HW #7 Answers

(1) $V(r) = De\,[1 - e^{-a(r-re)}]^2$

$V(r) = De\,[a(r-re) - \frac{a^2}{2}(r-re)^2 + \frac{a^3}{6}(r-re)^3 - \ldots]^2$

$V(r) = De\,[a^2(r-re)^2 - a^3(r-re)^3 + \frac{7}{12}a^4(r-re)^4\,]$

We know that $V(r) = \frac{1}{2}k(r-re)^2 + \gamma(r-re)^3 + \delta(r-re)^4 + \ldots$

So $k = 2Dea^2$

Now let $x = r-re$

We have already evaluated $\langle 0|x^4|0\rangle$ and $\langle 0|x^3|1\rangle$ and $\langle 0|x^3|3\rangle$, the relevant integrals for the first and second-order energies.

$\langle 0|x^4|0\rangle = \frac{3}{4}\frac{\hbar^2\omega^2}{k^2}$

$$\left.\begin{aligned} -\frac{|\langle 0|x^3|1\rangle|^2}{\hbar\omega} &= -\frac{9}{8}\frac{\hbar^2\omega^2}{k^3} \\ -\frac{|\langle 0|x^3|3\rangle|^2}{3\hbar\omega} &= -\frac{1}{4}\frac{\hbar^2\omega^2}{k^3} \end{aligned}\right]$$

combine to get $-\frac{11}{8}\frac{\hbar^2\omega^2}{k^3}$

So the energy of the $v=0$ vibrational level though second order perturbation theory is:

$E = \frac{1}{2}\hbar\omega + \frac{3}{4}\delta\frac{\hbar^2\omega^2}{k^2} - \gamma^2\left(\frac{11}{8}\right)\frac{\hbar^2\omega^2}{k^3}$

The vibrational energy can also be expressed as

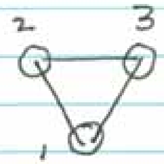
$E = \hbar\omega(v+\frac{1}{2}) - \omega_e x_e(v+\frac{1}{2})^2 + \ldots$

$= \frac{1}{2}\hbar\omega - \frac{1}{4}\omega_e x_e + \ldots$ when $v=0$

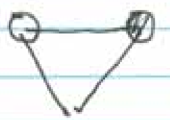
So $\omega_e x_e = -\frac{11}{2}\gamma^2\frac{\hbar^2\omega^2}{k^3} + 3\delta\frac{\hbar^2\omega^2}{k^2} = -\frac{\hbar^2\omega^2}{k^2}\left[\frac{11}{2}\frac{\gamma^2}{k} - 3\delta\right]$

$= \frac{1}{4}\frac{\omega_e^2\hbar^2}{De} = \frac{\tilde{\omega}_e^2}{4De} \leftarrow$ in cm^{-1}

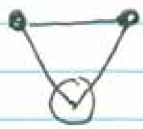
(2) Cyclopropenyl Hückel eigenvalues $\alpha+2\beta$, $2(\alpha-\beta)$



$E = \alpha + 2\beta$, $\psi = \frac{1}{\sqrt{3}}(\phi_1 + \phi_2 + \phi_3)$



$E = \alpha - \beta$, $\psi = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3)$



$E = \alpha - \beta$, $\psi = \sqrt{\frac{2}{3}}\,\phi_1 - \frac{1}{\sqrt{6}}(\varphi_2 + \varphi_3)$

The perturbation changes α at site 1 from -5 to -5.5 eV.

orbital 1 $\Delta E = \frac{1}{3}(-0.5)$ eV

orbital 2 $\Delta E = 0$

orbital 3 $\Delta E = \frac{2}{3}(-0.5)$ eV

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(3) $V = \frac{1}{2}kx_1^2 + \frac{1}{2}kx_2^2 + \frac{q^2}{R^3}x_1x_2$

Let $u = \frac{1}{\sqrt{2}}(x_1 + x_2)$, $v = \frac{1}{\sqrt{2}}(x_1 - x_2)$

Then $x_1 = \frac{1}{\sqrt{2}}(u+v)$, $x_2 = \frac{1}{\sqrt{2}}(u-v)$

$$V = \frac{1}{2}k\left[\frac{(u+v)^2 + (u-v)^2}{2}\right] + \frac{q^2}{R^3}\,\frac{(u+v)(u-v)}{2}$$

$$V = \frac{k}{4}(u^2 + v^2 + u^2 + v^2) + \frac{q^2}{2R^3}(u^2 - v^2)$$

$$V = \frac{k}{2}u^2 + \frac{q^2}{2R^3}u^2 + \frac{k}{2}v^2 - \frac{q^2}{2R^3}v^2$$

$$V = \left(\frac{k}{2} + \frac{q^2}{2R^3}\right)u^2 + \left(\frac{k}{2} - \frac{q^2}{2R^3}\right)v^2$$

$V = \frac{k'}{2}u^2 + \frac{k''}{2}v^2$, where k', k'' are new force constants

$$\omega' = \sqrt{k'/m} \quad , \quad \omega'' = \sqrt{k''/m}$$

$$\omega' = \sqrt{\frac{k}{m}}\sqrt{1+\frac{q^2}{kR^3}} = \sqrt{\frac{k}{m}}\left[1+\frac{q^2}{2kR^3} - \frac{q^4}{8k^2R^6}\cdots\right]$$

$$\omega'' = \sqrt{\frac{k}{m}}\sqrt{1-\frac{q^2}{kR^3}} = \sqrt{\frac{k}{m}}\left[1-\frac{q^2}{2kR^3} - \frac{q^4}{8k^2R^6}\cdots\right]$$

$$\tfrac{1}{2}\hbar(\omega'+\omega'') - \tfrac{2}{2}\hbar\omega = -\frac{\hbar q^4}{8k^2R^6}\omega = -\frac{1}{8}\frac{\hbar\omega\alpha^2}{R^6}$$

where one used $\alpha = q^2/k$

Actually the coupling between two alligned colinear dipoles is actually $-\frac{2q^2 x_1 x_2}{R^3}$, so the above result should actually be multiplied by 4.

Now on to the 2nd order PT treatment

$$-\frac{q^4}{R^6}\frac{|\langle 00|x_1x_2|11\rangle|^2}{2\hbar\omega} = -\frac{q^4}{R^6}\left(\frac{\hbar}{2m\omega}\right)^2\frac{1}{2\hbar\omega} = -\frac{q^4}{R^6}\frac{\hbar}{m^2\omega^3}$$

$$= -\tfrac{1}{8}\frac{\hbar\omega}{R^6}\alpha^2$$