

April 2007

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## Recommended Citation

David, Carl W., "Molecular Dynamics and the Diatomic Molecule as Harmonic Oscillator and Rigid Rotor" (2007). *Chemistry Education Materials*. 45.

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# Molecular Dynamics and the Diatomic Molecule as a Harmonic Oscillator and Rigid Rotor

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(Dated: April 19, 2007)

## I. SYNOPSIS

The transformation to the center of mass coordinate system (from the lab based one), when dealing with a molecule like HCl is explored. Note that this is a partial re-working of a published article, C. W. David, *Chemical Educator*, **5(11)**, 306, 2006.

## II. THE DYNAMICS OF A DIATOMIC MOLECULE IN GENERAL

When we consider a diatomic molecule and wish to treat it 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 and Cl nuclei as being harmonically, *vide supra* bound together (although if that were literally true, the molecule could never dissociate).

Of course, the proton could be a deuteron, and there are several isotopes of chlorine, so HCl is a misnomer, and instead, it is better to write  ${}^2_1\text{D}{}^{35}_{17}\text{Cl}$ , i.e., the entire isotopic description, so that the masses to be used, *vide ante*, will be correct.

Any discussion of the motions in this molecule starts with the classical motion, the translation, rotation, and vibration which the molecule undergoes. We here treat the vibration (classically) as precursor to treating the Harmonic Oscillator using Quantum Mechanics.

### A. Maple implementation of Molecular Dynamics of HCl

We will be doing molecular dynamics on the HCl molecule, so we introduce the Maple program which will effectuate our dynamics.

```
restart;  
with(inttrans):#needed for FFT  
printlevel := 0;
```

```
#start with HCl  
r_e := 1.3e-8;#cm (problem specific)  
m_H_1 := 1.0078/(6*10^(23)):#grams/atom  
m_H_2 := 2.01355/(6*10^(23)):#grams/atom Deuterium  
m_H_3 := 3.016049/(6*10^(23)):#grams/atom Tritium  
m_H := m_H_1;#choose your isotope  
m_Cl_35 := 34.9688/(6*10^(23)):#grams/atom  
m_Cl_37 := 36.9688/(6*10^(23)):#grams/atom  
m_Cl := m_Cl_35;#choose your isotope
```

We start with the molecule floating in space. The “proton” is at  $\vec{r}_H = [x_H, y_H, z_H]$  and the chloride is at  $\vec{r}_{Cl} = [x_{Cl}, y_{Cl}, z_{Cl}]$ . The molecule may or may not be tumbling, may or may not be translating (as a whole), but certainly, if we are not to waste our time, must be vibrating. That means that the “proton” and chloride are “beating” against each other, i.e., the distance of separation between them is sinusoidally varying.

```
r_H := [0,0,0]:  
r_Cl := [0,1.4e-8,0.4e-8]:
```

We have arbitrarily chosen to place the “proton” in the laboratory origin, and have the chloride, the heavier partner, at some point in the x=0 plane, i.e., the y-z plane.

For future work, we assign the velocity vectors next:

```
v_H := [0,0,0]:  
v_Cl := [0,0,0]:
```

where, for no particular reason, we’ve chosen to start the dynamics with the nuclei stationary! Parenthetically, we could choose  $v_z \neq 0$  for either the proton or the chloride nuclei, and induce an initial rotation (in addition to the induced vibration). Notice that we’ve chosen a value of  $r > r_e$ , which guarantees that some vibration will actually occur!

Next, we need to obtain the forces acting. For internal (Maple) reasons, we first define the forces as vectors; we will fill in values later.

```
F_H := [0,0,0]:  
F_Cl := [0,0,0]:  
F_H_p := [0,0,0]:  
F_Cl_p := [0,0,0]:
```

Lastly, we introduce the force constant (one of a plethora of literature values)

```
#k := +481:# Newton/Meter;  
k := 4.81e5:#dynes/angstrom
```

and the time step:

`h := 10^(-16):#(this is the time step in seconds)`

(note that  $10^{-12}$  seconds is a picosecond, and  $10^{-15}$  seconds is a femtosecond). In general, we have that

$$m_H \frac{d^2 \vec{r}_H}{dt^2} = F_H$$

where  $F_H$  is the force on the “proton”, and

$$m_{Cl} \frac{d^2 \vec{r}_{Cl}}{dt^2} = F_{Cl}$$

and  $F_{Cl}$  is the force on the chloride. There could be a gravitational force on each, there could be an external electric field pulling and pushing on each, but, as beginners, we assume that the only force operative is one between the “proton” and the chloride. In fact, we assume that force operates on the line connecting the two, and that  $F_H = -F_{Cl}$ , i.e., they are opposite to each other ( $\vec{F}_H = -\vec{F}_{Cl}$ ). We will call that force  $F$ , and note that if this is a typical diatomic molecule, then it is approximated by a Young’s law force of the form

$$F = -k(r - r_e)$$

where  $r_e$  is the equilibrium bond length! If  $r > r_e$  then we have a force attempting to bring the two nuclei back together again, while if  $r < r_e$  we have a repulsive force trying to separate them (push them apart). The potential energy function from which this force comes would be

$$V = \frac{k}{2} (r - r_e)^2$$

(remember,  $F = -\frac{\partial V}{\partial x}$ ,  $\vec{F} = -\nabla V$ ).

To more rigorously obtain the force, we write

$$V = \frac{k}{2} \left( \sqrt{(x_H - x_{Cl})^2 + (y_H - y_{Cl})^2 + (z_H - z_{Cl})^2} - r_e \right)^2$$

and note that  $r_e$  is about  $1.3\text{\AA}$ . This form allows us to obtain the force vectors properly, rather than in the form (above) which was more symbolic than anything. For the force on the “proton” in the x-direction we have

$$F_H^x = -\frac{\partial V}{\partial x_H}$$

which gives

$$F_H^x = -2\frac{k}{2} \frac{\left( \sqrt{(x_H - x_{Cl})^2 + (y_H - y_{Cl})^2 + (z_H - z_{Cl})^2} - r_e \right) \times \partial \left( \sqrt{(x_H - x_{Cl})^2 + (y_H - y_{Cl})^2 + (z_H - z_{Cl})^2} - r_e \right)}{\partial x_H} \quad (2.1)$$

or

$$F_H^x = -k(r - r_e) \frac{\partial \left( \sqrt{(x_H - x_{Cl})^2 + (y_H - y_{Cl})^2 + (z_H - z_{Cl})^2} - r_e \right)}{\partial x_H} \quad (2.2)$$

or

$$F_H^x = -k(r - r_e) \frac{1}{\sqrt{(x_H - x_{Cl})^2 + (y_H - y_{Cl})^2 + (z_H - z_{Cl})^2}} (x_H - x_{Cl}) \quad (2.3)$$

i.e.,

$$F_H^x = -\frac{k}{r} (r - r_e) (x_H - x_{Cl}) \quad (2.4)$$

with 5 other terms, corresponding to taking the derivatives with respect to y- and z- for the “proton” and with respect to x-, y-, and z- for the chloride.

Returning to the Maple code, we define the total potential energy, since we will be checking to see if the total energy, potential plus kinetic, is a constant during our simulation:

`V := (k/2)*(sqrt((r_H[1]-r_Cl[1])^2+`

`(r_H[2]-r_Cl[2])^2+(r_H[3]-r_Cl[3])^2)-r_e)^2:`

Finally, we define some simulation constants, specifically, since we know that the DFT works best when the number of datum is  $2^{\text{integer}}$ , we define `m` as that integer, i.e., the number of data points will be  $2^m$ .

```
m :=10;# FFT power of 2
n_stop := 2^m;
l := array(1..n_stop);
y := array(1..n_stop);
```

where  $m$  sets the power, and then  $n\_stop$  sets the number of data points to be collected. The output data from this simulation is going to be called 'l' (for length), it will be the instantaneous bond length as a function of the number of time steps.

Finally, we set up the loop for which will execute one time step of the simulation, one step of the Verlet algorithm.

```
for i from 1 by 1 to n_stop do
  r := r_H-r_Cl;
  r_mag := sqrt(r[1]^2+r[2]^2+r[3]^2):
```

Inside the loop, we calculate the force on each atom (nucleus) in each direction, using the appropriate force component.

```
F_H := -k*(r_mag-r_e)*(r_H-r_Cl)/r_mag:
F_Cl := -F_H:
```

and then we carry out the Verlet time step to the "prime"d system (denoted as  $_p$ ) where we do all three components at once:

```
r_H_p := r_H + h*v_H + ((h^2)/(2*m_H))*F_H:
r_Cl_p := r_Cl + h*v_Cl + ((h^2)/(2*m_Cl))*F_Cl:
```

The Verlet algorithm states:

- For the next time step, calculate

$$x_{next} = x_{old} + v_{old}\Delta t + \frac{F_{old}}{2m}(\Delta t)^2$$

- and calculate the next velocity as

$$v_{next} = v_{old} + \frac{(F_{new} + F_{old})\Delta t}{2m}$$

( $F_{new}$  is  $F(x_{next})$ ). for each particle. Then cycle around and use the new velocity to obtain the next position, etc..

In Maple, we now update the forces to the "prime"d (next) system,

```
r_p := r_H_p - r_Cl_p;
r_mag_p := sqrt(r_p[1]^2+r_p[2]^2+r_p[3]^2):

F_H_p := -k*(r_mag_p-r_e)*(r_H_p-r_Cl_p)/r_mag_p:
F_Cl_p := - F_H:
```

and update the velocities to the "primed"d (next) system,

```
v_H_p := v_H + (h/(2*m_H))*(F_H_p+F_H):
v_Cl_p := v_Cl + (h/(2*m_Cl))*(F_Cl_p+F_Cl):
```

and finally update the coordinates to the "prime"d (next) values:

```
r_H := r_H_p:#update coordinates
r_Cl := r_Cl_p:
v_H := v_H_p:#update velocities
v_Cl := v_Cl_p:
```

Now, there's some housekeeping for plotting purposes:

```
r_mag := sqrt(r[1]^2+r[2]^2+r[3]^2);
```

```
l[i] := r_mag*1e8;#Angstrom
y[i] := 0;#imaginary part
r_plot(i) := evalf(r_mag)*1e8;#Angstrom
end do;
i := 'i':#reset the value of the for loop variable
#SEQ := seq([i,r_plot(i)],i=1..n_stop):
PLOT(POINTS(seq([i,r_plot(i)],i=1..n_stop), SYMBOL(DIAMOND)))
FFT(m,l,y);
vu_0_cm_1 := 2886;#cm^(-1)
nu_0 := c*vu_0_cm_1;
i := 'i':
FreqSpectrum := [seq([(i-1),(2*mag(l[i],y[i])/(2^m))],i=1..n_stop)];
plot([seq(FreqSpectrum[j],j=2..20)],title="Fourier Transform")
```

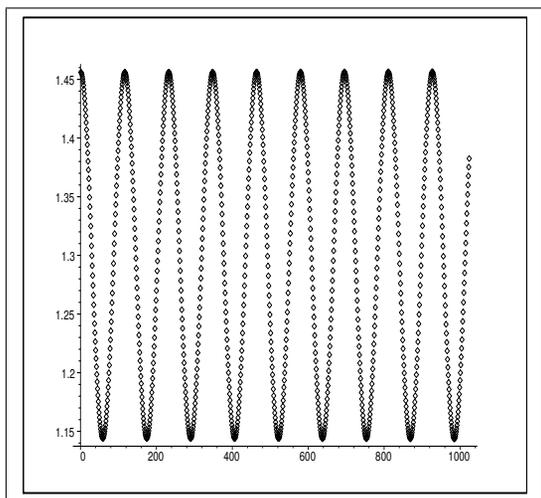


FIG. 1: HCl molecule’s amplitude of vibration as a function of time step.

We note that we can choose the value of “h” in the simulation, the size of the time step, and can adjust it as best as possible to get an exact integral number of periods inside our total time interval, i.e., in the  $2^m$  time steps. This allows us to calculate the frequency easily, i.e.,

$$\frac{\text{number of oscillations}}{\text{number of data points} \times h} = \nu = \frac{9}{1024 \times 1.021 \times 10^{-16}} = 8.608 \times 10^{13} \text{ cps}$$

which compares with a computed value of  $8.658 \times 10^{13}$  if  $k$  is  $4.81 \times 10^5$  dynes/cm ( $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ ). Otherwise, we are forced to locate the maximum in the Fourier Transform plot, shown in Figure 2 by reading it from the plot, and interpolate it’s position relative to the abscissa.

In our code,  $h$  is 0.1 femtoseconds, but if we adjust it to 1.021 femtoseconds, then one can observe almost exactly 9 periods, which allows the computation shown above.

### B. Checking the values

An acid test of molecular dynamics is that the energy is a constant. To test this requires a bit (not too much) of work. The following, when inserted into the “for” loop, at the end, accomplish the task:

```
v_H_mag := sqrt(v_H[1]^2+v_H[2]^2+v_H[3]^2);
v_Cl_mag := sqrt(v_Cl[1]^2+v_Cl[2]^2+v_Cl[3]^2);
KE(i) := 1/2*(m_H*v_H_mag^2+m_Cl*v_Cl_mag^2);
PE(i) := (k/2)*(r_mag-r_e)^2;
E_total(i) := evalf(KE(i)+PE(i));
```

In Figure 3 one sees that the fluctuations in the total energy are not trivially small, as hoped for!

### C. Adding a Cubic Term to the Potential

Changing the total potential energy to

$$V = \frac{k}{2}(r - r_e)^2 + k3 \times r - r_e)^3$$

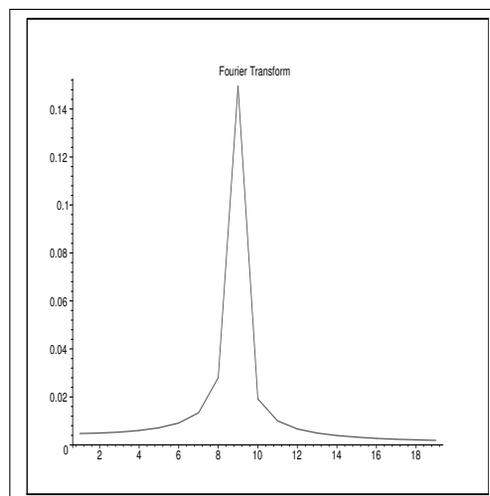


FIG. 2: HCl molecule’s Fourier Transform of the amplitude of vibration as a function of time step.

entails changing the force term in the for loop thusly:

$$F_H := -(k*(r\_mag-r\_e)*(r\_H-r\_Cl)/r\_mag + 3*k3*((r\_mag-r\_e)^2)*(r\_H-r\_Cl)/r\_mag);$$

Playing with  $k3$  results in changes to the frequency, which can be correlated with the perturbation calculations in “advanced” quantum mechanics when the time comes.

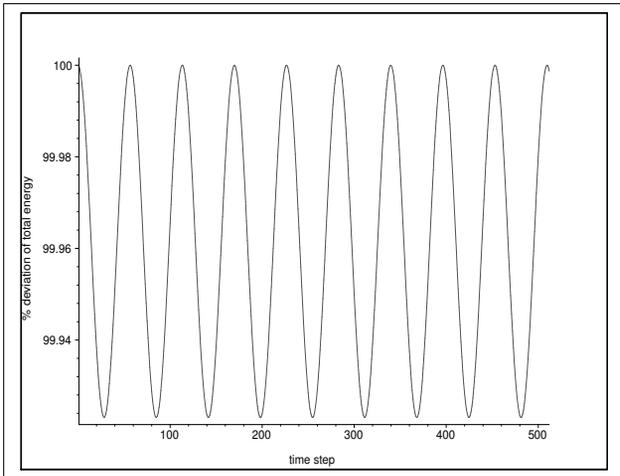


FIG. 3: Total energy (divided by the starting potential energy), after multiplying by  $10^2$ , i.e., very small fluctuations in energy being observed as a function of time

### III. SIMPLIFYING VIA THE CENTER OF MASS TRANSFORMATION

#### A. Defining the center of mass

We start with a laboratory coordinate system, denoted with “ $x$ ”, and look into converting to a moving coordinate system which is centered on the center of mass ( $X, Y, Z$ ) of the molecule, and which translates with the mass translation of the molecule and a new coordinate system,  $y$  which is located relative to the moving center of mass..

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

$$x_{Cl} = X_{cofm} + y_{Cl}$$

and

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

and with the origin at the center of mass so that we can

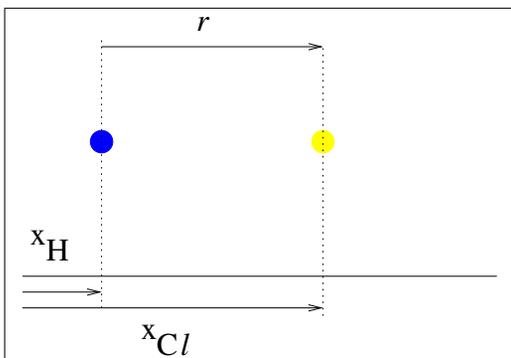


FIG. 4: HCl arbitrarily located

write

$$m_H \frac{d^2 x_H}{dt^2} = m_H \frac{d^2 y_H}{dt^2} + m_H \frac{d^2 X_{cofm}}{dt^2}$$

and

$$m_{Cl} \frac{d^2 x_{Cl}}{dt^2} = m_{Cl} \frac{d^2 y_{Cl}}{dt^2} + m_{Cl} \frac{d^2 X_{cofm}}{dt^2}$$

We wish to change coordinates to  $r = x_{Cl} - x_H$ . We then have

$$\dot{r} = \dot{x}_{Cl} - \dot{x}_H$$

and

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

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

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

Multiplying by  $m_H m_{Cl}$  we have

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

which can be rearranged to be:

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

$$m_H m_{Cl} \ddot{r} = m_H (F_{Cl}) - m_{Cl} (F_H)$$

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

$$m_H m_{Cl} \ddot{r} = -m_H (F_H) - m_{Cl} (F_H)$$

and, dividing through by  $m_H + m_{Cl}$  we have

$$\frac{m_H m_{Cl}}{m_H + m_{Cl}} \ddot{r} = F_H$$

which, since  $\mu$  is defined as

$$\frac{1}{\mu} = \frac{1}{m_H} + \frac{1}{m_{Cl}}$$

$$\mu \ddot{r} = F_H \quad (3.1)$$

Defining the force on the proton (or the chlorine) as

$$F_H = -k(r - r_e) = -F_{Cl}$$

where  $r_e$  is the equilibrium bond length for this molecule, the value of  $r$  where the force is zero and making  $r < r_e$

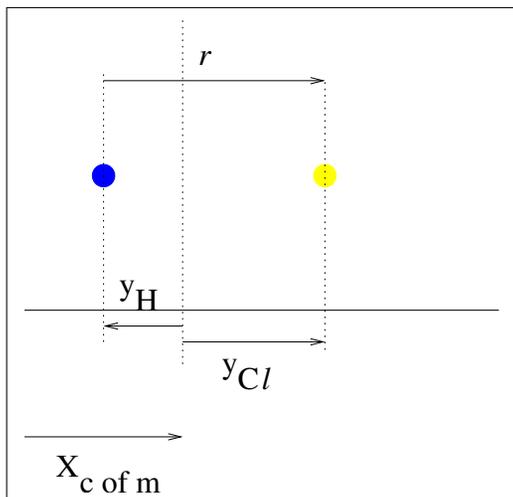


FIG. 5: HCl located at the center of mass

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

$$m_H x_H = m_{Cl} x_{Cl} \quad (3.2)$$

so

$$m_H \ddot{x}_H = m_{Cl} \ddot{x}_{Cl}$$

and we know that  $r = x_H - x_{Cl}$  so

$$\ddot{r} = \ddot{x}_H - \ddot{x}_{Cl}$$

or

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

can be re-written as

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

and dividing by  $m_{Cl} + m_H$  we have

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

or

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

i.e., we have a tautology!

### B. Inside the Center of Mass

In Equation 3.1 we have the basic equation of motion for a pseudo-particle of mass  $\mu$  subject to the force  $F$ . We then have

$$\mu \ddot{r} = -k(r - r_e)$$

It is traditional to re-write this as

$$\ddot{r} = -\frac{k}{\mu}(r - r_e)$$

and then change variable to something like “z”, i.e.,

$$z = r - r_e$$

so that

$$\ddot{r} = -\frac{k}{\mu}z = \ddot{z}$$

which employed a relative coordinate, relative to  $r_e$ .

It is well known that the solution to this differential equation is

$$z = A \cos\left(\sqrt{\frac{k}{\mu}}t\right) + B \sin\left(\sqrt{\frac{k}{\mu}}t\right)$$

where A and B are constants to be determined by the initial conditions of the problem. We then have

$$\omega = \sqrt{\frac{k}{\mu}}$$

is the value used in comparing the spectroscopic value to the molecular dynamics value, *vide ante*, with such marvelous success. Of course, the value of  $\omega$  is in radians/unit time, and needs a  $2\pi$  to convert to cycles per unit time (Hertz if unit time is seconds).

In our molecular dynamic sample, we chose B=0, and obtained a cosine for the displacement of the H versus the Cl.

### C. Conservation of Energy

If

$$z = A \cos \omega t; \omega = \sqrt{\frac{k}{\mu}}$$

and

$$\frac{\partial z}{\partial t} = -\omega A \sin \omega t$$

so that

$$\left(\frac{\partial z}{\partial t}\right)^2 = v^2 = \omega^2 A^2 \sin^2 \omega t$$

and

$$z^2 = A^2 \cos^2 \omega t$$

then, clearly, we can employ  $\sin^2 + \cos^2 = 1$  to advantage, to obtain a form involving  $\frac{1}{2}\mu v^2$  and  $\frac{k}{2}z^2$ . This leads to an expression for the total energy,

$$\frac{1}{2}\mu v^2 + \frac{k}{2}z^2$$

which is a constant, i.e., the conservation of energy as exemplified by the harmonic oscillator.

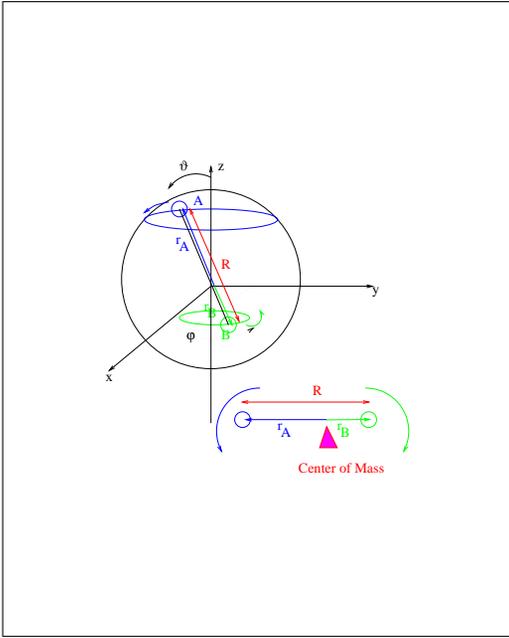


FIG. 6: The diatomic A-B molecule, in the center of mass coordinate system.

#### IV. ROTATION ABOUT THE CENTER OF MASS

The moment of inertia is computed relative to the center of mass, which for a diatomic molecule is easy to picture, it is the place where the "see-saw" balances, i.e., where the clockwise and counter clockwise torques balance each other out. We then have (see figure 6) (see Equation 3.2)

$$m_A r_A = m_B r_B \quad (4.1)$$

(A = Hydrogen and B = Chloride, or *vice versa*) as the condition for torque balance ("see-saw" equilibrium). Further, defining the internuclear distance as R, we have

$$R = r_A + r_B$$

Clearly

$$R^2 = r_A^2 + 2r_A r_B + r_B^2 \quad (4.2)$$

and, from Equation 4.1

$$0 = m_A^2 r_A^2 - 2m_A m_B r_A r_B + m_B^2 r_B^2 \quad (4.3)$$

so, multiplying Equation 4.2 by  $m_A m_B$  one has, upon adding the resultant to Equation 4.3,

$$m_A m_B R^2 = m_A m_B r_A^2 + m_A m_B r_B^2 + m_A^2 r_A^2 + m_B^2 r_B^2$$

which we rewrite as

$$m_A m_B R^2 = m_A (m_B + m_A) r_A^2 + m_B (m_A + m_B) r_B^2$$

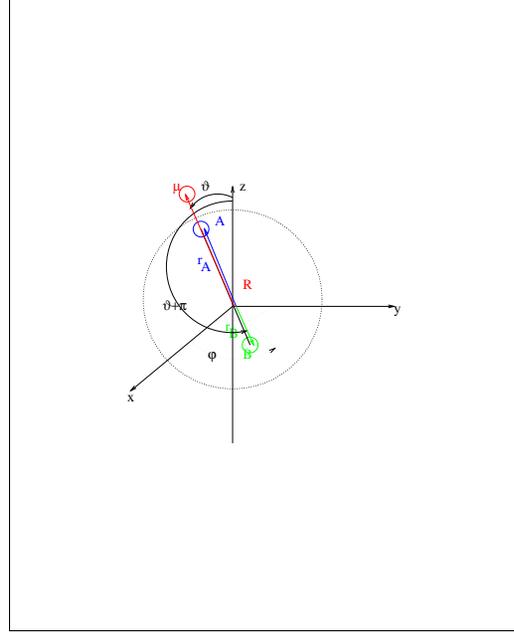


FIG. 7: The diatomic A-B molecule, in the center of mass coordinate system. The pseudo particle,  $\mu$ , is shown in red.

and since

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}$$

we have

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

which leads us to

$$\mu R^2 = m_A r_A^2 + m_B r_B^2 = I$$

i.e., we have obtained a pseudo particle (of mass  $\mu$ ) moment of inertia which mimics the two particle value. Said another way, when one is sitting on the center of mass of a two particle central force problem situation, then the moment of inertia of that two body system is identical in all respects to the moment of inertia of a single particle whose mass is the reduced mass, and whose separation from the origin is exactly equal to the sum of the two moment arms which separated the bodies in the first place.