Group Theory in Molecular Physics

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Difficulties of solving Schrodinger equation

- Obtaining electronic states and energy levels by solving Schrodinger equation is difficult because the configuration of a molecule in terms of electrons and nuclear is complex

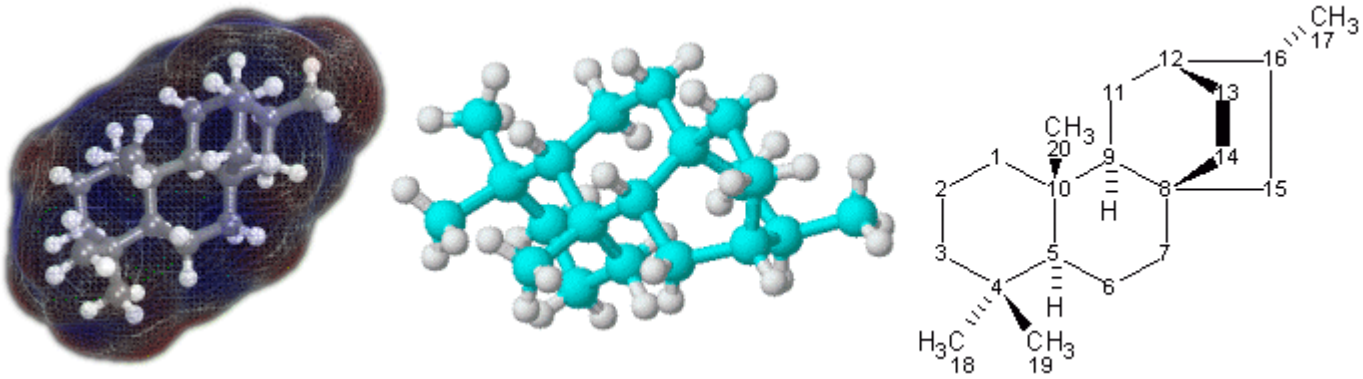

Image from wiki.

Electronic states, degeneracy and symmetry

Suppose we have a group of transformations $G=\{g|g\in G\}$ that acts on a Hilbert space V. Then V is a representation of G.

- The representation of G can split into irreducible representations $D^{(i)}(g)$. If $g|\psi\rangle = |\phi\rangle$, then we can say $|\psi\rangle$ and $|\phi\rangle$ are in the same irreps.
- If transformation operators has the same symmetries of Hamilton H, then [g, H] = 0. $|\psi\rangle$ and $|\phi\rangle$ are at the same energy level.
- All states in the same irreps are at the same energy level. Then if there are nontrivial irreps whose dimension is larger than 1, then there will be degenerate states.
- There is no degeneracy when G is abelian.

How to obtain character table

Procedure:

- Irreps can be obtained by acting a symmetry operator on a function that represents the spherically symmetric ground state of atoms.
- The first irrep is trivial.
- The first column of the character table is always the trace for the unit matrix representing the identity element or class.
- For all representations other than the identity representation Γ_1

$$\sum_k N_k \chi^{(\Gamma_i)}(\mathcal{C}_k) = 0. \qquad (3.43)$$

- Orthogonality

$$\sum_k \left[\chi^{(\Gamma_i)}(\mathcal{C}_k)\right]^* \chi^{(\Gamma_j)}(\mathcal{C}_k) N_k = h\delta_{\Gamma_i,\Gamma_j} \qquad (3.44)$$

$$\sum_{\Gamma_i} \left[\chi^{(\Gamma_i)}(\mathcal{C}_k)\right]^* \chi^{(\Gamma_i)}(\mathcal{C}_{k'}) = \frac{h}{N_k}\delta_{k,k'}. \qquad (3.45)$$

Table of point groups

The 32 Point Groups and Their Symbols				
System	Schoenflies symbol	Hermann-Mauguin symbol		Examples
		Full	Abbreviated	
Triclinic	C_1	1	1	
	$C_i, (S_2)$	$\bar{1}$	$\bar{1}$	Al_2SiO_5
Monoclinic	$C_{2v}, (C_{1h}), (S_1)$	m	m	KNO_2
	C_2	2	2	
	C_{2h}	$2/m$	$2/m$	
Orthorhombic	C_{2v}	$2mm$	mm	
	$D_2, (V)$	222	222	
	$D_{2h}, (V_h)$	$2/m\ 2/m\ 2/m$	mmm	I, Ga
Tetragonal	S_4	$\bar{4}$	$\bar{4}$	
	C_4	4	4	
	C_{4h}	$4/m$	$4/m$	$CaWO_4$
	$D_{2d}, (V_d)$	$\bar{4}2m$	$\bar{4}2m$	
	C_{4v}	$4mm$	$4mm$	
	D_4	422	42	
	D_{4h}	$4/m\ 2/m\ 2/m$	$4/mmm$	TiO_2, In, $\beta - Sn$
Rhombohedral	C_3	3	3	AsI_3
	$C_{3i}, (S_6)$	$\bar{3}$	$\bar{3}$	$FeTiO_3$
	C_{3v}	$3m$	$3m$	
	D_3	32	32	Se
	D_{3d}	$\bar{3}2/m$	$\bar{3}m$	Bi, As, Sb, Al_2O_3
Hexagonal	$C_{3h}, (S_3)$	$\bar{6}$	$\bar{6}$	
	C_6	6	6	
	C_{6h}	$6/m$	$6/m$	
	D_{3h}	$\bar{6}2m$	$\bar{6}2m$	
	C_{6v}	$6mm$	$6mm$	ZnO, NiAs
	D_6	622	62	CeF_3
	D_{6h}	$6/m\ 2/m\ 2/m$	$6/mmm$	Mg, Zn, graphite
Cubic	T	23	23	$NaClO_3$
	T_h	$2/m\bar{3}$	$m3$	FeS_2
	T_d	$\bar{4}3m$	$\bar{4}3m$	ZnS
	O	432	43	β-Mn
	O_h	$4/m\ \bar{3}\ 2/m$	$m3m$	NaCl, diamond, Cu

Symmetry of the NH3 molecule

Basis function

$(x^2+y^2)\ z^2$ → 1D irrep: A_1

z → 1D irrep: A_2

(xz, yz), (x^2-y^2, xy) → 2D irrep: E

Table 3.15: Character Table for Group C_{3v}

C_{3v} $(3m)$			E	$2C_3$	$3\sigma_v$
x^2+y^2, z^2	z	A_1	1	1	1
	R_z	A_2	1	1	−1
(x^2-y^2, xy) (xz, yz)	(x, y) (R_x, R_y)	E	2	−1	0

For all representations other than the identity representation Γ_1

$$\sum_k N_k \chi^{(\Gamma_i)}(\mathcal{C}_k) = 0. \qquad (3.43)$$

Orthogonality

$$\sum_k \left[\chi^{(\Gamma_i)}(\mathcal{C}_k)\right]^* \chi^{(\Gamma_j)}(\mathcal{C}_k) N_k = h\delta_{\Gamma_i,\Gamma_j} \qquad (3.44)$$

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Electronic states and irreps

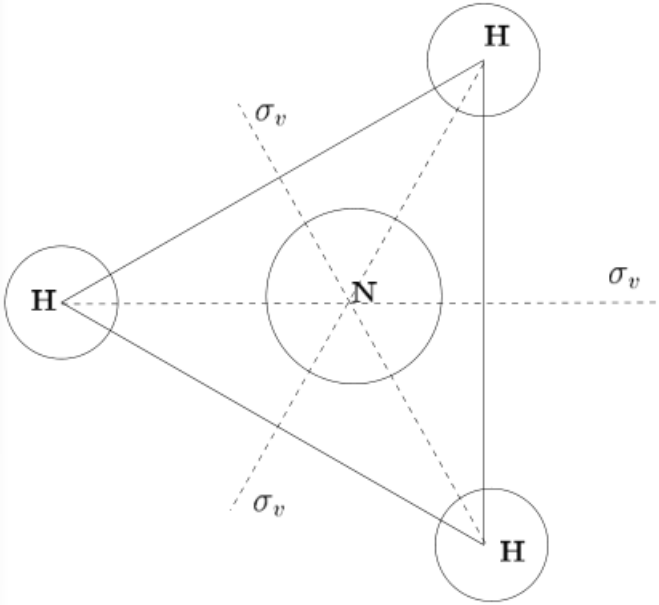


Figure 8.5: Schematic diagram of the symmetry operations for an NH_3 molecule (group C_{3v}) where the three hydrogen atoms are at the corners of an equilateral triangle and the N atom is along the normal through the midpoint of this triangle but not coplanar with the hydrogens.

Position never changes under symmetry operation

Trivial irrep

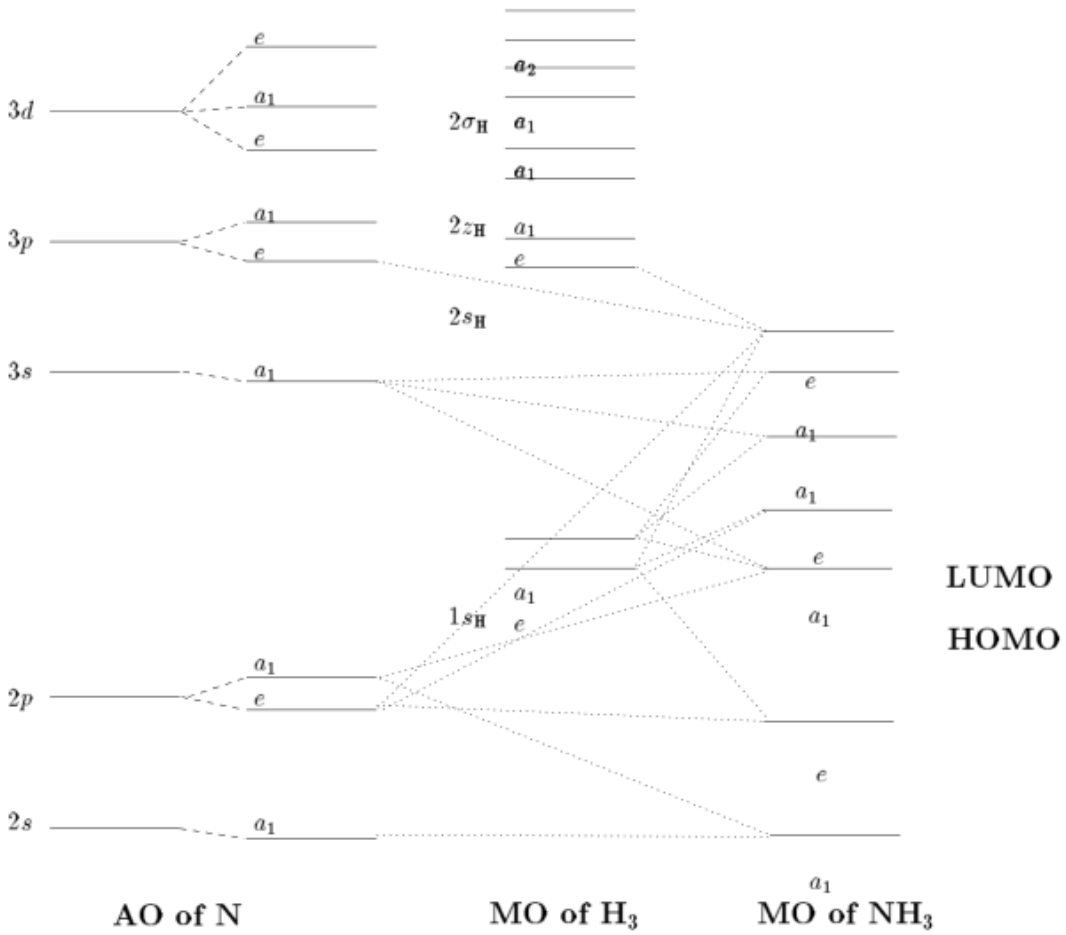
transform as the irrep

N $1s^2 2s^2 2p^3$ ⇨ l =1 ⇨ p_z $A_1(\Gamma_1)$

H $1s^1$ p_x and p_y $E(\Gamma_2)$

Electronic states of the NH3 molecule

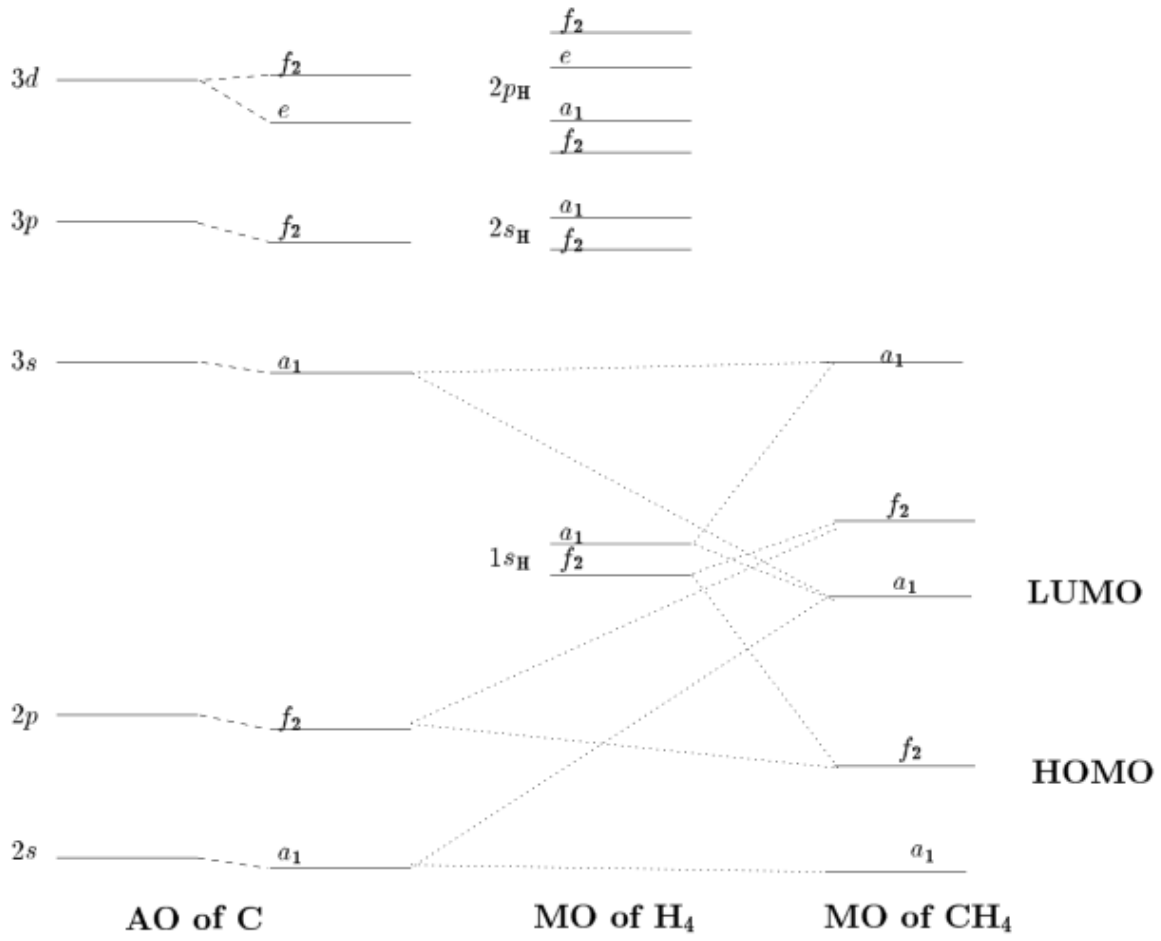
sp^3 hybridization



- The states with like symmetries will interact to form bonding and antibonding orbitals.
- States with unlike symmetries do not interact

- Atomic orbitals (AO) of nitrogen and the molecular orbitals (MO) for the cluster of three hydrogen atoms.
- The three electrons in the p state form bonds to the three hydrogen atoms.
- The higher levels are all antibonding states.

Electronic states of the CH4 molecule



- The states with like symmetries will interact to form bonding and antibonding orbitals.
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Molecular vibrations

Group theory help us figure out how radiation that is incident on a molecule induces electric dipole transitions (infrared activity) or in light scattering (Raman effect)

Each eigenvalue and its corresponding normal mode are labeled by its appropriate irrep because irreps do not couple with one another.

Procedure:

- Identify the symmetry operations and appropriate symmetry group G to describe the molecule in its equilibrium position.
- A molecular vibration involves the transformation properties of a vector.
- Find $\chi_{\text{equivalence}} = \chi^{\text{atom sites}}$, the characters for the equivalence transformation, which represents the number of atoms that are invariant under the symmetry operations of the group.
- Get irreps by using the following relation.

$$\chi_{\text{molecular vibrations}} = (\chi^{\text{atom sites}} \otimes \chi_{\text{vector}}) - \chi_{\text{translations}} - \chi_{\text{rotations}} \tag{9.7}$$

- Apply selection rule for C_{3V}.

Vibrations of the NH3 molecule

	E	$2C_3$	$3\sigma_v$	
$\chi^{\text{total}}_{\text{a.s.}}$	4	1	2	$\Rightarrow 2A_1 + E$
$\chi^{\text{H}}_{\text{a.s.}}$	3	0	1	$\Rightarrow A_1 + E$

$$\begin{aligned}\chi_{\text{molecular vibrations}} &= \chi^{\text{atom sites}} \otimes \chi_{\text{vector}} - \chi_{\text{translations}} - \chi_{\text{rotations}} \\ &= (2A_1 + E) \otimes (A_1 + E) - (A_1 + E) - (A_2 + E) \\ &= 2A_1 + 2E\end{aligned}$$

Symmetry in equilibrium (irreps)

Symmetry in atomic translations

Symmetry in molecular rotations

Symmetry in molecular translations and rotations should be excluded because we only consider vibration.

Vibration modes

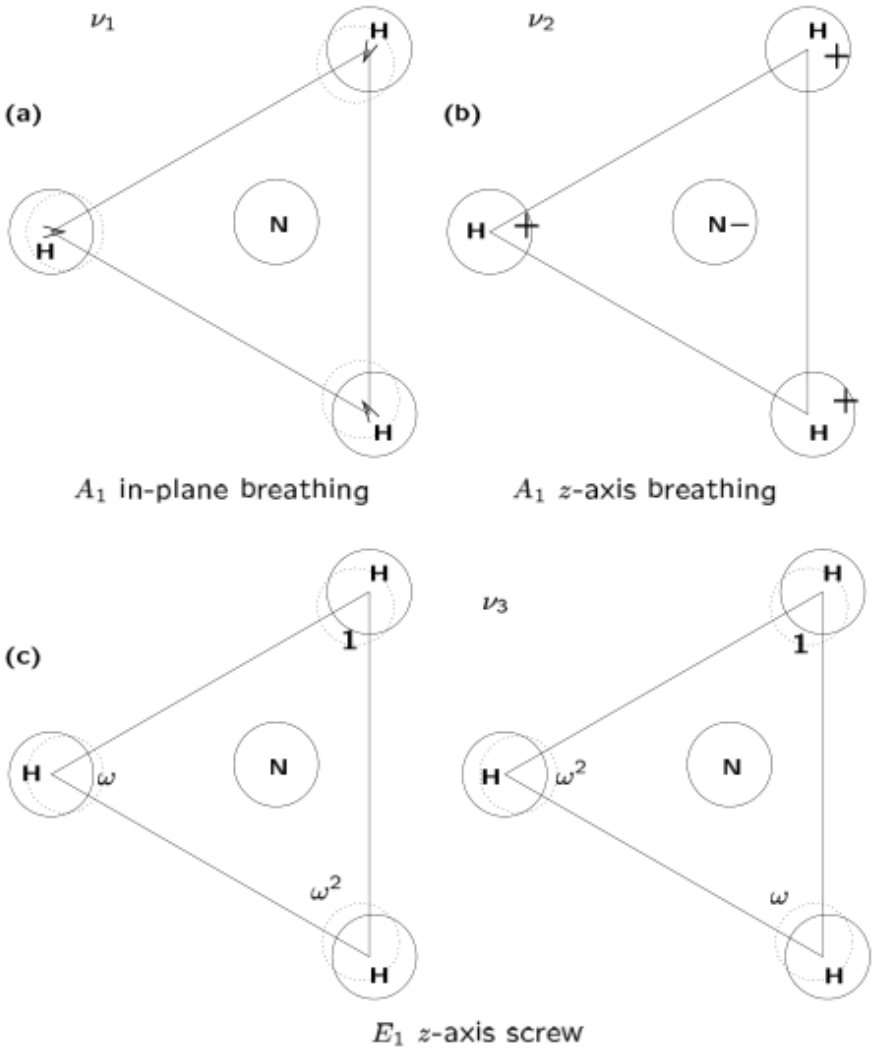

Figure 9.6: Normal modes for the NH_3 molecule: (a) the in-plane breathing mode, (b) the z-axis breathing mode, and (c) one partner of the in-plane mode of E symmetry; the second partner (complex conjugate of the first) is not shown. Also the other doubly-degenerate E mode for z-axis motion is not shown.

$$\omega = e^{2\pi i/3}$$

The Raman effect for NH3

P232

For the case of the NH_3 molecule which has C_{3v} symmetry (see §9.7.1), the Raman-active modes have the symmetries A_1 for x^2+y^2, z^2 and E for (x^2-y^2, xy) and (xz, yz) so that all the normal modes for the NH_3 molecule $(2A_1 + 2E)$ are Raman-active. Polarization selection rules imply that the A_1 modes are diagonal (i.e., scattering occurs when $\vec{E}_i \parallel \vec{E}_s$) while the E modes are off-diagonal (i.e., scattering occurs when $\vec{E}_i \perp \vec{E}_s$).

Symmetrical double well model

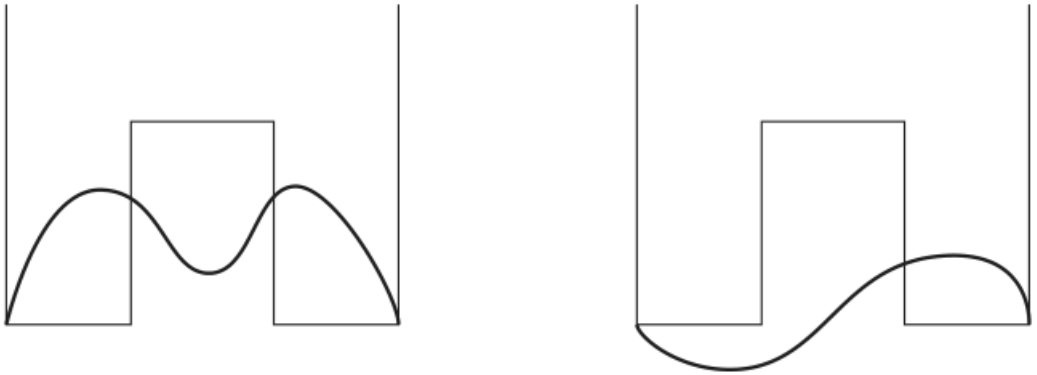

FIGURE 3 The symmetrical double well with the two lowest-lying states $|S\rangle$ (symmetrical) and $|A\rangle$ (antisymmetrical) shown.

$$|R\rangle = \frac{1}{\sqrt{2}}(|S\rangle + |A\rangle) \qquad |R, t_0 = 0; t\rangle = \frac{1}{\sqrt{2}}\left(e^{-iE_S t/\hbar}|S\rangle + e^{iE_A t/\hbar}|A\rangle\right)$$

$$= \frac{1}{\sqrt{2}} e^{-iE_S t/\hbar}\left(|S\rangle + e^{i(E_A - E_S)t/\hbar}|A\rangle\right).$$

$$|L\rangle = \frac{1}{\sqrt{2}}(|S\rangle - |A\rangle).$$

$$\omega = \frac{(E_A - E_S)}{\hbar}.$$

Nonstationarystates
Not parity eigenkets
Not energy eigenkets

System oscillates at the frequency dependent of the energy difference between symmetrical state and asymmetrical state

Oscillation of NH3

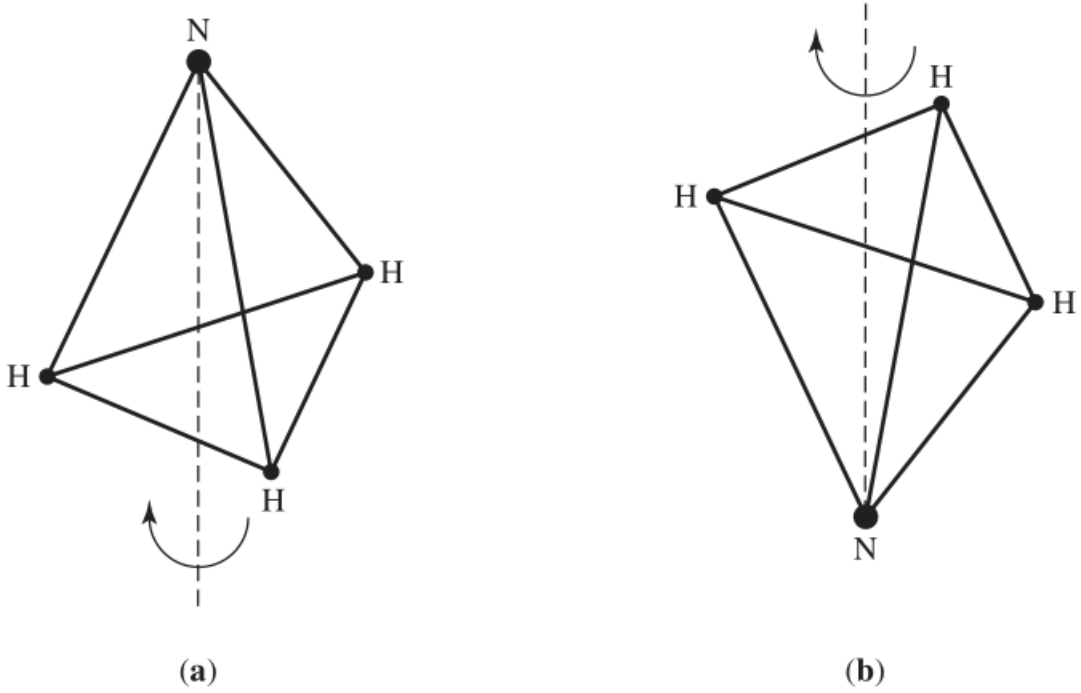

FIGURE 5 An ammonia molecule, NH_3, where the three H atoms form the three corners of an equilateral triangle.

- The up and down positions for the N atom are analogous to R and L of the double-well potential.
- The parity and energy eigenstates are superpositions of Figure 5a and Figure 5b

$$|R\rangle = \frac{1}{\sqrt{2}}(|S\rangle + |A\rangle)$$

$$|L\rangle = \frac{1}{\sqrt{2}}(|S\rangle - |A\rangle).$$

Oscillate at the frequency of 24,000MHz

Reference

- Sakurai, Jun John, and Eugene D. Commins. "Modern quantum mechanics, revised edition." (1995): 93-95.
- https://physics.stackexchange.com/questions/319096/what-is-the-relationship-between-symmetry-and-degeneracy-in-quantum-mechanics
- Dresselhaus, Mildred S., Gene Dresselhaus, and Ado Jorio. "Applications of group theory to the physics of solids." (2008).

Symmetry operations

- E = Identity
- C_n = rotation through $2\pi/n$. For example C_2 is a rotation of 180°. Likewise C_3 is a rotation of 120°, while C_6^2 represents a rotation of 60° followed by another rotation of 60° about the
- σ = reflection in a plane.
- σ_h = reflection in a "horizontal" plane. The reflection plane here is perpendicular to the axis of highest rotational symmetry.
- σ_v = reflection in a "vertical" plane. The reflection plane here contains the axis of highest symmetry.
- σ_d = reflection in a diagonal plane. The reflection plane here is a vertical plane which bisects the angle between the two fold axes $\perp$ to the principal symmetry axis. An example of a diagonal plane is shown in Fig. 3.1. σ_d is also called a dihedral plane.
- i = inversion which takes

$$\begin{cases} x \rightarrow -x \\ y \rightarrow -y \\ z \rightarrow -z \end{cases}$$

- S_n = improper rotation through $2\pi/n$, which consists of a rotation by $2\pi/n$ followed by a reflection in a horizontal plane.
- iC_n = compound rotation-inversion, which consists of a rotation followed by an inversion.