Tutorial: Direct product of the vector repr. for D_{3h}

- we know the characters of proper rotations C_φ and improper rotations S_φ for the vector repr. and general φ:

$$\chi^v(C_\varphi) = 1 + 2\cos\varphi \quad \text{and} \quad \chi^v(S_\varphi) = -1 + 2\cos\varphi$$

- thus, for the direct product $\Gamma^v \otimes \Gamma^v$ we get

$$\chi^{v\otimes v}(C_\varphi) = \chi^v(C_\varphi)^2 = (1+2\cos\varphi)^2$$
$$\chi^{v\otimes v}(S_\varphi) = \chi^v(S_\varphi)^2 = (-1+2\cos\varphi)^2$$

and specifically for elements of D_{3h}:

$$\chi^v(C_3) = 1+2\cos\tfrac{2\pi}{3} = 0 \ , \quad \chi^v(C_2) = 1+2\cos\pi = -1$$
$$\chi^v(S_3) = -1+2\cos\tfrac{2\pi}{3} = -2 \ , \quad \chi^v(\sigma = S_{2\pi}) = -1+2\cos 2\pi = 1$$

giving

D_{3h}	E	$2C_3$	$3\sigma_v$	σ_h	$2S_3$	$3C_2$	
Γ^v	3	0	1	1	-2	-1	squared
$\Gamma^{v\otimes v}$	9	0	1	1	4	1	

- the representation $\Gamma^{v\otimes v}$ decomposes into symmetric and antisymmetric parts $\Gamma^{v\otimes v} = \Gamma^{[v\otimes v]} \oplus \Gamma^{\{v\otimes v\}}$ with characters $\chi^{[v\otimes v]}(g) = \frac{1}{2}[\chi^v(g)^2 + \chi^v(g^2)]$, $\chi^{\{v\otimes v\}}(g) = \frac{1}{2}[\chi^v(g)^2 - \chi^v(g^2)]$

resulting in

$$\chi^{[v\otimes v]}(C_\varphi) = \frac{1}{2}[(1+2\cos\varphi)^2 + 1 + 2\cos 2\varphi] = 2\cos\varphi\,(1+2\cos\varphi)$$
$$\chi^{[v\otimes v]}(S_\varphi) = \frac{1}{2}[(-1+2\cos\varphi)^2 + 1 + 2\cos 2\varphi] = 2\cos\varphi\,(-1+2\cos\varphi)$$

and

$$\chi^{\{v\otimes v\}}(C_\varphi) = \frac{1}{2}[(1+2\cos\varphi)^2 - (1+2\cos 2\varphi)] = 1+2\cos\varphi = \chi^{pv}(C_\varphi)$$
$$\chi^{\{v\otimes v\}}(S_\varphi) = \frac{1}{2}[(-1+2\cos\varphi)^2 - (1+2\cos 2\varphi)] = 1-2\cos\varphi = \chi^{pv}(S_\varphi)$$

(we see that the antisymmetric subrepr. of $\Gamma^{v\otimes v}$ is equivalent to the pseudovector repr.)

- for D_{3h} we have for example

$$\chi^{[v\otimes v]}(C_3) = 2\cos\tfrac{2\pi}{3}\cdot\chi^v(C_3) = 0 \ , \quad \chi^{[v\otimes v]}(S_3) = 2\overbrace{\cos\tfrac{2\pi}{3}}^{-\frac{1}{2}}\cdot\overbrace{\chi^v(S_3)}^{-2} = 2$$
$$\chi^{[v\otimes v]}(C_2) = 2\cos\pi\cdot\chi^v(C_2) = 2 \ , \quad \chi^{[v\otimes v]}(\sigma) = 2\cos 2\pi\,\chi^v(\sigma) = 2$$

(T9)

- finally, we can deco-pose these repr. ~~into~~ into IRs

	D_{3h}	E	$2C_3$	$3\sigma_v$	σ_h	$2S_3$	$3C_2$	D_{3h}	C_{3v}	D_{3h}	C_{3v}
	A_1'	1	1	1	1	1	1		z	z^2, x^2+y^2	z^2, x^2+y^2
	A_2'	1	1	-1	1	1	-1	R_z	R_z		
	E'	2	-1	0	2	-1	0	(x,y)	$(x,y),(R_x,R_y)$	(xy, x^2-y^2)	$(xz,yz),(xy,x^2-y^2)$
	A_1''	1	1	-1	-1	-1	1				
	A_2''	1	1	1	-1	-1	-1	z			
	E''	2	-1	0	-2	1	0	(R_x,R_y)		(xz,yz)	
								see (T6)		see below	
squared	Γ^v	3	0	1	1	-2	-1	$= E' \oplus A_2''$ (as (x,y) and z)			
	$\Gamma^{v\otimes v}$	9	0	1	1	4	1	$= 2A_2' \oplus A_2' \oplus E' \oplus 2E''$			
+	$\Gamma^{[v\otimes v]}$	6	0	2	2	2	2	$= 2A_1' \oplus E' \oplus E''$ (as $x^2, y^2, z^2, xy, xz, yz$)			
	$\Gamma^{\{v\otimes v\}}$	3	0	-1	-1	2	-1	$= A_2' \oplus E''$ (as (R_x,R_y) and R_z)			

- assignment of functions $x^2, y^2, z^2, xy, xz, yz$ to IRs of D_{3h}:

  - we can consider these functions as components of the tensor product $\vec{x} \otimes \vec{x}$ where $\vec{x} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$ (this product has only symmetric part)
  - because $\vec{x}$ transforms as $\vec{x}' = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = D^v(g) \begin{pmatrix} x \\ y \\ z \end{pmatrix}$ for any $g \in D_{3h}$

    we can write for example

    $$x'x' = x'^2 = \left(D^v_{11}(g)\, x + D^v_{12}(g)\, y + D^v_{13}(g)\, z \right)^2$$

    and in a similar way for other combinations $y'^2, z'^2, x'y', x'z', y'z'$
  - from these transformations we can find which functions mix with each other and because we already know that $\Gamma^{[v\otimes v]} = 2A_1' \oplus E' \oplus E''$ from characters we look for 2 invariant (A_1') functions and two pairs of functions belonging to E' and E''
  - as $D^v(g)$ are orthogonal matrices for all point groups (magnitude of $\vec{x}$ is preserved), we can assign $x^2+y^2+z^2$ directly to A_1' (totally symmetric function) and because D_{3h} has only one main axis C_3 (as the z-axis), also x^2+y^2 and z^2 are independent invariants

(note that $x^2+y^2+z^2$ corresponds to s orbitals, and $2z^2-x^2-y^2$ do one of d orbitals)

T10

- furthermore, as z is independent of (x,y) for D_{3h} action, we can guess that xz and yz will form a pair and the second pair will be xy and x^2-y^2 (orthogonal complement to x^2+y^2)

- to find which pair belongs to E' we can apply for example reflection σ_h because the characters for this element differ in E' and E''

- $x, y,$ and z transform under σ_h as

$$\left.\begin{array}{l} x' = x \\ y' = y \\ z' = -z \end{array}\right\} \overset{\text{thus}}{\Longrightarrow} \quad \begin{array}{l} x'z' = -xz \\ y'z' = -yz \end{array} \quad \text{or} \quad \begin{pmatrix} x'z' \\ y'z' \end{pmatrix} = \overset{D_1(\sigma_h)}{\overset{\shortparallel}{\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}}} \begin{pmatrix} xz \\ yz \end{pmatrix}$$

$$\Rightarrow \chi_1(\sigma_h) = -2$$

and thus (xz, yz) belongs to E'' representation

- for the second pair we get

$$\begin{array}{l} x'y' = xy \\ x'^2 - y'^2 = x^2 - y^2 \end{array} \quad \text{or} \quad \begin{pmatrix} x'y' \\ x'^2-y'^2 \end{pmatrix} = \overbrace{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}}^{D_2(\sigma_h)} \begin{pmatrix} xy \\ x^2-y^2 \end{pmatrix} \Rightarrow \chi_2(\sigma_h) = 2$$

corresponding to E'

- one can easily check that also other characters are the same as for E'' or E', for example for C_3 we have

$$\left.\begin{array}{l} x' = -\frac{1}{2}x - \frac{\sqrt{3}}{2}y \\ y' = \frac{\sqrt{3}}{2}x - \frac{1}{2}y \\ z' = z \end{array}\right\} \Rightarrow \quad \left.\begin{array}{l} x'z' = -\frac{1}{2}xz - \frac{\sqrt{3}}{2}yz \\ y'z' = \frac{\sqrt{3}}{2}xz - \frac{1}{2}yz \end{array}\right\} \chi_1(C_3) = -1$$

$$x'y' = \left(-\frac{1}{2}x - \frac{\sqrt{3}}{2}y\right)\left(\frac{\sqrt{3}}{2}x - \frac{1}{2}y\right) = -\frac{1}{2}xy - \frac{\sqrt{3}}{4}(x^2-y^2)$$

$$x'^2 - y'^2 = \left(-\frac{1}{2}x - \frac{\sqrt{3}}{2}y\right)^2 - \left(\frac{\sqrt{3}}{2}x - \frac{1}{2}y\right)^2 = \sqrt{3}xy - \frac{1}{2}(x^2-y^2)$$

$$\Rightarrow \chi_2(C_3) = -1$$

but it is not necessary it is clear from the decomposition that these pairs belong either to E' or to E'' and we can use the simplest case (here σ_h) to determine the assignment