Chem237: Lecture 15

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1 Classical Normal Mode Analysis

1.1 Harmonic Approximation

We start by writing the hamiltonian for our system of interest with N degrees of freedom,

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + V(r_1, \ldots, r_N) \tag{1}$$

where our coorindate vector is $\mathbf{r} = \begin{bmatrix} r_1 \\ \vdots \\ r_N \end{bmatrix}$. We can invoke the **Harmonic approximation**, which says that the potential $V(\mathbf{r})$ can be expressed as a taylor expansion about a minimum r_o

$$V(r) = V(r_o) + \sum_j \Big(\frac{\partial V}{\partial r_j}\Big)(r - r_o) + \frac{1}{2}\sum_{ij} r_i K_{ij} r_j + \ldots \tag{2}$$

where $\mathbf{K}$ is called the **Hessian** and is defined as

$$k_{ij} = \frac{\partial^2 V}{\partial r_i r_j}. \tag{3}$$

Since our potential is expanded about a minimum, we can say that $\frac{\partial V(r_o)}{\partial r_i} = 0$. If we neglect higher order terms and assume that $V(r_o) \approx 0$, then we obtain an approximate potential

$$V(r) \approx \frac{1}{2}\sum_{ij} r_i K_{ij} r_j. \tag{4}$$

The hamiltonian can then be written in terms of matrices as

$$\mathbf{H} \approx \frac{1}{2}\mathbf{P}^T\mathbf{M}^{-1}\mathbf{P} + \frac{1}{2}\mathbf{r}^T\mathbf{K}\mathbf{r} \tag{5}$$

We have effectively turned our system into one where each degree of freedom can be approximated as a harmonic oscillator. The equations of motion for each degree of freedom can be solved by using Hamilton's equations:

$$\begin{aligned} \dot{p}_i &= -\frac{\partial H}{\partial r_i} \\ \dot{r}_i &= \frac{\partial H}{\partial p_i} \end{aligned} \tag{6}$$

However, this can be difficult when we have a system of coupled oscillators.

1.2 Normal Mode Coordinates

One way to get around this problem is by transforming our original coordinates into a set of normal mode coordinates. This decouples all of our degrees of freedom and turns our system into one of N independent harmonic oscillators, each with a normal mode frequency ω_i. If our mass matrix $\mathbf{M}$ is not diagonal, we could perform an eigenvalue

decomposition and use the corresponding eigenvectors to find a diagonal matrix for $\mathbf{M}$, which would just be a matrix of its eigenvalues. Instead, we will introduce mass scaled coordinates to get rid of our mass matrix from the hamiltonian. These coordinates can be defined as:

$$\begin{aligned} r_i' = \sqrt{m_i} r_i \quad &\iff \quad \mathbf{r}' = \mathbf{M}^{1/2}\mathbf{r} \\ p_i' = \frac{1}{\sqrt{m_i}} p_i \quad &\iff \quad \mathbf{P}' = \mathbf{M}^{-1/2}\mathbf{P} \\ K_{ij}' = \frac{1}{\sqrt{m_i m_j}} K_{ij} \quad &\iff \quad \mathbf{K}' = \mathbf{M}^{-1/2}\mathbf{K}\mathbf{M}^{1/2} \end{aligned} \tag{7}$$

So H becomes,

$$H = \frac{1}{2}\mathbf{K}'^{T}\mathbf{K} + \frac{1}{2}\mathbf{r}'^{T}\mathbf{K}'\mathbf{r}' \tag{8}$$

where $\mathbf{K}$' is now our mass-scaled Hessian.

1.3