Lecture 28

Motions of Polyatomic Molecule - Normal Mode

Study Goal of This Lecture

- Normal mode analysis

28.1 Polyatomic Molecule

In previous lecture, we talk about the rot-vibration spectrum of diatomic molecule. In this lecture we are going to introduce the motion of polyatomic molecule. Recall that there are 3 translational, 3(2) rotational and $3N-6(3N-5)$ vibrational mode for non-linear(linear) N-atoms molecule. How do we know and how to find out those motion? We have to introduce the technique of normal mode analysis.

28.1.1 Normal Mode Analysis

As we apply Born-Oppenheimer approximation to seperate the nuclear part and electronic part wavefunction of the molecule, we say that we can seen as that motions of the atom(specifically, nuclear) are on the potential energy surface. Now supposed the molecule is in its equlibrium structure, it also means that it is in the local minimum of the potential energy surface, then recall what we were taught in introducing "why learn the harmonic oscillator", it is naturally for us to investigate the small motions around the minumum via quadratic approximation.

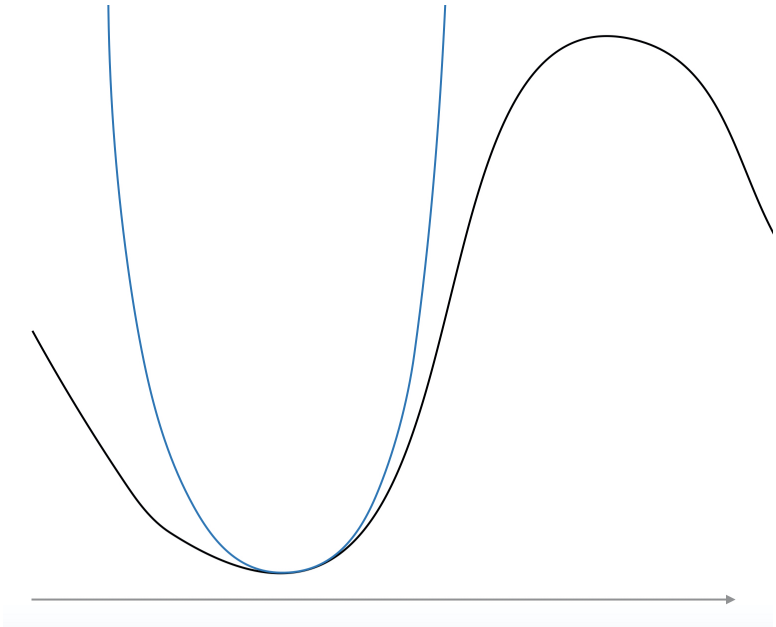

Figure 28.1: Quadratic Approximation. Harmonic approximation always good around minimal.

We can use "independent" vibrational mode to describe the motions! This technique is called normal mode analysis.

Consider the Hamiltonian:

$$\begin{aligned}
\hat{H} &= \hat{T} + \hat{V} \\
&= \sum_{i}^{3N} \frac{\hat{P}_i^2}{2M_i} + \hat{V} \\
&= \sum_{i}^{3N} \frac{\hat{P}_i^2}{2M_i} + \Big\{ \cancelto{0}{V(\vec{r}_0)} + \sum_{i}^{3N} \cancelto{0}{\frac{\partial V}{\partial x_i}\Big|_{\vec{r}=\vec{r}_0}} (x_i - x_{i;0}) \\
&+ \sum_{i,j}^{3N} \frac{1}{2} \frac{\partial^2 V}{\partial x_i \partial x_j}\Big|_{\vec{r}=\vec{r}_0} (x_i - x_{i;0})(x_j - x_{j;0}) \Big\} \\
&= \sum_{i}^{3N} \frac{\hat{P}_i^2}{2M_i} + \sum_{i,j}^{3N} \frac{1}{2} \frac{\partial^2 V}{\partial x_i \partial x_j}\Big|_{\vec{r}=\vec{r}_0} (x_i - x_{i;0})(x_j - x_{j;0}) \\
&= \sum_{i}^{3N} \frac{\hat{P}_i^2}{2M_i} + \sum_{i,j}^{3N} \frac{1}{2} k_{ij} (x_i - x_{i;0})(x_j - x_{j;0})
\end{aligned} \tag{28.1}$$

Since we expand the potential around the equilibrium, the first derivatives are zero and we also can set the absolute potential be zero (It will not affect the calculation).

Now we focus on the force constant, and write it in the matrix form. (It has a name termed Hessian matrix.)

$$(V'')_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j}\Big|_{\vec{r}=\vec{r}_0} \tag{28.2}$$

The normal mode analysis requires that we use forces in the "mass-weighted coordinate"

$$q_i = \sqrt{m_i} x_i. \tag{28.3}$$

Then

$$F = M^{-1/2} V'' M^{-1/2} \tag{28.4}$$

where

$$M = \begin{pmatrix} m_1 & 0 & 0 & 0 \\ 0 & m_2 & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & m_{3N} \end{pmatrix}, \tag{28.5}$$

$$M^{-1/2} = \begin{pmatrix} m_1^{-1/2} & 0 & 0 & 0 \\ 0 & m_2^{-1/2} & 0 & 0 \\ 0 & 0 & \ddots & 0 \\ 0 & 0 & 0 & m_{3N}^{-1/2} \end{pmatrix}. \tag{28.6}$$

Finally, we diagonize the matrix F

$$FQ_i = k_i Q_i, \tag{28.7}$$

it yields the eigenvectors and eigenvalues.

If V'' is defined in 3N Cartesian coordinates, then six of them will be zero. This correspond to three translational and three rotational motions. For other modes, the frequencies are

$$\nu_i = \frac{\sqrt{k_i}}{2\pi} \tag{28.8}$$

k_i is already mass-wighted.

and the Q_i vector is the displacement corresponding to the "motion" of the mode.

28.1.2 Example: Coupled String

Let's consider a simple system of 1-D coupled string, i.e. 3-atom molecule in 1-D. The potential is

$$V = \frac{1}{2}k(x_2 - x_1 - l_0)^2 + \frac{1}{2}k(x_3 - x_2 - l_0)^2 \tag{28.9}$$

therefore,

$$\begin{aligned}
\frac{\partial V}{\partial x_1} &= -k(x_2 - x_1 - l_0), \\
\frac{\partial V}{\partial x_2} &= k(x_2 - x_1 - l_0) - k(x_3 - x_2 - l_0), \\
\frac{\partial V}{\partial x_3} &= k(x_3 - x_2 - l_0).
\end{aligned} \tag{28.10}$$

So

$$V'' = \begin{pmatrix} k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{pmatrix}, \tag{28.11}$$

$$M^{1/2} = \begin{pmatrix} \frac{1}{\sqrt{m_1}} & 0 & 0 \\ 0 & \frac{1}{\sqrt{m_2}} & 0 \\ 0 & 0 & \frac{1}{\sqrt{m_3}} \end{pmatrix}, \tag{28.12}$$

thus

$$F = \begin{pmatrix} \frac{k}{m_1} & -\frac{k}{\sqrt{m_1 m_2}} & 0 \\ -\frac{k}{\sqrt{m_1 m_2}} & \frac{2k}{m_2} & \frac{-k}{\sqrt{m_1 m_2}} \\ 0 & \frac{-k}{\sqrt{m_1 m_2}} & \frac{k}{m_3} \end{pmatrix}. \tag{28.13}$$

Solving the seqular equation:

$$|F - \lambda I| = 0, \tag{28.14}$$

$$\begin{vmatrix} \frac{k}{m_1} - \lambda & \frac{-k}{\sqrt{m_1 m_2}} & 0 \\ \frac{k}{\sqrt{m_1 m_2}} & \frac{2k}{m_2} - \lambda & \frac{-k}{\sqrt{m_1 m_2}} \\ 0 & \frac{-k}{\sqrt{m_1 m_2}} & \frac{k}{m_1} - \lambda \end{vmatrix} = 0 \tag{28.15}$$

the equation leads to

$$\begin{aligned}
\lambda_1 = \frac{k}{m_1}, Q_1 &\sim \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \\
\lambda_2 = 0, Q_2 &\sim \begin{pmatrix} 1 \\ \sqrt{\frac{m_2}{m_1}} \\ 1 \end{pmatrix} \\
\lambda_3 = \frac{m_1 + m_2}{m_1 m_2} \times k, Q_3 &\sim \begin{pmatrix} 1 \\ -2\sqrt{\frac{m_1}{m_2}} \\ 1 \end{pmatrix}
\end{aligned} \tag{28.16}$$

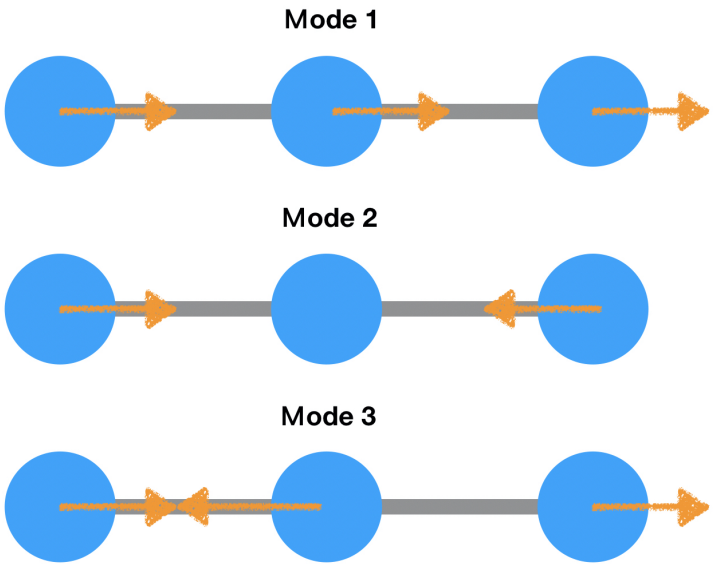

Figure 28.2: Normal Mode of three atoms in 1-D.

We can see λ_i are the new force constant of each mode and the vector tells us how each atom moves. The second mode is the translational motion.

Results of normal mode analysis are useful for

1. Vibrational spectroscopy
2. Indentify stable structures
3. Thermodynamic data