The Harmonic Oscillator, Diatomic Molecule Adaptation*

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When one considers a diatomic molecule, and wishes to treat it (in some manner) as a harmonic oscillator, i.e., we wish to begin a discussion of the IR spectrum of this moiety, we need to understand what our model actually is.

Consider a molecule of HCℓ in the gas phase. It consists of a proton, a chlorine nucleus, and many (18) electrons. Usually, we think of 16 of these electrons as being "inner" shell electrons on the chlorine, and two of these electrons as "binding" the proton to the chlorine nucleus (and its tightly bound non-involved electrons). The binding electrons make it possible to "think" of the H-Cℓ nuclei as being harmonically bound together (although if that were literally true, the molecule could never dissociate).

If we align the molecule along the x-axis, then we have

$$x_{C\ell} = X_{cofm} + y_{C\ell}$$

and

$$x_H = X_{cofm} + y_H$$

with the origin at the center of mass, so that we can write

$$m_H \frac{d^2 x_H}{dt^2} = m_H \frac{d^2 y_H}{dt^2} + m_H \frac{d^2 X_{cofm}}{dt^2}$$
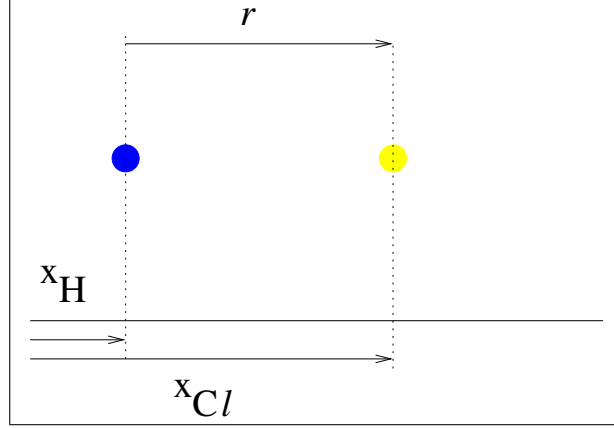
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*l2h2:ho1a.tex

Figure 1: HCℓ arbitrarily located

and

$$m_{C\ell}\frac{d^2x_{C\ell}}{dt^2} = m_{C\ell}\frac{d^2y_{C\ell}}{dt^2}m_{C\ell}\frac{d^2X_{cofm}}{dt^2}$$

We wish to change coördinates to $r = x_{C\ell} - x_H$. We then have

$$\dot{r} = \dot{x}_{C\ell} - \dot{x}_H$$

and

$$\frac{d^2r}{dt^2} = \ddot{r} = \frac{d^2x_{C\ell}}{dt^2} - \frac{d^2x_H}{dt^2} = \frac{d^2y_{C\ell}}{dt^2} + \frac{d^2X_{cofm}}{dt^2} - \frac{d^2y_H}{dt^2} - \frac{d^2X_{cofm}}{dt^2}$$

where one sees that we get an immediate cancelation of the center of mass terms, i.e.,

$$\frac{d^2r}{dt^2} = \ddot{r} = \frac{d^2y_{C\ell}}{dt^2} - \frac{d^2y_H}{dt^2}$$

Multiplying by $m_H m_{C\ell}$ we have

$$m_H m_{C\ell}\ddot{r} = m_H m_{C\ell}\frac{d^2y_{C\ell}}{dt^2} - m_H m_{C\ell}\frac{d^2y_H}{dt^2}$$

which can be rearranged to be:

$$m_H m_{C\ell}\ddot{r} = m_H\left(m_{C\ell}\frac{d^2y_{C\ell}}{dt^2}\right) - m_{C\ell}\left(m_H\frac{d^2y_H}{dt^2}\right)$$

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$$m_H m_{C\ell} \ddot{r} = m_H \left(F_{C\ell} \right) - m_{C\ell} \left(F_H \right)$$

but since one force is opposite to the other, we have, choosing one arbitrarily,

$$m_H m_{C\ell} \ddot{r} = -m_H \left(F_H \right) - m_{C\ell} \left(F_H \right)$$

so, dividing throught my $m_H + m_{C\ell}$ we have

$$\frac{m_H m_{C\ell}}{m_H + m_{C\ell}} \ddot{r} = F_{C\ell}$$

which, since μ is defined as

$$\frac{1}{\mu} = + \frac{1}{m_H} + \frac{1}{m_{C\ell}}$$

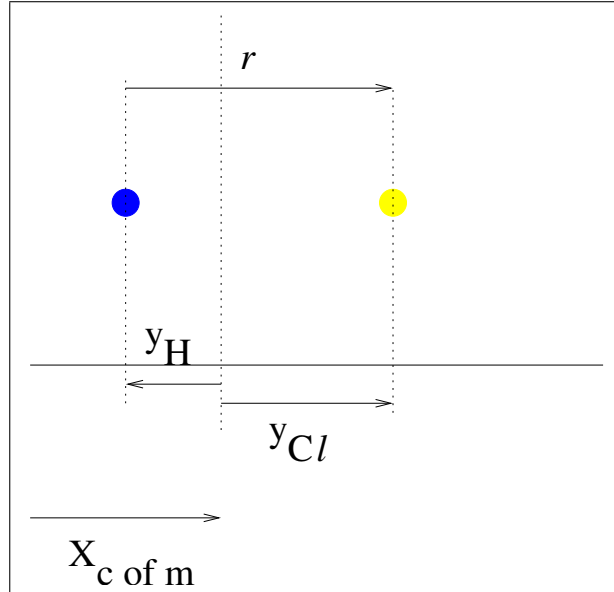$$\mu \ddot{r} = F_{C\ell}$$

Figure 2: HCℓ located at the center of mass

and defining the force on the proton (of the chlorine fragment) as

$$F_{C\ell} = -k(r - r_e)$$

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where r_e is the equilibrium bond length for this molecule, the value of r where the force is zero and making $r < r_e$ results in a repulsive force trying to separate the nuclei, and making $r > r_e$ results in an attractive force trying to pull them back together.

The center of mass is defined as the teeter-totter point of the see-saw, i.e., the place where

$$m_H x_H = m_{C\ell} x_{C\ell}$$

so

$$m_H \ddot{x}_H = m_{C\ell} \ddot{x}_{C\ell}$$

and we know that $r = x_{C\ell} - x_H$ so

$$\ddot{r} = \ddot{x}_{C\ell} - \ddot{x}_H$$

or

$$m_{C\ell} m_H \ddot{r} = m_{C\ell} m_H \ddot{x}_{C\ell} - m_{C\ell} m_H \ddot{x}_H$$

can be re-written as

$$m_{C\ell} m_H \ddot{r} = m_H (m_{C\ell} \ddot{x}_{C\ell}) - m_{C\ell} (m_H \ddot{x}_H)$$

and dividing by $m_{C\ell} + m_H$ we have

$$\frac{m_{C\ell} m_H}{m_{C\ell} + m_H} \ddot{r} = m_H (m_{C\ell} \ddot{x}_{C\ell}) - m_{C\ell} (m_H \ddot{x}_H)$$