6.2: Classical Description of the Vibration of a Diatomic Molecule

A classical description of the vibration of a diatomic molecule is needed because the quantum mechanical description begins with replacing the classical energy with the Hamiltonian operator in the Schrödinger equation. It also is interesting to compare and contrast the classical description with the quantum mechanical picture.

The motion of two particles in space can be separated into translational, vibrational, and rotational motions. The internal motions of vibration and rotation for a two-particle system can be described by a single reduced particle with a reduced mass μ located at r.

For a diatomic molecule, Figure $6.2.1$, the vector r corresponds to the internuclear axis. The magnitude or length of r is the bond length, and the orientation of r in space gives the orientation of the internuclear axis in space. Changes in the orientation correspond to rotation of the molecule, and changes in the length correspond to vibration. The change in the bond length from the equilibrium bond length is the normal vibrational coordinate Q for a diatomic molecule.

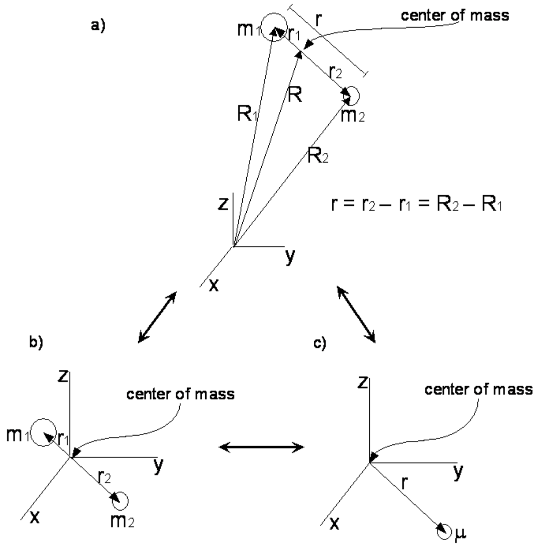

Figure $6.2.1$: The diagram shows the coordinate system for a reduced particle. R_1 and R_2 are vectors to m_1 and m_2. R is the resultant and points to the center of mass. (b) Shows the center of mass as the origin of the coordinate system, and (c) expressed as a reduced particle.

We can use Newton's equation of motion

$$\vec{F} = m\vec{a} \tag{6.2.1}$$

to obtain a classical description of how a diatomic molecule vibrates. In this equation, the mass, m, is the reduced mass μ of the molecule, the acceleration, a, is d^2Q/dt^2, and the force, f, is the force that pulls the molecule back to its equilibrium bond length. If we consider the bond to behave like a spring, then this restoring force is proportional to the displacement from the equilibrium length, which is Hooke's Law

$$F = -kQ \tag{6.2.2}$$

where k is the **force constant**. Hooke's Law says that the force is proportional to, but in opposite direction to, the displacement, Q. The force constant, k, reflects the stiffness of the spring. The idea incorporated into the application of Hooke's Law to a diatomic molecule is that when the atoms move away from their equilibrium positions, a restoring force is produced that increases proportionally with the displacement from equilibrium. The potential energy for such a system increases quadratically with the displacement. (See Exercise $6.2.9$ below.)

$$V(Q) = \frac{1}{2}kQ^2 \tag{6.2.3}$$

Hooke's Law or the harmonic (i.e. quadratic) potential given by Equation 6.2.3 is a common approximation for the vibrational oscillations of molecules. The magnitude of the force constant k depends upon the nature of the chemical bond in molecular systems just as it depends on the nature of the spring in mechanical systems. The larger the force constant, the stiffer the spring or the stiffer the bond. Since it is the electron distribution between the two positively charged nuclei that holds them together, a double bond with more electrons has a larger force constant than a single bond, and the nuclei are held together more tightly. In fact IR and other vibrational spectra provide information about the molecular composition of substances and about the bonding structure of molecules because of this relationship between the electron density in the bond and the bond force constant. Note that a stiff bond with a large force constant is not necessarily a strong bond with a large dissociation energy.

Example 6.2.1

a. Show that minus the first derivative of the harmonic potential energy function in Equation 6.2.3 with respect to Q is the Hooke's Law force.
b. Show that the second derivative is the force constant, k.
c. At what value of Q is the potential energy a minimum; at what value of Q is the force zero?
d. Sketch graphs to compare the potential energy and the force for a system with a large force constant to one with a small force constant.

In view of the above discussion, Equation 6.2.1 can be rewritten as

$$\frac{d^2Q(t)}{dt^2} + \frac{k}{\mu}Q(t) = 0 \tag{6.2.4}$$

Equation 6.2.4 is the equation of motion for a classical harmonic oscillator. It is a linear second-order differential equation that can be solved by the standard method of factoring and integrating as described in Chapter 5.

Example 6.2.2

Substitute the following functions into Equation 6.2.4 to show that they are both possible solutions to the classical equation of motion.

$$Q(t) = Q_0 e^{i\omega t} \text{and} Q(t) = Q_0 e^{-i\omega t} \tag{6.2.5}$$

where

$$\omega = \sqrt{\frac{k}{\mu}} \tag{6.2.6}$$

Note that the Greek symbol ω for frequency represents the angular frequency $2\pi\nu$.

Example 6.2.3

Show that sine and cosine functions also are solutions to Equation 6.2.4.

Example 6.2.4

Using the sine function, sketch a graph showing the displacement of the bond from its equilibrium length as a function of time. Such motion is called **harmonic**. Show how your graph can be used to determine the frequency of the oscillation. Obtain an equation for the velocity of the object as a function of time, and plot the velocity on your graph also. Note that momentum is mass times velocity so you know both the momentum and position at all times.

Example 6.2.5

Identify what happens to the frequency of the motion as the force constant increases in one case and as the mass increases in another case. If the force constant is increased by 9 times and the mass is increased by 4 times, by what factor does the frequency change?

The energy of the vibration is the sum of the kinetic energy and the potential energy. The momentum associated with the vibration is

$$P_Q = \mu \frac{dQ}{dt} \tag{6.2.7}$$

so the energy can be written as

$$E = T + V = \frac{P_Q^2}{2\mu} + \frac{k}{2} Q^2 \tag{6.2.8}$$

Example 6.2.6

What happens to the frequency of the oscillation as the vibration is excited with more and more energy? What happens to the maximum amplitude of the vibration as it is excited with more and more energy?

Example 6.2.7

If a molecular vibration is excited by collision with another molecule and is given a total energy E_{hit} as a result, what is the maximum amplitude of the oscillation? Is there any constraint on the magnitude of energy that can be introduced?

We can generalize this discussion to any normal mode in a polyatomic molecule. The normal coordinate associated with a normal mode can be thought of as a vector Q, with each component giving the displacement amplitude of a particular atom in a particular direction. Equation 6.2.4 then applies to the length of this vector $Q = |Q|$. As Q increases, it means the displacements of all the atoms that move in that normal mode increase, and the restoring force increases as well.
