Solutions to Problem Set 4/Problem 4
Physics 480 / Fall 1999
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Problem 4: Vibrations of Linear Triatomic Molecule

(a) By using the definition

$$\begin{aligned} y_1 &= \frac{m_Y\,(x_1 + x_3) \,+\, m_X\, x_2}{m_X + 2m_Y} \\ y_2 &= x_2 - x_1 \\ y_3 &= x_3 - x_2 \ , \end{aligned} \tag{1}$$

one can get

$$\begin{aligned} \frac{\partial}{\partial x_1} &= \frac{\partial y_1}{\partial x_1}\frac{\partial}{\partial y_1} + \frac{\partial y_2}{\partial x_1}\frac{\partial}{\partial y_2} + \frac{\partial y_3}{\partial x_1}\frac{\partial}{\partial y_3} \\ &= \frac{m_Y}{m_X + 2m_Y}\frac{\partial}{\partial y_1} - \frac{\partial}{\partial y_2} \ ; \end{aligned} \tag{2}$$

$$\begin{aligned} \frac{\partial}{\partial x_2} &= \frac{\partial y_1}{\partial x_2}\frac{\partial}{\partial y_1} + \frac{\partial y_2}{\partial x_2}\frac{\partial}{\partial y_2} + \frac{\partial y_3}{\partial x_2}\frac{\partial}{\partial y_3} \\ &= \frac{m_X}{m_X + 2m_Y}\frac{\partial}{\partial y_1} + \frac{\partial}{\partial y_2} - \frac{\partial}{\partial y_3} \ ; \end{aligned} \tag{3}$$

$$\begin{aligned} \frac{\partial}{\partial x_3} &= \frac{\partial y_1}{\partial x_3}\frac{\partial}{\partial y_1} + \frac{\partial y_2}{\partial x_3}\frac{\partial}{\partial y_2} + \frac{\partial y_3}{\partial x_3}\frac{\partial}{\partial y_3} \\ &= \frac{m_Y}{m_X + 2m_Y}\frac{\partial}{\partial y_1} + \frac{\partial}{\partial y_3} \ . \end{aligned} \tag{4}$$

The kinetic energy of the system is

$$\begin{aligned} \hat{T} &= -\frac{\hbar^2}{2\,m_Y}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_3^2}\right) - \frac{\hbar^2}{2\,m_X}\frac{\partial^2}{\partial x_2^2} \\ &= -\frac{\hbar^2}{2\,m_Y}\left[\left(\frac{m_Y}{m_X + 2m_Y}\frac{\partial}{\partial y_1} - \frac{\partial}{\partial y_2}\right)^2 + \left(\frac{m_Y}{m_X + 2m_Y}\frac{\partial}{\partial y_1} + \frac{\partial}{\partial y_3}\right)^2\right] \\ &\quad -\frac{\hbar^2}{2\,m_X}\left(\frac{m_X}{m_X + 2m_Y}\frac{\partial}{\partial y_1} + \frac{\partial}{\partial y_2} - \frac{\partial}{\partial y_3}\right)^2 \\ &= -\frac{\hbar^2}{2\,(m_X + 2m_Y)}\frac{\partial^2}{\partial y_1^2} - \frac{\hbar^2}{2}\left(\frac{1}{m_Y} + \frac{1}{m_Y}\right)\left(\frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial y_3^2}\right) \\ &\quad +\frac{\hbar^2}{m_X}\frac{\partial}{\partial y_2}\frac{\partial}{\partial y_3} \ ; \end{aligned} \tag{5}$$

and the potential energy function part is

$$V \;=\; \frac{1}{2}\,k_0\,[\,y_2^2 \;+\; y_3^2\,] \;+\; k_1\,y_2\,y_3 \;\;. \tag{6}$$

Then the Hamiltonian of the system can be written as:

$$\begin{aligned}
\hat{H} \;&=\; \hat{T} \,+\, \hat{V} \\
&=\; -\frac{\hbar^2}{2\,(m_X + 2m_Y)}\,\frac{\partial^2}{\partial y_1^2} \;+\; \hat{H}_1(y_2, y_3)
\end{aligned} \tag{7}$$

where

$$\begin{aligned}
\hat{H}_1(y_2, y_3) \;&=\; -\,\frac{\hbar^2}{2}\left(\frac{1}{m_X} \,+\, \frac{1}{m_Y}\right)\left(\frac{\partial^2}{\partial y_2^2} \,+\, \frac{\partial^2}{\partial y_3^2}\right) \\
&\quad +\frac{\hbar^2}{m_X}\,\frac{\partial}{\partial y_2}\,\frac{\partial}{\partial y_3} \;+\; \frac{1}{2}\,k_0\,(y_2^2 \;+\; y_3^2) \;+\; k_1\,y_2\,y_3 \;.
\end{aligned} \tag{8}$$

(b) Employ the transformation

$$\begin{aligned}
z_2 \;&=\; y_2 \;+\; c_2\,y_3 \\
z_3 \;&=\; y_2 \;+\; c_3\,y_3 \;,
\end{aligned} \tag{9}$$

the kinetic energy part of $\hat{H}_1(y_2, y_3)$ can be written as

$$\begin{aligned}
\hat{T}_1(y_2, y_3) \;&=\; -\,\frac{\hbar^2}{2}\left(\frac{1}{m_X} \,+\, \frac{1}{m_Y}\right)\left[\left(\frac{\partial}{\partial z_2} \,+\, \frac{\partial}{\partial z_3}\right)^2 \,+\, \left(c_2\,\frac{\partial}{\partial z_2} \,+\, c_3\,\frac{\partial}{\partial z_3}\right)^2\right] \\
&\quad -\frac{\hbar^2}{m_X}\left(\frac{\partial}{\partial z_2} \,+\, \frac{\partial}{\partial z_3}\right)\left(c_2\,\frac{\partial}{\partial z_2} \,+\, c_3\,\frac{\partial}{\partial z_3}\right) \\
&=\; -\,\frac{\hbar^2}{2}\left[\left(\frac{1}{m_X} \,+\, \frac{1}{m_Y}\right)(\,1 \,+\, c_2\,c_3\,) \,-\, \frac{c_3 \,+\, c_2}{m_X}\right]\frac{\partial}{\partial z_2}\,\frac{\partial}{\partial z_3} \\
&\quad -\,\frac{\hbar^2}{2}\left[\left(\frac{1}{m_X} \,+\, \frac{1}{m_Y}\right)(\,1 \,+\, c_3^2\,) \,-\, \frac{c_3}{m_X}\right]\frac{\partial^2}{\partial z_2^2} \\
&\quad -\,\frac{\hbar^2}{2}\left[\left(\frac{1}{m_X} \,+\, \frac{1}{m_Y}\right)(\,1 \,+\, c_2^2\,) \,-\, \frac{c_2}{m_X}\right]\frac{\partial^2}{\partial z_2^2} \;.
\end{aligned} \tag{10}$$

For the potential part, first, we express y_2 and y_3 as a function of z_2 and z_3 from (9)

$$\begin{aligned}
y_2 \;&=\; \frac{c_3\,z_2 \;-\; c_2\,z_3}{c_3 \;-\; c_2} \\
y_3 \;&=\; \frac{z_2 \;-\; z_3}{c_2 \;-\; c_3} \;\;,
\end{aligned} \tag{11}$$

and substitute (11) into (6), so that

$$V = \frac{1}{2\,(c_2 - c_3)^2} \, \{ \, z_2^2 \, (\, k_0 \; - \; 2 \, k_1 \, c_3 \; + \; k_0 \, c_3^2 \,) \\ + 2 \, z_2 \, z_3 \; [\, k_1 \, (c_2 \; + \; c_3) \; - \; k_0 (1 \; + \; c_2 \, c_3) \,] \\ + z_3^2 \, (\, k_0 \; - \; 2 \, k_1 \, c_2 \; + \; k_0 \, c_2^2 \,) \} \; . \tag{12}$$

Let the coefficients of the crossterms $\frac{\partial}{\partial z_2} \frac{\partial}{\partial z_3}$ and $z_2 \, z_3$ in (10) and (12) to be 0, i. e.

$$\begin{cases} \; (\, 1/m_X \; + \; 1/m_Y \,) \; (\, 1 \; + \; c_2 \, c_3 \,) \; - (\, c_3 \; + \; c_2 \,) \, / \, m_X \; = \; 0 \\ \; k_1 \, (c_2 \; + \; c_3) \; - \; k_0 (1 \; + \; c_2 \, c_3) \; = \; 0 \; . \end{cases} \tag{13}$$

The solution of (13) is

$$\begin{cases} c_2 \; = \; 1 \\ c_3 \; = \; -1 \end{cases} \; ; \; \text{or} \; \begin{cases} c_2 \; = \; -1 \\ c_3 \; = \; 1 \end{cases} \; . \tag{14}$$

The derivations from (9) to (14) can be actually done either by hand or by `Mathematica` (see the notebook).

The two solutions in (14) are actually equivalent. Now we just pick up one, $c_2 \; = \; 1, c_3 \; = \; -1$, such that

$$z_2 = y_2 \; + \; y_3 \\ z_3 = y_2 \; - \; y_3 \; . \tag{15}$$

Then $\hat{H}_1(y_2, y_3)$ can be given as:

$$\hat{H}_1 \; = \; -\frac{\hbar^2}{2m_2} \frac{\partial^2}{\partial z_2^2} \; + \; \frac{1}{2} \, k_2' \, z_2^2 \; - \; \frac{\hbar^2}{2m_3} \frac{\partial^2}{\partial z_3^2} \; + \; \frac{1}{2} \, k_3' \, z_3^2 \; . \tag{16}$$

where

$$m_2 \; = \; \frac{m_Y}{2} \; , \; k_2' \; = \; \frac{k_0 + k_1}{2} \; ; \\ m_3 \; = \; \frac{m_X m_Y}{2(2m_Y + m_X)} \; , \; k_3' \; = \; \frac{k_0 - k_1}{2} \; . \tag{17}$$

The correspondent normal mode frequencies are:

$$\omega_2 \; = \; \sqrt{\frac{k_2'}{m_2}} \; = \; \sqrt{\frac{k_0 + k_1}{m_Y}} \; ; \\ \omega_3 \; = \; \sqrt{\frac{k_3'}{m_3}} \; = \; \sqrt{\frac{k_0 - k_1}{m_Y} \left(1 + \frac{2m_X}{m_Y} \right)} \; . \tag{18}$$

(c) In the normal coordinate, we know that $\phi_1(y_1)$ is a plane wave; $\phi_2(z_2)$ and $\phi_3(z_3)$ are two independent harmonic oscillators. So the wave function for them can be written as

$$\begin{aligned}
\phi_1(y_1) &= \exp\left[ipy_1\right] \\
\phi_2(z_2) &= \sqrt{\frac{\alpha_2}{2^n n!\sqrt{\pi}}}e^{-\alpha_2^2 z_2^2/2}H_n(\alpha_2 z_2) \\
\phi_3(z_3) &= \sqrt{\frac{\alpha_3}{2^l l!\sqrt{\pi}}}e^{-\alpha_3^2 z_3^2/2}H_l(\alpha_3 z_3) \quad .
\end{aligned} \tag{19}$$

where

$$\begin{aligned}
\alpha_2 &= \sqrt{\frac{\sqrt{m_2 k_2'}}{\hbar}} = \sqrt{\frac{\sqrt{m_Y(k_0'+k_1')}}{2\hbar}} \ ; \\
\alpha_3 &= \sqrt{\frac{\sqrt{m_3 k_3'}}{\hbar}} = \sqrt{\frac{1}{2\hbar}\sqrt{\frac{m_Y m_X(k_0'-k_1')}{2m_Y+m_X}}} \ .
\end{aligned} \tag{20}$$

The vibrational energy levels of this system are:

$$E_{l,n} = (n+\frac{1}{2})\,\hbar\omega_2 + (l+\frac{1}{2})\,\hbar\omega_3 \ ; n,l = 0,1,2,... \ . \tag{21}$$

So the general wave function as a function of y_1, y_2 and y_3 will be:

$$\begin{aligned}
\psi(y_1,y_2,y_3,t) &= \sum_{n,l=0}^{\infty}\frac{1}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}\mathrm{d}p\,\omega_{nl}(p) \\
&\quad \exp\left\{ipy_1 - it\left[\frac{p^2}{2m\hbar}+(n+\frac{1}{2})\,\omega_2+(l+\frac{1}{2})\,\omega_3\right]\right\} \\
&\quad \sqrt{\frac{\alpha_2}{2^n n!\sqrt{\pi}}}e^{-\alpha_2^2(y_2+y_3)^2/2}H_n(\alpha_2(y_2+y_3)) \\
&\quad \sqrt{\frac{\alpha_3}{2^l l!\sqrt{\pi}}}e^{-\alpha_3^2(y_2-y_3)^2/2}H_l(\alpha_3(y_2-y_3)) \\
&= \sum_{n,l=0}^{\infty}\frac{\sqrt{\alpha_2\alpha_3}}{\pi\sqrt{2^{n+l+1}\hbar n! l!}}\int_{-\infty}^{\infty}\mathrm{d}p\,\omega_{nl}(p) \\
&\quad H_n(\alpha_2(y_2+y_3))\,H_l(\alpha_3(y_2-y_3)) \\
&\quad \exp\left\{-\alpha_2^2(y_2+y_3)^2/2-\alpha_3^2(y_2-y_3)^2/2+ipy_1\right\} \\
&\quad \exp\left\{-it\left[\frac{p^2}{2m\hbar}+(n+\frac{1}{2})\,\omega_2+(l+\frac{1}{2})\,\omega_3\right]\right\} \quad .
\end{aligned} \tag{22}$$

(d) Using $m_X = 12$ u; $m_Y = 16$ u, where $1u = 1.66\times10^{-27}$ Kg, and $k_0 = 580$ Kcal/molÅ^2 and $k_1 = 0$, one can find

$$\omega_2 = 930.893 \text{ cm}^{-1} \ ;$$

$$\omega_3 = 1471.87\ \mathrm{cm}^{-1}\,. \tag{23}$$

The percentage errors for ω_2 and ω_3 comparing to the experiment are 30.4% and 37.3% respectively.

(e) From the Fig 1, one can see that there is a net dipole moment for the normal mode of ω_3, but no net dipole moment for the normal mode of ω_2. This means that there is no interaction between the normal mode of ω_2 and the infrared light, and it can not be excited. So only the normal mode with $\omega_3 = \sqrt{\frac{k_0-k_1}{m_Y}\left(1+\frac{2m_X}{m_Y}\right)}$ can absorb energy from the light and be excited.

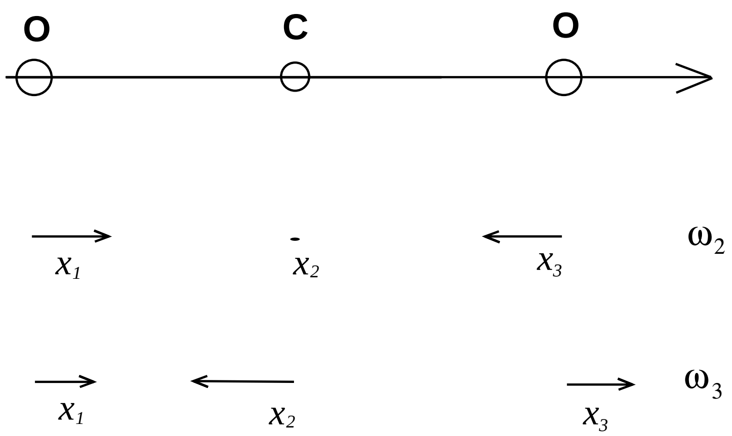

Figure 1: The two normal modes of the CO_2 molecule.

(f) One can find out the vibrational quantum numbers of certain state by counting the number of nodes (the points where the wave function is 0) along its normal coordinate. From the solution of part **(e)**, we find that the normal coordinate for mode ω_2 is along $y_2 + y_3 = z_2$, and the normal coordinate for mode ω_3 is along $y_2 - y_3 = z_3$,where z_2 and z_3 will have a spatial pattern of one dimensional harmonic oscillator. In Fig.**??** (a), there is no node, so it represents the ground state, where $n2 = 0$ and $n3 = 0$. In Fig.**??** (b), there is no node along $y_2 - y_3 = z_3$, but there are 5 nodes along $y_2 + y_3 = z_2$. So it represents an excited state, where $n2 = 5$ and $n3 = 0$. In Fig.**??** (c), there are 4 nodes along $y_2 - y_3 = z_3$, and there are 5 nodes along $y_2 + y_3 = z_2$ so that it represents another excited state, where n2=5 and $n3 = 4$.