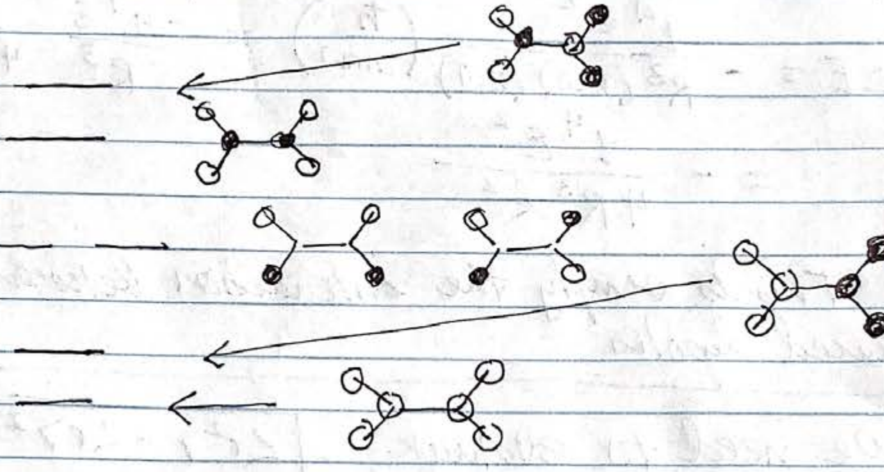
Chem 2430, Exam #3

1.



The 2nd and third orbitals are predicted to be degenerate in Hückel theory due to the restriction to nearest neighbor interactions.

There are two electrons in the pair of degenerate orbitals. So there will be three low-lying singlet states and a low-lying triplet state. If we label the degenerate orbitals as "a" and "b" we have

$ab + ba$	(S)
$ab - ba$	(T)
$a^2 + b^2$	(S)
$a^2 - b^2$	(S)

The molecule probably twists nonplanar as that would remove the repulsion between the CH_2 groups.

2.
$$H = -\frac{1}{2m}\frac{d^2}{dx_1^2} - \frac{1}{2m}\frac{d^2}{dx_2^2} + \frac{1}{2}kx_1^2 + \frac{1}{2}kx_2^2$$

$$+ q_1 \mathcal{E} x_1 + q_2 \mathcal{E} x_2 - \frac{2q_1 q_2 x_1 x_2}{R^3}$$

At 2nd order $\Delta E = \frac{\langle 0|q\mathcal{E}x_1|1\rangle^2}{-\omega} + \frac{\langle 0|q\mathcal{E}x_2|1\rangle^2}{-\omega}$ | $q_1 = q_2$

$$= \frac{2q^2\mathcal{E}^2 \langle 0|x|1\rangle^2}{-\omega} = -\frac{q^2\mathcal{E}^2}{k}$$

which is 2x the energy lowering of one oscillator

At third order we have

$$\Delta E = -\frac{q^4 \varepsilon^2}{R^3 (\hbar\omega)(\hbar\omega)} \left(\frac{\hbar}{2m\omega}\right)^2 = \frac{-q^4 \varepsilon^2}{R^3} \frac{1}{4m^2\omega^4}$$

$$= -\frac{q^4 \varepsilon^2}{4R^3 k^2}$$

This is simply the interaction between the two induced dipoles.

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3. We need to evaluate $\sqrt{\langle r^2\rangle - \langle r\rangle^2}$

$$\langle r\rangle = 3/2 \qquad \langle r^2\rangle = 3$$

$$\sqrt{\langle r^2\rangle - \langle r\rangle^2} = \sqrt{3}/2$$

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4. $V = \frac{1}{2}kx^2 + 0.01x^4$, $k = 0.1$, $m = 1000$.

$$\psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2}, \quad \alpha = \omega m/\hbar$$

(a) $E = \frac{\hbar\omega}{2} + 0.01\langle 0|x^4|0\rangle$

$$= \frac{\hbar\omega}{2} + 0.01 \frac{\hbar^2}{4m\omega^2} 3 = \frac{3}{4}\frac{1}{(1000)(.1)} + \frac{\hbar\omega}{2}$$

$$E = \frac{\omega}{2} + 0.0075 \text{ (in a.u.)}$$

(b) for $\psi = e^{-ax^2/2}$

$$E = \frac{\frac{a}{2m}\sqrt{\frac{\pi}{a}} + \left(\frac{1}{2}k - \frac{a^2}{2m}\right)\frac{\sqrt{\pi}}{2a^{3/2}} + 0.01\,\frac{3}{4}\,\frac{\sqrt{\pi}}{a^{5/2}}}{\sqrt{\frac{\pi}{a}}}$$

$$= \frac{a}{4m} + \frac{k}{4a} + 3/4\,\frac{0.01}{a^2}$$

$$\partial E/\partial a = 0 = \frac{1}{4m} - \frac{k}{4a^2} - 3/4\,\frac{(2)\,0.01}{a^3}$$

or $\frac{a^3}{4m} - \frac{ka}{4} - 3/4\,\frac{2(0.01)}{a^3}$

$\rightarrow$ ~~$a = 0.038$, vs 0.01~~ for the purely harmonic problem.

$a = 10.2875$ vs 10