CHARACTER TABLE

Unit-IV

A table containing all I.R's. of a point group and their characters w.r. to each symm. operation is called character table. The I.R's are denoted as Γ_1, Γ_2, Γ_3 ...... (Bethe not.) and A_1, A_2, B_1, B_2 ..... (Mulliken notation).

Γ_i terms are Bethe notations and A, B are Mulliken notations

For C_{2v} group :→

Symmetry elements are —
E, $C_2(z)$, $\sigma_v(xz)$ $\sigma_v'(yz)$ ....

order of the group = 4
No. of classes = 4
No. of I.R's = 4
No. of classes = No. of I.R's = 4

vector x or orbital p_x forms a basis for I.R. Γ_1'
" y " " p_y " " " " " Γ_2'
" z " " p_z " " " " " Γ_3

And R_z i.e rotation about z-axis forms a basis for I.R. Γ_4.

The 3×3 matrices of different operations are —

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$C_2(z) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & +1 \end{pmatrix}$$

$$\sigma_v(xz) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\sigma_v(yz) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The four matrices are blocked factored int
1 X 1 matrices.

Thus,

$$\Gamma_1'(E) = (1)$$

$$\Gamma_2'(E) = (1)$$

$$\Gamma_3'(E) = (1)$$

$$\Gamma_1'(C_2) = (-1)$$

$$\Gamma_2'(C_2) = (-1)$$

$$\Gamma_3'(C_3) = (+1)$$ and so on

!! Read gemma.

Thus the 3 I.R's. of each operation are as

I.R	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	Ba
Γ_1'	1	-1	1	-1	x
Γ_2'	1	-1	-1	1	Y
Γ_3'	1	1	1	1	z

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As, there are four classes, there would be four I.R's. Let the fourth I.R have the characters a, b, c, d. So that we have the character table as -

Notations χ		Elements			
Bethe	Mulliken	E	C_2	$\sigma_v(xz)$	$\sigma(yz)$
Γ_1	B_1	1	-1	1	-1
Γ_2	B_2	1	-1	-1	1
Γ_3	A_1	1	1	1	1
Γ_4		a	b	c	d

By orthogonality rule :→.

$$\sum \Gamma_1 \cdot \Gamma_4$$

$$= 1\times a + (-1)\times b + 1\times c + (-1)\times d = 0$$

or, $a - b + c - d = 0$

or, $a + c = b + d$

and

$$\sum \Gamma_3 \cdot \Gamma_4 = 1\times a + 1\times b + 1\times c + 1\times d =$$

or, $a + b + c + d = 0$

$\therefore a + c = -(b+d)$

or, $a + c = 0$ $\quad$ ($\because a+c = b+$ from ab

$\cdot e \cdot -1$

a is the character of identity (E).

$\therefore a = +1$

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$\sum T_2 \cdot T_4 = 1\times a + (-1)\times b + (-1)\times c + 1\times d = 0$

or, $a - b - c + d = 0$

or, $a - b = c - d$

or, $a + d = b + c$

Since,

(i) $a + b + c + d = 0$ $\quad (\because a+b = c+d)$

or, $a + c + a + c = 0$

or, $2a + 2c = 0$

or, $a + c = 0$ $\quad (\because a = 1)$

or, $a = -c = -1$.

(ii) $a + b + c + d = 0$ $\quad (\because a+d = b+c)$

or, $a + d + a + d = 0$

or, $2a + 2d = 0$

or $a + d = 0$ $\quad (\because a = 1)$

or, $d = -a = -1$

(iii) $a + b + c + d = 0$

or, $1 + b - 1 - 1 = 0$

or $b - 1 = 0$

or, $b = 1$

$\therefore T_4$ gives $a = 1$, $b = 1$, $c = -1$, $d = -1$

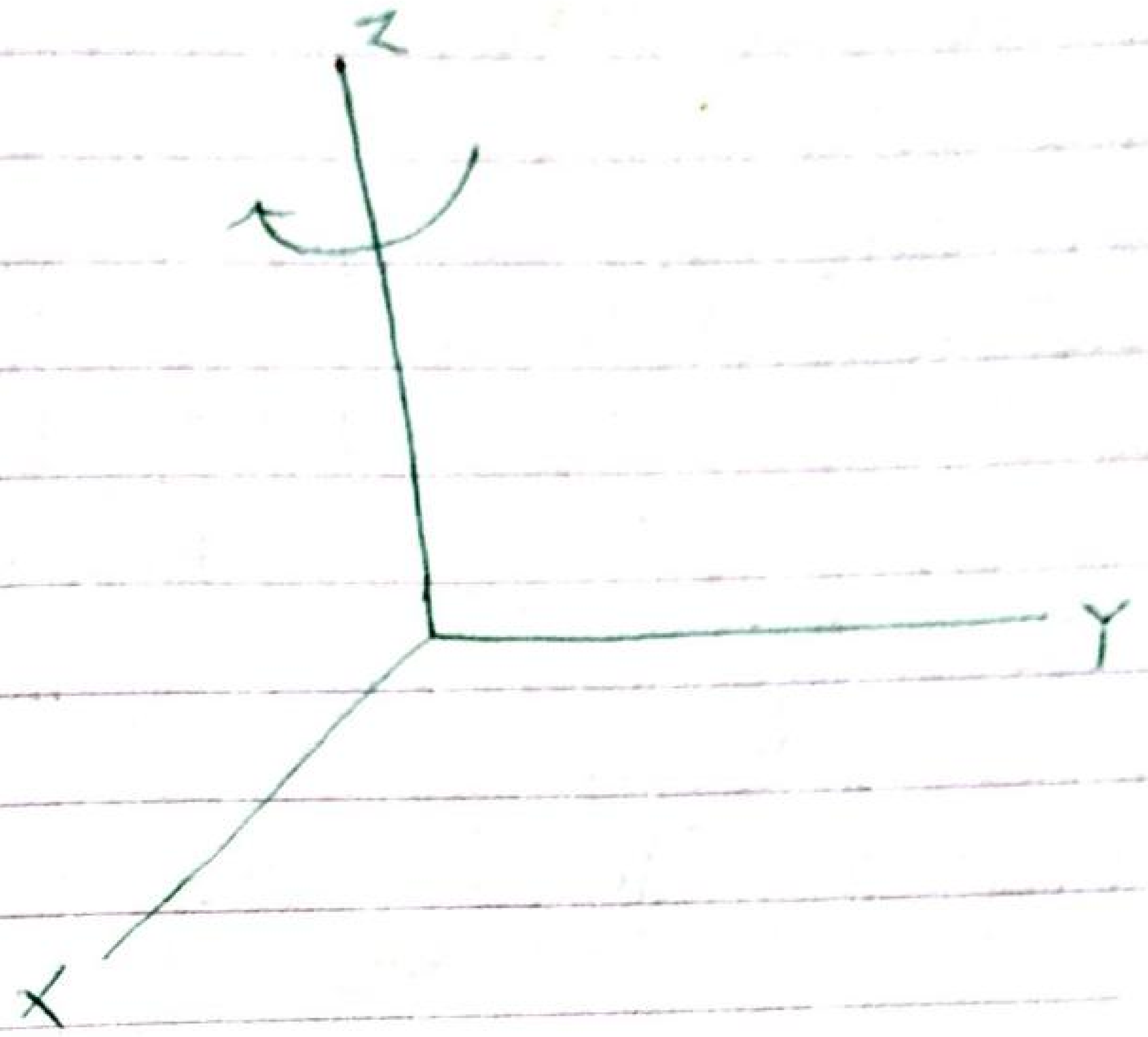
i.e.

Notation			Elements		
Character (χ)		E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
Bethe	Mulliken				
T_1'	B_1	1	-1	1	-1
T_2'	B_2	1	-1	-1	1
T_3'	A_1	1	1	1	1
T_4	A_2	1	1	-1	-1

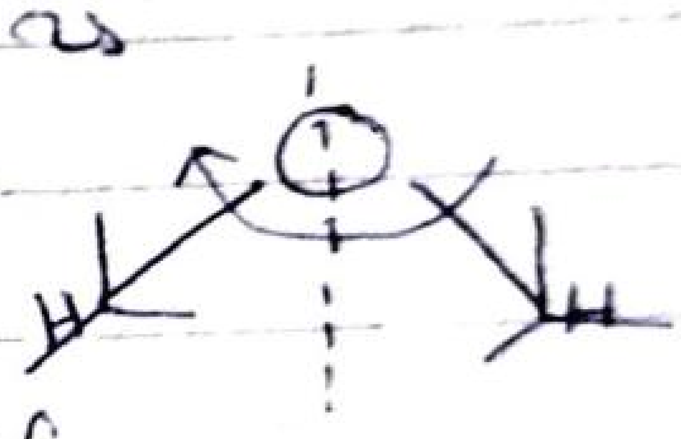
as $b = +$, $T_4 - A_2$

For determining T_4.

T_4 is generated using rotations R_x, R_y, R_z.

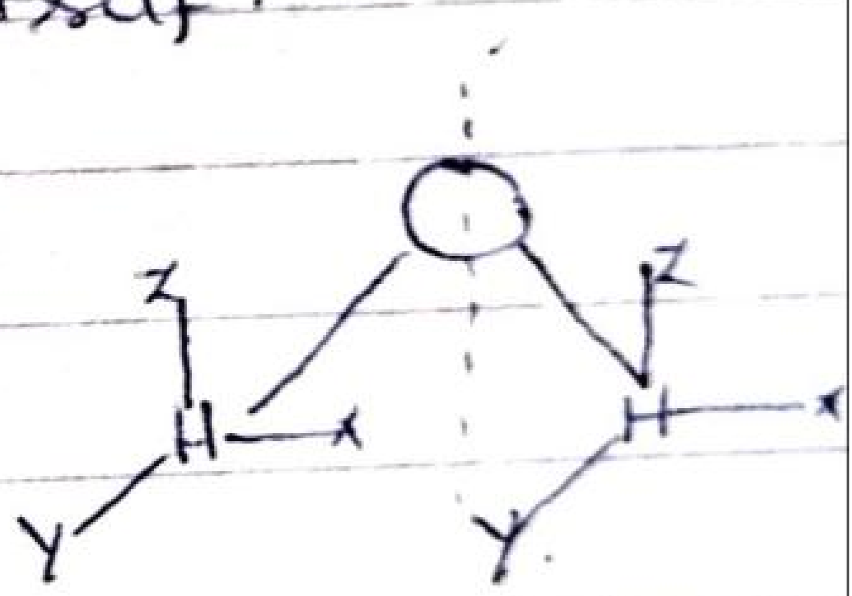


Identity (E) turns the molecule into itself and hence transformation matrix is



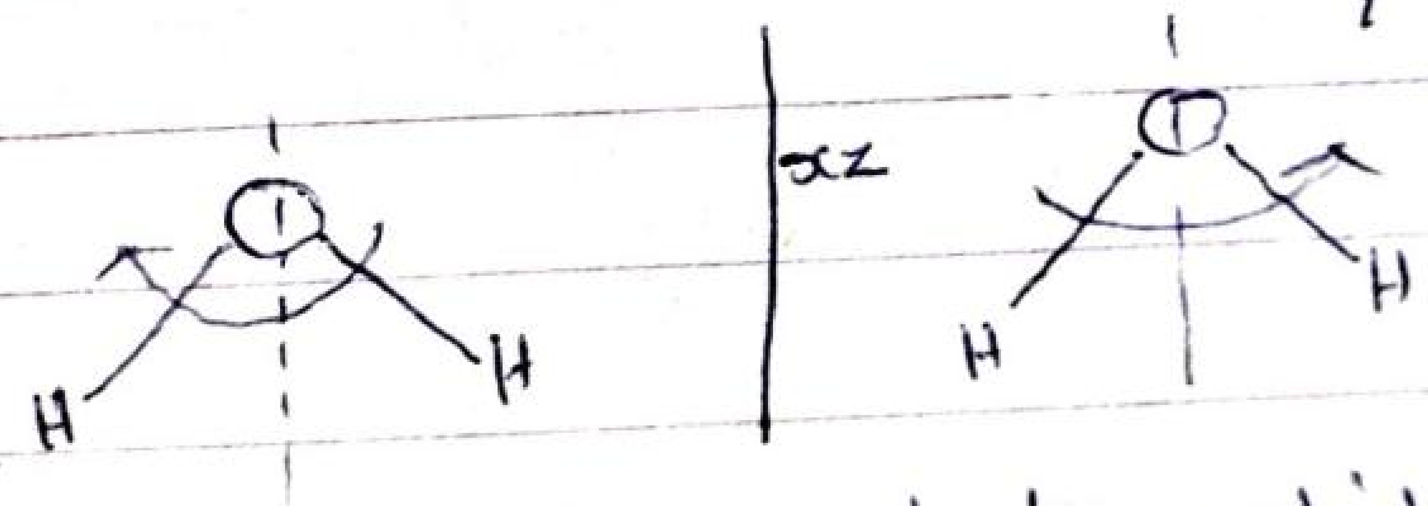
$$E = +1$$

$C_2(z)$ turns it into itself.



$$\therefore C_2(z) = (1)$$

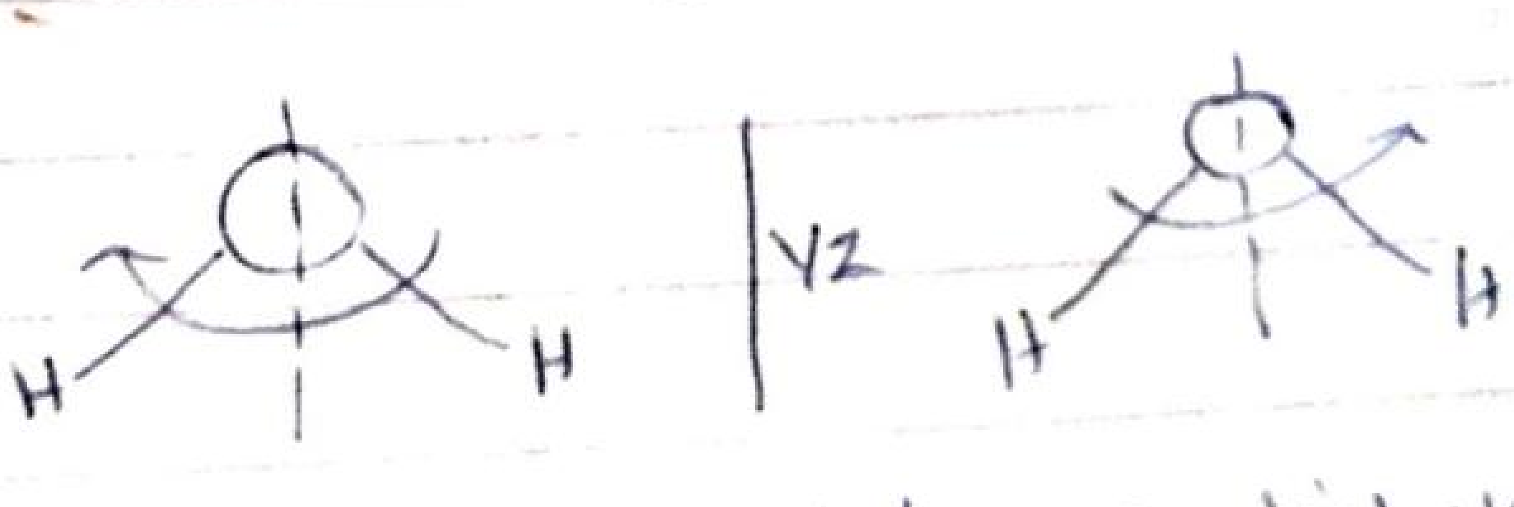
$\sigma(xz) \rightarrow$.



The rotation is turned to anticlockwise form clockwise.

$$\therefore \sigma(xz) = -1$$

$\sigma_{yz} \rightarrow$



The rotation is turned to anticlockwise from clockwise. $\therefore \sigma(yz) = -1$.

Hence, using R_z (rotation along z-axis)

Characters are

$E = 1$, $C = 1$, $\sigma_{xz} = -1$, $\sigma_{yz} = -1$

and hence the character table.

Character (χ)		Notation				
Bethe	Mulliken	E	$C_2(z)$	σ_{xz}	σ_{yz}	Basis
Γ_1	B_1	1	-1	1	-1	x, R_y
Γ_2	B_2	1	-1	-1	1	y, R_x
Γ_3	A_1	1	1	1	1	z
Γ_4	A_2	1	1	-1	-1	R_z

I.R. or Symmetry species (A_1, A_2, B_1, B_2) of C_{2v} or H_2O using orbitals as ~~below~~ → basis :→

Group = C_{2v}

Symm. elements are — E, $C_2(z)$, σ_v(xz)

$\sigma'_v(yz)$

Mutually conjugate operations = 4

∴ Classes = 4

∴ I.R's. = 4

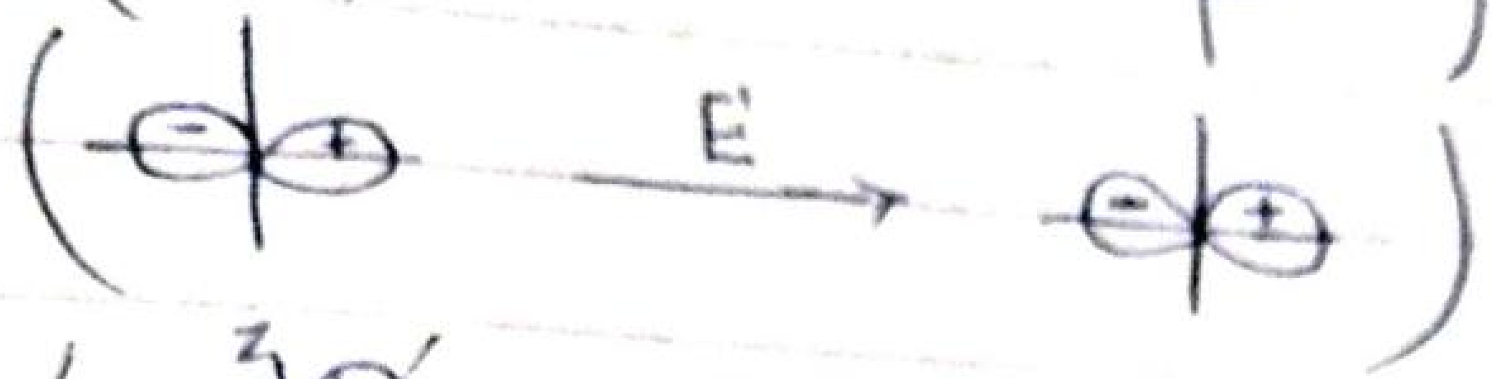
Let the I.R's be $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$

Taking orbitals as the basis functions:

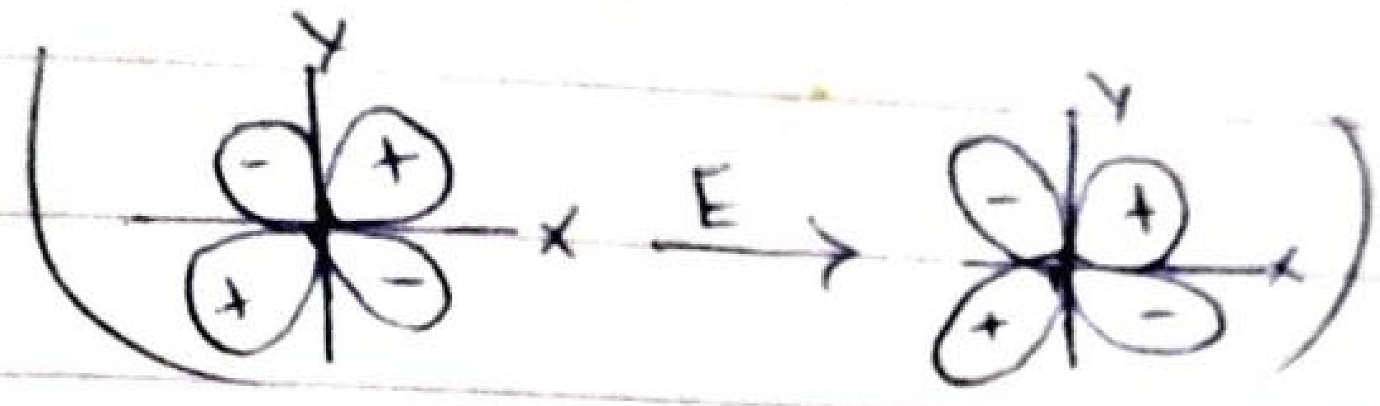
s, p_x, p_y, d_{xy}.

Under 'E' operation :→

$E(s) \rightarrow$  $\rightarrow s' = \chi E(s) = +1$

$E(p_x) \rightarrow$  $\rightarrow p'_{(x)} = \chi E(p_x) = +1$

$E(p_y) \rightarrow$  $\rightarrow p'_{(y)} \rightarrow \chi E(p_y) = +1$

$E(d_{xy}) \rightarrow$  $\rightarrow d'_{(xy)} = \chi E(d_{xy}) = +1$

i.e

s	- transforms	as	s'
p_x	"	"	p'_x
p_y	"	"	p'_y
d_{xy}	"	"	d'_{xy}

$$s' = 1s + 0p_x + 0p_y + 0d_{xy}.$$
$$p'_x = 0s + 1p_x + 0p_y + 0d_{xy}.$$
$$p'_y = 0s + 0p_x + 1p_y + 0d_{xy}$$
$$d'_{xy} = 0s + 0p_x + 0p_y + 1d_{xy}.$$

The corresponding matrix (4×4) is

$$E = \begin{pmatrix} s \\ p_x \\ p_y \\ d_{xy} \end{pmatrix} = \begin{pmatrix} s' \\ p'_x \\ p'_y \\ d'_{xy} \end{pmatrix} = \begin{pmatrix} \boxed{1} & 0 & 0 & 0 \\ 0 & \boxed{1} & 0 & 0 \\ 0 & 0 & \boxed{1} & 0 \\ 0 & 0 & 0 & \boxed{1} \end{pmatrix} \begin{pmatrix} s \\ p_x \\ p_y \\ d_{xy} \end{pmatrix}$$

The above 4 dimensional matrix representation is block factored as shown above.

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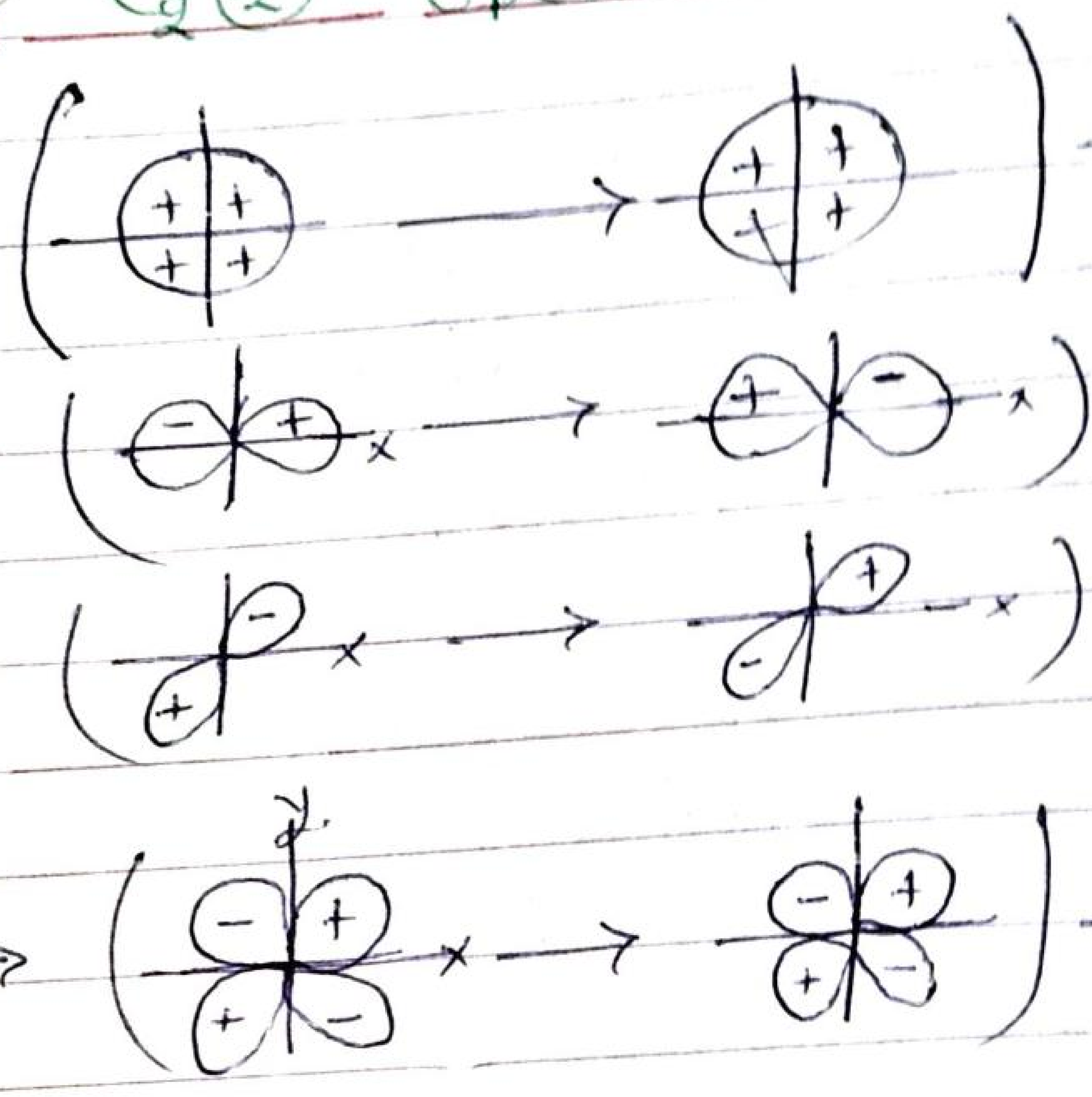
$$E - \chi(\Gamma_1') = 1$$
$$\chi(\Gamma_2') = 1$$
$$\chi(\Gamma_3') = 1$$
$$\chi(\Gamma_4') = 1$$

Under $C_2(z)$ operation :→



$C_2(s) \rightarrow$ → $s' = 1s$

$C_2(p_x) \rightarrow$ → $p'_x = -1\,p_x$

$C_2(p_y) \rightarrow$ → $p'_y = -1\,p_y$

$C_2(d_{xy}) \rightarrow$ → $d'_{xy} = 1\,d_{xy}$

Hence, matrix representation is

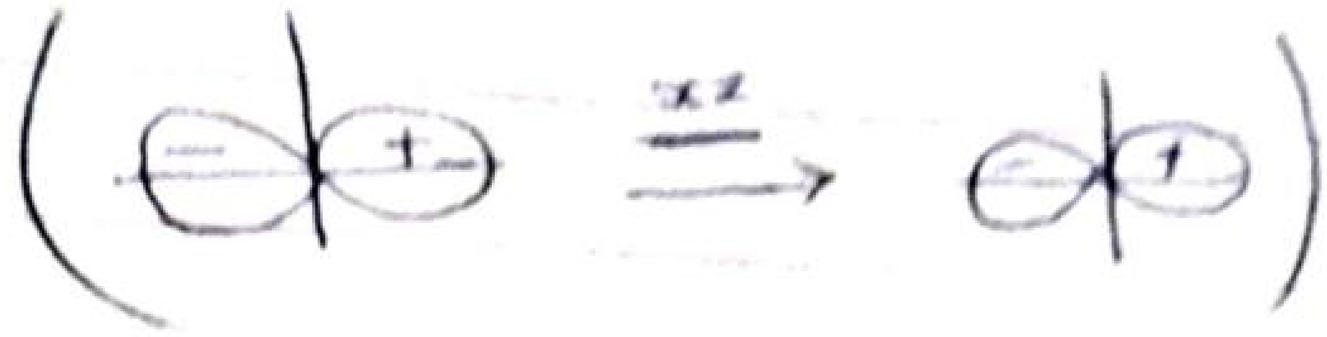
$$C_2 = \begin{pmatrix} s' \\ p'_x \\ p'_y \\ d'_{xy} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} s \\ p_x \\ p_y \\ d_{xy} \end{pmatrix}$$

Thus,

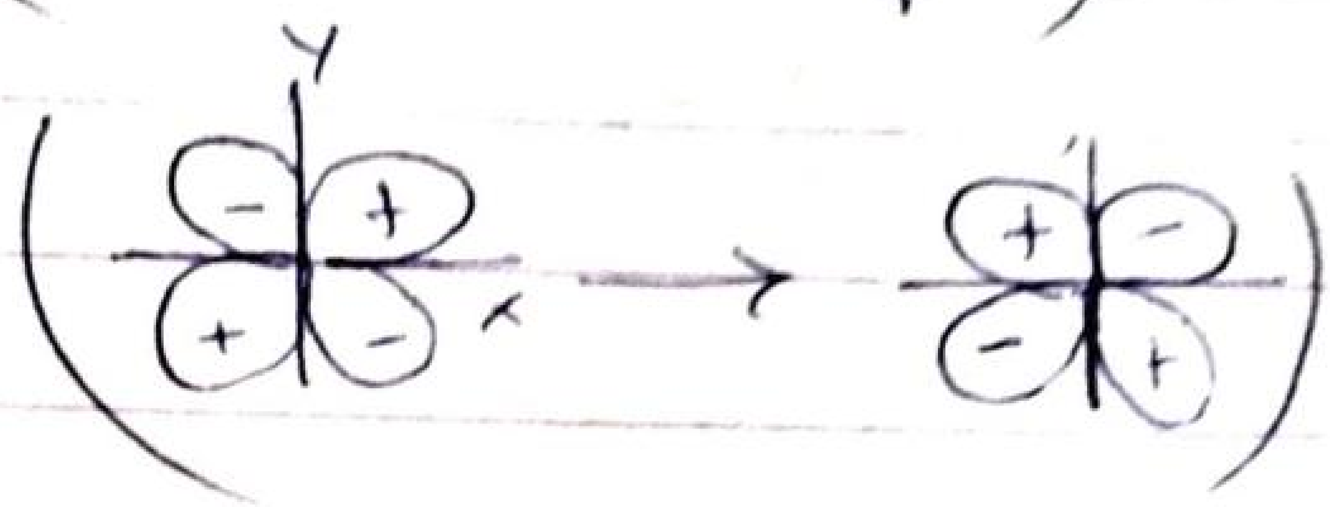
$$C_2 - \chi(\Gamma_1') = 1$$
$$\chi(\Gamma_2') = -1$$
$$\chi(\Gamma_3') = -1$$
$$\chi(\Gamma_4') = 1$$

Under $\sigma_v(xz)$ operation :→

$\sigma_v(xz)(s) \rightarrow$  $\rightarrow s' = +1 s$

$\sigma_v(xz)(p_x) \rightarrow$  $\rightarrow p'_x = +1 p_x$

$\sigma_v(xz)(p_y) \rightarrow$  $\rightarrow p'_y = -1 p_y$.

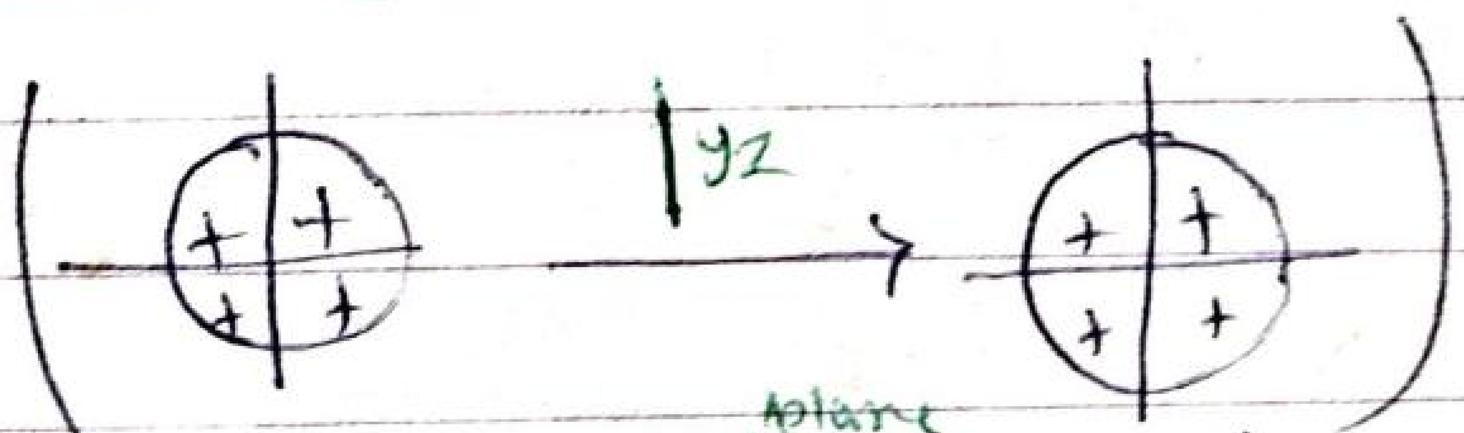
$\sigma_v(xz)(d_{xy}) \rightarrow$  $\rightarrow d'_{xy} = -1 d_{xy}$.

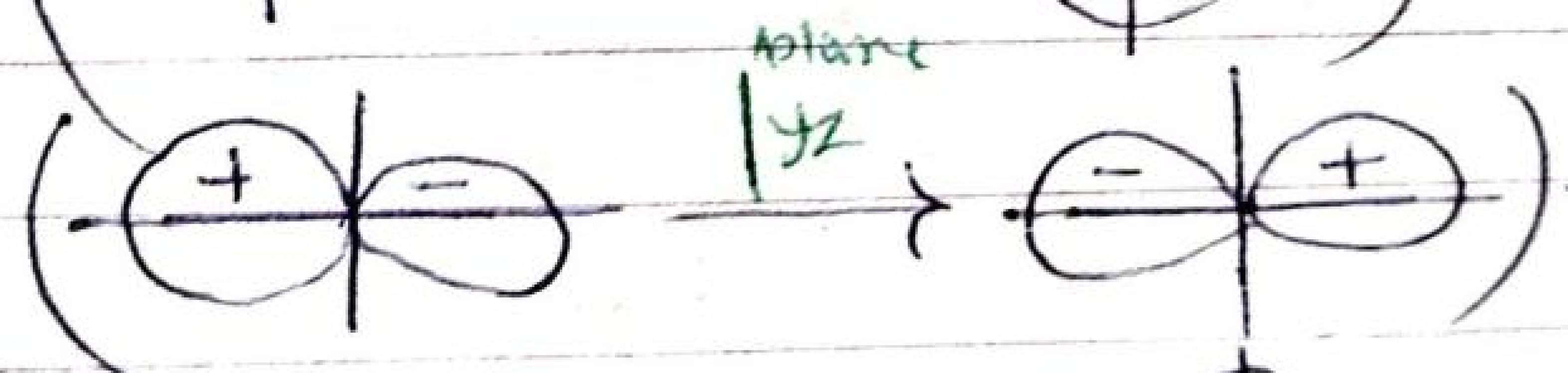
Hence,

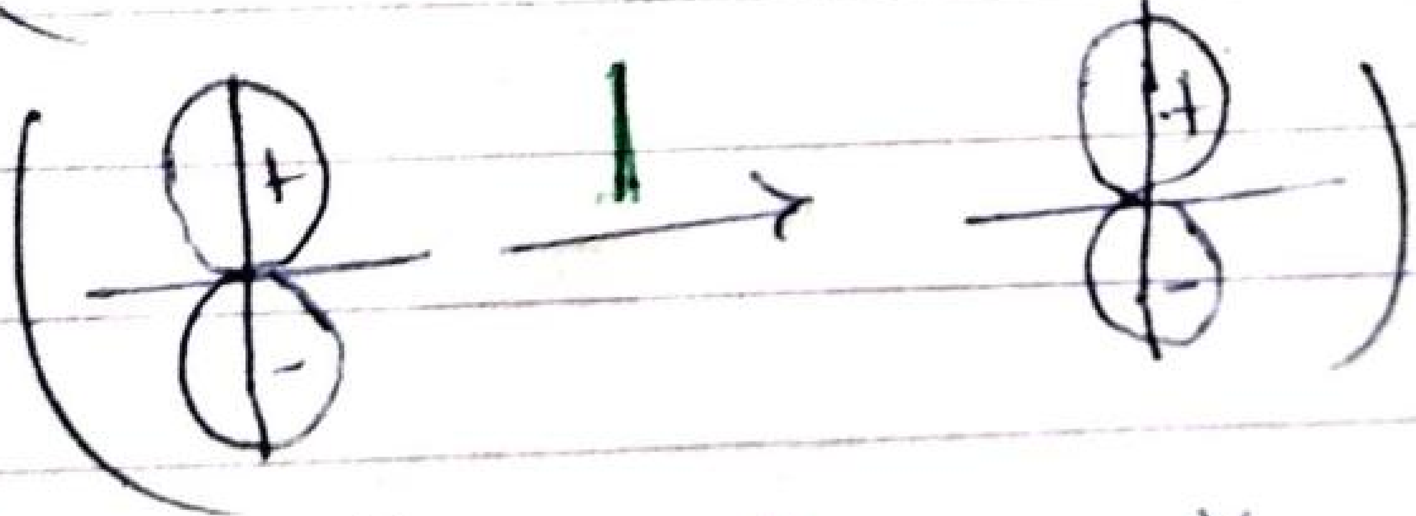
$\sigma_v(xz)$ —

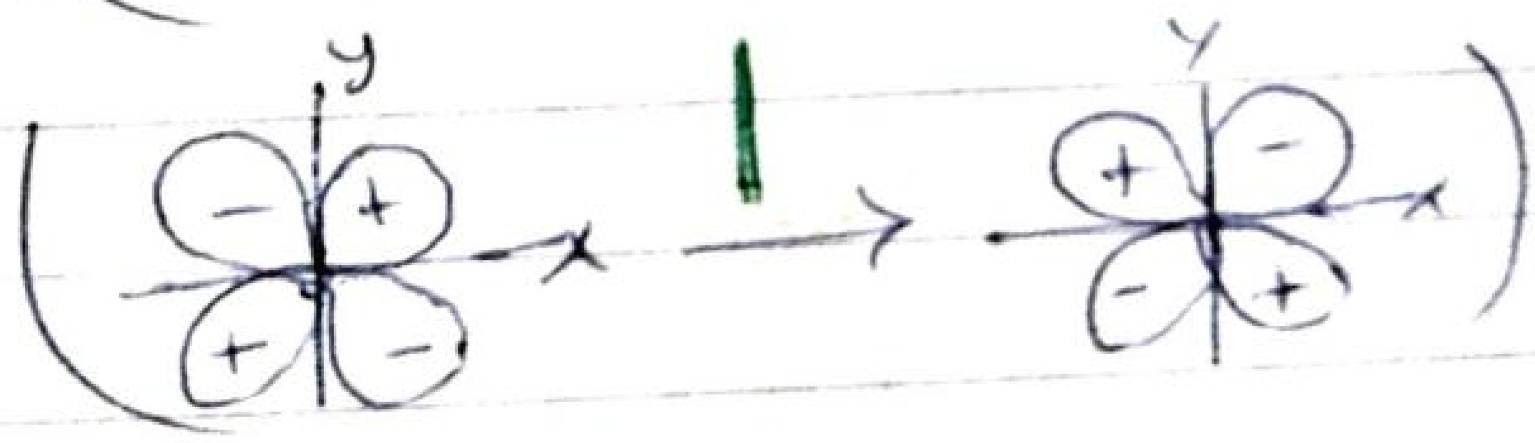
$$\chi(\Gamma_1) = 1$$
$$\chi(\Gamma_2) = +1$$
$$\chi(\Gamma_3) = -1$$
$$\chi(\Gamma_4) = -1$$

Under $\sigma'_v(yz)$ operation :→

$\sigma'_v(yz)(s) \rightarrow$  $\rightarrow s' = +1 s$

$\sigma'_v(yz)(p_x) \rightarrow$  $\rightarrow p'_x = -1 p_x$

$\sigma'_v(yz)(p_y) \rightarrow$  $\rightarrow p'_y = 1 p_y$.

$\sigma'_v(yz)(d_{xy}) \rightarrow$  $\rightarrow d'_{xy} = -1 d_{xy}$

Hence,

$$\sigma'_v(yz) - \chi(\Gamma_1) = +1$$
$$\chi(\Gamma_2) = -1$$
$$\chi(\Gamma_3) = +1$$
$$\chi(\Gamma_4) = -1$$

Thus the charecter table is as –

Notations		Elements				
Bethe	Mulliken	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$	Basis
Γ_1	A_1	1	1	1	1	s
Γ_2	B_1	1	-1	1	-1	p_x
Γ_3	B_2	1	-1	-1	1	p_y
Γ_4	A_2	1	1	-1	-1	d_{xy}.

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