Advanced Quantum Mechanics & Spectroscopy (CHEM 7520)

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Week 4-6: Vibrations of polyatomic molecules

II. QUANTUM MECHANICS OF MOLECULAR VIBRATIONS

1) During our discussion of the rotational spectroscopy, we obtained the rotational Hamiltonian by replacing the classical quantities by the operators. In the discussion of molecular vibrations we in principle could do the same. As an exercise, we will take a different approach. We will start with a general expression for the vibrational Hamiltonian and the Schrödinger equation and demonstrate that we can convert these quantum mechanical expressions to the form obtained in the classical description.

2) The *vibrational Schrödinger equation* for an N-atom molecule has the following form:

$$\hat{H}_{vib} |\Psi_{vib}\rangle = E |\Psi_{vib}\rangle \tag{1}$$

where the *vibrational Hamiltonian* is given by

$$\hat{H}_{vib} = -\frac{\hbar^2}{2} \sum_{\alpha=1}^{N} \frac{1}{m_\alpha} \left(\frac{\partial^2}{\partial x_\alpha^2} + \frac{\partial^2}{\partial y_\alpha^2} + \frac{\partial^2}{\partial z_\alpha^2} \right) + V(\mathbf{x_1}, \mathbf{x_2}, \ldots, \mathbf{x_N}) \tag{2}$$

The first term corresponds to the vibrational kinetic energy operator $\hat{T}$ and the second term is the potential energy $\hat{V}$. In Eq. (2) both operators are expressed in terms of the Cartesian displacement coordinates $\mathbf{x}_\alpha = (x_\alpha, y_\alpha, z_\alpha)$ that we defined during the classical description. As we discussed before, it is convenient to introduce the mass-weighted Cartesian coordinates ($q_1 = \sqrt{m_1}x_1, q_2 = \sqrt{m_1}y_1, \ldots$), which allows to write the kinetic energy operator in a more compact form:

$$\hat{T} = -\frac{\hbar^2}{2} \sum_{i=1}^{3N} \frac{\partial^2}{\partial q_i^2} \tag{3}$$

Similarly, the potential energy function can be expanded in a Taylor series about

the equilibrium positions and approximated using the second-order expression:

$$V(q_1,\ldots,q_{3N}) \approx V_e + \frac{1}{2}\sum_{i=1}^{3N}\sum_{k=1}^{3N} W_{ik}q_iq_k \tag{4}$$

$$W_{ik} \equiv \left(\frac{\partial^2 V}{\partial q_i \partial q_k}\right)_e \tag{5}$$

Combining these results, we obtain for the vibrational Hamiltonian:

$$\hat{H}_{vib} = -\frac{\hbar^2}{2}\sum_{i=1}^{3N}\frac{\partial^2}{\partial q_i^2} + \frac{1}{2}\sum_{i=1}^{3N}\sum_{j=1}^{3N} W_{ij}q_iq_j \tag{6}$$

In the above equation the constant term V_e does not affect the vibrational wavefunctions and simply shifts the eigenvalue; therefore, we set it to zero ($V_e = 0$).

3) We now consider a unitary transformation of the coordinates q_i that makes W_{ij} diagonal. As before, we define:

$$Q_k = \sum_{i=1}^{3N} U_{ik}q_i \qquad \mathbf{U^T U} = \mathbf{U U^T} = \mathbf{1} \tag{7}$$

$$\mathbf{Q} = \mathbf{U^T q} \qquad \mathbf{q} = \mathbf{U Q} \tag{8}$$

The corresponding derivatives can be written as:

$$\frac{\partial}{\partial q_i} = \sum_{k=1}^{3N}\frac{\partial Q_k}{\partial q_i}\frac{\partial}{\partial Q_k} = \sum_{k=1}^{3N} U_{ik}\frac{\partial}{\partial Q_k} \tag{9}$$

$$\frac{\partial^2}{\partial q_i^2} = \sum_{k=1}^{3N}\sum_{l=1}^{3N} U_{ik}U_{il}\frac{\partial^2}{\partial Q_k \partial Q_l} \tag{10}$$

$$\sum_{i=1}^{3N}\frac{\partial^2}{\partial q_i^2} = \sum_{k=1}^{3N}\sum_{l=1}^{3N}\frac{\partial^2}{\partial Q_k \partial Q_l}\sum_{i=1}^{3N} U_{ik}U_{il} \tag{11}$$

$$\sum_{i=1}^{3N}\frac{\partial^2}{\partial q_i^2} = \sum_{k=1}^{3N}\frac{\partial^2}{\partial Q_k^2} \tag{12}$$

Thus, $\hat{T}$ is separable in the basis of Q_k as well. Similarly, for the potential energy

operator we obtain:

$$\hat{V} = \frac{1}{2} \sum_{k=1}^{3N} \lambda_k Q_k^2 \tag{13}$$

4) We are left with the following Schrödinger equation in normal coordinates:

$$\left[-\frac{\hbar^2}{2} \sum_{k=1}^{3N-6} \frac{\partial^2}{\partial Q_k^2} + \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2 \right] |\Psi_{vib}\rangle = E |\Psi_{vib}\rangle \tag{14}$$

where *it is now restricted to the internal vibrational modes only*, i.e. those with nonzero eigenvalues λ_k. The translations and rotations are thus separated from the problem. We note that the Hamiltonian can be written as a sum of terms, each of which involves only one normal coordinate (sum of the uncoupled harmonic-oscillator Hamiltonians):

$$\hat{H} = \sum_{k=1}^{3N-6} \hat{H}_k \tag{15}$$

$$\hat{H}_k = -\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_k^2} + \frac{1}{2} \lambda_k Q_k^2 \tag{16}$$

Thus, according to the separation of variables theorem, *the eigenfunction of $\hat{H}$ can be written in the product form*

$$|\Psi_{vib}\rangle = \prod_{k=1}^{3N-6} |\psi_{k,v_k}(Q_k)\rangle \tag{17}$$

and *the solution of the Schrödinger equation* (14) *is equivalent to the solution of* $3N-6$ *one-dimensional Schrödinger equations*:

$$\hat{H}_k |\psi_{k,v_k}(Q_k)\rangle = \varepsilon_k |\psi_{k,v_k}(Q_k)\rangle \tag{18}$$

The solution of Eq. (18) is well-known, *it is a solution of the one-dimensional harmonic-oscillator problem*. The eigenvalues and eigenfunctions have the form:

$$E = \sum_{k=1}^{3N-6} \varepsilon_k = \sum_{k=1}^{3N-6} \hbar \omega_k \left(v_k + \frac{1}{2} \right) \tag{19}$$

$$|\psi_{k,v_k}(Q_k)\rangle = \frac{1}{\sqrt{2^{v_k}(v_k!)}} \left(\frac{\alpha_k}{\pi} \right)^{1/4} e^{-\frac{1}{2} \alpha_k Q_k^2} H_{v_k}(\sqrt{\alpha_k} Q_k) \tag{20}$$

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$$\omega_k = \sqrt{\lambda_k} \qquad \alpha_k = \frac{\sqrt{\lambda_k}}{\hbar} \qquad (21)$$

where functions H_{v_k} are known as **Hermite polynomials**. If all vibrational quantum numbers are zero ($v_k = 0$), we obtain expression for the ground-state energy, which is often called the **zero-point vibrational energy** (ZPVE):

$$E_0 = \frac{1}{2} \sum_{k=1}^{3N-6} \hbar \omega_k \qquad (22)$$

The ground-state vibrational wavefunction has the form:

$$|\Psi_{vib}\rangle = \prod_{k=1}^{3N-6} \left(\frac{\alpha_k}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha_k Q_k^2} \qquad (23)$$

(We note that in principle Eq. (17) should satisfy Pauli principle and thus be symmetric or antisymmetric with respect to the permutation of the nuclear coordinates, depending on whether the nuclei are fermions or bosons. For example, if the nuclei are fermions, the harmonic oscillator wavefunction should be a Slater determinant and the form in Eq. (17) will be an approximation. In practice, this approximation holds very well for vibrations at low energies and is always used.)

5) *We summarize that for molecules vibrating in deep potential wells near equilibrium, the total vibrational wavefunction is a product of one-dimensional harmonic oscillator wavefunctions in normal coordinates. The total vibrational energy is the sum of the quantized vibrational energies for each normal mode. The vibrational frequencies are obtained by diagonalizing the mass-weighted force constant matrix.*

6) *Each vibrational state can be characterized by the combination of quantum numbers v_k for each normal mode k. These vibrational quantum numbers are usually written in parenthesis: $(v_1, v_2, \ldots, v_{3N-6})$. Levels with one $v_k = 1$ and all other $v_i = 0$ ($i \neq k$) are called* **fundamental levels**. *Levels with one $v_k > 1$ and all other $v_i = 0$ ($i \neq k$) are called* **overtone levels**. *Levels with more than one non-zero v_k are called* **combination levels**.

7) The frequencies of most diatomic molecules are high enough to make the population of the excited vibrational levels negligible at room temperature. For polyatomics, it is common to have low-energy vibrational levels that are appreciably populated at room temperature.

8) If the two vibrational levels have the same energy they are called **degenerate**. For the ground state there is only one possible set of quantum numbers $(0, 0, \ldots, 0)$. Therefore, *the ground vibrational level is always non-degenerate*. If all of the normal modes are non-degenerate (i.e., *there is no degenerate eigenvalues of the force constant matrix*), then the excited vibrational levels should also be non-degenerate. In this case, it is still possible that two vibrational levels can become accidentally degenerate (or near-degenerate). For example, a fundamental level $(1, 0, \ldots)$ can become accidentally degenerate with an overtone level $(0, 3, \ldots)$ if it happens that $\omega_1 \approx 3\omega_2$. *The probability of the accidental degeneracy increases rapidly with the size of the molecule, such degeneracies are very common for the polyatomic molecules.* If the two vibrational levels are accidentally degenerate and have the same symmetry, their vibrational wavefunctions may strongly interact. In this case (known as the Fermi resonance), the harmonic approximation usually breaks down and the anharmonicity splits the vibrational levels apart, leading to the loss of the degeneracy. In molecules with high symmetry that belong to non-abelian symmetry point groups, it is possible to have degenerate normal modes and, therefore, many of the excited vibrational levels are degenerate.