① (a)

$$E^{(0)} = \frac{\hbar^2}{2I} J(J+1) \qquad \mathbb{H}^{\circ} = \frac{\hbar^2}{2I}\begin{bmatrix} 0 & & & & & \\ & 2 & & & \bigcirc & \\ & & 6 & & & \\ & & & 12 & & \\ & \bigcirc & & & 20 & \\ & & & & & 30 \ldots \end{bmatrix}$$

$$h = -\mu\mathcal{E}\cos\theta$$

$$h\,Y_{JM} = -\mu\mathcal{E}\left\{\left[\frac{J^2-M^2}{(2J-1)(2J+1)}\right]^{1/2} Y_{J-1,M} + \left[\frac{(J+1)^2-M^2}{(2J+1)(2J+3)}\right]^{1/2} Y_{J+1,M}\right\}$$

$$hY_{00} = -\mu\mathcal{E}\left\{0 + \left(\frac{1}{3}\right)^{1/2} Y_{10}\right\}$$

$$hY_{10} = -\mu\mathcal{E}\left\{\left(\frac{1}{3}\right)^{1/2} Y_{00} + \left(\frac{4}{3\cdot 5}\right)^{1/2} Y_{20}\right\}$$

$$hY_{11} = -\mu\mathcal{E}\left\{0 + \left(\frac{\cancel{3}}{\cancel{3}\cdot 5}\right)^{1/2} Y_{21}\right\}$$

$$hY_{1-1} = -\mu\mathcal{E}\left\{0 + \left(\frac{\cancel{3}}{\cancel{3}\cdot 5}\right)^{1/2} Y_{2-1}\right\}$$

$$hY_{20} = -\mu\mathcal{E}\left\{\left(\frac{4}{3\times 5}\right)^{1/2} Y_{10} + \left(\frac{9}{5\times 7}\right)^{1/2} Y_{30}\right\}$$

etc.

$$h = -\mu\mathcal{E}\;\begin{array}{c|ccccccccc} & \overset{J=0}{M=0} & \overbrace{M=-1 \quad\; 0 \quad\; 1}^{J=1} & & & \overbrace{-2 \quad -1 \quad 0 \quad +1 \quad +2}^{J=2 \quad \text{etc.}} & & & & \\ \hline 00 & 0 & 0 & \frac{1}{\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 1\bar{1} & 0 & 0 & 0 & 0 & 0 & \frac{1}{\sqrt{5}} & 0 & 0 & 0 \\ 10 & \frac{1}{\sqrt{3}} & 0 & 0 & 0 & 0 & 0 & \frac{2}{\sqrt{15}} & 0 & 0 \\ 11 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{\sqrt{5}} & 0 \\ 2\bar{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 2\bar{1} & 0 & \frac{1}{\sqrt{5}} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 20 & 0 & 0 & \frac{2}{\sqrt{15}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 21 & 0 & 0 & 0 & \frac{1}{\sqrt{5}} & 0 & 0 & 0 & 0 & 0 \\ 22 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{array}$$

$$E^{(2)}_{JM} = -\frac{|\langle J-1, M | h | JM\rangle|^2}{\epsilon_{J-1}-\epsilon_J} - \frac{|\langle J+1, M | h | JM\rangle|^2}{\epsilon_{J+1}-\epsilon_J}$$

(b)

$$E_{JM} = E^{(0)}_{JM} + E^{(1)}_{JM} + E^{(2)}_{JM}$$

$$= \frac{\hbar^2}{2I} J(J+1) + \underbrace{\langle JM | h | JM \rangle}_{\text{always zero}} - \frac{\frac{(J^2-M^2)}{(2J-1)(2J+1)} \cdot \mu^2 \mathcal{E}^2}{\underbrace{[(J-1)J - J(J+1)]\frac{\hbar^2}{2I}}_{-2J}} - \frac{\frac{((J+1)^2 - M^2) \cdot \mu^2 \mathcal{E}^2}{(2J+1)(2J+3)}}{\underbrace{[(J+1)(J+2) - J(J+1)]\frac{\hbar^2}{2I}}_{2(J+1)}}$$

Two lowest energy levels become changed to

$$E_{00} = 0 + 0 - \frac{\left(\frac{-\mu \mathcal{E}}{\sqrt{3}}\right)^2}{2\frac{\hbar^2}{2I} - 0} = \frac{-\mu^2 \mathcal{E}^2}{3\hbar^2/I}$$

$$E_{10} = \frac{2\hbar^2}{2I} + 0 - \frac{\left(\frac{-\mu \mathcal{E}}{\sqrt{3}}\right)^2}{0 - \frac{2\hbar^2}{2I}} - \frac{\left(\frac{-2\mu \mathcal{E}}{\sqrt{15}}\right)^2}{\frac{2(3)\hbar^2}{2I} - \frac{2\hbar^2}{2I}}$$

$$= \frac{\hbar^2}{I} + \frac{\mu^2 \mathcal{E}^2}{3\hbar^2/I} - \frac{4\mu^2 \mathcal{E}^2}{15(2\hbar^2/I)}$$

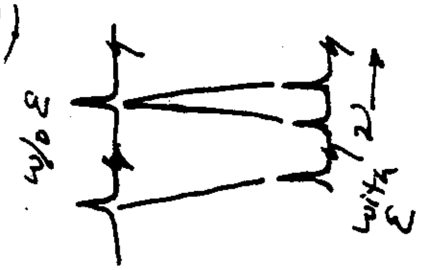
$$= \frac{\hbar^2}{I} + \frac{\mu^2 \mathcal{E}^2}{5\hbar^2/I}$$

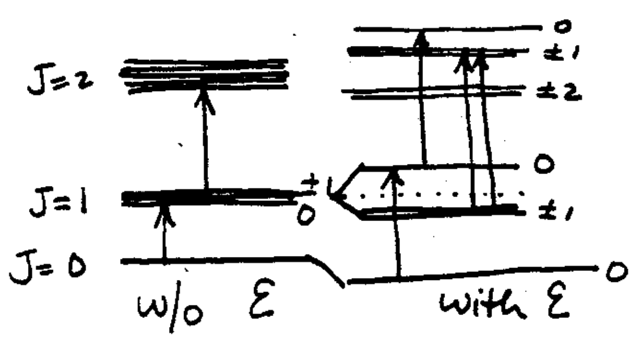
$$E_{11} = E_{1-1} = \frac{\hbar^2}{I} + 0 - \frac{\left(\frac{-\mu \mathcal{E}}{\sqrt{5}}\right)^2}{\frac{2(3)\hbar^2}{2I} - \frac{2\hbar^2}{2I}} = \frac{\hbar^2}{I} - \frac{\mu^2 \mathcal{E}^2}{10\hbar^2/I}$$

(c) $$\Psi_{00} = Y_{00}(\theta,\phi) - \frac{\left(\frac{-\mu\mathcal{E}}{\sqrt{3}}\right)}{\frac{2\hbar^2}{2I}-0}\, Y_{10}(\theta,\phi)$$

$$\Psi_{00} = Y_{00}(\theta,\phi) + \underbrace{\frac{\mu\mathcal{E}}{\sqrt{3}\,\hbar^2/I}}_{\text{small}}\, Y_{10}(\theta,\phi)$$

(d)





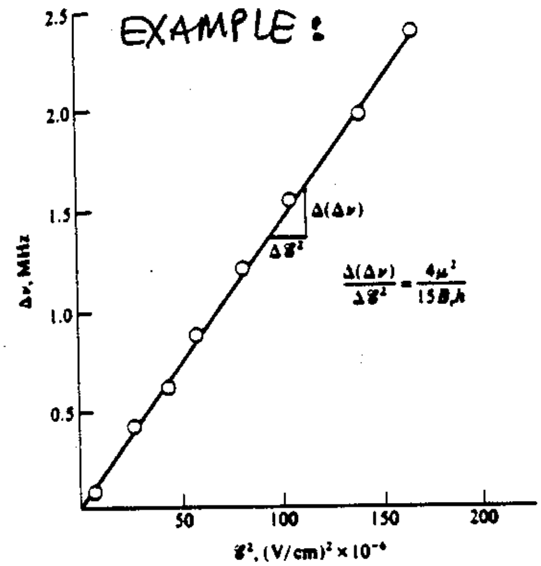


FIGURE 14.13
Stark effect for CO.

$\Delta M = 0$ since no ϕ in transition operator

$\Delta J = \pm 1$ since $\cos\theta\, Y_{JM} = \sim Y_{J-1,M} + \sim Y_{J+1,M}$

(e) The ~~shift~~ frequency of the first transition $|00\rangle \to |10\rangle$ $= \dfrac{\mu^2\mathcal{E}^2}{\hbar^2/I}\left(\dfrac{1}{3}+\dfrac{1}{5}\right)$

Thus if $\mathcal{E}$ is accurately known and the moment of inertia is of course obtained from the frequency of the first transition in the absence of the field, $\hbar^2/I$, then μ can be obtained. Also can get μ from the splitting of the second peak when $\mathcal{E}$ is applied, as in the example shown above

② (a) Eigenfunctions of H_1 are:

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad m = 0, \pm 1, \pm 2, \cdots$$

(b) Eigenvalues are found by:

$$\frac{-\hbar^2}{2m_e R^2} (im)^2 \frac{1}{\sqrt{2\pi}} e^{im\phi} = E_m \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

$$E_m = \frac{m^2 \hbar^2}{2m_e R^2}$$

(c) H_2 commutes with H_1 : Show this:

$$H_2 = H_1 + \frac{\mu_B}{\hbar} B_z \cdot \frac{\hbar}{i} \frac{d}{d\phi} + \frac{e^2 B_z^2}{8mc^2} R^2 \quad \leftarrow x^2+y^2$$

$$[H_2, H_1] = [H_1, H_1] + \left[\frac{\mu_B B_z}{\hbar} \cdot \frac{\hbar}{i} \frac{d}{d\phi}, \frac{-\hbar^2}{2m_e R^2} \frac{d^2}{d\phi^2}\right]$$

$$+ \left[\frac{e^2 B_z^2}{8mc^2} R^2, \frac{-\hbar^2}{2m_e R^2} \frac{d^2}{d\phi^2}\right]$$

$= 0$ since H_1 commutes with itself, $\frac{d}{d\phi}$ commutes with $\frac{d^2}{d\phi^2}$, and a constant commutes with $\frac{d^2}{d\phi^2}$

(d) Since H_2 commutes with H_1, the eigenfunctions of H_2 are also

$$\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \quad m = 0, \pm 1, \pm 2, \cdots$$

Get the eigenvalues: We will need

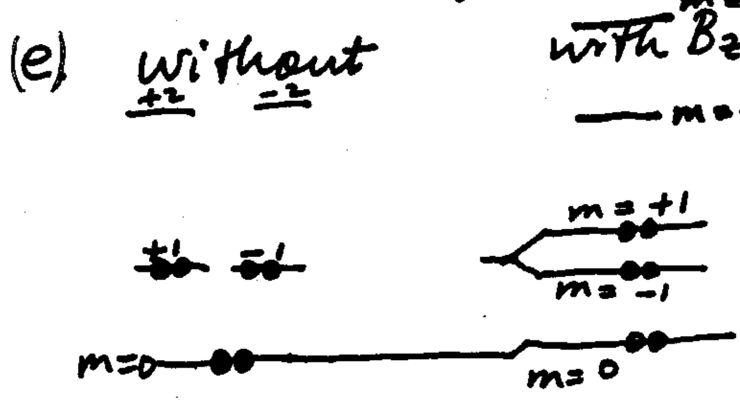
$$\frac{\hbar}{i}\frac{d}{d\phi}\psi_m(\phi) = \frac{\hbar}{i}\frac{d}{d\phi}\frac{1}{\sqrt{2\pi}}e^{im\phi} = \frac{\cancel{i}m\hbar}{\cancel{i}}\frac{e^{im\phi}}{\sqrt{2\pi}}$$

$$H_z\psi_m(\phi) = \underbrace{\frac{m^2\hbar^2}{2m_eR^2}}_{E_m}\psi_m(\phi) + \frac{\mu_B B_z}{\hbar}\cdot m\hbar\,\psi_m(\phi) + \frac{e^2B_z^2}{8m_ec^2}R^2\psi_m(\phi)$$

$$= \underbrace{\left[\frac{m^2\hbar^2}{2m_eR^2} + (\mu_B B_z)m + \frac{e^2B_z^2R^2}{8m_ec^2}\right]}\psi_m(\phi)$$

These are the eigenvalues

(e)



$$E = \frac{\hbar^2}{2m_eR^2} + \mu_B B_z + \frac{e^2B_z^2R^2}{8m_ec^2}$$

$$E = \frac{\hbar^2}{2m_eR^2} - \mu_B B_z + \frac{e^2B_z^2R^2}{8m_ec^2}$$

$$E = \frac{e^2B_z^2R^2}{8m_ec^2}$$

(f) see above assignments of 6 electrons into states. By separation of variables we get eigenvalues which are a simple sum

$$E_{ground} = 2\left\{0 + 1^2 + (-1)^2\right\}\frac{\hbar^2}{2m_eR^2}$$

and eigenfunctions which are a simple PRODUCT

$$\Psi_{ground}(1,2,3,4,5,6) = \frac{1}{\sqrt{2\pi}}\cdot\frac{1}{\sqrt{2\pi}}\cdot\frac{1}{\sqrt{2\pi}}e^{i\phi_3}\cdot\frac{1}{\sqrt{2\pi}}e^{i\phi_4}\cdot\frac{1}{\sqrt{2\pi}}e^{-i\phi_5}\cdot\frac{1}{\sqrt{2\pi}}e^{-i\phi_6}$$

In the presence of a field the wavefunctions are the same, so Ψ_{ground} is the same and the energy is

$$E_{ground} = \frac{e^2B_z^2R^2}{8m_ec^2}\cdot 6 + 2\left\{0+1^2+(-1)^2\right\}\frac{\hbar^2}{2m_eR^2}$$

(g) $\dfrac{-\partial^2E}{\partial B_z^2} = \dfrac{12e^2R^2}{8m_ec^2}$, the "ring-current" contribution to magn. susceptibility of Benzene

(3) $E_n^{(0)} = \frac{n^2 h^2}{8ma^2}$ the eigenvalues of the unperturbed particle on a line.

$$E_n^{(1)} = \int_0^a \psi_n^*(x)\, h\, \psi_n(x)\,dx = -q\mathcal{E}\, x_{nn} = -q\mathcal{E}\frac{a}{2}$$

$$E_n^{(2)} = -\sum_{k\neq n} \frac{|h_{kn}|^2}{E_k^{(0)}-E_n^{(0)}} = -\sum_{k\neq n}\frac{|h_{kn}|^2}{\frac{h^2}{8ma^2}(k^2-n^2)}$$

$$= -\sum_{k\neq n} \frac{(q\mathcal{E})^2 |x_{kn}|^2}{\frac{h^2}{8ma^2}(k^2-n^2)} = -\frac{8ma^2}{h^2} q^2\mathcal{E}^2 \sum_{k\neq n}\frac{|x_{kn}|^2}{k^2-n^2}$$

$$= -\frac{8ma^2}{h^2} q^2 \mathcal{E}^2 \left(\frac{4a}{\pi^2}\right)^2 \sum_{k\neq n} \frac{kn\{(-1)^{k-n}-1\}^2}{(k^2-n^2)^5}$$

is zero whenever $(k-n)$ is even

$$\Psi_n = \psi_n^{(0)} + \psi_n^{(1)}$$

$$\psi_n^{(1)} = -\sum_{k\neq n}\frac{h_{kn}}{E_k^{(0)}-E_n^{(0)}}\cdot \psi_k^{(0)}(x)$$

$$= -\frac{8ma^2}{h^2}\sum_{k\neq n} \frac{-q\mathcal{E}\, x_{kn}}{k^2-n^2}\, \psi_k^{(0)}(x)$$

$$= +\frac{8ma^2}{h^2} q\mathcal{E}\, \frac{4a}{\pi^2} \sum_{k\neq n} \frac{kn\{(-1)^{k-n}-1\}}{(k^2-n^2)^3}\, \psi_k^{(0)}(x)$$

The two lowest levels

$$E_1^{(2)} = -\frac{8ma^2}{h^2} q^2\mathcal{E}^2 \left(\frac{-8a}{\pi^2}\right)^2 \sum_{\substack{k=\text{even}\\ \text{only}}} \frac{(1\cdot k)^2}{(k^2-1^2)^3}$$

$$E_2^{(2)} = -\frac{8ma^2}{h^2} q^2\mathcal{E}^2 \left(\frac{-8a}{\pi^2}\right)^2 \sum_{\substack{k=\text{odd}\\ \text{only}}} \frac{(2k)^2}{(k^2-2^2)^3}$$

$$E_1 = \frac{1^2 h^2}{8ma^2} - q\mathcal{E}\frac{a}{2} + \underset{\substack{\uparrow \\ \text{from previous page}}}{E_1^{(2)}} \qquad E_2 = \frac{2^2 h^2}{8ma^2} - q\mathcal{E}\frac{a}{2} + \underset{\substack{\nearrow \\ \text{from previous page}}}{E_2^{(2)}}$$

The wavefunctions correct to first order

$$\Psi_1(x) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{\pi}{a}x\right) + \frac{8ma^2}{h^2} q\mathcal{E}\left(\frac{-8a}{\pi^2}\right) \sum_{\substack{k=\text{even} \\ \text{only}}} \frac{k}{(k^2-1)^3} \psi_k^{(0)}(x)$$

$$\Psi_2(x) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{2\pi}{a}x\right) + \frac{8ma^2}{h^2} q\mathcal{E}\left(\frac{-8a}{\pi^2}\right) \sum_{\substack{k=\text{odd} \\ \text{only}}} \frac{2k}{(k^2-1)^3} \psi_k^{(0)}(x)$$

Or else, take quantities directly from given matrix:

$$E_1 = \frac{1^2 h^2}{8ma^2} - q\frac{\mathcal{E}a}{2} - 8\frac{ma^2}{h^2} q^2\mathcal{E}^2 \left(\frac{-8a}{\pi^2}\right)^2 \left\{ \frac{(2/9)^2}{2^2-1^2} + \frac{(4/225)^2}{4^2-1^2} + \frac{(6/1225)^2}{6^2-1^2} + \cdots \right\}$$

$$E_2 = \frac{2^2 h^2}{8ma^2} - q\frac{\mathcal{E}a}{2} - 8\frac{ma^2}{h^2} q^2\mathcal{E}^2 \left(\frac{-8a}{\pi^2}\right)^2 \left\{ \frac{(2/9)^2}{1^2-2^2} + \frac{(6/25)^2}{3^2-2^2} + \frac{(10/441)^2}{5^2-1^2} + \frac{(14/2025)^2}{7^2-1^2} + \cdots \right\}$$

$$\Psi_1(x) = \left(\frac{2}{a}\right)^{1/2} \sin\frac{\pi}{a}x + \frac{8ma^2}{h^2} q\mathcal{E}\left(\frac{-8a}{\pi^2}\right) \left\{ \frac{2/9}{2^2-1^2}\psi_2^{(0)}(x) + \frac{(4/225)}{4^2-1^2}\psi_4^{(0)}(x) + \frac{(6/1225)}{6^2-1^2}\psi_6^{(0)}(x) + \cdots \right\}$$

$$\Psi_2(x) = \left(\frac{2}{a}\right)^{1/2} \sin\frac{2\pi}{a}x + \frac{8ma^2}{h^2} q\mathcal{E}\left(\frac{-8a}{\pi^2}\right) \left\{ \frac{2/9}{1^2-2^2}\psi_1^{(0)}(x) + \frac{6/25}{3^2-2^2}\psi_3^{(0)}(x) + \frac{10/441}{5^2-2^2}\psi_5^{(0)}(x) + \cdots \right\}$$

To evaluate the matrix elements of operator x in the complete set of eigenfunctions of a particle on a line between 0 and a : We already know the diagonal elements are equal to $a/2$

$$x_{mn} = \int_0^a \Psi_m{}^*(x) x \Psi(x) dx \qquad \text{for } m \neq n$$

$$= \frac{2}{a}\int_0^a \sin\left(\frac{m\pi x}{a}\right) x \sin\left(\frac{n\pi x}{a}\right) dx$$

Given the identity: $\quad 2\sin(mx)\sin(nx) = \cos[(m\text{-}n)x] - \cos[(m\text{+}n)x]$

$$x_{mn} = \frac{1}{a}\int_0^a \left\{ x\cos\left[\frac{(m-n)\pi x}{a}\right] - x\cos\left[\frac{(m+n)\pi x}{a}\right] \right\} dx$$

Given the integral : $\quad \int x\cos(px)dx = \frac{x\sin(px)}{p} + \frac{\cos(px)}{p^2}$

$$x_{mn} = \frac{1}{a}\left[\frac{x\sin\frac{(m-n)\pi x}{a}}{\frac{(m-n)\pi}{a}} + \frac{\cos\frac{(m-n)\pi x}{a}}{\frac{(m-n)^2\pi^2}{a^2}} - \frac{x\sin\frac{(m+n)\pi x}{a}}{\frac{(m+n)\pi}{a}} - \frac{\cos\frac{(m+n)\pi x}{a}}{\frac{(m+n)^2\pi^2}{a^2}} \right]_0^a$$

sin is zero at both upper and lower limits, so we have:

$$x_{mn} = \frac{1}{a}\left[\frac{\cos\frac{(m-n)\pi}{a} - 1}{\frac{(m-n)^2\pi^2}{a^2}} - \frac{\cos\frac{(m+n)\pi}{a} - 1}{\frac{(m+n)^2\pi^2}{a^2}} \right]$$

When m-n = even, m+n = even also, in which case, $\cos(m\text{-}n)\pi = +1$ and $\cos(m\text{+}n)\pi = +1$, so that both numerators in the above equation are zero and $x_{mn} = 0$.

On the other hand, when m-n = odd, m+n = odd also, in which case $\cos(m\text{-}n)\pi = -1$

$$x_{mn} = \frac{a}{\pi^2}\left[\frac{\cos[(m-n)\pi]-1}{(m-n)^2} - \frac{\cos[(m+n)\pi]-1}{(m+n)^2} \right]$$

$$= \frac{a}{\pi^2}\left[\frac{-2}{(m-n)^2} - \frac{-2}{(m+n)^2} \right] = \frac{-2a}{\pi^2}\left[\frac{1}{(m-n)^2} - \frac{1}{(m+n)^2} \right]$$

$$= \frac{-2a}{\pi^2}\left[\frac{(m+n)^2-(m-n)^2}{(m-n)^2(m+n)^2} \right] = \frac{-2a}{\pi^2}\left[\frac{4mn}{(m-n)(m+n)(m-n)(m+n)} \right]$$

$$= \frac{-8a}{\pi^2}\left[\frac{mn}{(m^2-n^2)^2} \right]$$

Thus, $\quad x_{mn} = (4a/\pi^2) mn\{(-1)^{m-n} - 1\}\,\{m^2 - n^2\}^{-2}$ for $m \neq n$