Normal Coordinate Analysis and the Vibrational Spectrum

T. Daniel Crawford, *Virginia Tech*

This document outines the fundamental theory and algorithmic steps for calculating the vibrational spectrum of a polyatomic molecule. The essential theoretical step is the transformation of the kinetic and potential energy operators from simple Cartesian displacement coordinates to so called "normal coordinates" (linear combinations of mass-weighted displacement coordinates), in which the Hamiltonian may be written as a sum of independent harmonic oscillators. We use a notation based on that used in the text, *Molecular Vibrations*, by Wilson, Decius, and Cross, McGraw-Hill, 1955.

I. Fundamental Theory

Given an equilibrium molecular structure consisting of N atoms with Cartesian coordinates of the i-th atom, a_i, b_i, c_i, we may define corresponding displacement coordinates for the i-th atom as

$$\Delta x_i \equiv x_i - a_i \qquad \Delta y_i \equiv y_i - b_i \qquad \Delta z_i \equiv z_i - c_i$$

In this coordinate system, the kinetic energy operator of the atoms becomes

$$\hat{T} = -\frac{\hbar^2}{2} \sum_{i=1}^{N} \frac{1}{m_i} \left\{ \frac{\partial^2}{\partial \Delta x_i^2} + \frac{\partial^2}{\partial \Delta y_i^2} + \frac{\partial^2}{\partial \Delta z_i^2} \right\}$$

We may remove the explicit dependence of this operator on the atomic masses, $\{m_i\}$, by converting to $3N$ mass-weighted cartesian displacement coordinates, defined as

$$q_1 \equiv \sqrt{m_1}\Delta x_1 \qquad q_2 \equiv \sqrt{m_1}\Delta y_1 \qquad q_3 \equiv \sqrt{m_1}\Delta z_1 \qquad q_4 \equiv \sqrt{m_2}\Delta x_2 \dots$$

The kinetic energy operator then becomes

$$\hat{T} = -\frac{\hbar^2}{2} \sum_{i}^{3N} \frac{\partial^2}{\partial q_i^2}.$$

The potential energy operator, $\hat{V}$, is often too complicated to represent analytically for all values of the $\{q_i\}$ because that would require constructing the complete potential energy hypersurface, i.e. solving (approximately) the electronic Schrödinger equation across all possible coordinates. If instead we limit our analysis to only "small" displacements, then we may represent $\hat{V}$ has a Taylor expansion about the equilibrium geometry, *viz.*,

$$\hat{V} = V_0 + \sum_{i}^{3N} \left(\frac{\partial V}{\partial q_i} \right)_0 q_i + \frac{1}{2} \sum_{i,j}^{3N} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 q_i q_j + \dots,$$

where the subscript 0 denotes the equilibrium geometry. The leading V_0 term may be eliminated by redefining the zero of energy, and the first-derivatives are zero because the equilibrium geometry is, by definition, stationary. If we further assume that terms beyond the quadratic contribution are neglible (the *harmonic* approximation), the potential becomes

$$\hat{V} = \frac{1}{2} \sum_{i,j}^{3N} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 q_i q_j = \frac{1}{2} \sum_{i,j}^{3N} F_{ij} q_i q_j,$$

where the matrix of second-derivatives (known as the "mass-weighted Hessian matrix")

$$F_{ij} \equiv \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0.$$

We may choose a new coordinate system – the "normal" coordinate system – defined as that which diagonalizes the mass-weighted Hessian:

$$Q_i \equiv \sum_j^{3N} L_{ji} q_j,$$

where

$$\mathbf{FL} = \mathbf{L\Lambda},$$

i.e., the columns of the $\mathbf{L}$ matrix are the eigenvectors of $\mathbf{F}$, and Λ is a diagonal matrix of the eigenvalues of $\mathbf{F}$. Furthermore, it may be shown (see Wilson, Decius, and Cross), that six of these eigenvalues (five for linear molecules) are zero and that the corresponding normal coordinates represent rotations and translations. Eliminating these, the *vibrational* Schrödinger equation becomes

$$\left[-\frac{\hbar^2}{2} \sum_i^{3N-6} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \sum_i^{3N-6} \lambda_i Q_i^2 \right] \Psi_{\mathrm{v}} = E_{\mathrm{v}} \Psi_{\mathrm{v}}.$$

The vibrational Hamiltonian is simply a sum of independent harmonic oscillator Hamiltonians, each of which is a function of a different Q_i. Thus, the total vibrational wave function is a product of $3N - 6$ harmonic oscillator wave functions, each of which depends on a quantum number υ_i,

$$\Psi_{\mathrm{v}} = \prod_i^{3N-6} \left(\frac{1}{2^{\upsilon_i} \upsilon_i!} \right)^{1/2} \left(\frac{\alpha_i}{\pi} \right)^{1/4} e^{-\frac{1}{2}\alpha_i Q_i^2} H_{\upsilon_i}(\sqrt{\alpha_i} Q_i),$$

where H_{υ_i} denotes the υ_i-th Hermite polynomial and

$$\alpha_i \equiv \frac{\sqrt{\lambda_i}}{\hbar}.$$

The total vibrational energy is a sum of harmonic oscillator energies,

$$E_{\mathrm{v}} = \sum_i^{3N-6} \varepsilon_i = \sum_i^{3N-6} \hbar\omega_i \left(\upsilon_i + \frac{1}{2} \right),$$

where $\omega_i \equiv \sqrt{\lambda_i}$ is the (harmonic) vibrational frequency of the *i*-th normal mode.

II. Basic Normal Coordinate Analysis Algorithm

1. Read the geometry from the `geom.dat` file, just as in Project #1.

2. Read the Hessian matrix from `hessian.dat`. The integer on the first line is the number of atoms, while the remaining values represent the second-derivatives of the potential energy (the sum of the electronic and nuclear repulsion energies) with respect to the (non-mass-weighted) Cartesian coordinates of the atoms,

$$F_{ij} = \frac{\partial^2 V}{\partial q_i \partial q_j},$$

given in atomic units (E_h/a_0^2). The file contains $(3N)^2$ entries, and the data are ordered in three columns, *viz.*,

$$
\begin{array}{ccc}
F_{x_1,x_1} & F_{x_1,y_1} & F_{x_1,z_1} \\
F_{x_1,x_2} & F_{x_1,y_2} & F_{x_1,z_2} \\
& \cdots & \\
F_{x_2,x_1} & F_{x_2,y_1} & F_{x_2,z_1} \\
& \cdots &
\end{array}
$$

3. Mass-weight the Hessian matrix:

$$F_{ij}^M = \frac{F_{ij}}{\sqrt{m_i m_j}}$$

where m_i represents the atomic mass of the atom corresponding to coordinate i. Use atomic mass units (u).

4. Diagonalize the mass-weighted Hessian:

$$\mathbf{F}^M \mathbf{L} = \mathbf{L} \mathbf{\Lambda}$$

5. Calculate the harmonic vibrational frequencies in cm^{-1}:

$$\omega_i = \text{constant} \times \sqrt{\lambda_i}.$$