## Advanced Quantum Mechanics & Spectroscopy (CHEM 7520)

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## Week 4-6: Vibrations of polyatomic molecules

## I. CLASSICAL MECHANICS OF MOLECULAR VIBRATIONS

1) We have discussed that the nuclear motion can be separated into translational, rotational, and vibrational motions. If the molecule has *N* nuclei, then the nuclear wavefunction is a function of 3*N* coordinates. The translational wavefunction depends on three coordinates that define the position of the center of mass in a space-fixed coordinate system. For a nonlinear molecule, the rotational wavefunction depends on three Euler angles ( $\theta$ ,  $\phi$ , and  $\chi$ ) that define the orientation of the principal axes *a*, *b*, and *c* with respect to a nonrotating set of axes with origin at the center of mass. For linear molecules, the rotational quantum number *K* = 0, and the wavefunction only depends on  $\theta$  and  $\phi$ . Thus, the *vibrational wavefunction will depend on* (3*N* – 5) *or* (3*N* – 6) *coordinates for linear or nonlinear molecules*, respectively.

2) As we discussed before, in the description of molecular vibrations we work in the coordinate system that has its origin at the center of mass of the molecule and its axes directed along the principal axes of rotation (a, b, c).

3) In the classical mechanical description, our model for molecular vibration is a set of N point masses (nuclei), each of which vibrates about an equilibrium position (determined by solving the electronic Schrödinger equation). If  $a_{\alpha}$ ,  $b_{\alpha}$ , and  $c_{\alpha}$  are the Cartesian coordinates of the nucleus  $\alpha$ , and  $a_{\alpha,e}$ ,  $b_{\alpha,e}$ , and  $c_{\alpha,e}$ are the *equilibrium values* of these coordinates, we can define the 3N **Cartesian displacement coordinates**:

$$x_{\alpha} = a_{\alpha} - a_{\alpha,e} \qquad y_{\alpha} = b_{\alpha} - b_{\alpha,e} \qquad z_{\alpha} = c_{\alpha} - c_{\alpha,e} \tag{1}$$

These coordinates measure the displacement of each nucleus from equilibrium. Since there is (3N - 5) or (3N - 6) vibrational coordinates, *not all displacement coordinates are independent*. They are connected by five or six relations, which specify how the axes (a, b, c) rotate and translate with the molecule. 4) The classical kinetic energy of vibration about the equilibrium positions:

$$T = \frac{1}{2} \sum_{\alpha=1}^{N} m_{\alpha} \left[ \left( \frac{\mathrm{d}x_{\alpha}}{\mathrm{d}t} \right)^2 + \left( \frac{\mathrm{d}y_{\alpha}}{\mathrm{d}t} \right)^2 + \left( \frac{\mathrm{d}z_{\alpha}}{\mathrm{d}t} \right)^2 \right]$$
(2)

To simplify this equation, we define the mass-weighted Cartesian displacement coordinates  $q_1, \ldots, q_{3N}$ :

$$q_1 = \sqrt{m_1} x_1$$
  $q_2 = \sqrt{m_1} y_1$   $q_3 = \sqrt{m_1} z_1$  (3)

$$q_4 = \sqrt{m_2} x_2 \qquad \dots \qquad q_{3N} = \sqrt{m_N} z_N \tag{4}$$

Then, the kinetic energy has the form:

$$T = \frac{1}{2} \sum_{i=1}^{3N} \left( \frac{\mathrm{d}q_i}{\mathrm{d}t} \right)^2 = \frac{1}{2} \sum_{i=1}^{3N} \dot{q}_i^2 \tag{5}$$

$$T = \frac{1}{2} \begin{pmatrix} \dot{q}_1 & \dot{q}_2 & \dots & \dot{q}_{3N} \end{pmatrix} \begin{pmatrix} \dot{q}_1 \\ \dot{q}_2 \\ \vdots \\ \dot{q}_{3N} \end{pmatrix} = \frac{1}{2} \dot{\mathbf{q}}^{\mathbf{T}} \dot{\mathbf{q}}$$
(6)

5) The *potential energy of vibration* is a function of  $x_1, \ldots, z_N$ ; hence it can be written as a function of the mass-weighted coordinates  $q_1, \ldots, q_{3N}$ . For a molecule, the vibrational potential energy is given by U, the sum of the electronic energy and the nuclear repulsions (the solution of the electronic Schrödinger equation):

$$V = U(q_1, \dots, q_{3N}) \tag{7}$$

From now on, we will use *V* to denote the vibrational potential energy. We can *expand the potential energy in a Taylor series* about the equilibrium positions  $(q_1 = q_2 = ... = q_{3N} = 0)$ :

$$V = V_e + \sum_{i=1}^{3N} \left(\frac{\partial V}{\partial q_i}\right)_e q_i + \frac{1}{2} \sum_{i=1}^{3N} \sum_{k=1}^{3N} \left(\frac{\partial^2 V}{\partial q_i \partial q_k}\right)_e q_i q_k$$
$$+ \frac{1}{6} \sum_{i=1}^{3N} \sum_{j=1}^{3N} \sum_{k=1}^{3N} \left(\frac{\partial^3 V}{\partial q_i \partial q_j \partial q_k}\right)_e q_i q_j q_k + \dots$$
(8)

where  $V_e$  is the equilibrium electronic energy (including nuclear repulsion) and the

subscript *e* indicates that the derivatives are evaluated at the equilibrium nuclear configuration. At the equilibrium, the potential energy is a minimum:

$$\left(\frac{\partial V}{\partial q_i}\right)_e = 0, \qquad i = 1, \dots, 3N \tag{9}$$

We will neglect terms higher than quadratic in the Taylor expansion. If the vibrations are small, this is a good approximation. We obtain:

$$V = V_e + \frac{1}{2} \sum_{i=1}^{3N} \sum_{k=1}^{3N} W_{ik} q_i q_k$$
(10)

$$W_{ik} \equiv \left(\frac{\partial^2 V}{\partial q_i \partial q_k}\right)_e \tag{11}$$

$$V = V_e + \frac{1}{2} \mathbf{q}^{\mathrm{T}} \mathbf{W} \mathbf{q}$$
(12)

The matrix W is called the mass-weighted Cartesian force constant matrix.

6) To find equations of motion for the classical mechanical vibration of molecules, we use the Newton's second law ( $F_x = ma_x$ ). The *x*-component of the force acting on each atom is given by:

$$F_{x,\alpha} = -\frac{\partial V}{\partial x_{\alpha}} = m_{\alpha} \frac{\mathrm{d}^2 x_{\alpha}}{\mathrm{d}t^2}$$
(13)

We can rewrite this equation using the mass-weighted coordinates  $q_i = \sqrt{m_{\alpha}} x_{\alpha}$ :

$$\frac{\partial V}{\partial x_{\alpha}} = \frac{\partial V}{\partial q_i} \frac{\partial q_i}{\partial x_{\alpha}} = m_{\alpha}^{1/2} \frac{\partial V}{\partial q_i}$$
(14)

$$\frac{\mathrm{d}^2 x_\alpha}{\mathrm{d}t^2} = \frac{\mathrm{d}^2}{\mathrm{d}t^2} \left(\frac{q_i}{m_\alpha^{1/2}}\right) = \frac{1}{m_\alpha^{1/2}} \frac{\mathrm{d}^2 q_i}{\mathrm{d}t^2} \tag{15}$$

This leads to:

$$\frac{\mathrm{d}^2 q_i}{\mathrm{d}t^2} + \frac{\partial V}{\partial q_i} = 0 , \quad i = 1, \dots, 3N$$
(16)

Here, V is given by Eq. (10) and contains a double sum over the coordinates  $q_i$ .

Hence, the derivative  $\frac{\partial V}{\partial q_i}$  will contain a single sum over  $q_i$ :

$$\frac{d^2 q_i}{dt^2} + \sum_{j=1}^{3N} W_{ij} q_j = 0 , \quad i = 1, \dots, 3N$$
(17)

$$\ddot{\mathbf{q}} + \mathbf{W}\mathbf{q} = 0 \tag{18}$$

This is a coupled system of differential equations that involves all  $q_i$ 's, which makes the solution of this system of equations very complicated.

7) To solve this system of coupled equations, we seek a unitary transformation of the coordinates  $q_i$  to a new set of coordinates which will be *uncoupled*. We consider

$$Q_k = \sum_{i=1}^{3N} U_{ik} q_i \qquad \mathbf{U}^{\mathbf{T}} \mathbf{U} = \mathbf{U} \mathbf{U}^{\mathbf{T}} = \mathbf{1}$$
(19)

$$\mathbf{Q} = \mathbf{U}^{\mathbf{T}} \mathbf{q} \qquad \mathbf{q} = \mathbf{U} \mathbf{Q} \tag{20}$$

Thus, the equations of motion become:

$$\mathbf{U}\ddot{\mathbf{Q}} + \mathbf{W}\mathbf{U}\mathbf{Q} = 0 \tag{21}$$

$$\ddot{\mathbf{Q}} + \mathbf{U}^{\mathrm{T}} \mathbf{W} \mathbf{U} \mathbf{Q} = 0 \tag{22}$$

We choose **U** such that

$$\mathbf{U}^{\mathbf{T}}\mathbf{W}\mathbf{U} = \mathbf{\Lambda} = \begin{bmatrix} \lambda_1 & 0 & \dots & 0 \\ 0 & \lambda_2 & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \lambda_{3N} \end{bmatrix}$$
(23)

Hence, the transformation matrix **U** is the eigenvector matrix of the real and symmetric force constant matrix **W**. We can obtain **U** by diagonalizing the matrix **W** or by solving the secular equation  $det(W_{ij} - \delta_{ij}\lambda_i) = 0$ . Then, the system of differential equations becomes uncoupled:

$$\ddot{\mathbf{Q}} + \mathbf{A}\mathbf{Q} = 0 \tag{24}$$

$$\frac{\mathrm{d}^2 Q_i}{\mathrm{d}t^2} + \lambda_i Q_i = 0 , \quad i = 1, \dots, 3N$$
(25)

The solutions of these differential equations have the form:

$$Q_i = B_i \sin(\sqrt{\lambda_i}t + b_i), \quad i = 1, \dots, 3N$$
(26)

where  $B_i$  and  $b_i$  are some constants. Transforming  $Q_i$  back to the old set of the mass-weighted Cartesian coordinates, we get:

$$q_{k} = \sum_{i=1}^{3N} A_{ki} \sin(\sqrt{\lambda_{i}}t + b_{i}) , \quad k = 1, \dots, 3N$$
(27)

where  $A_{ki} = U_{ki}B_i$ . Eqs. (26) and (27) demonstrate that the solutions of the equations of motion correspond to the harmonic vibrations. The constants  $\sqrt{\lambda_i}$ ,  $b_i$ , and  $B_i$  contain information about the vibrational frequency, phase, and amplitude, respectively.

8) The coordinates  $Q_k$  are called **normal coordinates** and the vibrations associated with these coordinates are called **normal modes**. Let us look at what these modes physically represent. We consider a special case with only one non-zero constant  $B_m \neq 0$  ( $B_i = 0, i \neq m$ ), i.e. only one normal mode with non-zero amplitude. In this case, Eq. (27) contains a single term representing the contribution from the normal mode *m* for each  $q_k$ :

$$q_k = A_{km}\sin(\sqrt{\lambda_m}t + b_m), \quad k = 1, \dots, 3N$$
(28)

We see that the *coordinates of each atom vibrate in phase with one another with the same frequency*: when *t* has increased by  $T_m = \frac{2\pi}{\sqrt{\lambda_m}}$ , the sine function has gone through one cycle. Thus the vibrational frequency is given by:

$$\mathbf{v}_m = \frac{1}{T_m} = \frac{\sqrt{\lambda_m}}{2\pi} = \frac{\omega_m}{2\pi} \tag{29}$$

where  $\omega_m = \sqrt{\lambda_m}$  is the angular frequency. We note that the amplitudes  $A_{km}$  are in general different for each atom since  $A_{km} = U_{km}B_m$  and the elements of  $U_{km}$  can be different for different *k*.

9) We summarize that a normal mode vibration is the one in which all the nuclei undergo harmonic motion with the same frequency and move in phase, but generally with different amplitudes. The general classical solution for vibrations of polyatomic molecules near equilibrium is an arbitrary superposition of normal modes. The normal coordinate coefficients  $U_{km}$  and the normal frequencies

 $v_m = \frac{\sqrt{\lambda_m}}{2\pi}$  are determined by diagonalizing the mass-weighted Cartesian force constant matrix **W**.

10) In the basis of normal coordinates, expressions for the vibrational kinetic and potential energies simplify:

$$T = \frac{1}{2} (\mathbf{U}\dot{\mathbf{Q}})^{\mathbf{T}} \mathbf{U}\dot{\mathbf{Q}} = \frac{1}{2} \dot{\mathbf{Q}}^{\mathbf{T}} \dot{\mathbf{Q}}$$
(30)

$$T = \frac{1}{2} \sum_{i=1}^{3N-6} \dot{Q}_i^2 \tag{31}$$

$$V = V_e + \frac{1}{2} \mathbf{q}^{\mathrm{T}} \mathbf{U} \mathbf{\Lambda} \mathbf{U}^{\mathrm{T}} \mathbf{q} = V_e + \frac{1}{2} \mathbf{Q}^{\mathrm{T}} \mathbf{\Lambda} \mathbf{Q}$$
(32)

$$V = V_e + \frac{1}{2} \sum_{i=1}^{3N-6} \lambda_i Q_i^2$$
(33)

The reason we have omitted contributions for the last six  $Q_i$ 's is that the three translational and three rotational coordinates are not harmonic motions, therefore, their  $\lambda_i = 0$  rigorously for i = 3N - 5, ..., 3N (in our notation, these coordinates with zero eigenvalues are labeled as 3N - 5, ..., 3N). Thus, for a nonlinear molecule there are 3N - 6 normal modes with  $\lambda_i \neq 0$  that correspond to internal (vibrational) motions. For a linear molecule, there is one less rotational coordinate, and thus there are 3N - 5 vibrational normal modes (the summation limits need to be appropriately modified in the above equations). If the molecule is not at its equilibrium geometry, the three  $\lambda_i$  corresponding to the rotational motion can have small non-zero values due to forces acting on atoms to rotate back to the equilibrium position.