Solution for Group Theory PS3

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1. a) Choose $2xy$ as a partner of x^2-y^2 to get the representation by unitary matrices.

D_3	E	C_3	C_3^2	$C_{2\alpha}$	$C_{2\beta}$	$C_{2\gamma}$
x	x	$-\frac{1}{2}x+\frac{\sqrt{3}}{2}y$	$-\frac{1}{2}x-\frac{\sqrt{3}}{2}y$	x	$-\frac{1}{2}x-\frac{\sqrt{3}}{2}y$	$-\frac{1}{2}x+\frac{\sqrt{3}}{2}y$
y	y	$-\frac{\sqrt{3}}{2}x-\frac{1}{2}y$	$\frac{\sqrt{3}}{2}x-\frac{1}{2}y$	$-y$	$-\frac{\sqrt{3}}{2}x+\frac{1}{2}y$	$\frac{\sqrt{3}}{2}x+\frac{1}{2}y$
$2xy$	$2xy$	$-\frac{1}{2}(2xy)+\frac{\sqrt{3}}{2}(x^2-y^2)$	$-\frac{1}{2}(2xy)-\frac{\sqrt{3}}{2}(x^2-y^2)$	$-2xy$	$\frac{1}{2}(2xy)+\frac{\sqrt{3}}{2}(x^2-y^2)$	$\frac{1}{2}(2xy)-\frac{\sqrt{3}}{2}(x^2-y^2)$
x^2-y^2	x^2-y^2	$-\frac{\sqrt{3}}{2}(2xy)-\frac{1}{2}(x^2-y^2)$	$\sqrt{3}/2\,(2xy)-\frac{1}{2}(x^2-y^2)$	x^2-y^2	$\sqrt{3}/2\,(2xy)-1/2\,(x^2-y^2)$	$-\sqrt{3}/2\,(2xy)-\frac{1}{2}(x^2-y^2)$

$\Rightarrow$

	E	C_3	C_3^2	$C_{2\alpha}$	$C_{2\beta}$	$C_{2\gamma}$
$D_{(x,y)}$	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}-1/2&-\sqrt{3}/2\\\sqrt{3}/2&-1/2\end{pmatrix}$	$\begin{pmatrix}-1/2&\sqrt{3}/2\\-\sqrt{3}/2&-1/2\end{pmatrix}$	$\begin{pmatrix}1&0\\0&-1\end{pmatrix}$	$\begin{pmatrix}-1/2&-\sqrt{3}/2\\-\sqrt{3}/2&1/2\end{pmatrix}$	$\begin{pmatrix}-1/2&\sqrt{3}/2\\\sqrt{3}/2&1/2\end{pmatrix}$
$D_{(2xy,x^2-y^2)}$	$\begin{pmatrix}1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}-1/2&-\sqrt{3}/2\\\sqrt{3}/2&-1/2\end{pmatrix}$	$\begin{pmatrix}-1/2&\sqrt{3}/2\\-\sqrt{3}/2&-1/2\end{pmatrix}$	$\begin{pmatrix}-1&0\\0&1\end{pmatrix}$	$\begin{pmatrix}1/2&\sqrt{3}/2\\\sqrt{3}/2&-1/2\end{pmatrix}$	$\begin{pmatrix}1/2&-\sqrt{3}/2\\-\sqrt{3}/2&-1/2\end{pmatrix}$

$$\Rightarrow \quad U D_{(x,y)} U^{+} = D_{(2xy,\,x^2-y^2)}$$

where $U = \begin{pmatrix}0&1\\-1&0\end{pmatrix}$

Notice $U^{+} \equiv \tilde{U}^{*} = U^{-1}$ $\Rightarrow$ unitary matrix.

b) Using $\hat{P}_{kl}^{(\Gamma_n)} = \frac{l_n}{h} \sum_R D^{(\Gamma_n)}(R)_{kl}^* \hat{P}_R$,

show

$$\hat{P}_{11}^{(E)}(xy) = xy, \quad \hat{P}_{21}^{(E)}(xy) = \frac{1}{2}(x^2 - y^2)$$

c) For E′ representation,

$$D(E) = D(\sigma_h) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad D(C_{2\alpha}) = D(\sigma_{v\alpha}) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$D(C_3) = D(S_3) = \begin{pmatrix} -1/2 & +\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} \qquad D(C_{2\beta}) = D(\sigma_{v\beta}) = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix}$$

$$D(C_3^2) = D(S_3^2) = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} \qquad D(C_{2\gamma}) = D(\sigma_{v\gamma}) = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix}$$

For E″ representation, we get the same matrices as for E′ representation for the following matrices,

$D(E)$, $D(C_3)$, $D(C_3^2)$, $D(\sigma_{v\alpha})$, $D(\sigma_{v\beta})$, $D(\sigma_{v\gamma})$

otherwise,

$$D(\sigma_h) = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}, \quad D(S_3) = \begin{pmatrix} 1/2 & -\sqrt{3}/2 \\ +\sqrt{3}/2 & 1/2 \end{pmatrix}, \quad D(S_3^2) = \begin{pmatrix} 1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix}$$

$$D(C_{2\alpha}) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \quad D(C_{2\beta}) = \begin{pmatrix} 1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}; \quad D(C_{2\gamma}) = \begin{pmatrix} 1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}$$

2 a)

Table B.14. D_{3d}

D_{3d}		Basis	E	$2C_3$	$3C_2'$	I	$2IC_3$	$3\sigma_v$	L
A_{1g}	Γ_1^+	z^2	1	1	1	1	1	1	L_1
A_{2g}	Γ_2^+	$x_1y_2 - y_1x_2$	1	1	−1	1	1	−1	L_2
E_g	Γ_3^+	$\{zx, zy\}$	2	−1	0	2	−1	0	L_3
A_{1u}	Γ_1^-	$3x^2y - y^3$	1	1	1	−1	−1	−1	L_1'
A_{2u}	Γ_2^-	z	1	1	−1	−1	−1	1	L_2'
E_u	Γ_3^-	$\{x, y\}$	2	−1	0	−2	1	0	L_3'

b) 4 one-dimensional and 2 two-dimensional irreducible representations.

c) By inspection.

	E	$2C_3$	$3C_2'$	i	$2iC_3$	$3\sigma_v$
atom sites χ	6	0	0	0	0	2

$= A_{1g} + E_g + A_{2u} + E_u$

$$\hat{P}^{(A_{1g})}(a) = \frac{1}{6}(a+b+c+d+e+f)$$

$$\hat{P}^{(A_{2u})}(a) = \frac{1}{6}(a-b+c-d+e-f)$$

$$\hat{P}_{11}^{(E_g)}(a) = \frac{1}{6}(2a-b-c+2d-e-f)$$

$$\hat{P}_{22}^{(E_g)}(b) = \frac{1}{4}(b-c+e-f)$$

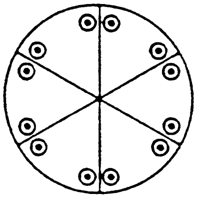
$$\hat{P}_{11}^{(E_u)}(a) = \frac{1}{6}(2a+b-c-2d-e+f)$$

$$\hat{P}_{22}^{(E_u)}(b) = \frac{1}{4}(b+c-e-f)$$

d)

Symbols: D_{6h} – $6/mmm$

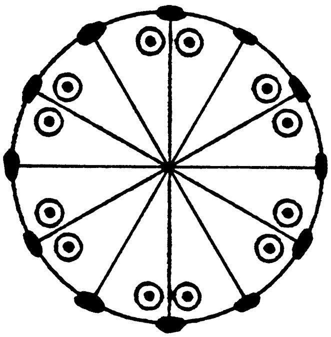
Generators: $\begin{pmatrix} 1/2 & \sqrt{3}/2 & 0 \\ -\sqrt{3}/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

Diagram: 

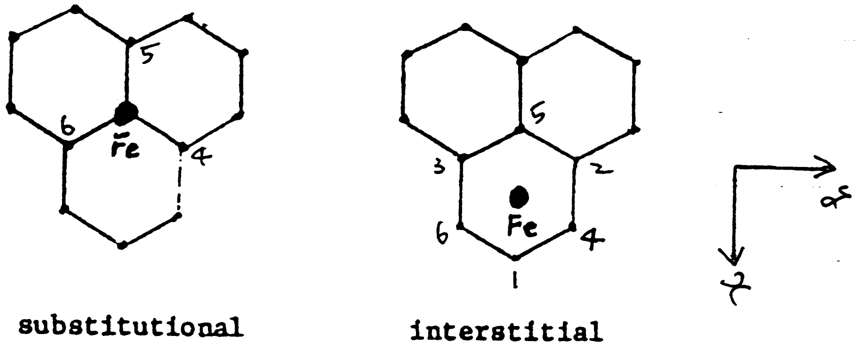
Character table:

$6/mmm$	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0

e)

Diagram: 

3. Honeycomb lattice with impurity



Coordinates

1. $\vec{r}_1 = (a, 0)$ 2. $\vec{r}_2 = \frac{a}{2}(-1, \sqrt{3})$ 3. $\vec{r}_3 = \frac{a}{2}(-1, -\sqrt{3})$

4. $\vec{r}_4 = \frac{a}{2}(1, \sqrt{3})$ 5. $\vec{r}_5 = (-a, 0)$ 6. $\vec{r}_6 = \frac{a}{2}(1, -\sqrt{3})$

a) We want to study $V_{crystal}(x, y)$ at a point very close to the impurity. Therefore, we can assume $\frac{x}{a}, \frac{y}{a} \ll 1$, if the impurity is located at the origin.
Let's define $\bar{x} \equiv x/a$, $\bar{y} \equiv y/a$, $\delta^2 \equiv \bar{x}^2 + \bar{y}^2$

If V_i is the potential on the impurity acted by the atom at location "i", the difference in crystal potential between the interstitial and substitutional impurities is (including only 1st nearest neighbors):

$$\Delta V \equiv V_{interstitial} - V_{substitutional} = V_1 + V_2 + V_3$$

$$V_i = \frac{e}{|\vec{x} - \vec{r}_i|}$$

$$V_1 = \frac{e}{[(x-a)^2+y^2]^{1/2}} \cong \frac{e}{a}\left\{1 - \frac{1}{2}\overbrace{(\delta^2 - 2\bar{x})}^{\varepsilon \atop \equiv} + \frac{3}{8}\varepsilon^2 - \frac{5}{16}\varepsilon^3 + \cdots\right\}$$

$$V_2 = \frac{e}{[(y+\frac{a}{2})^2+(y-\frac{\sqrt{3}}{2}a)^2]^{1/2}} = \frac{e}{a}\left\{1 - \frac{1}{2}(\delta^2 - \bar{x} - \sqrt{3}\bar{y}) + \frac{3}{8}(\quad)^2 + \cdots\right\}$$

$$V_3 = \frac{e}{[(x+\frac{a}{2})^2+(y+\frac{\sqrt{3}}{2}a)^2]^{1/2}} = \frac{e}{a}\left\{1 - \frac{1}{2}(\delta^2 + \bar{x} + \sqrt{3}\bar{y}) + \frac{3}{8}(\quad)^2 + \cdots\right\}$$

$$\Delta V = \frac{e}{a}\left\{3 - \frac{3}{2}\delta^2 + \frac{3}{8}(6\bar{y}^2 + 6\bar{x}^2) + O(\bar{x}^3, \bar{y}^3)\right\}$$

$$= \frac{3e}{a}\left\{1 + \frac{1}{4a^2}(x^2+y^2)\right\} + O((x/a)^3, (y/a)^3)$$

[This solution is inherited from the previous years, and does not explicitly consider the displacement in z direction. If we consider it explicitly, we get the following potentials.

$V_{\text{substitutional}}(x,y,z)$

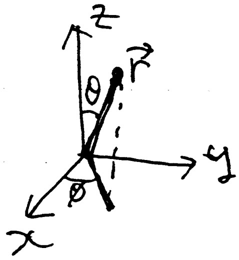
$$= \frac{e}{a}\left\{3 + \frac{9}{4}(\bar{x}^2+\bar{y}^2) - \frac{3}{2}\bar{r}^2 - \frac{15}{8}\bar{y}(3\bar{x}^2 - \bar{y}^2) + O(\bar{r}^4)\right\}$$

$V_{\text{interstitial}}(x,y,z)$

$$= \frac{2e}{a}\left\{3 + \frac{9}{4}(\bar{x}^2+\bar{y}^2) - \frac{3}{2}\bar{r}^2 + O(\bar{r}^4)\right\}$$]

b) $V_{interstitial}(x,y,z) \simeq \frac{6e}{a} + \frac{2e}{a}\left[\frac{9}{4}(\bar{x}^2+\bar{y}^2) - \frac{3}{2}\bar{r}^2\right]$

$= \frac{6e}{a} + \frac{3e}{2a}\left[\bar{r}^2 - 3\bar{z}^2\right]$



Let $z = r\cos\theta$

$= \frac{6e}{a} + \frac{3e}{2a}\left(\frac{r}{a}\right)^2\left[1 - 3\cos^2\theta\right]$

Now, $Y_{0,0} = \frac{1}{\sqrt{4\pi}}$, $Y_{2,0} = \sqrt{\frac{5}{4\pi}}\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)$

Therefore,

$V_{interstitial} = \sqrt{4\pi}\,\frac{e}{a}\left[6Y_{0,0}(\theta,\phi) - \frac{3}{\sqrt{5}}\left(\frac{r}{a}\right)^2 Y_{2,0}(\theta,\phi)\right]$

c) Substitutional: $D_{3h} = D_3 \otimes \sigma_h$

Table 3.30: Character Table for Group D_{3h}

$D_{3h} = D_3 \otimes \sigma_h$ ($\bar{6}m2$)			E	σ_h	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$
x^2+y^2, z^2		A_1'	1	1	1	1	1	1
	R_z	A_2'	1	1	1	1	−1	−1
		A_1''	1	−1	1	−1	1	−1
	z	A_2''	1	−1	1	−1	−1	1
(x^2-y^2, xy)	(x, y)	E'	2	2	−1	−1	0	0
(xz, yz)	(R_x, R_y)	E''	2	−2	−1	1	0	0

interstitial: $D_{6h} = D_6 \otimes i$ (or $D_6 \otimes \sigma_h$)

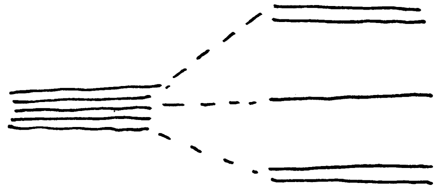
Table 3.28: Character Table for Group D_6

D_6 (622)			E	C_2	$2C_3$	$2C_6$	$3C_2'$	$3C_2''$
x^2+y^2, z^2		A_1	1	1	1	1	1	1
	R_z, z	A_2	1	1	1	1	−1	−1
		B_1	1	−1	1	−1	1	−1
		B_2	1	−1	1	−1	−1	1
(xz, yz)	(x, y), (R_x, R_y)	E_1	2	−2	−1	1	0	0
(x^2-y^2, xy)		E_2	2	2	−1	−1	0	0

(d) & (e) <u>d-level</u>

		D_{3h}		D_{6h}
$\psi_1 = 2z^2 - x^2 - y^2$	$\longrightarrow$	A_1'	$\longrightarrow$	A_{1g}
$\left.\begin{array}{l}\psi_2 = xz \\ \psi_3 = yz\end{array}\right\}$	$\longrightarrow$	E''	$\longrightarrow$	E_{1g}
$\left.\begin{array}{l}\psi_4 = x^2 - y^2 \\ \psi_5 = xy\end{array}\right\}$	$\longrightarrow$	E'	$\longrightarrow$	E_{2g}

Splitting (in both cases)



(f) The placement of the impurity in any of the two 2 dimensional crystal fields does not affect much the orbitals which are oriented in the z-direction (or the z component of the orbitals). Therefore,

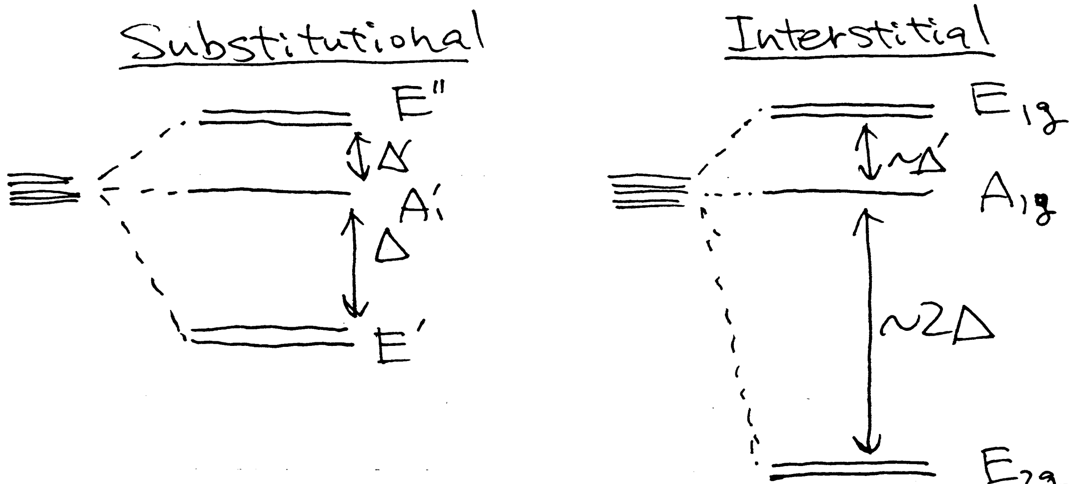
$\psi_1 = 3z^2 - r^2$ remains essentially uneffected (bonding state)

$\psi_{2,3} = \begin{cases} xz \\ yz \end{cases}$ (antibonding state) As they have a higher energy, those orbitals will be unoccupied.

$\psi_{4,5} = \begin{cases} x^2 - y^2 \\ xy \end{cases}$ (bonding state) As they have a lower energy, these will be the orbitals that the electrons will occupy.

$\longrightarrow$ cont.

As the interstitial impurity has six nearest neighbors, the energy of this states will be lower in the D_{6h} case than in the D_{3h} case, where there are only 3 nearest neighbors. Thus, the level structure will look like:



4 a) E

main axis

$2C_5, 2C_5^2$ (rotation about the axis of the stretch)

$5C_2'$ (rotation about the axis perpendicular to the main axis)

i (inversion)

$2iC_5, 2iC_5^2, 5iC_2' = 5\sigma_d$

b) D_{5d}

c) We first write down the characters of G_u and H_g as the reducible representation in D_{5d}

D_{5d}	E	$2C_5$	$2C_5^2$	$5C_2'$	i	$2S_{10}^{-1}$	$2S_{10}$	$5\sigma_d$
H_g	5	0	0	1	5	0	0	1
G_u	4	-1	-1	0	-4	1	1	0

By using the decomposition rules,

(i) H_g :

$$a_{1g} = \frac{1}{20}(5+0+0+5+5+0+0+5) = 1$$

$$e_{1g} = \frac{1}{20}(10+0+0+0+10+0+0+0) = 1$$

$$e_{2g} = \frac{1}{20}(10+0+0+0+10+0+0+0) = 1$$

$$\therefore H_g = A_{1g} + E_{1g} + E_{2g}$$

(ii) G_u :

$$e_{1u} = \frac{1}{20}(8-2(\tau-1)+2\tau+0+8-2(\tau-1)+2\tau) = 1$$

$$e_{2u} = \frac{1}{20}(8+2\tau-2(\tau-1)+0+8+2\tau-2(\tau-1)+0) = 1$$

$$\therefore G_u = E_{1u} + E_{2u}$$

Table 3.39: Character table for I_h.

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}^3$	$12S_{10}$	$20S_3$	15σ	$(h=120)$
A_g	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	$x^2+y^2+z^2$
F_{1g}	+3	$+\tau$	$1-\tau$	0	-1	+3	τ	$1-\tau$	0	-1	R_x, R_y, R_z
F_{2g}	+3	$1-\tau$	$+\tau$	0	-1	+3	$1-\tau$	τ	0	-1	
G_g	+4	-1	-1	+1	0	+4	-1	-1	+1	0	
H_g	+5	0	0	-1	+1	+5	0	0	-1	+1	$2z^2-x^2-y^2$ x^2-y^2 xy xz yz
A_u	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	
F_{1u}	+3	$+\tau$	$1-\tau$	0	-1	-3	$-\tau$	$\tau-1$	0	+1	(x,y,z)
F_{2u}	+3	$1-\tau$	$+\tau$	0	-1	-3	$\tau-1$	$-\tau$	0	+1	(x^3,y^3,z^3)
G_u	+4	-1	-1	+1	0	-4	+1	+1	-1	0	$x(z^2-y^2)$ $y(x^2-z^2)$ $z(y^2-x^2)$ xyz
H_u	+5	0	0	-1	+1	-5	0	0	+1	-1	

where $\tau = (1+\sqrt{5})/2$.
Note: C_5 and C_5^{-1} are in different classes, labeled $12C_5$ and $12C_5^2$ in the character table. Then $iC_5 = S_{10}^{-1}$ and $iC_5^{-1} = S_{10}$ are in the classes labeled $12S_{10}^3$ and $12S_{10}$, respectively. Also $iC_2 = \sigma_v$.

From the character table in the lecture note, we know the basis functions of H_g are:

$$H_g: \begin{cases} 2z^2-x^2-y^2 \\ x^2-y^2 \\ xy \\ xz \\ yz \end{cases}$$

The corresponding basis functions for the splitting multiplets are found by inspection

A_{1g} : $2z^2-x^2-y^2$

E_{1g} : (xz, yz)

E_{2g} : (x^2-y^2, xy)

Similarly

$$G_u \begin{cases} x(z^2-y^2) \\ y(x^2-z^2) \\ z(y^2-x^2) \\ xyz \end{cases}$$

$\Rightarrow$ basis functions for E_{1u} and E_{2u}

d) The characters of the full rotation group $\Gamma^{(2)}_{rot}$ for the operations in I_h group are.

	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12iC_5$	$12iC_5^2$	$20iC_3$	$15iC_2$
$\Gamma^{(2)}_{rot}$	5	0	0	-1	1	5	0	0	-1	1

where
$$\chi^{\Gamma^{(2)}}(C_5) = \frac{\sin(4+1)\cdot\frac{2\pi}{5}}{\sin(\frac{\pi}{5})} = 0$$

$$\chi^{\Gamma^{(2)}}(C_3) = \frac{\sin(4+1)\cdot\frac{2\pi}{3}}{\sin(\frac{\pi}{3})} = -1 \quad , etc.$$

We can see that the characters are the same as that of H_g in I_h group. Therefore,
$$\Gamma^{(2)}_{rot} = H_g .$$
So, the 5-d levels will remain degenerate in an icosahedral crystal field.