

Modeling Molecular Vibrations as Simple

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Spring 1997

Abstract

Differential equations provide a means of modeling the vibrational motion in simple molecules, such as HCl.

1 Introduction

When this project was first assigned, I had difficulty coming up with any ideas for a topic. I wanted to choose a subject that was challenging, but not something that was beyond my abilities to study. I also thought it was important to choose a topic that I was genuinely interested in and wanted to research. In my organic chemistry class, we frequently use the technique of infrared molecular absorption spectroscopy to identify molecules. It was not long before I came to a section in my chemistry textbook that dealt with this subject. A picture in the book showed a molecule that was connected by springs, which reminded me of the harmonic oscillator systems that I had studied. Upon further investigation, I discovered that infrared spectroscopy was based on the vibrational motion of the atoms in molecules, which can be described by systems of differential equations. It was then that I decided to choose this subject for my project.

The simplest molecular system which undergoes vibrational motion can be represented by a diatomic molecule. The individual atoms of such a molecule are in a state of constant motion. If this motion is to be fully described by a mathematical model, then six variables would need to be introduced representing the x, y, and z coordinates of the two atoms in 3-dimensional space. As far as vibrational motion is concerned, however, only one coordinate is necessary to describe the fundamental mode of vibration. This coordinate represents motion along the axis of the bond. The other five coordinates would describe the translational and rotational motion of the molecule. These particular motions do not result in a net change of the dipole moment of the molecule, which is a necessary condition of infrared activity, thus I will not be concerned with them.

The individual oscillations of the atoms in a diatomic molecule are coupled, therefore they can be combined into a single system representing a mass connected by a spring to a fixed location. Only one variable is needed to describe

the displacement of this mass about its equilibrium position. Classical Newtonian physics can then be applied to describe the motion of the system. The fundamental physical principle involved is the equation for Newton's second law of motion, in which f is force, m is mass, and a is acceleration:

$$f = ma$$

Using the knowledge that the acceleration of a particle is really the second derivative of its position and that the force will be equal to the negative derivative of the potential energy function,

$$f = -\frac{dU}{dx} = -kx$$

where U is potential energy, k is a constant, and x is position, the equation becomes the more familiar harmonic oscillator equation:

$$\frac{d^2x}{dt^2} = -\frac{k}{m}x$$

Before proceeding any further, the equation should be modified to represent the original coupled oscillators. The masses of the individual atoms need to be combined in some manner that represents the mass of the simplified system. This can be done by introducing μ , the reduced mass, which is essentially the mass felt by the molecule at the center of gravity:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

It should also be noted that x actually represents the equilibrium value for the bond length minus the actual value at any time, t . Therefore, as x oscillates, the distance between the atoms periodically increases and decreases. When the reduced mass is substituted for m , the equation becomes:

$$\frac{d^2x}{dt^2} + \frac{k}{\mu}x = 0$$

Differential equations of this form have exponential solutions, therefore we can substitute the general solution, $x = e^{\lambda t}$, into the differential equation and solve for the eigenvalue, λ .

$$\begin{aligned}\lambda^2 e^{\lambda t} + e^{\lambda t} &= 0 \\ \lambda^2 + 1 &= 0 \\ \lambda &= \pm i \sqrt{\frac{k}{\mu}}\end{aligned}$$

Choosing either eigenvalue will yield the same result, therefore I chose the positive complex root and placed it back into the general solution to obtain the following exponential complex solution:

$$x(t) = e^{i(\sqrt{\frac{k}{\mu}})t}$$

Using Euler's identity ($e^{i\theta t} = \cos \theta t + i \sin \theta t$) and the fact that both the imaginary and real parts of the equation are linearly independent solutions, the general solution with constants A_1 and A_2 becomes:

$$x(t) = A_1 \cos\left(\left(\sqrt{\frac{k}{\mu}}\right)t\right) + A_2 \sin\left(\left(\sqrt{\frac{k}{\mu}}\right)t\right)$$

The variable, x , corresponds to the changing length of the bond, in which $x = 0$ represents the equilibrium length at which the potential energy is minimized. To simplify the problem by discarding one of the terms, I will impose the initial condition, $x(0) = 0$.

$$\begin{aligned} x(0) &= A_1 \cos\left(\left(\sqrt{\frac{k}{\mu}}\right)(0)\right) + A_2 \sin\left(\left(\sqrt{\frac{k}{\mu}}\right)(0)\right) = 0 \\ x(0) &= A_2 = 0 \end{aligned}$$

Therefore,

$$x(t) = A_2 \sin\left(\left(\sqrt{\frac{k}{\mu}}\right)t\right)$$

At this point in the calculations, it becomes necessary to choose an actual molecule so that numerical values for the force constant, k , and the reduced mass, μ , can be determined. I will use hydrogen chloride (HCl) as an example. The masses of the H and Cl atoms can be easily obtained by using molecular weights and Avogadro's number. The force constant, however, was more elusive, but luckily I did obtain its approximate value. The calculations for removing the constants is outlined below:

$$\begin{aligned} m_1(H) &\approx [1.0079 \text{ g/mol}] \left[\frac{1}{6.0221367 \times 10^{23}} \text{ mol} \right] \approx 1.6737 \times 10^{-24} \text{ g} \\ m_2(Cl) &\approx [35.4527 \text{ g/mol}] \left[\frac{1}{6.0221367 \times 10^{23}} \text{ mol} \right] \approx 5.8871 \times 10^{-23} \text{ g} \\ \mu &= \left[\frac{m_1 m_2}{m_1 + m_2} \right] \approx (1.6274 \times 10^{-24} \text{ g}) \\ k &\approx 5.16 \times 10^{-5} \text{ dyn/cm} \\ x(t) &\approx A_2 \sin((5.6309 \times 10^9)t) \end{aligned}$$

The only thing that has not been solved for is the amplitude, A_2 , which may not be so easy to find. The frequency of the oscillations, however, are readily apparent. The frequency can be found with the following equations, where ν is the standard frequency, γ is the wavenumber, which is commonly used in spectroscopy, and c is the speed of light:

$$\begin{aligned} \nu &= \frac{\sqrt{\frac{k}{\mu}}}{2\pi} \approx 8.962 \times 10^8 \text{ s}^{-1} \\ \gamma &= \frac{\nu}{c} \approx 2989.4 \text{ cm}^{-1} \end{aligned}$$

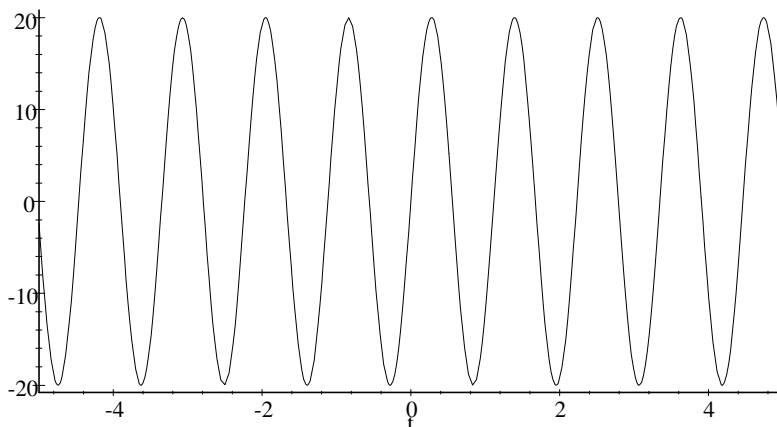


Figure 1: Graph of the changing bond length in an HCl molecule.

This calculated wavenumber is an extremely accurate estimate of the actual fundamental, vibrational absorption band of HCl, which has been experimentally shown to occur at about 2886 cm^{-1} . Assuming a value of 20 pm for the value of A_2 , which seems reasonable considering the measured average bond distance is around 127 pm, a graph of the change in bond length versus time can now be drawn. For simplicity's sake, the time access has been scaled in nanoseconds..

$$x(t) \approx 20 \sin((5.6309)t)$$

Although this graph is not particularly interesting, it does seem to demonstrate that the complex motion of the atoms in molecules can be modeled using classical physics and mathematics. The vibrational motions of this particular molecule, and for that matter, any diatomic molecule, are easy to describe with differential equations.

In terms of cartesian coordinates, with each successive addition of an atom to a molecular system, three new variables enter into the equations of motion, making them more difficult to handle. A system with N separate particles requires 3N coordinates to describe the positions and motion for each separate part, however, there are several techniques that help to simplify a complicated problem. For example, it was previously noted that six (five for linear molecules) of the variables in a multi-component system will describe only the pure rotational and translation motion of the molecule. The other $3N-6$ coordinates will describe the vibrational motion for which infrared absorption can occur. Motion along these coordinates are known as the normal vibrational modes of the system. One of the ways in which the analysis of polyatomic molecules can be made easier is through the use of matrix and summation notation. A set of

N equations for the motion of undamped harmonic oscillator can be condensed to the following form:

$$\frac{d^2 x_i}{dt^2} - \frac{f_i}{m_i} = 0, \quad i = 1, 2, 3, 4, \dots, 3N$$

By using such equations like the one above, not only is the work made easier by entailing less repetitious writing of equations, but also there seems to be less chance for making mistakes. When left in the form in this form, the major difficulty in solving the equations arises as a result of the f_i terms. As in the case of the diatomic molecule, the potential energy function is often to remove the f_i terms. A particularly useful method of handling equations of motion involves the formulation of the Lagrange equations for the system, which are of the form:

$$\frac{d}{dt} \cdot \frac{\partial L}{\partial q'_i} - \frac{\partial L}{\partial q_i} = 0, \quad i = 1, 2, 3 \dots 3N$$

L is defined as the excess of kinetic energy (T) over potential energy (V),

$$L = T - V$$

and the q_i terms are the coordinates of the particle involved.

T can be found in the following manner by using the well known equation for kinetic energy:

$$\begin{aligned} KE &= \frac{1}{2}mv^2 \\ T &= \frac{1}{2} \sum_i m_i (x'_i)^2 \end{aligned}$$

The potential energy is a function of the position of the particle and can be found by expanding a Taylor series centered at $x = 0$.

$$V = V_0 + \sum_i \left(\frac{\partial V}{\partial x_i} \right)_0 x_i + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0 x_i x_j + \dots$$

The potential energy function is assumed to be zero at $x = 0$, thus the V_0 term disappears. In a stable molecule, the equilibrium position at $x = 0$ is a potential minimum, thus the first derivative at this point will be zero and the linear term will also vanish.

$$V = \frac{1}{2} \sum_{i,j} a_{ij} x_i x_j$$

where a_{ij} is a constant and $a_{ij} = a_{ji}$.

These equations can be simplified if the mass is removed from any terms, therefore let $x_i = \frac{y_i}{\sqrt{m_i}}$ and $a_{ij} = \frac{b_{ij}}{\sqrt{m_i m_j}}$ which makes

$$T = \frac{1}{2} \sum_i (y'_i)^2$$

$$V = \frac{1}{2} \sum_{i,j} b_{ij} y_i y_j$$

The next step is to find L , which was defined earlier, and put it into the Lagrange transformation equation.

$$L = \frac{1}{2} \sum_i (y'_i)^2 - \frac{1}{2} \sum_{i,j} b_{ij} y_i y_j$$

$$\frac{d}{dt} \cdot \frac{\partial L}{\partial q'_i} - \frac{\partial L}{\partial q_i} = y''_i + \sum_{j} b_{ij} y_j = 0$$

$$y''_i + \sum_{j} b_{ij} y_j = 0$$

Because the solutions of this equation are usually of the form, $x = a \sin \left(\sqrt{\frac{k}{m}} \right) t$, we can let $y_i = y_i^0 \sin t \left(\sqrt{\lambda} \right)$, which yields:

$$-\lambda y_i^0 \sin \left(t \sqrt{\lambda} \right) + y_i^0 b_{ij} \sin \left(t \sqrt{\lambda} \right) + \sum_j b_{ij} y_j^0 \sin \left(t \sqrt{\lambda} \right) = 0$$

$$\sum_j b_{ij} y_j^0 + y_i^0 b_{ij} - y_i^0 \lambda = 0$$

$$\sum_j b_{ij} y_j^0 + (b_{ij} - \lambda) y_i^0 = 0$$

The results above represent a system of $3N$ equations in terms of y_i^o and λ , which are essentially the amplitudes and frequencies of solutions to the equations of motion. The $b_{ij} - \lambda$ and b_{ij} terms are the coefficients of these equations and can be shown using a matrix such as the one below.

$b_{11} - \lambda$	b_{12}	b_{13}	b_{14}	b_{15}	b_{16}
b_{12}	$b_{22} - \lambda$	b_{23}	b_{24}	b_{25}	b_{26}
b_{13}	b_{23}	$b_{33} - \lambda$	b_{34}	b_{35}	b_{36}
b_{14}	b_{24}	b_{34}	$b_{44} - \lambda$	b_{45}	b_{46}
b_{15}	b_{25}	b_{35}	b_{45}
b_{16}	b_{26}	b_{36}	b_{46}	$b_{ij} - \lambda$

The coefficient matrix above can be a very useful tool. It can be solved for λ by setting the determinant equal to zero to yield $3N$ values for the λ terms in the original equations. Another way that it can be used is to find the relative amplitudes, y_i , of the displacement equations. I decided to do this for my simple system to see how well the method worked.

If the positions of the atoms in the HCl molecule along the bond are x_1 for H and x_2 for Cl, then the equation for the potential energy of the coupled system

would be determined by the distance between the particles, and the following equations can be formed:

$$\begin{aligned} V &= \frac{1}{2}k(x_1 - x_2)^2 \\ V &= \frac{1}{2}kx_1^2 - kx_1x_2 + kx_2^2 \\ T &= \frac{1}{2}m_1(x_1')^2 + \frac{1}{2}m_2(x_2')^2 \end{aligned}$$

If mass is removed from the variables, that is x_i becomes $\frac{x_i}{\sqrt{m_i}}$ and k becomes $\frac{k}{\sqrt{m_i m_j}}$, then the Lagrange transformation will yield the following two equations:

$$\begin{aligned} x_1'' + kx_1 + kx_2 &= 0 \\ x_2'' + kx_1 + kx_2 &= 0 \end{aligned}$$

The k values will represent the b_{ij} terms from the coefficient matrix and the when masses are substituted back, the following matrix will result:

$$\begin{array}{cc} \frac{k}{m_1} - \lambda & \frac{k}{\sqrt{m_1 m_2}} \\ \frac{k}{\sqrt{m_1 m_2}} & \frac{k}{m_2} - \lambda \end{array}$$

If A_1 and A_2 are the amplitudes of solutions to the equations of motion, then the matrix will give the following two equations:

$$\begin{aligned} A_1 \left(\frac{k}{m_1} - \lambda \right) + A_2 \frac{k}{\sqrt{m_1 m_2}} &= A_1 = - \frac{A_2 \frac{k}{\sqrt{m_1 m_2}}}{\left(\frac{k}{m_1} - \lambda - 1 \right)} \\ A_2 \left(\frac{k}{m_2} - \lambda \right) + A_1 \frac{k}{\sqrt{m_1 m_2}} &= A_2 = - \frac{A_1 \frac{k}{\sqrt{m_1 m_2}}}{\left(\frac{k}{m_2} - \lambda - 1 \right)} \end{aligned}$$

When the constants and masses are substituted into one of the equations using the previously determined values, then the ratio of A_1 to A_2 can be determined.

$$\begin{aligned} \frac{\frac{(5.16 \times 10^{-5})}{\sqrt{(1.6737 \times 10^{-24})(5.8871 \times 10^{-23})}}}{\left(\frac{(5.16 \times 10^{-5})}{(1.6737 \times 10^{-24})} - (3.1707 \times 10^{19}) - 1 \right)} &= -5.9267 \\ A_1 &= 5.9267 A_2 \end{aligned}$$

The equations of motion are now defined below, where x_1 is the H atom position and x_2 is the Cl position. When A_2 is set equal to one, a graph of the relative displacements of the atoms can be drawn.

$$\begin{aligned} x_1(t) &\approx 5.9267 A_2 \sin((5.6309 \times 10^9)t) \\ x_2(t) &\approx A_2 \sin((5.6309 \times 10^9)t) \end{aligned}$$

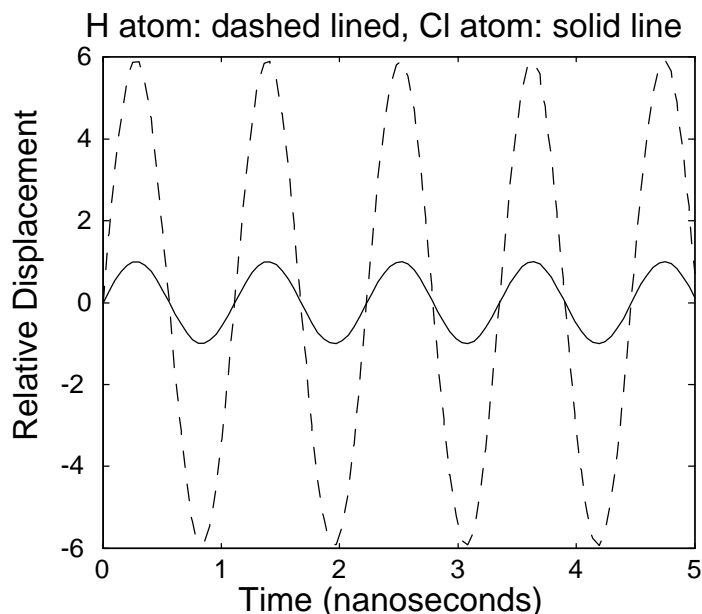


Figure 2:

The graph in Figure 2 is consistent with what one would expect based on the differences in mass of the two atoms. The curve with the large amplitude is obviously the hydrogen atom, which would undergo larger displacements because of its smaller size, and the smaller one is for Cl. Upon determining the relative amplitudes of the displacements, I have come to the conclusion that this is about as far as I can go with this particular system. I will leave the analysis of more complicated systems to people who actually know what they are doing. While working on this project, I tried to analyze some more difficult systems, but the math became too involved for my level of ability. After studying the molecular vibrations and absorption of infrared light by molecules, I have come to the painful conclusion that there is still much more for me to learn about mathematics and physics.

References

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