Molecular symmetry group
I. Introduction

Full permutation-inversion group

$$\mathcal{F} = \mathcal{S}_{n_1} \otimes \cdots \otimes \mathcal{S}_{n_m} \otimes \mathcal{I}$$

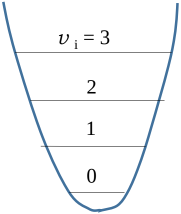
$\mathcal{S}_{n_j}$ = group of permutation of n_j identical nuclei of jth kind
$\mathcal{I} = \{e, e^*\}$ = inversion group

Molecular symmetry group is $\mathcal{F}$ with non-realizable ("useless") elements excluded, i.e., without operations transforming between (practically) degenerate equilibrium configurations

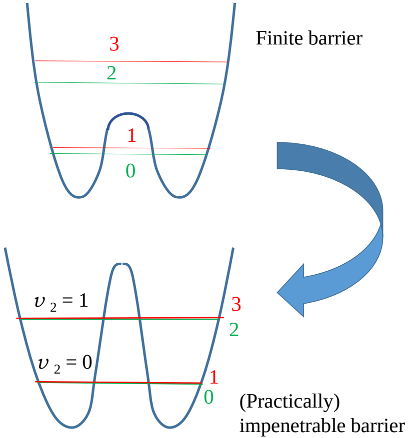
We can often relate the MSG to a point group of the equilibrium configuration of a *rigid* molecule.

XH_3 molecule

Inversion motion ("umbrella" vibration mode)



Planar configuration



$|+\rangle = (|R\rangle + |L\rangle)/\sqrt{2}$

$|-\rangle = (|R\rangle - |L\rangle)/\sqrt{2}$

X = chemical element of the V group of the periodic table

Molecule	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Inv. splitting (s^{-1})	2.38×10^{10}	$\sim 10^{-3}$	$\sim 10^{-8}$	$\sim 10^{-14}$	$\sim 10^{-18}$
	Experiment	Theory			

Schwerdtfeger, Laakkonen & Pyykkö, J. Chem. Phys. **96**, 6807 (1992)

Inversion splitting is not resolvable $\Leftrightarrow$ two degenerate levels

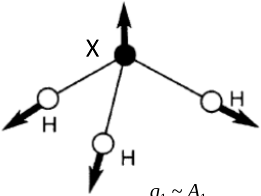
Molecule with a pyramidal structure; MSG is C_{3v}

3 classes $\Leftrightarrow$ 3IRs with the following table of characters

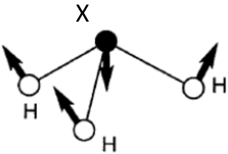
g	e	C_3	σ_v	
permut. of H′s	e	(ijk)	$(ij)^*$	
A_1	1	1	1	$\{3\} \otimes \mathfrak{g}$ or $\{1,1,1\} \otimes \mathfrak{u}$
A_2	1	1	−1	$\{1,1,1\} \otimes \mathfrak{g}$ or $\{3\} \otimes \mathfrak{u}$
E	2	−1	0	$\{2,1\} \otimes \mathfrak{g}$ or $\{2,1\} \otimes \mathfrak{u}$

$\mathfrak{g}$ ($\mathfrak{u}$) is the symmetric (antisymmetric) IR of $\mathcal{I}$

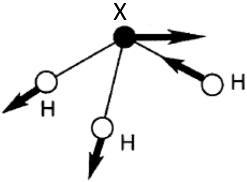
PH_3, AsH_3, SbH_3, BiH_3 molecules
Normal vibrtational coordinates (not including inversion!)



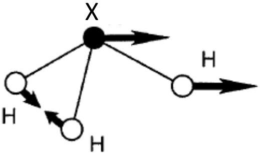
$q_1 \sim A_1$



$q_2 \sim A_1$



$q_3 \sim E$



$q_4 \sim E$

Coordinate part of the wave function of XH_3

$$\Psi = \Psi_{el} \otimes \Psi_v \otimes \Psi_r$$

For the ground state $\Psi_{el} \sim A_1$

$$\Psi_v = \Psi_{v_1} \otimes \Psi_{v_2} \otimes \Psi_{v_3} \otimes \Psi_{v_1}$$

$$\Psi_{v_1} \sim A_1, \qquad \Psi_{v_2} \sim A_1$$

For double-degenerate normal modes $j = 3, 4$, the level with the energy $\hbar\omega_j(v_j + \frac{1}{2})$ has the degeneracy $v_j + 1$; the decomposition in IRs A_1, A_2, E is analogous to that for the NH_3 molecule

Rotational levels:

K	Ψ_r
$K = 0$	A_1 (J even) or A_2 (J odd)
$K \bmod 3 = 1, 2$	E
$K \neq 0, \quad K \bmod 3 = 0$	$A_1 \oplus A_2$

Finally, we obtain $\Psi \sim A_1,\;$ or $A_2,\;$ or E
In terms of $\mathcal{F}$,

$$\Psi \sim (\{\lambda\} \otimes \mathfrak{g}) \oplus (\{\tilde{\lambda}\} \otimes \mathfrak{u})$$

The presence of two types of symmetry reflects the degeneracy of inversion doublet states.
The symmetry of the spin w.f. is determined by the Fermi–Dirac or Bose–Einstein statistics of the identical nuclei.