C_{4v} 

Finding irreducible representations for P_x, P_y, P_z, R_x, R_y, R_z, all d orbitals in a molecule w/ C_{4v} symmetry

1) Determine where symmetry elements are in your molecule

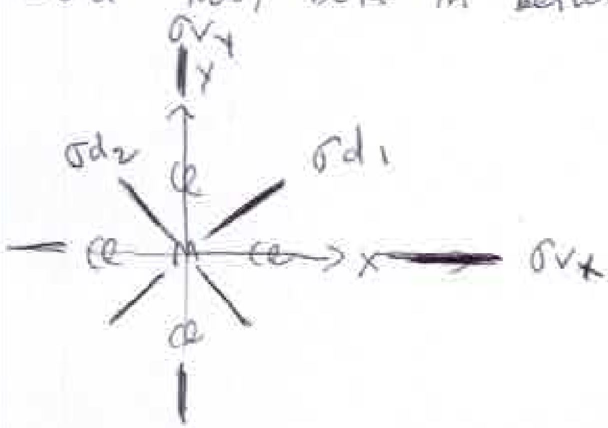
E

$2C_4$ (C_4 & C_4^3) along z axis

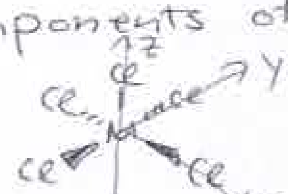
C_2 along z axis

$2\sigma_v$ one along xz plane, one along yz plane

$2\sigma_d$ two, both in between x & y axes



2) Derive characters for different components of your molecule



A) Straight forward derivations

P_z 

$\xrightarrow{E}$ 1

$\xrightarrow{C_4 \text{ or } C_4^3}$ 1

$\xrightarrow{C_2}$ 1

$\xrightarrow{\sigma_{v_x} \text{ or } y}$ 1

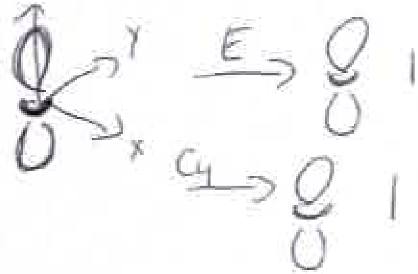
$\xrightarrow{\sigma_{d_1} \text{ or } 2}$ 1

Characters for $\boxed{P_z}$

1 1 1 1 1

↳ correspond to $\boxed{A_1}$

d_{z^2}



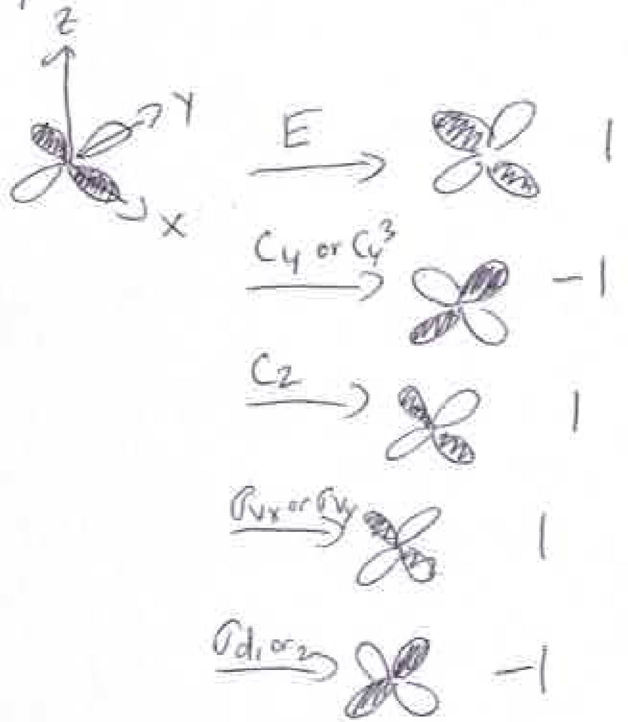
Characters for $\boxed{d_{z^2}}$

1 1 1 1 1

↳ correspond to $\boxed{A_1}$

... all operations will give (+1)

$d_{x^2-y^2}$

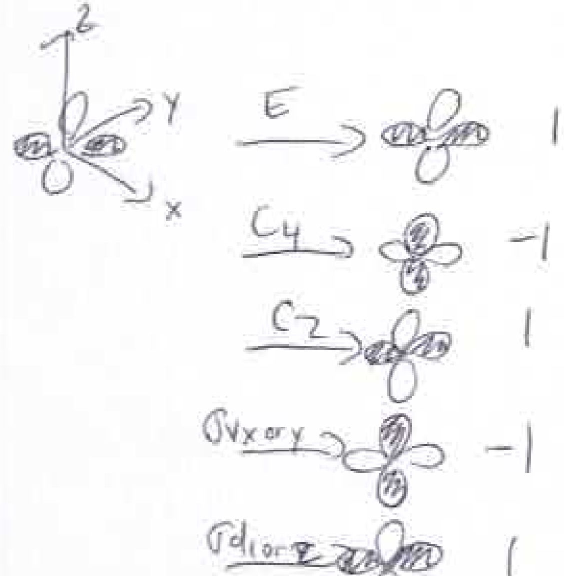


Characters for $\boxed{d_{x^2-y^2}}$

1 −1 1 1 −1

↳ correspond to $\boxed{B_1}$

d_{xy}

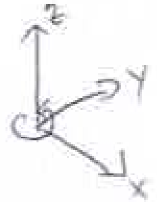


Characters for $\boxed{d_{xy}}$

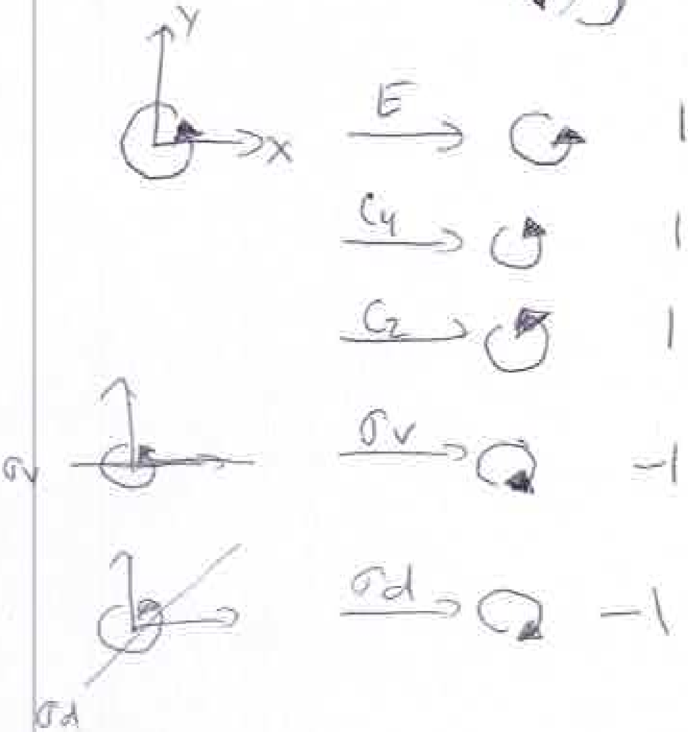
1 −1 1 −1 1

↳ correspond to $\boxed{B_2}$

$R_z \rightarrow$ rotation about z-axis



Easier to see if you look at it from above (looking down z-axis)



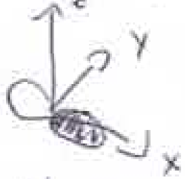
Characters for $\boxed{R_z}$

1 1 1 -1 -1

↳ corresponds to $\boxed{A_2}$

B) More complicated

p_x



$\Downarrow$ Easier to look at in xy plane

$\xrightarrow{E}$ 1

$\xrightarrow{C_4}$ 0 ← no overlap with original, give a character of 0!

$\xrightarrow{C_2}$ -1

$\xrightarrow{\sigma_v}$ 1 or -1 $\Rightarrow$ 0

$\uparrow \sigma_{v\,xz}$ $\quad \uparrow \sigma_{v\,yz}$

The two σ_v operations give opposite characters. The end result of 0 comes from the average of the two characters.

$$\frac{1+(-1)}{2} = 0$$

$\xrightarrow{\sigma_d}$ 0

Characters for p_x: 1 0 -1 0 0

* This does not match any of the irreducible representations!

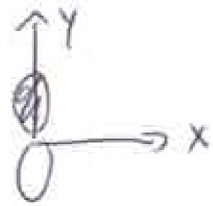
* In addition, sum of squares X class coefficients does not equal the order of the group!

$h = 1 + 2 + 1 + 2 + 2 = 8 \rightarrow$ order

$$1(1)^2 + 2(0)^2 + 1(-1)^2 + 2(0)^2 + 2(0)^2 = 2$$

$\Rightarrow$ This means that p_x has to be combined with something else in order to make a valid irreducible representation!

Let's try p_y



$\xrightarrow{E}$  1

$\xrightarrow{C_4}$  0

$\xrightarrow{C_2}$  -1

$\xrightarrow{\sigma_v}$ -1 or 1 $\Rightarrow 0$ (same as with p_x!)

$\uparrow$ $\sigma_{v\,xz}$ $\quad$ $\uparrow$ $\sigma_{v\,yz}$

$\xrightarrow{\sigma_d}$  0

Characters for p_y: $1 \quad 0 \quad -1 \quad 0 \quad 0$

$\Rightarrow$ same as p_x!

$\Rightarrow$ p_x and p_y <u>transform</u> together in C_{4v} point group ~~because~~

$\Rightarrow$ add up their characters to form a irreducible representation

p_x	1	0	-1	0	0
$+\ p_y$	1	0	-1	0	0
(p_x, p_y)	2	0	-2	0	0

$\rightarrow$ corresponds to "E"

$$1(2)^2 + 2(0)^2 + 1(-2)^2 + 2(0)^2 + 2(0)^2 = 8 \rightarrow \text{order of group}$$

Thus, p_x and p_y combine to form doubly degenerate E representation!

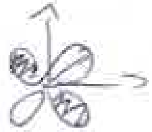
Similar things happen w/ d_{xz} and d_{yz}

d_{xz}

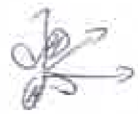
(in xz plane) $\xrightarrow{E}$  1

$\xrightarrow{C_4}$  0

(in yz plane

$\xrightarrow{C_2}$  -1

$\xrightarrow{\sigma_v}$ 1 or -1 $\Rightarrow$ 0

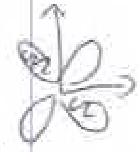
$\xrightarrow{\sigma_d}$  0

in yz plane

d_{yz}

 $\xrightarrow{E}$ 

(in yz plane)

$\xrightarrow{C_4}$  0

in xz plane

$\xrightarrow{C_2}$  -1

$\xrightarrow{\sigma_v}$ -1 or 1 $\Rightarrow$ 0

$\xrightarrow{\sigma_d}$  0

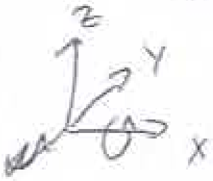
in xz

d_{xz}	1	0	-1	0	0
d_{yz}	1	0	-1	0	0
(xz, yz)	2	0	-2	0	0

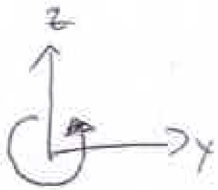
$\rightarrow E$

Similar things happen w/ R_x & R_y

R_x



R_y



$\xrightarrow{E}$ 1

$\xrightarrow{C_4}$ 0 (goes to y axis)

$\xrightarrow{C_2}$ −1

$\xrightarrow{\sigma_v}$ 1 or −1 ⇒ 0

$\xrightarrow{\sigma_d}$ 0

$\xrightarrow{E}$

$\xrightarrow{C_4}$ 0

$\xrightarrow{C_2}$ −1

$\xrightarrow{\sigma_v}$ 0

$\xrightarrow{\sigma_d}$ 0

R_x	1	0	−1	0	0
R_y	1	0	−1	0	0
(R_x, R_y)	2	0	−2	0	0

You will only be expected to do these with point groups when $C_n = C_2$ or C_4

↑ principal rotation axis