Algebraic and Geometric Methods in Engineering and Physics - The symmetries of the Ammonia Molecule as an example for point group symmetries of molecules

Conrad Meerpohl

10. January 2024

1 Point group symmetries

Frequently, molecules have certain symmetries in their structure. The point group symmetries describe molecules that have a unique equilibrium configuration with no observable tunneling between equivalent configurations. The study of point group symmetries is useful since it allows to efficiently study all molecules in one point symmetry group at the same time since chemically related molecules in the same point symmetry group have similar properties as, for example, similar bonding schemes, molecular bonding diagrams and spectroscopic properties.

The symmetries of molecules are diveded in five categories:

- **Identity** (E): Every molecule has of course the identity symmetry which leaves the molecule unchanged.
- **Rotational axis** (C_n): An axis around which a rotation of $\frac{360}{n}$ degree takes place which leaves the molecule unchanged. A molecule can have more than one rotational axes. The axis with largest n is called **principal axis**
- **Plane symmetry** (σ): A plane on which the molecule is reflected. If the plane is parallel to the principal axis we call this plane symmetry **vertical** and we use the symbol σ_v. If the plane is perpendicular to the principal axis we call it horizontal and use σ_h.
- **Inversion center** (i): A molecule has this symmetry if for every atom of this molecule a an identical atom is diametrically opposite of the center of the molecule with equal distance to the center.
- **Rotation-reflection** (S_n): An axis with a rotation by $\frac{360}{n}$ followed by a reflection on a perpendicular plane

The molecules themselves can then be divided depending on the symmetries they have. For example the point group called C_1 consists of all molecules without non-trival symmetries (for example bromochlorofluoromethane). Another example is the point group C_{nv} which consists all molecules with symmetries $E, C_n, n \cdot \sigma_v$. In the following we want to further examine the point group C_{3v} which consists the ammonia molecule. Other molecules in this point group are phosphorus oxychloride and cobalt tetracarbonyl hydride.

2 The ammonia molecule as an example of C_{3v}

We want to study the symmetries of the ammonia molecule which consists of one nitrogen atom and three hydrogen atoms. The ammonia molecule has of course the trivial symmetry. Furthermore it has a rotational symmetry C_3 and three plane symmetries σ_v.

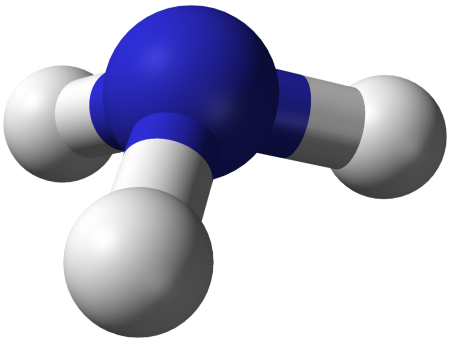

Figure 1: The ammonia molecule

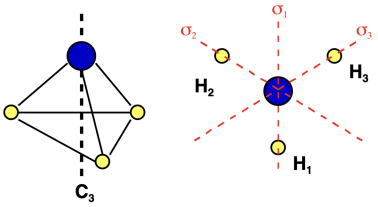

Figure 2: The (non-trivial) symmetries of the ammonia molecule

Since the one nitrogen atom remains in the same position under each symmetry, it is easy to see that the symmetries of the ammonia molecule and hence of C_{3v} is isomorphic to the symmetric group S_3 where we identify $C_3 \cong (123), C_3^2 = (132), \sigma_1 = (2,3), \sigma_2 = (13), \sigma_3 = (12)$, and we get the following multiplication table:

C_{3v}	E	C_3	C_3^2	σ_1	σ_2	σ_3
E	E	C_3	C_3^2	σ_1	σ_2	σ_3
C_3	C_3	C_3^2	E	σ_3	σ_1	σ_2
C_3^2	C_3^2	E	C_3	σ_2	σ_3	σ_1
σ_1	σ_1	σ_2	σ_3	E	C_3	C_3^2
σ_2	σ_2	σ_3	σ_1	C_3^2	E	C_3
σ_3	σ_3	σ_1	σ_2	C_3	C_3^2	E

For this group we can find the following (irreducible) representations

- The trivial representation, which in this context is called A_1:

$$A_{1,E} = A_{1,C_3} = A_{1,C_3^2} = A_{1,\sigma_1} = A_{1,\sigma_2} = A_{1,\sigma_3} = 1$$

- The representation A_2 defined as follows:

$$A_{2,E} = A_{2,C_3} = A_{2,C_3^2} = 1, A_{2,\sigma_1} = A_{2,\sigma_2} = A_{2,\sigma_3} = -1$$

- The irreducible representation E which we already know from Homework 7:

$$E_E = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad E_{C_3} = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$$
$$E_{C_3^2} = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} \quad E_{\sigma_1} = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$$
$$E_{\sigma_2} = \begin{pmatrix} 1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} \quad E_{\sigma_3} = \begin{pmatrix} 1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$$

We can easily calculate the characters of these representations, which for A_1 and A_2 are equal to the representation itself. For E we calculate:

$$\chi_E(E) = 2, \chi_E(C_3) = \chi_E(C_3^2) = -1, \chi_E(\sigma_1) = \chi_E(\sigma_2) = \chi_E(\sigma_3) = 0$$

Using the characters we can check that these representations are indeed irreducible since by *Corollary 2.2.100* a representation is irreducible iff $\langle \chi_\phi, \chi_\phi \rangle = 1$, indeed

$$\langle \chi_E, \chi_E \rangle = \frac{1}{6}(2^2 + 2(-1)^2) = 1$$

(for A_1, A_2 this is trivial). With this we can conclude that the representation ψ given by

$$\psi_E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \psi_{C_3} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\psi_{C_3^2} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \quad \psi_{\sigma_1} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

$$\psi_{\sigma_2} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \quad \psi_{\sigma_3} = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix})$$

is equivalent to the direct sum of A_1 and E, $\psi \sim A_1 \oplus E$. This follows from the fact, that two (finite-dimensional) representations that have equal characters are equivalent, which has been shown on Homework 8 ($\chi_\psi = \chi_E + 1 = \chi_E + \chi_{A_1}$).

The (irreducible) representations of these point group symmetries and their characteristics are used to study molecular orbits or the vibrations of the molecules, since the symmetry operations commute with the "vibration-electronic Hamiltonian" when we interpret the symmetries as symmetries of the vibration-electronic coordinates. Here the symmetries reduce the complexity of the system similar as to *2.2.7 Application to civil engineering.*

Reference

Blinder, Quantum Chemistry Spring Term 2002 Chapter 12, https://public.websites.umich.edu/ chem461/