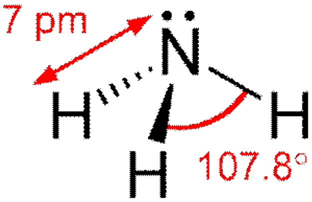
L30-Ammonia Molecule

Friday, November 11, 2016 09:03

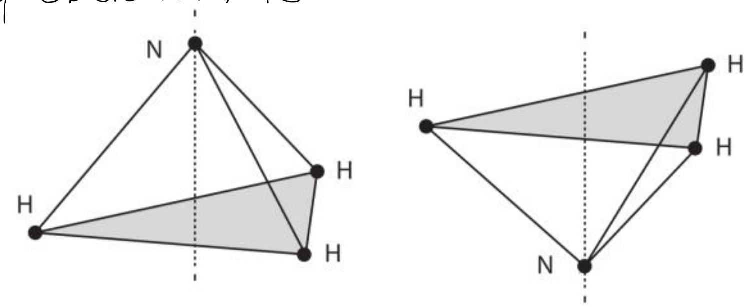
* The ammonia molecule has 2 states:
  $|1\rangle$ N atom above the H triangle
  $|2\rangle$ N atom below the H triangle



The two states are symmetric in energy, but neither is an energy eigenstate becouse of an interaction energy, $-A$ representing the probability of tunnelling from one state to the other

The Hamiltonian (total energy operator) is:

$$\mathcal{H} = \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix}$$



a) Solve the TISE:

$$\hat{H}|\psi\rangle = E|\psi\rangle \qquad \begin{pmatrix} E_0 & -A \\ -A & E_0 \end{pmatrix}\psi = E\psi \qquad \begin{pmatrix} E_0-E & -A \\ -A & E_0-E \end{pmatrix}\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$\begin{vmatrix} E_0-E & -A \\ -A & E_0-E \end{vmatrix} = (E_0-E)^2 - A^2 = 0 \qquad E_I = E_0 - A$$

$$E = E_0 \pm A \qquad E_{II} = E_0 + A$$

$$E_I: \quad \begin{pmatrix} A & -A \\ -A & A \end{pmatrix}\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \qquad |I\rangle = \psi_1|1\rangle + \psi_2|2\rangle \qquad \psi_2 = \psi_1$$

$$= \frac{1}{\sqrt{2}}(|1\rangle + |2\rangle) \qquad \text{normalized.}$$

$$E_{II}: \quad \begin{pmatrix} A & A \\ A & A \end{pmatrix}\begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \qquad |II\rangle = \psi_1|1\rangle + \psi_2|2\rangle \qquad \psi_2 = -\psi_1$$

$$= \frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)$$

b) Change basis to the energy eigenstates with a Unitary Transformation.

$$|\psi\rangle = \psi_1|1\rangle + \psi_2|2\rangle \qquad = \psi_I|I\rangle + \psi_{II}|II\rangle$$

$$= \psi_I \left[\frac{1}{\sqrt{2}}(|1\rangle + |2\rangle\right] + \psi_{II}\left[\frac{1}{\sqrt{2}}(|1\rangle - |2\rangle)\right]$$

$$= \frac{1}{\sqrt{2}}(\psi_I + \psi_{II})\,|1\rangle + \frac{1}{\sqrt{2}}(\psi_I - \psi_{II})\,|2\rangle$$

Thus $\underbrace{\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}}_{\psi} = \underbrace{\frac{1}{\sqrt{2}}\begin{pmatrix}1 & 1\\ 1 & -1\end{pmatrix}}_{R}\underbrace{\begin{pmatrix}\psi_I\\ \psi_{II}\end{pmatrix}}_{\psi'}$ or $\psi = R\,\psi'$

$\psi' = R^{-1}\psi = R^{\dagger}\psi$

Because $|\psi_I\rangle$ and $|\psi_{II}\rangle$ are orthonormal [$\mathcal{H}$ is Hermitian]

$$R^{\dagger}R = \frac{1}{\sqrt{2}}\begin{pmatrix}1 & 1\\ 1 & -1\end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix}1 & 1\\ 1 & -1\end{pmatrix} = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix} = I$$

c) Evolve the state $\psi = \begin{pmatrix}a\\ b\end{pmatrix}$ ie $|\psi\rangle = a|1\rangle + b|2\rangle$ in time:

$$\mathcal{H}|\psi\rangle = i\hbar\frac{\partial}{\partial t}|\psi\rangle \qquad \begin{pmatrix}E_I & \\ & E_{II}\end{pmatrix}\begin{pmatrix}\psi_I(t)\\ \psi_{II}(t)\end{pmatrix} = i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\psi_I(t)\\ \psi_{II}(t)\end{pmatrix}$$

$$\frac{d\psi_n}{\psi_n} = \frac{E_n}{i\hbar}dt = -i\omega_n dt \qquad E_I = \hbar\omega_I \quad E_{II} = \hbar\omega_{II}$$

$$\psi_n(t) = \psi_n(0)\,e^{-i\omega_n t} \qquad \begin{pmatrix}\psi_I(t)\\ \psi_{II}(t)\end{pmatrix} = \begin{pmatrix}\psi_I(0)\,e^{-i\omega_I t}\\ \psi_{II}(0)\,e^{-i\omega_{II} t}\end{pmatrix} = \underbrace{\begin{pmatrix}e^{-i\omega_I t} & 0\\ 0 & e^{-i\omega_{II} t}\end{pmatrix}}_{U'(t) = e^{-i\mathcal{H}t/\hbar}}\begin{pmatrix}\psi_I(0)\\ \psi_{II}(0)\end{pmatrix}$$

$$\psi'(t) = U'(t)\,\psi'(0)$$

$$\psi(t) = R\psi'(t) = RU'(t)\,\psi'(0) = RU'(t)R^{\dagger}\,\psi(0) = U(t)\,\psi(0)$$

$$U(t) = RU'(t)R = \frac{1}{\sqrt{2}}\begin{pmatrix}1 & 1\\ 1 & -1\end{pmatrix}\begin{pmatrix}e^{-i\omega_I t} & 0\\ 0 & e^{-i\omega_{II} t}\end{pmatrix}\frac{1}{\sqrt{2}}\begin{pmatrix}1 & 1\\ 1 & -1\end{pmatrix}$$

$\omega_I = \omega_0 - \Delta\omega$

$\omega_{II} = \omega_0 + \Delta\omega$

$$= \frac{1}{2}\begin{pmatrix}e^{-i\omega_I t} + e^{-i\omega_{II} t} & e^{-i\omega_I t} - e^{-i\omega_{II} t}\\ e^{-i\omega_I t} - e^{-i\omega_{II} t} & e^{-i\omega_I t} + e^{-i\omega_{II} t}\end{pmatrix}$$

$\hbar\omega_0 = E_0$

$\hbar\Delta\omega = -A$

$$= e^{-i\omega_0 t}\begin{pmatrix}\cos(\Delta\omega t) & i\sin(-\Delta\omega t)\\ i\sin(-\Delta\omega t) & \cos(\Delta\omega t)\end{pmatrix} \qquad U^{\dagger}U = I$$

so $\begin{pmatrix} \Psi_1(t) \\ \Psi_2(t) \end{pmatrix} = U(t) \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} \cos(\Delta\omega t) \cdot a + i \sin(-\Delta\omega t) \cdot b \\ i \sin(-\Delta t) \cdot a + \cos(\Delta\omega t) \cdot b \end{pmatrix} e^{-i\omega t}$