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Electric Fields

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The Energy Levels of NH_3 in an Electric Field

The 2×2 representation

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

$$\hat{H}_0\psi_n = E_n\psi_n, \qquad ,n = 0, 1, \ldots$$

In the presence of an electric field,

$$\hat{H}_0 \to \hat{H} = \hat{H}_0 - \boldsymbol{d} \cdot \boldsymbol{E}.$$

If x is the coordinate associated with inversion and $\boldsymbol{E} = \mathcal{E}\hat{\imath}$, 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 ψ_0 and ψ_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

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

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

$\hat{H}$ as a Geometrical Transformation

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

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

If

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

then

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

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 θ transforms a point (located with cylindrical coordinates r, ϕ 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

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

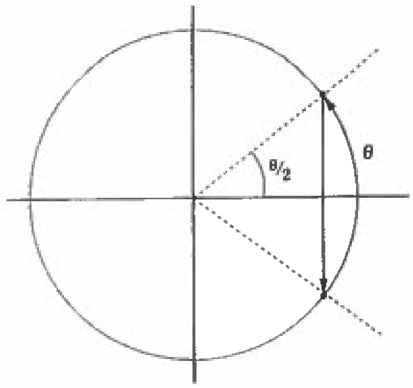
the effect of the Hermitian operator $\hat{M}$ is the same as application of two transformations,

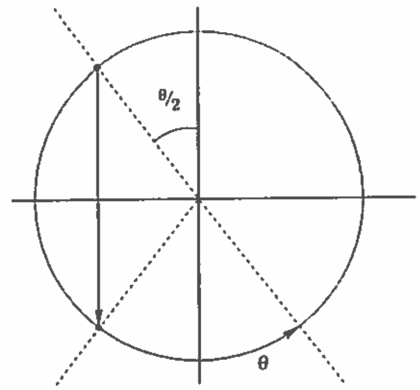
(1) a reflection about the $x = 0$ line, followed by

(2) a rotation by an angle θ.

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

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

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

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

and the corresponding eigenvalues are

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

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