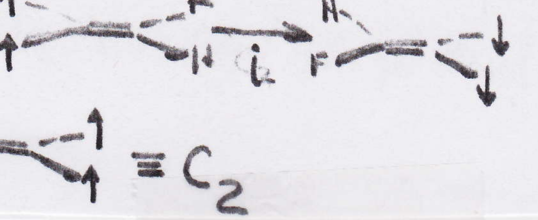
2. 

The operations are:
E

remember to multiply
(column) x (row)

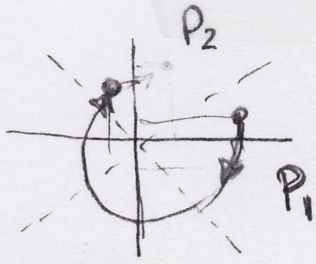
	E	C_2	i	σ_h
E	E	C_2	i	σ_h
C_2	C_2	E	σ_h	i
i	i	σ_h	E	C_2
σ_h	σ_h	i	C_2	E

for example:

$(i)\times(C_2) =$ 

$(\sigma_h)\times(i) =$

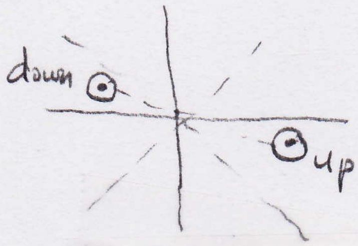
4. a)



$$\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

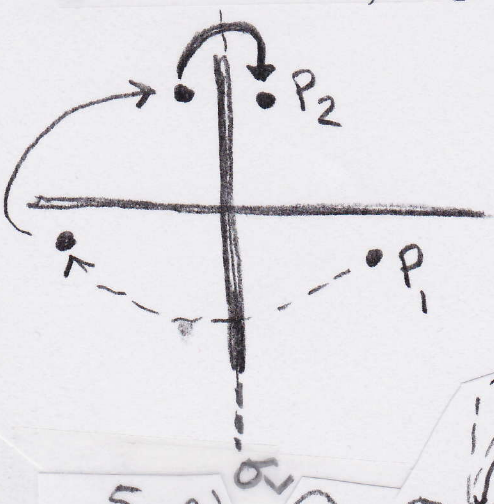
$$x_2 = (0)x_1 + (-1)y_1 + (0)z_1$$
$$y_2 = (1)x_1 + (0)y_1 + (0)z_1$$
$$z_2 = (0)x_1 + (0)y_1 + (1)z_1$$
$$\therefore \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

b)



$$x_2 = (-1)x_1 + (0)y_1 + (0)z_1$$
$$y_2 = (0)x_1 + (-1)y_1 + (0)z_1$$
$$z_2 = (0)x_1 + (0)y_1 + (-1)z_1$$
$$\therefore \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

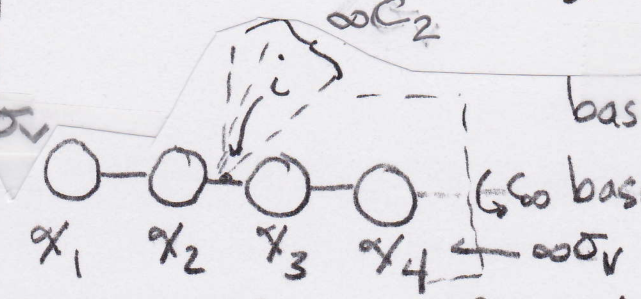
c) Use, say σ_v



$$\sigma_v C_4 \sigma_v = C_4^3$$

you could have used the other σ_v; the σ_d's, any C_2, etc.

5. a)



basis 1: α_1, α_4

basis 2: α_2, α_3

	$D_{\infty h}$	E	$2C_\infty$	∞C_v	i	$2S_\infty$	∞C_2
for α_1, α_4	Γ_1	2	2	2	0	0	0
for α_2, α_3	Γ_2	2	2	2	0	0	0

$\Gamma_1 = \sigma_g^+ + \sigma_u^+$ $\Gamma_2 = \sigma_g^+ + \sigma_u^+$

$D_{\infty h}$	E	C_∞	C_v	i	S_∞	C_2
α_1	α_1	α_1	α_1	α_4	α_4	α_4
α_2	α_2	α_2	α_2	α_3	α_3	α_3

$$\psi_{1\sigma_g^+} \propto (1)\chi_1 + (1)\chi_1 + (1)\chi_1 \cdots (\infty)\chi_1 + (1)\chi_4 + (1)\chi_4 \cdots (\infty)\chi_4$$
$$\propto \chi_1 + \chi_4$$

$$\psi_{2\sigma_g^+} \propto (1)\chi_2 + (1)\chi_2 + (1)\chi_2 \cdots (\infty)\chi_2 + (1)\chi_3 + (1)\chi_3 + \cdots (\infty)\chi_3$$
$$\propto \chi_2 + \chi_3$$

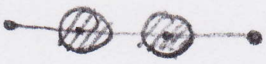
Normalizing:

$$\langle \psi_{1\sigma_g^+} | \psi_{1\sigma_g^+} \rangle = \langle \chi_1 + \chi_4 | \chi_1 + \chi_4 \rangle = \chi_1^2 + \chi_4^2 + 2\chi_1\chi_4 = 2 + 2S_{14}$$

$$\therefore \psi_{1\sigma_g^+} = \frac{1}{\sqrt{2+2S_{14}}}(\chi_1 + \chi_4) \equiv$$ 

likewise

$$\langle \psi_{2\sigma_g^+} | \psi_{2\sigma_g^+} \rangle = \langle \chi_2 + \chi_3 | \chi_2 + \chi_3 \rangle = \chi_2^2 + \chi_3^2 + 2\chi_2\chi_3 = 2 + 2S_{23}$$

$$\therefore \psi_{2\sigma_g^+} = \frac{1}{\sqrt{2+2S_{23}}}(\chi_2 + \chi_3) \equiv$$ 

Obviously, $\psi_{1\sigma_g^+}$ & $\psi_{2\sigma_g^+}$ can interact with eachother $\therefore$

$$\psi_1 \propto (\psi_{1\sigma_g^+} + \psi_{2\sigma_g^+}) \quad \& \quad \psi_2 \propto (\psi_{1\sigma_g^+} - \psi_{2\sigma_g^+})$$

Thus, with normalization and $S_{12} = S_{23} = S_{34}$; $S_{13} = S_{24}$ - if the H's are equally space

$$\psi_1 = \frac{1}{\sqrt{4+6S_{12}+4S_{13}+2S_{14}}}(\chi_1 + \chi_2 + \chi_3 + \chi_4) \equiv$$ 

$$\psi_2 = \frac{1}{\sqrt{4-2S_{12}-4S_{13}+2S_{14}}}(\chi_1 - \chi_2 - \chi_3 + \chi_4) \equiv$$ 

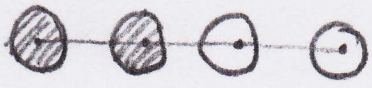
$$\psi_{1\sigma_u^+} \propto (1)\chi_1 + (1)\chi_1 + (1)\chi_1 \cdots (\infty)\chi_1 + (-1)\chi_4 + (-1)\chi_4 + (-1)\chi_4 \cdots (\infty)\chi_4$$
$$\propto \chi_1 - \chi_4$$

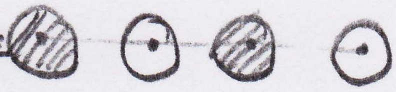
$$\psi_{2\sigma_u^+} \propto (1)\chi_2 \cdots (\infty)\chi_2 + (-1)\chi_3 \cdots -(\infty)\chi_3$$
$$\propto \chi_2 - \chi_3$$

normalizing $\psi_{1\sigma_u^+} = \frac{1}{\sqrt{2-2S_{14}}}(\chi_1 - \chi_4) \equiv$ 

$\psi_{2\sigma_u^+} = \frac{1}{\sqrt{2-2S_{23}}}(\chi_2 - \chi_3) \equiv$ 

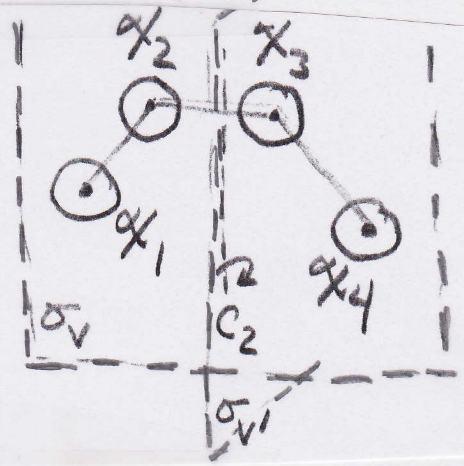
again $\psi_{1\sigma_u^+}$ & $\psi_{2\sigma_u^+}$ can be combined to give

$\psi_3 = \frac{1}{\sqrt{4+2S_{12}-4S_{13}-2S_{14}}}(\chi_1 + \chi_2 - \chi_3 - \chi_4) \equiv$ 

$\psi_4 = \frac{1}{\sqrt{4-6S_{12}+4S_{13}-2S_{14}}}(\chi_1 - \chi_2 + \chi_3 - \chi_4) \equiv$ 

<u>note</u> while $S_{12} = S_{23} = S_{34}$ (if the hydrogens are equally spaced) S_{13} and $S_{14} \approx 0$ because of the long distance

<u>note</u>: MO's from an extended Hückel calculation are on the next page.

b) 

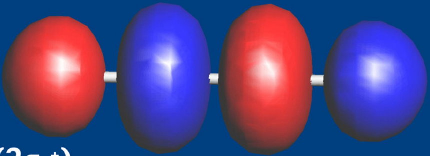
C_{2v} symmetry

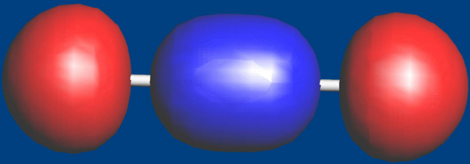
basis 1 = χ_1, χ_4

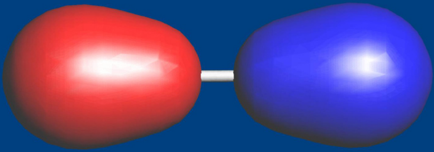
basis 2 = χ_2, χ_3

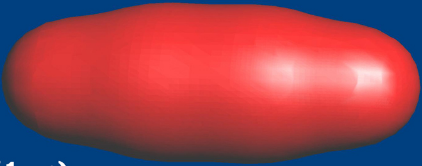
	C_{2v}	E	C_2	σ_v	σ_v'	
for χ_1, χ_4	$\Gamma_1 =$	2	0	2	0	$= a_1 + b_1$
for χ_2, χ_3	$\Gamma_2 =$	2	0	2	0	$= a_1 + b_1$

C_{2v}	E	C_2	σ_v	σ_v'
χ_1	χ_1	χ_4	χ_1	χ_4
χ_2	χ_2	χ_3	χ_2	χ_3


$\psi(2\sigma_u^+)$


$\psi(2\sigma_g^+)$


$\psi(1\sigma_u^+)$

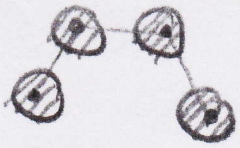

$\psi(1\sigma_g^+)$

$$\psi_{1a_1} \propto (1)\chi_1 + (1)\chi_4 + (1)\chi_1 + (1)\chi_4$$
$$\propto \chi_1 + \chi_4$$
$$\therefore \psi_{1a_1} = \frac{1}{\sqrt{2+2S_{14}}}(\chi_1 + \chi_4) \equiv$$

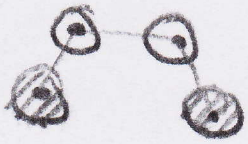
$$\psi_{2a_1} \propto (1)\chi_2 + (1)\chi_3 + (1)\chi_2 + (1)\chi_3$$
$$\propto \chi_2 + \chi_3$$
$$\therefore \psi_{2a_1} = \frac{1}{\sqrt{2+2S_{23}}}(\chi_2 + \chi_3) \equiv$$

Taking combinations of ψ_{1a_1} & ψ_{2a_1} and $S_{12} = S_{23} = S_{34}$, $S_{13} = S_{24}$

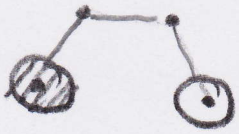
$$\psi_1 = \frac{1}{\sqrt{4+6S_{12}+4S_{13}+2S_{14}}}(\chi_1 + \chi_2 + \chi_3 + \chi_4) \equiv$$



$$\psi_2 = \frac{1}{\sqrt{4-2S_{12}-4S_{13}+2S_{14}}}(\chi_1 - \chi_2 - \chi_3 + \chi_4) \equiv$$

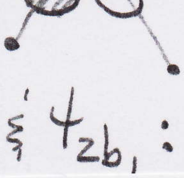


$$\psi_{1b_1} \propto (1)\chi_1 + (-1)\chi_4 + (1)\chi_1 + (-1)\chi_4$$
$$\propto \chi_1 - \chi_4$$
$$\psi_{1b_1} = \frac{1}{\sqrt{2-2S_{14}}}(\chi_1 - \chi_4) \equiv$$



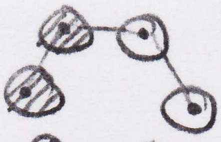
$$\psi_{2b_1} \propto (1)\chi_2 + (-1)\chi_3 + (1)\chi_2 + (-1)\chi_3$$

$$\psi_{2b_1} \propto \chi_2 - \chi_3$$
$$\therefore \psi_{2b_1} = \frac{1}{\sqrt{2-2S_{23}}}(\chi_2 - \chi_3) \equiv$$

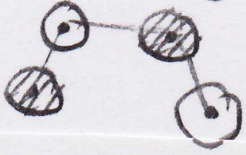


Again, taking combinations of ψ_{1b_1} & ψ_{2b_1}:

$$\psi_3 = \frac{1}{\sqrt{4+2S_{12}-4S_{13}-2S_{14}}}(\chi_1+\chi_2-\chi_3-\chi_4) \equiv$$



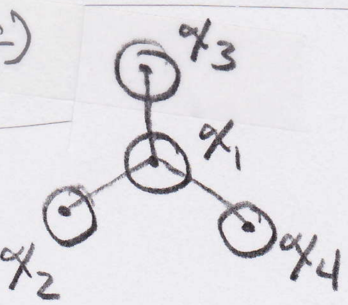
$$\psi_4 = \frac{1}{\sqrt{4-6S_{12}+4S_{13}-2S_{14}}}(\chi_1-\chi_2+\chi_3-\chi_4) \equiv$$



Notice that the form of the SALC's does not change on going from the linear to the C_{2v} geometry. Plots of the MO's are shown on the next page.

** For the remaining problems I will not show all of the steps to get the SALC's. Be sure to work through them carefully.

c)



basis 1 – χ_1

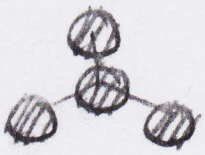
basis 2 – χ_2, χ_3, χ_4

$\Gamma_1 = a_1'$

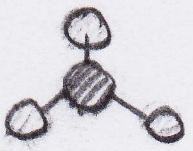
$\Gamma_2 = a_1' + e'$

$a_1' = \chi_1 \qquad a_1' = \frac{1}{\sqrt{3+6S_{23}}}(\chi_2+\chi_3+\chi_4)$

$$\therefore \psi_1 = \frac{1}{\sqrt{2+2S}}(\psi_{1a_1'} + \psi_{2a_1'}) \equiv$$

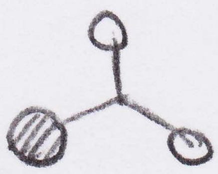


$$\psi_2 = \frac{1}{\sqrt{2-2S}}(\psi_{1a_1'} - \psi_{2a_1'}) \equiv$$

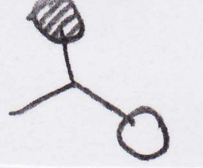


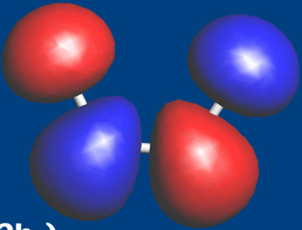
For e' set recall that the Schmidt orthogonalization must be used

$$\psi_3 = \frac{1}{\sqrt{6-6S_{23}}}(2\chi_2-\chi_3-\chi_4) \equiv$$

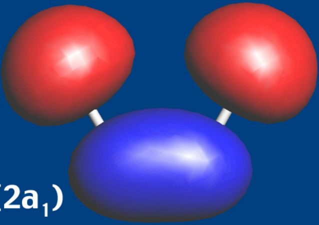


$$\psi_4 = \frac{1}{\sqrt{2-2S_{23}}}(\chi_3-\chi_4) \equiv$$

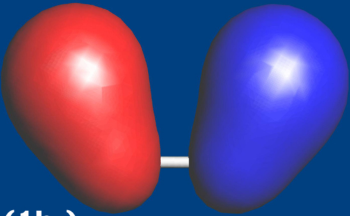




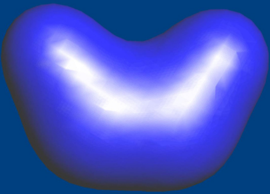
$\psi(2b_1)$



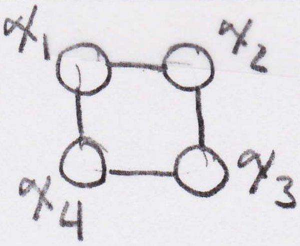
$\psi(2a_1)$



$\psi(1b_1)$

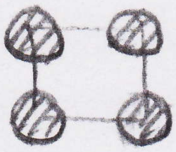


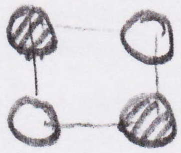
$\psi(1a_1)$

d) 

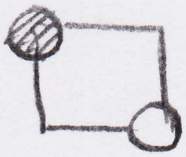
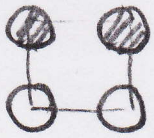
basis = $\chi_1, \chi_2, \chi_3, \chi_4$

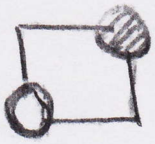
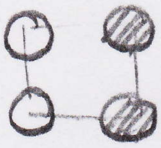
$\Gamma = a_{1g} + b_{2g} + e_u$

$$\psi_{a_{1g}} = \frac{1}{\sqrt{4+8S_{12}+4S_{13}}}(\chi_1+\chi_2+\chi_3+\chi_4) \equiv$$ 

$$\psi_{b_{2g}} = \frac{1}{\sqrt{4-8S_{12}+4S_{13}}}(\chi_1-\chi_2+\chi_3-\chi_4) \equiv$$ 

in this case the Schmidt process is not necessary

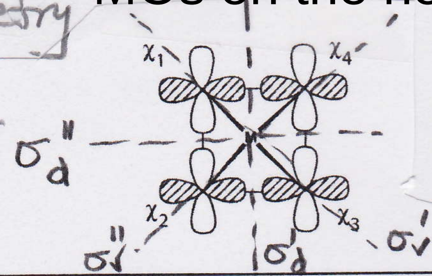
$$\psi_{e_u} = \frac{1}{\sqrt{2-2S_{13}}}(\chi_1-\chi_3) \equiv$$  $\equiv$ 

$$\psi_{e_u} = \frac{1}{\sqrt{2-2S_{13}}}(\chi_2-\chi_4) \equiv$$  $\equiv$ 

6. C_{4v} symmetry

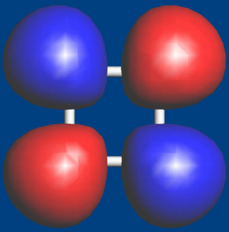
MOs on the next page

(This is easier than D_{4h} & will result in the same form for the SALC's)

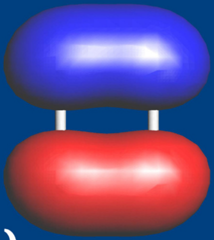


C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
E	2	0	-2	0	0
Γ =	4	0	0	-2	0 = $e + a_2 + b_2$

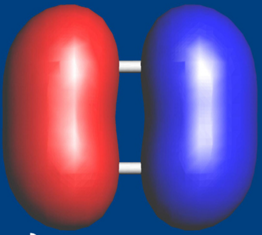
C_{4v}	E	C_4	C_4^3	C_2	σ_v'	σ_v''	σ_d'	σ_d''
χ_1	χ_1	$-\chi_4$	$-\chi_2$	χ_3	$-\chi_1$	$-\chi_3$	χ_4	χ_2
χ_2	χ_2	$-\chi_1$	$-\chi_3$	χ_4	$-\chi_4$	$-\chi_2$	χ_3	χ_1



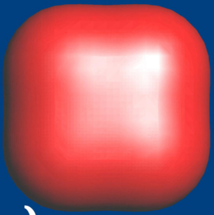
$\psi(b_{2g})$



$\psi(e_u)$

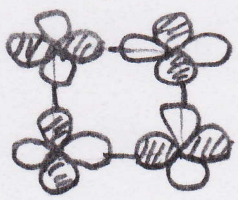


$\psi(e_u)$

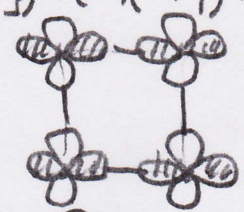


$\psi(a_{1g})$

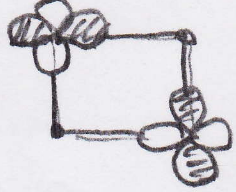
$$\psi_{a_2} \propto (1)\chi_1 + (1)(-\chi_4) + (1)(-\chi_2) + (1)\chi_3 + (-1)(-\chi_1) + (-1)(-\chi_3) + (-1)(\chi_2)$$
$$\propto \chi_1 - \chi_2 + \chi_3 - \chi_4 \equiv$$



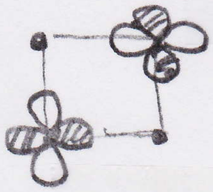
$$\psi_{b_2} \propto 1(\chi_1) + (-1)(-\chi_4) + (-1)(-\chi_2) + 1(\chi_3) + (-1)(-\chi_1) + (-1)(-\chi_3) + 1(\chi_4) + 1(\chi_2)$$
$$\propto \chi_1 + \chi_2 + \chi_3 + \chi_4 \equiv$$



$$\psi_e \propto 2(\chi_1) - 2(\chi_3) \propto \chi_1 - \chi_3 \equiv$$



$$\psi_e' \propto 2(\chi_2) - 2(\chi_4) \propto \chi_2 - \chi_4 \equiv$$



note $\langle \psi_e | \psi_e' \rangle = 0$

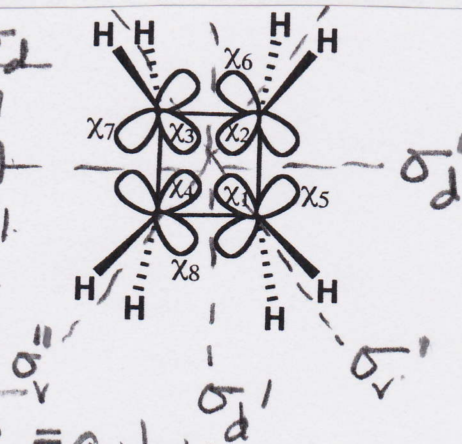
so ψ_e & ψ_e' are orthogonal – no need to do the Schmidt orthogonalization

7. C_{4v} symmetry again (D_{4h} is much more cumbersome)

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
a_1	1	1	1	1	1
a_2	1	1	1	−1	−1
b_1	1	−1	1	1	−1
b_2	1	−1	1	−1	1
e	2	0	−2	0	0
basis I	4	0	0	2	0
basis II	4	0	0	−2	0

basis I $= a_1 + b_1 + e$

basis II $= a_2 + b_2 + e$



picking σ_v and σ_d the alternate way just inverts b_1 and b_2

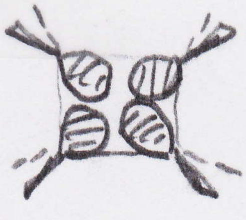
$\chi_1 - \chi_4$ basis I

$\chi_5 - \chi_8$ basis II

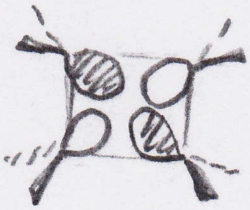
For basis I – assigning phases:

	E	C_4	C_4^3	C_2	σ_v'	σ_v''	σ_d''	σ_d'
χ_1	χ_1	χ_4	χ_2	χ_3	χ_1	χ_3	χ_2	χ_4
χ_2	χ_2	χ_1	χ_3	χ_4	χ_4	χ_2	χ_1	χ_3

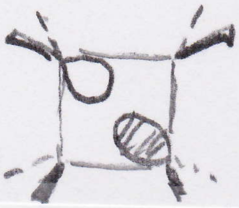
$$\psi_{a_1} \propto \chi_1 + \chi_4 + \chi_2 + \chi_3 + \chi_1 + \chi_3 + \chi_2 + \chi_4$$
$$= 2(\chi_1 + \chi_2 + \chi_3 + \chi_4) \propto \chi_1 + \chi_2 + \chi_3 + \chi_4$$



$$\psi_{b_1} \propto \chi_1 - \chi_4 - \chi_2 + \chi_3 + \chi_1 + \chi_3 - \chi_2 - \chi_4$$
$$= 2(\chi_1 - \chi_2 + \chi_3 - \chi_4) \propto \chi_1 - \chi_2 + \chi_3 - \chi_4$$

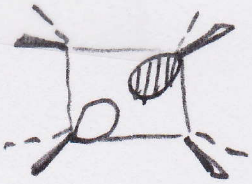


$$\psi_{1e} \propto 2\chi_1 - 2\chi_3$$
$$\propto \chi_1 - \chi_3$$



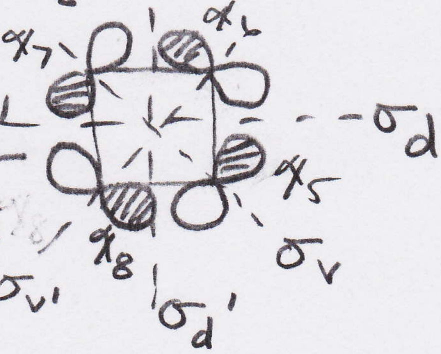
NOTE: ψ_{1e} & $\psi_{1e'}$ are already orthogonal

$$\psi_{1e'} \propto 2\chi_2 - 2\chi_4$$
$$\propto \chi_2 - \chi_4$$

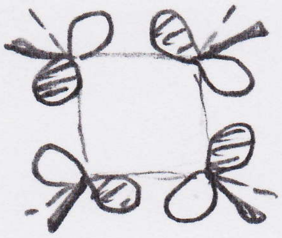


For basis II – assigning phases:

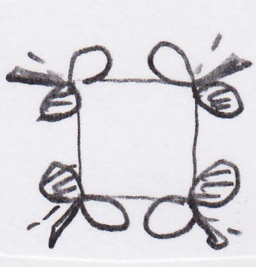
	E	C_4	C_4^3	C_2	σ_v'	σ_v''	σ_d''	$\sigma_d^{\perp}$
χ_5	χ_5	χ_8	χ_6	χ_7	$-\chi_5$	$-\chi_7$	$-\chi_6$	$-\chi_8$
χ_6	χ_6	χ_5	χ_7	χ_8	$-\chi_8$	$-\chi_6$	$-\chi_5$	$-\chi_7$



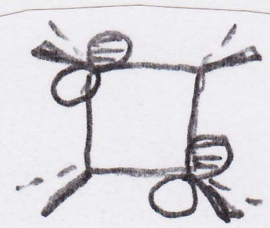
$$\psi_{a_2} \propto \chi_5 + \chi_8 + \chi_6 + \chi_7 + \chi_5 + \chi_7 + \chi_6 + \chi_8$$
$$= 2(\chi_5 + \chi_6 + \chi_7 + \chi_8)$$
$$\propto \chi_5 + \chi_5 + \chi_7 + \chi_8$$



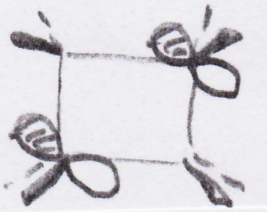
$$\psi_{b_2} \propto \chi_5 - \chi_8 - \chi_6 + \chi_7 + \chi_5 + \chi_7 - \chi_6 - \chi_8$$
$$= 2(\chi_5 - \chi_6 + \chi_7 - \chi_8)$$
$$\propto \chi_5 - \chi_6 + \chi_7 - \chi_8$$



$$\psi_{2e} \propto 2\chi_5 - 2\chi_7$$
$$\propto \chi_5 - \chi_5$$



$$\psi_{2e'} \propto 2\chi_6 - \chi_8$$
$$\propto \chi_6 - \chi_8$$



again ψ_{2e} & $\psi_{2e'}$ are orthogonal

It is important to realize that one can take any combination of phases for the members of a basis and come up with exactly the same shape of the SALC's. However, it is easier to start with the all-bonding combination, or, if this is not possible like the p AOs in this problem (basis II), then use the all-antibonding combination to start with.

The orbitals are:

— b_2
— $2a_1$
— $1a_1$

for H_3^+ there are two electrons. Thus we can have

b_2	—	—	—	—	↓	↑	↑↓	↓	↑
$2a_1$	—	↓	↑	↑↓	↑	↑	—	—	—
$1a_1$	↑↓	↑	↑	—	—	—	—	↑	↑
	$^1A_1$	$^1A_1$	$^3A_1$	$^1A_1$	$^1B_2$	$^3B_2$	$^1A_1$	$^1B_2$	$^3B_2$