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# Electric Fields

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## The Energy Levels of NH<sub>3</sub> in an Electric Field

### The 2×2 representation

Let  $\hat{H}_0$  be the Hamiltonian in the absence of an electric field. Suppose

$$\hat{H}_0\psi_n = E_n\psi_n, \quad , n = 0, 1, \dots$$

In the presence of an electric field,

$$\hat{H}_0 \rightarrow \hat{H} = \hat{H}_0 - d \cdot \mathbf{E}.$$

If  $x$  is the coordinate associated with inversion and  $\mathbf{E} = \mathcal{E}\hat{i}$ , then

$$\hat{H} = \hat{H}_0 - q(\hat{x} - x_{cm})\mathcal{E},$$

with  $q$  the charge associated with changing the conformation of the molecule.

We will look (as an approximation) for eigenvectors of  $\hat{H}$  in the subspace spanned by  $\{\psi_0, \psi_1\}$ . Using  $\psi_0$  and  $\psi_1$  as a basis set,

$$\hat{H}_0 = \begin{bmatrix} E_0 & 0 \\ 0 & E_1 \end{bmatrix}.$$

Let the phases of the basis vectors be chosen so that

$$\ell = \langle \psi_0 | (\hat{x} - x_{cm}) \psi_1 \rangle = \langle \psi_1 | (\hat{x} - x_{cm}) \psi_0 \rangle.$$

Since symmetry requires

$$\langle \psi_0 | (\hat{x} - x_{cm}) \psi_0 \rangle = \langle \psi_1 | (\hat{x} - x_{cm}) \psi_1 \rangle = 0,$$

$$\hat{H} = \begin{bmatrix} E_0 & -q\ell\mathcal{E} \\ -q\ell\mathcal{E} & E_1 \end{bmatrix}. \quad (1)$$



**$\hat{H}$  as a Geometrical Transformation**

By shifting the origin and moving factors around,  $\hat{H}$  can be written

$$\hat{H} = \frac{E_0 + E_1}{2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} - \sqrt{\frac{1}{4}(E_1 - E_0)^2 + (q\ell\mathcal{E})^2} \begin{bmatrix} \frac{E_1 - E_0}{\sqrt{\frac{1}{4}(E_1 - E_0)^2 + (q\ell\mathcal{E})^2}} & \frac{q\ell\mathcal{E}}{\sqrt{\frac{1}{4}(E_1 - E_0)^2 + (q\ell\mathcal{E})^2}} \\ \frac{q\ell\mathcal{E}}{\sqrt{\frac{1}{4}(E_1 - E_0)^2 + (q\ell\mathcal{E})^2}} & -\frac{E_1 - E_0}{\sqrt{\frac{1}{4}(E_1 - E_0)^2 + (q\ell\mathcal{E})^2}} \end{bmatrix}.$$

If

$$\sin \theta = \frac{q\ell\mathcal{E}}{\sqrt{\frac{1}{4}(E_1 - E_0)^2 + (q\ell\mathcal{E})^2}},$$

then

$$\hat{H} = \frac{E_0 + E_1}{2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} - \sqrt{\frac{1}{4}(E_1 - E_0)^2 + (q\ell\mathcal{E})^2} \begin{bmatrix} \cos \theta & \sin \theta \\ \sin \theta & -\cos \theta \end{bmatrix} \quad (2)$$

with  $-\frac{\pi}{2} < \theta < \frac{\pi}{2}$  corresponding to  $-\infty < \mathcal{E} < \infty$ .

It follows from (2) that the eigenvectors of  $\hat{H}$  are the eigenvectors of

$$\hat{M} = \begin{bmatrix} \cos \theta & \sin \theta \\ \sin \theta & -\cos \theta \end{bmatrix}.$$

Now a rotation by an angle  $\theta$  transforms a point (located with cylindrical coordinates  $r, \phi$  in the  $x, y$ -plane)

$$x = r \cos \phi$$

$$y = r \sin \phi$$

into

$$x' = r \cos(\phi + \theta) = r \cos \phi \cos \theta - r \sin \phi \sin \theta = x \cos \theta - y \sin \theta$$

$$y' = r \sin(\phi + \theta) = r \sin \phi \cos \theta + r \cos \phi \sin \theta = y \cos \theta + x \sin \theta$$

In matrix notation,

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}.$$

Since

$$\hat{M} = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix},$$

the effect of the Hermitian operator  $\hat{M}$  is the same as application of two transformations,

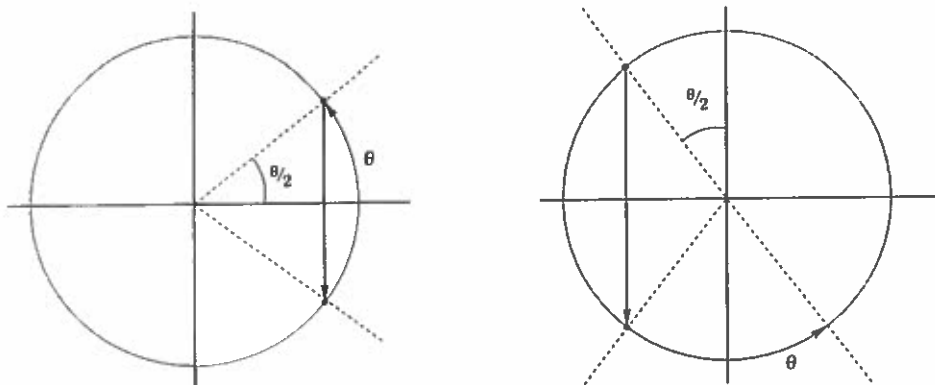
(1) a reflection about the  $x = 0$  line, followed by

(2) a rotation by an angle  $\theta$ .



## The eigenvectors and eigenvalues

There are only two directions which are left invariant by this transformation,



The direction  $\theta/2$  is left invariant by  $\hat{M}$  and the direction  $(\theta + \pi)/2$  is reversed. The eigenvectors and eigenvalues are

$$\begin{bmatrix} \cos \frac{\theta}{2} \\ \sin \frac{\theta}{2} \end{bmatrix}, \quad +1; \quad \begin{bmatrix} -\sin \frac{\theta}{2} \\ \cos \frac{\theta}{2} \end{bmatrix}, \quad -1.$$

$\hat{H}$  has the same eigenvectors,

$$|\epsilon_0\rangle = \begin{bmatrix} \cos \frac{\theta}{2} \\ \sin \frac{\theta}{2} \end{bmatrix} \quad \text{and} \quad |\epsilon_1\rangle = \begin{bmatrix} -\sin \frac{\theta}{2} \\ \cos \frac{\theta}{2} \end{bmatrix},$$

and the corresponding eigenvalues are

$$\epsilon_0 = \frac{E_0 + E_1}{2} - \sqrt{(E_1 - E_0)^2/4 + (q\ell\mathcal{E})^2} = \frac{E_0 \cos^2 \frac{\theta}{2} + E_1 \sin^2 \frac{\theta}{2}}{\cos^2 \frac{\theta}{2} - \sin^2 \frac{\theta}{2}},$$

$$\epsilon_1 = \frac{E_0 + E_1}{2} + \sqrt{\frac{1}{4}(E_1 - E_0)^2 + (q\ell\mathcal{E})^2} = \frac{E_0 \sin^2 \frac{\theta}{2} + E_1 \cos^2 \frac{\theta}{2}}{\cos^2 \frac{\theta}{2} - \sin^2 \frac{\theta}{2}}.$$

