

4.1: The Potential Energy Surface for a Diatomic Molecule

5.2: The Equation for a Harmonic-Oscillator Model of a Diatomic Molecule Contains the Reduced Mass of the Molecule Consider the **potential energy surface** for a diatomic molecule. The functional form can be seen in the following graph.

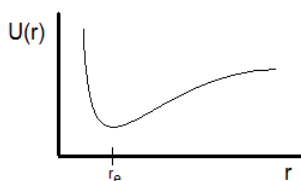


Figure 4.1.1

In the surface, it is easy to see the “hard wall” on the left side, where the repulsive force between atoms is strong (which is why the curve is so steep) and the “soft wall” on the right side of the well, where the restorative force of the chemical bond exists. The bond length at the potential minimum is indicated by r_e , the equilibrium bond length.

The function can be expressed as a [Taylor series expansion](#). For convenience, we can define $x = (r - r_e)$. We will also define the zero of energy to be the bottom of the potential well. Given these definitions and the Taylor expansion about $x = 0$ which can be expressed by

$$U(x) = U(0) + \left. \frac{d}{dx} U(x) \right|_{x=0} (x) + \frac{1}{2} \left. \frac{d^2}{dx^2} U(x) \right|_{x=0} (x^2) + \frac{1}{6} \left. \frac{d^3}{dx^3} U(x) \right|_{x=0} (x^3) + \dots$$

We can evaluate these terms qualitatively based on the above diagram and the definitions provided above. The first two terms of the expansion are zero, by the choice of the zero of energy and because the derivative is zero at the potential minimum. The third and fourth terms are simplified by making the following substitutions

$$\left. \frac{d^2}{dx^2} U(x) \right|_{x=0} \equiv k \text{ and } \left. \frac{d^3}{dx^3} U(x) \right|_{x=0} \equiv \gamma$$

The new function can be rewritten as

$$U(x) = \frac{1}{2} k x^2 + \frac{1}{6} \gamma x^3 + \dots$$

And if the series is truncated at the x^2 term, it yields the familiar Harmonic Oscillator potential energy function that corresponds to a Hook’s Law oscillator.

$$U(x) = \frac{1}{2} k x^2$$

Transforming to Center of Mass Coordinates

Consider a diatomic molecule that can be modeled as two masses (m_1 and m_2) attached by a spring that has a force constant k . The location of atom 1 is z_1 and that of atom 2 is z_2 . The equilibrium length of the spring is r_e .

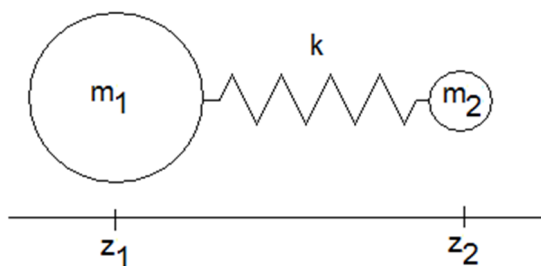


Figure 4.1.2

The force acting on either atom can be expressed in two ways.

$$F = ma$$

and

$$F = -kx$$

where m is either m_1 or m_2 and x is the displacement from the equilibrium distance, given by

$$x = (z_2 - z_1 - r_e)$$

The force acting on atom 1 is in the opposite direction of that acting on atom 2. This suggests two equations that will govern the motion of atom 1 and atom 2 respectively.

$$m_1 \frac{d^2}{dt^2} z_1 = k(z_2 - z_1 - r_e) \quad \text{and} \quad -m_2 \frac{d^2}{dt^2} z_2 = k(z_2 - z_1 - r_e)$$

Dividing both equations by the masses yields the following pair of equations.

$$\frac{d^2}{dt^2} z_1 = \frac{k}{m_1} (z_2 - z_1 - r_e) \quad \text{and} \quad -\frac{d^2}{dt^2} z_2 = \frac{k}{m_2} (z_2 - z_1 - r_e)$$

Add these two equations yields

$$\frac{d^2}{dt^2} z_1 - \frac{d^2}{dt^2} z_2 = \left(\frac{1}{m_1} + \frac{1}{m_2} \right) k (z_2 - z_1 - r_e)$$

The term $\left(\frac{1}{m_1} + \frac{1}{m_2} \right)$ has important significance, as it is the reciprocal of the reduced mass.

$$\begin{aligned} \left(\frac{1}{m_1} + \frac{1}{m_2} \right) &= \frac{m_1 + m_2}{m_1 m_2} = \frac{1}{\mu} \\ \mu &= \frac{m_1 m_2}{m_1 + m_2} \end{aligned}$$

The reduced mass is introduced as a consequence of moving to center of mass coordinates. It is the mass of a single object that would move with the same frequency of oscillation were it attached to a fixed point by a spring of the same force constant. It is important to note that μ has units of mass. Also, in the limit that m_1 and m_2 have the same value (let's call it m_1)

$$\begin{aligned} \mu &= \frac{m_1 m_1}{m_1 + m_1} \\ &= \frac{m_1^2}{2m_1} = \frac{m_1}{2} \end{aligned}$$

This result makes a great deal of sense because for equal masses, the motion of the molecule will involve equal and opposite motions of the two atoms relative to the center of mass (which will be the middle of the bond.) Thus, a single mass oscillating with the same frequency is moving relative to a distance that is in the middle of the spring. Hence, the mass will have to be half of the mass of one of the atoms, or the frequency would be different.

The other important limit is when one mass is significantly larger than the other. Consider what happens when $m_1 \gg m_2$

$$\begin{aligned} \mu &= \frac{m_1 m_2}{m_1 + m_2} \\ &\approx \frac{m_1 m_2}{m_1} = m_2 \end{aligned}$$

This result makes a great deal of sense because if one mass is significantly larger than the other, it will be the light atom that undergoes the larger motion. In the limit that $m_1 = \infty$, the center of mass is located at z_1 and the heavy atom becomes a fixed point in the motion.

The next task is to simplify things further by introducing a mass-weighted coordinate, Z .

$$Z \equiv \frac{m_1 z_1 + m_2 z_2}{m_1 + m_2}$$

This expression gives the location of the center of mass of the molecule. The utility of this substitution is found in taking the difference of the two equations

$$m_1 \frac{d^2}{dt^2} z_1 = k(z_2 - z_1 - r_e) \quad \text{and} \quad -m_2 \frac{d^2}{dt^2} z_2 = k(z_2 - z_1 - r_e)$$

which yields

$$\begin{aligned} m_1 \frac{d^2}{dt^2} z_1 + m_2 \frac{d^2}{dt^2} z_2 &= 0 \\ \frac{d^2}{dt^2} (m_1 z_1 + m_2 z_2) &= 0 \end{aligned}$$

Dividing both sides by $(m_1 + m_2)$ yields

$$\begin{aligned} \left(\frac{1}{m_1 + m_2} \right) \frac{d^2}{dt^2} (m_1 z_1 + m_2 z_2) &= 0 \\ \frac{d^2}{dt^2} \left(\frac{m_1 z_1 + m_2 z_2}{m_1 + m_2} \right) &= 0 \end{aligned}$$

Finally, making the substitution for the center of mass

$$\frac{d^2}{dt^2} Z = 0$$

which tells us that the center of mass of the system does not move in time.

This page titled [4.1: The Potential Energy Surface for a Diatomic Molecule](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by [Patrick Fleming](#).