Professor Per Jensen, Ph.D.
Physical and Theoretical Chemistry
School of Mathematics and Natural Sciences

Fundamentals of Molecular Symmetry ***Exercises***

Week 4/11

4.1 The CNPI group of PH_3 is

$$\boldsymbol{D}_{3\mathrm{h}}(\mathrm{M}) = \{E, (123), (132), (12), (23), (13), E^*, (123)^*, (132)^*, (12)^*, (23)^*, (13)^*\}$$

with the irreducible representations

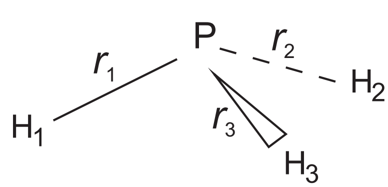
$\boldsymbol{D}_{3\mathrm{h}}(\mathrm{M})$:	E	(123)	(23)	E^*	$(123)^*$	$(23)^*$
	1	2	3	1	2	3
$A_1{}'$:	1	1	1	1	1	1
$A_1{}''$:	1	1	1	−1	−1	−1
$A_2{}'$:	1	1	−1	1	1	−1
$A_2{}''$:	1	1	−1	−1	−1	1
E' :	2	−1	0	2	−1	0
E'':	2	−1	0	−2	1	0

Decompose the following reducible representations of $\boldsymbol{D}_{3\mathrm{h}}(\mathrm{M})$ into their irreducible components:

E	(123)	(12)	E^*	$(123)^*$	$(12)^*$
4	4	0	0	0	0
4	1	0	4	1	0
8	2	0	0	0	0
8	−4	0	−8	4	0
12	0	0	0	0	0
16	−2	0	−8	4	0
40	10	0	0	−30	0

4.2 Before you start solving this problem, it may be helpful to have a look at the solution to Problem 3.2!

The three protons in the PH_3 molecule are labeled by $i = 1, 2, 3$. The bond length between the P nucleus and proton i is denoted r_i.



Determine the representation of $\boldsymbol{C}_{3\mathrm{v}}(\mathrm{M})$ generated by r_1, r_2, r_3. The irreducible representations of $\boldsymbol{C}_{3\mathrm{v}}(\mathrm{M})$ have the characters

$\boldsymbol{C}_{3\mathrm{v}}(\mathrm{M})$	E	(123),(132)	$(12)^*$,$(23)^*$,$(13)^*$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Use projection operators in the form

$$P_{mm}^{\Gamma_i} = \frac{l_i}{h} \sum_R D^{\Gamma_i}[R]_{mm}^* R,$$

where l_i is the dimension of Γ_i, and $D^{\Gamma_i}[R]$ is the representation matrix in Γ_i for R. to determine the linear combinations of r_1, r_2, r_3 that transform irreducibly. In forming the projection operators for the irreducible representation E, use the elements of the following 2×2 matrices known from the lecture

$$\left\{\mathbf{M}^E, \mathbf{M}^{(123)}, \mathbf{M}^{(132)}, \mathbf{M}^{(12)^*}, \mathbf{M}^{(23)^*}, \mathbf{M}^{(31)^*}\right\}$$

where

$$\mathbf{M}^{E} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad \mathbf{M}^{(12)^*} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

$$\mathbf{M}^{(123)} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \qquad \mathbf{M}^{(23)^*} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix},$$

$$\mathbf{M}^{(132)} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \qquad \mathbf{M}^{(31)^*} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}.$$

Verify that the transformation properties of the coordinates with E symmetry are described by these matrices.