MOLECULAR VIBRATIONS

Here we wish to investigate molecular vibrations and draw a similarity between the theory of molecular vibrations and Hückel theory.

1. SIMPLE HARMONIC OSCILLATOR

Recall that the energy of a one-dimensional harmonic oscillator is given by the sum of the kinetic and potential energy. Suppose a particle of mass m is moving in a potential given by $V(x) = \frac{1}{2}kx^2$ in one-dimension, then, the Hamiltonian is given by

$$H = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2 \tag{1}$$

where the first term is the kinetic energy and the second the potential energy.

Classically, the particle obeys Newton's Law, which states that:

$$m\ddot{x} = -\frac{dV}{dx} \tag{2}$$

giving rise to the following equation of motion upon substituting the form of the potential $V(x) = \frac{1}{2}kx^2$:

$$m\ddot{x} = -kx \tag{3}$$

which solves to give oscillatory solutions having the form of sin, cos or exponential. We could choose the cosine form:

$$x(t) = A\cos(\omega t + \phi) \tag{4}$$

where A and ϕ are constants determined by initial conditions (since Eq. (3) is a second-order differential equation, we expect two constants here) and ω is the *angular frequency* given by

$$\omega = \sqrt{\frac{k}{m}} \tag{5}$$

Using Eq. (5), we could write the Hamiltonian as

$$H = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}m\omega^2 x^2 \tag{6}$$

2. Diatomic molecule

Now, consider a diatomic molecule having atoms with masses m_1 and m_2 interacting through a harmonic potential described with a force constant k. Assuming that the motion of the two nuclei is confined to one dimension, the Hamiltonian of the problem becomes

$$H = \frac{1}{2}\sum_i m_i \dot{x_i}^2 + \frac{1}{2}k(x_1 - x_2)^2 \tag{7}$$

where x_1 and x_2 are the displacement coordinates relative to the equilibrium geometry of the molecule (Fi. 1).

Figure 1. Displacement coordinates of a diatomic molecule.

We first introduce a *mass-weighted* coordinate:

$$q_i = \sqrt{m_i}x_i \tag{8}$$

to remove any explicit mass dependence from Eq. (7):

$$\begin{aligned}
H &= \frac{1}{2}\sum_i \dot{q_i}^2 + \frac{1}{2}k\left(\frac{q_1}{\sqrt{m_1}} - \frac{q_2}{m_2}\right)^2 \\
&= \cdots + \frac{1}{2}\left(\frac{k}{m_1}q_1^2 - 2\frac{k}{\sqrt{m_1 m_2}}q_1 q_2 + \frac{k}{m_2}q_2^2\right)^2 \\
&= \frac{1}{2}\sum_i \dot{q_i}^2 + \frac{1}{2}\sum_{ij} q_i K_{ij} q_j
\end{aligned} \tag{9}$$

where K is the *dynamical* or *Hessian matrix* given, in this case, by

$$\mathbf{K} = \begin{pmatrix} \dfrac{k}{m_1} & -\dfrac{k}{\sqrt{m_1 m_2}} \\ -\dfrac{k}{\sqrt{m_1 m_2}} & \dfrac{k}{m_2} \end{pmatrix} \tag{10}$$

We can find the eigenvalues and eigenvectors of the dynamical matrix K by solving

$$|\mathbf{K} - \lambda\mathbf{I}| = 0 \tag{11}$$

The solutions can be written as

$$\sum_j K_{ij}c_j^{(n)} = \lambda_n c_i^{(n)} \tag{12}$$

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where the superscript n refers to the nth normailsed eigenvector, and λ_n the corresponding eigenvalue.

Since the matrix $\mathbf{K}$ is Hermitian (indeed $\mathbf{K}$ is symmetric since all its components are real), their eigenvectors are orthogonal, we can also normalised them to give orthonormal eigenvectors:

$$\sum_i c_i^{(n)} c_i^{(m)} = \delta_{mn} \tag{13}$$

Now we wish to find *normal mode coordinates*, Q_i, in terms of (a linear combination of) scaled atomic displacements q_i, such that these normal modes are *decoupled* from each other and can be analysed separately. Expressed more formally, we wish to be able to write the Hamiltonian in Eq. (9) in a *diagonal* form:

$$H = \sum_i \left(\frac{1}{2} \dot{Q}_i^2 + \frac{1}{2} \omega_i^2 Q_i^2 \right). \tag{14}$$

Since the Hamiltonian Eq. (9) contains the atomic displacements q_i, we consider the following *coordinate transform*:

$$q_i = \sum_n c_i^{(n)} Q_n \tag{15}$$

i.e., writing the scaled coordinates as a linear combination of the normal mode coordinates, where the coefficients $c_i^{(n)}$ is the ith component of the nth normalised eigenvector from Eq. (12).

Substituting this into the Hamiltonian of the system Eq. (9), we have

$$\begin{aligned}
H &= \frac{1}{2} \sum_i \dot{q_i}^2 + \frac{1}{2} \sum_{ij} q_i K_{ij} q_j \\
&= \frac{1}{2} \sum_i \left[\sum_n c_i^{(n)} \dot{Q}_n \right] \left[\sum_m c_i^{(m)} \dot{Q}_m \right] + \frac{1}{2} \sum_{ij} \left[\sum_n c_i^{(n)} Q_n \right] K_{ij} \left[\sum_m c_i^{(m)} Q_m \right] \\
&= \frac{1}{2} \sum_{mn} \dot{Q}_n \left[\sum_i c_i^{(n)} c_i^{(m)} \right] \dot{Q}_m + \frac{1}{2} \sum_{mn} \left[\sum_{ij} c_i^{(n)} K_{ij} c_i^{(m)} \right] Q_m \\
&= \frac{1}{2} \sum_{mn} \dot{Q}_n \delta_{mn} \dot{Q}_m + \frac{1}{2} \sum_{mn} \lambda_m \delta_{mn} Q_m \\
&= \frac{1}{2} \sum_n \dot{Q}_n^2 + \frac{1}{2} \sum_n \lambda_n Q_n^2 \tag{16}
\end{aligned}$$

where in achieving the second last line, we used the equations from Eq. (12) and (13). This now indeed has the diagonal form of Eq. (14) in which we identify the eigenvalues from solving the dynamical matrix as

$$\lambda_n = \omega_n^2 \tag{17}$$

At this stage, after solving for the eigenvalues and the eigenvectors of the dynamical matrix, we are finally able to write the normal mode coordinates as a linear combination of the (scaled) atomic displacements. We have the coordinate transform Eq. (15), left multiply by transpose of another eigenvector and using the orthonormality condition of Eq. (13), we have

$$\sum_i c_i^{(m)} q_i = \sum_i c_i^{(m)} \sum_n c_i^{(n)} Q_n = \sum_n \left[\sum_i c_i^{(m)} c_i^{(n)} \right] Q_n = \sum_n \delta_{mn} Q_n = Q_m$$

$$\Leftrightarrow \qquad Q_n = \sum_i c_i^{(n)} q_i \qquad \text{(free relabelling of } m \to n) \tag{18}$$

Now, the above equation write the normal mode coordinates as a linear combination of the mass-scaled atomic displacements so that each normal mode is decoupled from the other normal modes (Ref Eq. 16). To solve the system of molecular motions for the diatomic system, one is then required to solve the diagonalisation of the dynamical matrix in Eq. (10). This is left to the readers as a simple exercise.

3. Generalisation to polyatomics

Consider a molecule consisting of N atoms. Classically, the Hamiltonian for molecular vibrations has the general form

$$H = -\frac{1}{2} \sum_i^{3N} m_i \dot{R}_i^2 + V(\mathbf{R}) \tag{19}$$

where $\mathbf{R}_i$ is the position vector for atom i, m_i is the mass of the atom with components R_i ($i = 1, \cdots, 3N$). The positions of all nuclei can be written as

$$\mathbf{R} \equiv \{\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N\} \tag{20}$$

The quantum expression is given instead by

$$\hat{H} = \frac{1}{2} \sum_i \frac{1}{m_i} \hat{p}^2 + V(\mathbf{R}) = -\frac{1}{2} \sum_i \frac{1}{m_i} \frac{\partial^2}{\partial R_i^2} + V(\mathbf{R}) \tag{21}$$

However, we will note that using the mass-weighted coordinate in Eq. (8), we can get the dynamical matrix using the potential term $V(\mathbf{R})$ alone.

Suppose the molecule is at equilibrium geometry, denoted by

$$\mathbf{R}^{(0)} \equiv \{\mathbf{R}_1^{(0)}, \mathbf{R}_2^{(0)}, \cdots, \mathbf{R}_N^{(0)}\}, \tag{22}$$

we can define any nuclear motions relative to the equilibrium geometry by

$$\mathbf{R}_i = \mathbf{R}_i^{(0)} + \mathbf{x_i} \tag{23}$$

where $\mathbf{x_i}$ is a collection of 3 coordinate displacements for nucleus i:

$$\mathbf{x_i} = (x_1, x_2, x_3). \tag{24}$$

The condition for equilibrium geometry for a molecule is given by

$$\left(\frac{\partial V}{\partial x_i}\right)_0 = 0 \tag{25}$$

where the subscript 0 denotes that the partial derivatives are evaluated at equilibrium geometry. For small-amplitude displacements around the equilibrium, we can Taylor-expand the potential energy as

$$V(\mathbf{R}) = V_0 + \frac{1}{2}\sum_{ij}\left(\frac{\partial^2 V}{\partial x_i \partial x_j}\right)_0 x_i x_j + \text{cubic terms } x_i x_j x_k + \cdots \tag{26}$$

where $V_0 = V(\mathbf{R}^{(0)})$. Note that the linear term vanishes due to equilibrium condition.

In the harmonic approximation, the Taylor expansion above is truncated after the quadratic terms. Comparing the quadratic term above with the potential energy term (the second term) in Eq. (9), and using the mass-weighted coordinates in Eq. (8), we can see that[1] the dynamical matrix is given by

$$K_{ij} = \frac{1}{\sqrt{m_i m_j}}\left(\frac{\partial^2 V}{\partial x_i \partial x_j}\right)_0 \tag{27}$$

$$= \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0 \tag{28}$$

We now have a general method for solving for normal modes of a system with a potential energy V. We can construct the dynamical matrix from it using Eq. (28). We then solve for its eigenvalues and eigenvectors to give the (square) of the vibrational frequencies (Eq. 17) and the normal mode coordinates (Eq. 18). This is indeed the same approach we use in solving the Hückel secular equations. Of course, symmetry could be used to simplify the solving of these matrices.

4. Parallels between Hückel theory and molecular vibrations analysis

Although the two areas appear to be very different, in actual fact, the ways to solve these problems are very similar. We note the following resemblance between Hückel theory and molecular vibrations analysis:

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[1]you could do a change of variable differentiation by using chain rule

Hückel Theory	Molecular Vibrations
atomic orbitals, ϕ_i	mass-weighted coordinates, q_i
molecular orbitals, ψ_i	normal mode coordinates, Q_n
Hückel matrix, H_{ij}	dynamical matrix, K_{ij}
orbital energies, ϵ_n	squared frequencies, ω_n^2
symmetry orbitals, θ_Γ	symmetry-adapted linear combination of displacements, Q_Γ

TABLE 1. Close resemblance between Hückel theory and molecular vibrations.