Advanced Quantum Mechanics & Spectroscopy (CHEM 7520)

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Week 2-3: Rotations of polyatomic molecules

I. NUCLEAR MOTION OF POLYATOMIC MOLECULES

1) Within the Born-Oppenheimer approximation, the Schrödinger equation for the nuclei is expressed as

$$\hat{H}_N |\Psi_N\rangle = (\hat{T}_N + U) |\Psi_N\rangle = E |\Psi_N\rangle \tag{1}$$

where the nuclear Hamiltonian \hat{H}_N is a sum of the **nuclear kinetic energy** \hat{T}_N and the potential energy U derived from solving the electronic Schrödinger equation. For a diatomic molecule, it is easy to convert the classical nuclear kinetic energy terms into quantum-mechanical ones by choosing a proper coordinate system. For an arbitrary polyatomic molecule, such manipulations are rather complex, so we only discuss the results.

2) The classical expression for the kinetic energy of a polyatomic molecule can be written as

$$T_N = T_{trans} + T_{rot} + T_{vib} + T_{vib-rot}$$
(2)

where T_{trans} is the *translational kinetic energy* of the molecule as a whole (simply, a constant), T_{rot} is the *rotational kinetic energy*, T_{vib} is the *vibrational kinetic energy*, and $T_{vib-rot}$ is the *interaction between rotation and vibration*. The total classical-mechanical Hamiltonian function also includes the potential energy U, which is a function of the relative positions of the nuclei.

- 3) We choose the coordinate system as follows:
 - The translation is described by specifying the Cartesian coordinates of the center of mass relative to the *space-fixed coordinate system*.
 - The rotation is described by specifying the orientation of the molecule relative to the *nonrotating coordinate system* with the origin at the center of mass that translates with the molecule.

- The vibration is described by specifying the atomic coordinates relative to the *molecule-fixed coordinate system* that rotates with the molecule and has its origin at the center of mass.
- The *molecule-fixed coordinate system* is also used to solve the electronic Schrödinger equation.

4) Since T_{trans} is just a constant, we can set it to zero (i.e., assume no net translational motion). The $T_{vib-rot}$ term is difficult to deal with, but it's usually small. For now, we will assume that $T_{vib-rot} \approx 0$, but we will come back to this approximation later in the course (for some polyatomic molecules this term can be significant). The T_{rot} term depends on the instantaneous nuclear configurations. Since vibrations are typically much faster than rotations, we can calculate T_{rot} approximately by averaging over vibrational motion.

5) Within these approximations, the **classical-mechanical Hamiltonian** function has the form:

$$H_N = T_{rot} + [T_{vib} + U] \tag{3}$$

where we combined the last two terms because they depend on the relative nuclear coordinates, while the T_{rot} term averaged over vibrations does not. The quantum-mechanical Hamiltonian thus can be written as:

$$\hat{H}_N = \hat{T}_{rot} + \left[\hat{T}_{vib} + U\right] = \hat{H}_{rot} + \hat{H}_{vib} \tag{4}$$

Since \hat{H}_N approximately separates into two parts, the *nuclear wavefunction* $|\Psi_N\rangle$ *is approximately a product of rotational and vibrational wavefunctions* and the energy is the sum of the rotational and vibrational components. We can find these energies and wavefunctions by solving the rotational and vibrational Schrödinger equations, respectively.

II. CLASSICAL MECHANICS OF RIGID ROTATIONS

1) Before we consider quantum mechanics of the molecular rotation, we first briefly summarize results from classical mechanics. We assume that the molecule is a rigid rotor with a configuration averaged by vibrational motions. Thus, we can consider the molecule as a collection of point masses m_i located at positions $r_i = (x_i, y_i, z_i)$ in a Cartesian coordinate system (x, y, z), which origin is located at the center of mass.

2) The classical rotational kinetic energy can be expressed as:

$$T_{rot} = \frac{1}{2} \sum_{ij} \omega_i I_{ij} \omega_j = \frac{1}{2} \boldsymbol{\omega}^{\mathrm{T}} \mathbf{I} \boldsymbol{\omega}$$
(5)

where ω_i are the components of the **angular velocities** (ω_x , ω_y , ω_z) along the axes *x*, *y*, and *z*. The matrix **I** is the rotational **inertia tensor**:

$$\mathbf{I} = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{bmatrix}$$
(6)

where the diagonal elements are called moments of inertia

$$I_{xx} = \sum_{i} m_i (y_i^2 + z_i^2)$$
(7)

$$I_{yy} = \sum_{i} m_i (x_i^2 + z_i^2)$$
(8)

$$I_{zz} = \sum_{i} m_i (x_i^2 + y_i^2)$$
(9)

and the off-diagonal elements are referred to as products of inertia

$$I_{xy} = I_{yx} = -\sum_{i} m_i x_i y_i \tag{10}$$

$$I_{xz} = I_{zx} = -\sum_{i} m_i x_i z_i \tag{11}$$

$$I_{yz} = I_{zy} = -\sum_{i} m_i y_i z_i \tag{12}$$

The inertia tensor contains information about the molecular structure and atomic masses.

3) Note that in the space-fixed coordinate system the coordinates of atoms change with time as the molecule rotates, and thus the inertia tensor is time-dependent. However, *in the molecule-fixed coordinate system the inertia tensor is time-independent*. We also note that in the absence of external perturbations, *the molecule must conserve its kinetic energy* T_{rot} .

4) Let's assume that (x, y, z) refers to the molecule-fixed coordinate system where **I** is time-independent. Although **I** is in general non-diagonal, we can always rotate

the axes (x, y, z) into a new coordinate system (a, b, c) where I is diagonal:

$$\mathbf{I} = \begin{bmatrix} I_a & 0 & 0\\ 0 & I_b & 0\\ 0 & 0 & I_c \end{bmatrix}$$
(13)

$$I_a = \sum_{i}^{2} m_i (b_i^2 + c_i^2)$$
(14)

$$I_b = \sum_{i}^{b} m_i (a_i^2 + c_i^2)$$
(15)

$$I_c = \sum_{i} m_i (a_i^2 + b_i^2)$$
(16)

where I_a, I_b, I_c are called **principal moments of inertia** (eigenvalues of I) and the axes (a, b, c) which diagonalize I are called **principal axes of rotation** (eigenvectors of I). To summarize, here are the steps for determining the principal axes and the principal moments:

(a) Attach an arbitrary coordinate system to the body and compute the center of mass

$$\mathbf{R_{cm}} = \frac{1}{M} \sum_{i} m_i \mathbf{r_i}$$
(17)

- (b) Translate the coordinate system to place the center of mass at the origin. Recompute all coordinates of the particles in this reference frame
- (c) Compute the inertia tensor in this body-fixed, center-of-mass reference frame
- (d) Find the eigenvalues and eigenvectors of the inertia tensor

$$\mathbf{I}\,\mathbf{v}_{\alpha} = I_{\alpha}\,\mathbf{v}_{\alpha} \tag{18}$$

The \mathbf{v}_{α} are the principal axes and the I_{α} are the principal moments

5) We can visualize the inertia tensor as follows. For every possible axis α through the center of mass, we compute the moment of inertia

$$I_{\alpha} = \sum_{i} m_{i} r_{i}^{2} \tag{19}$$

(r_i is the perpendicular distance from the particle of mass m_i to the axis α) and lay off on each side of the center of mass a distance numerically equal to $I_{\alpha}^{-1/2}$. The resulting surface in three dimensions is the **ellipsoid of inertia**. The equation for

the ellipsoid of inertia is

$$I_{xx}x^{2} + I_{yy}y^{2} + I_{zz}z^{2} + 2I_{xy}xy + 2I_{xz}xz + 2I_{yz}yz = 1$$
(20)

In the principal coordinate system, we obtain:

$$I_a a^2 + I_b b^2 + I_c c^2 = 1 (21)$$

- 6) Facts that aid rapid determination of the principal axes:
- (a) The principal axes are mutually orthogonal because the inertia tensor is symmetric
- (b) Any plane of symmetry contains two principal axes and is perpendicular to a third principal axis, because any symmetry operation must send the inertia ellipsoid into itself
- (c) Any axis of rotation is a principal axis. If it is a C_n axis for n > 2, the plane perpendicular to the axis is a **principal plane** corresponding to degenerate moments of inertia. In this case, the inertia ellipsoid becomes an **ellipsoid of revolution**
- (d) A molecule with two or more non-coincident C_n axes $n \ge 3$ has all three moments of inertia equal. In this case, the *inertia ellipsoid becomes a sphere* (any axis through the center of mass is a principal axis)

7) By convention, the principal axes are labeled as (a, b, c) such that the principal moments are

$$I_a \le I_b \le I_c \tag{22}$$

The rotational constants are defined as (in cm^{-1}):

$$A = \frac{1}{hc} \left(\frac{\hbar^2}{2I_a}\right) \tag{23}$$

$$B = \frac{1}{hc} \left(\frac{\hbar^2}{2I_b}\right) \tag{24}$$

$$C = \frac{1}{hc} \left(\frac{\hbar^2}{2I_c}\right) \tag{25}$$

where $A \ge B \ge C$.

8) Rotors are classified as follows:

(a) Spherical tops

$$I_c = I_b = I_a \qquad A = B = C \tag{26}$$

There exists only one unique rotational constant, which is labeled as B. Examples: CH₄, SF₆, basketball.

(b) Linear molecules

$$I_c = I_b > I_a = 0 \tag{27}$$

Only one unique rotation rotational constant labeled B that is equal to C. Examples: HCN, CO₂, NNO, diatomics.

(c) Symmetric tops

i. Prolate symmetric top

$$I_c = I_b > I_a \neq 0 \qquad A > B = C \tag{28}$$

There exist two unique rotational constants, *A* and *B*, where B < A. Examples: CH₃I, allene, football.

ii. Oblate symmetric top

$$I_c > I_b = I_a \qquad A = B > C \tag{29}$$

There exist two unique rotational constants, *B* and *C*, where B > C. Examples: NH₃, benzene, frisbee.

(d) Asymmetric tops

$$I_c > I_b > I_a \qquad A > B > C \tag{30}$$

There exist three unique rotational constants, A, B, and C. Examples: H₂O, H₂CO, C₂H₄.

(e) If $I_c \approx I_b > I_a$, the molecule is a **prolate near-symmetric top**. If $I_c > I_b \approx I_a$, the molecule is an **oblate near-symmetric top**.

9) The character table for the point group of a molecule indicates whether it is an asymmetric top, a symmetric top, or a spherical top by showing how the (a, b, c) axes [which correspond to some choice of (x, y, z)] transform.

(a) Asymmetric top: *a*, *b*, and *c* are unique and transform as one-dimensional irreducible representation.

- (b) Symmetric top: (a,b) or (b,c) pair transforms as a two-dimensional irrep. The other axis is unique and transforms as a **one-dimensional** irrep.
- (c) Spherical top: (a, b, c) triplet transforms as a three-dimensional irrep.
- 10) Using the principal axes, the kinetic energy expression simplifies:

$$T_{rot} = \frac{1}{2}\boldsymbol{\omega}^{\mathrm{T}}\mathbf{I}\boldsymbol{\omega} = \frac{1}{2}\left(I_a\omega_a^2 + I_b\omega_b^2 + I_c\omega_c^2\right)$$
(31)

11) In addition to the angular velocity and the inertia tensor, we can define the rotational **angular momentum** vector as:

$$\mathbf{J} = \mathbf{I}\boldsymbol{\omega} \tag{32}$$

The angular momentum is the rotational equivalent of the linear momentum. In the absence of external perturbations, *the molecule must conserve its angular momentum*. We can express the kinetic energy in terms of the angular momentum as follows:

$$T_{rot} = \frac{1}{2} \mathbf{J}^{\mathbf{T}} \mathbf{I}^{-1} \mathbf{J}$$
(33)

Using the principal axes, the components of the angular momentum vector are:

$$J_a = I_a \omega_a \qquad J_b = I_b \omega_b \qquad J_c = I_c \omega_c \tag{34}$$

Thus, the kinetic energy takes the form:

$$T_{rot} = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c} = H_{rot}$$
(35)

We also note the rotational kinetic energy is the only term in the classical rotational Hamiltonian function of a rigid body, thus $H_{rot} = T_{rot}$.

12) Depending on the rotational type of the molecule, the classical Hamiltonian expression may simplify:

(a) Spherical tops

$$H_{rot} = \frac{J_a^2 + J_b^2 + J_c^2}{2I_b} = \frac{hc}{\hbar^2} B J^2$$
(36)

(b) Linear molecules

$$H_{rot} = \frac{hc}{\hbar^2} B J^2 \tag{37}$$

(c) Symmetric tops

i. Prolate symmetric top

$$H_{rot} = \frac{hc}{\hbar^2} \left[A J_a^2 + B (J_b^2 + J_c^2) \right] = \frac{hc}{\hbar^2} \left[(A - B) J_a^2 + B J^2 \right]$$
(38)

ii. Oblate symmetric top

$$H_{rot} = \frac{hc}{\hbar^2} \left[BJ^2 + (C - B)J_c^2 \right]$$
(39)

(d) Asymmetric tops

There is no simplification:

$$H_{rot} = \frac{hc}{\hbar^2} \left[AJ_a^2 + BJ_b^2 + CJ_c^2 \right]$$
(40)