Jan 2009

Problem 2: A two-state system (10 points)

We can approximate the ammonia molecule NH_3 by a simple two-state system. The three H nuclei are in a plane, and the N nucleus is at a fixed distance either above or below the plane of the H's. Each is approximately a stationary state with some energy E_0. But there is a small amplitude for transition from up to down. Thus the total Hamiltonian is $H = H_0 + H_1$, where

$$H_0 = \begin{pmatrix} E_0 & 0 \\ 0 & E_0 \end{pmatrix} \quad \text{and} \quad H_1 = \begin{pmatrix} 0 & -A \\ -A & 0 \end{pmatrix}$$

with $|A| \ll |E_0|$.

(a) Find the exact eigenvalues of H. (*1 points*)

(b) Now suppose the molecule is in an electric field that distinguishes the two states. The new Hamiltonian is $H = H_0 + H_1 + H_2$, where

$$H_2 = \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix}$$

Find the new exact energy levels. (*1 points*)

(c) Apply perturbation theory and find the energy levels to the lowest non-vanishing order for $\epsilon_i \ll |A|$. Compare the results to the exact answer in (b). (*4 points*)

(d) Apply perturbation theory and find the energy levels to the lowest non-vanishing order for $\epsilon_i \gg |A|$. Compare the results to the exact answer in (b). (*4 points*)

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Quantum #2

$$H_0 = \begin{bmatrix} E_0 & 0 \\ 0 & E_0 \end{bmatrix} \qquad H_1 = \begin{bmatrix} 0 & -A \\ -A & 0 \end{bmatrix}$$

$$H = H_0 + H_1 = \begin{bmatrix} E_0 & -A \\ -A & E_0 \end{bmatrix}$$

a) Using the eigenvalue equation $\det(H - \lambda \mathbb{I}) = 0$

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

$$= E_0^2 - 2\lambda E_0 + \lambda^2 - A^2$$

$$= \lambda^2 - 2E_0\lambda + (E_0^2 - A^2)$$

$$\hookrightarrow \lambda = \frac{2E_0 \pm \sqrt{4E_0^2 - 4(1)(E_0^2 - A^2)}}{2}$$

$$= \frac{2E_0 \pm \sqrt{\cancel{4E_0^2} - \cancel{4E_0^2} + 4A^2}}{2}$$

$$= E_0 \pm A$$

b) $H_2 = \begin{bmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{bmatrix}$

$$H = H_0 + H_1 + H_2 = \begin{bmatrix} E_0 + \epsilon_1 & -A \\ -A & E_0 + \epsilon_2 \end{bmatrix}$$

Again, as above:

$$\begin{vmatrix} E_0 + \epsilon_1 - \lambda & -A \\ -A & E_0 + \epsilon_2 - \lambda \end{vmatrix} = 0 = (E_0 + \epsilon_1 - \lambda)(E_0 + \epsilon_2 - \lambda) - (-A)^2$$

$$= E_0^2 + E_0\epsilon_2 - E_0\lambda + \epsilon_1 E_0 + \epsilon_1\epsilon_2 - \lambda\epsilon_1 - \lambda E_0 - \epsilon_2\lambda + \lambda^2 - A^2$$

$$= \lambda^2 - (2E_0 + \epsilon_1 + \epsilon_2)\lambda + (E_0^2 + E_0[\epsilon_1 + \epsilon_2] + \epsilon_1\epsilon_2 - A^2)$$

$$\hookrightarrow \lambda = \frac{2E_0 + \epsilon_1 + \epsilon_2 \pm \sqrt{4E_0^2 - 4(1)(E_0^2 + E_0[\epsilon_1 + \epsilon_2] + \epsilon_1\epsilon_2 - A^2)}}{2}$$

$$= \frac{2E_0 + \epsilon_1 + \epsilon_2 \pm \sqrt{4A^2 - 4E_0(\epsilon_1 + \epsilon_2) - 4\epsilon_1\epsilon_2}}{2}$$

#2 (cont.)

c) Assume H_2 is a perturbation on $H = H_0 + H_1$. Therefore, use non-degenerate perturbation theory, and we must solve for eigenvectors of $H = H_0 + H_1$

$\Rightarrow$ Using the eigenvector equation $H\vec{a} = \lambda \vec{a}$

$$\begin{bmatrix} E_0 & -A \\ -A & E_0 \end{bmatrix}\begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = \lambda \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} \quad \Rightarrow \quad \begin{aligned} E_0 a_1 - A a_2 &= \lambda a_1 \\ -A a_1 + E_0 a_2 &= \lambda a_2 \end{aligned}$$

* for $\lambda = E_0 + A$

$$E_0 a_1 - A a_2 = E_0 a_1 + A a_1$$

$$-A a_2 = A a_1$$

$$-a_2 = a_1$$

$$\hookrightarrow \vec{a} = \begin{bmatrix} 1 \\ -1 \end{bmatrix} \cdot \frac{1}{\sqrt{2}}$$

* for $\lambda = E_0 - A$

$$E_0 a_1 - A a_2 = E_0 a_1 - A a_1$$

$$-A a_2 = -A a_1$$

$$a_2 = a_1$$

$$\vec{a} = \begin{bmatrix} 1 \\ 1 \end{bmatrix} \cdot \frac{1}{\sqrt{2}}$$

$$\Rightarrow |E_0 + A\rangle = \langle 1, -1 \rangle \cdot \frac{1}{\sqrt{2}}$$

$$|E_0 - A\rangle = \langle 1, 1 \rangle \cdot \frac{1}{\sqrt{2}}$$

* Dot product verifies orthogonality

$$\frac{1}{2}[(1 \cdot 1) + (1 \cdot -1)] = 0$$

In general $\Delta E_n^{(1)} = \langle n^{(0)} | V | n^{(0)} \rangle$

$$\hookrightarrow \Delta E_1^{(1)} = \langle E + A | H_2 | E + A \rangle$$

$$= \frac{1}{2}\begin{bmatrix} 1 & -1 \end{bmatrix} \begin{bmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{bmatrix} \begin{bmatrix} 1 \\ -1 \end{bmatrix}$$

$$= \frac{1}{2}\begin{bmatrix} 1 & -1 \end{bmatrix} \begin{bmatrix} \epsilon_1 \\ -\epsilon_2 \end{bmatrix}$$

$$= \frac{1}{2}(\epsilon_1 + \epsilon_2)$$

$$\hookrightarrow \Delta E_2^{(1)} = \langle E - A | H_2 | E - A \rangle$$

$$= \frac{1}{2}\begin{bmatrix} 1 & 1 \end{bmatrix} \begin{bmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{bmatrix} \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

$$= \frac{1}{2}(\epsilon_1 + \epsilon_2)$$

*If $\epsilon_i \ll A$, our exact energies are

$$E \approx \frac{2E_0 + \epsilon_1 + \epsilon_2 \pm \sqrt{4A^2 - \cancelto{0}{4E_0(\epsilon_1 + \epsilon_2)} - 4\epsilon \ldots}}{2}$$

$$= E_0 \pm A + \epsilon_1 + \epsilon_2$$

which matches what we get from perturbation theory

#2 (cont.)

d) If $\epsilon_i >> |A|$, then $H = H_0 + H_2$ and H_1 is our perturbation

↳ $\lambda = E_0 + \epsilon_1$

$\vec{a} = \langle 1, 0 \rangle$ and $\langle 0, 1 \rangle$

$\Rightarrow |E_0 + \epsilon_1\rangle = \langle 1, 0 \rangle$ * Dot product verifies orthogonality

$|E_0 + \epsilon_2\rangle = \langle 0, 1 \rangle$

Again as in part c

$$\Delta E_n^{(1)} = \langle n^{(0)} | V | n^{(0)} \rangle$$

$$\Delta E_1^{(1)} = \langle E_0 + \epsilon_1 | H_1 | E_0 + \epsilon_1 \rangle = \begin{bmatrix} 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & -A \\ -A & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \cdot \frac{1}{2} = \frac{1}{2} \begin{bmatrix} 1 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ -A \end{bmatrix} = 0$$

$$\Delta E_2^{(1)} = \langle E_0 + \epsilon_1 | H_1 | E_0 + \epsilon_1 \rangle = \begin{bmatrix} 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & -A \\ -A & 0 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \cdot \frac{1}{2} = \frac{1}{2} \begin{bmatrix} 0 & 1 \end{bmatrix} \begin{bmatrix} -A \\ 0 \end{bmatrix} = 0$$

*We must proceed to $\Delta E_n^{(2)}$ which requires $|n^{(1)}\rangle$

$$|n^{(1)}\rangle = \sum_{k \neq n}' \frac{V_{kn}}{E_n^{(0)} - E_k^{(0)}} |k^{(0)}\rangle$$

* remember that n and k refer to Energy eigen values

$$↳ |(E_0 + \epsilon_1)^{(1)}\rangle = \frac{\langle E_0 + \epsilon_2 | H_1 | E_0 + \epsilon_1 \rangle}{(E_0 + \epsilon_1) - (E_0 + \epsilon_2)} |E_0 + \epsilon_2\rangle = \frac{-A}{\epsilon_1 - \epsilon_2} |E_0 + \epsilon_2\rangle$$

$$↳ |(E_0 + \epsilon_2)^{(1)}\rangle = \frac{\langle E_0 + \epsilon_1 | H_1 | E_0 + \epsilon_2 \rangle}{(E_0 + \epsilon_2) - (E_0 + \epsilon_1)} |E_0 + \epsilon_1\rangle = \frac{-A}{\epsilon_2 - \epsilon_1} |E_0 + \epsilon_1\rangle$$

*In general, our second order correction formula is: $\Delta E_n^{(2)} = \langle n^{(0)} | V | n^{(1)} \rangle = \sum_{k \neq n}' \frac{|V_{kn}|^2}{E_n^{(0)} - E_k^{(0)}}$

$$\Rightarrow \Delta E_1^{(2)} = \frac{A^2}{\epsilon_1 - \epsilon_2} \qquad \Delta E_2^{(2)} = \frac{A^2}{\epsilon_2 - \epsilon_1}$$

#2 (cont.)

d) This gives us energies of: $E_0 + \epsilon_1 + \dfrac{A^2}{\epsilon_1 - \epsilon_2} \approx E_1$

$$E_0 + \epsilon_2 + \frac{A^2}{\epsilon_2 - \epsilon_1} \approx E_2$$

* Returning to our exact solution

$$E_i = \frac{2E_0 + \epsilon_1 + \epsilon_2 \pm \sqrt{\cancel{4A^2}^{\approx 0} - 4E_0(\epsilon_1 + \epsilon_2) - 4\epsilon_1\epsilon_2}}{2}$$

$$= E_0 + \frac{\epsilon_1 + \epsilon_2}{2} \pm \sqrt{E_0(\epsilon_1 + \epsilon_2) - \epsilon_1\epsilon_2}$$

$$= E_0 + \frac{\epsilon_1 + \epsilon_2}{2} \mp E_0(\epsilon_1 + \epsilon_2)\sqrt{1 + \frac{\epsilon_1\epsilon_2}{E_0(\epsilon_1 + \epsilon_2)}}$$

$$= E_0 + \frac{\epsilon_1 + \epsilon_2}{2} \mp E_0(\epsilon_1 + \epsilon_2)\left[1 + \frac{1}{2}\left(\frac{\epsilon_1\epsilon_2}{E_0(\epsilon_1 + \epsilon_2)}\right) \overset{\text{ignore}}{\cancel{- \frac{1}{8}\left(\frac{\epsilon_1\epsilon_2}{E_0(\epsilon_1 + \epsilon_2)}\right)^2}} + \ldots\right]$$

$$= E_0 + \frac{\epsilon_1 + \epsilon_2}{2} \mp \left[E_0(\epsilon_1 + \epsilon_2) + \frac{1}{2}\epsilon_1\epsilon_2\right]$$

↳