

13.1: Rotational Motions of Rigid Molecules

In Chapter 3 and Appendix G the energy levels and wavefunctions that describe the rotation of rigid molecules are described. Therefore, in this Chapter these results will be summarized briefly and emphasis will be placed on detailing how the corresponding rotational Schrödinger equations are obtained and the assumptions and limitations underlying them.

Linear Molecules

As given in Chapter 3, the Schrödinger equation for the angular motion of a rigid (i.e., having fixed bond length R) diatomic molecule is

$$\frac{\hbar^2}{2\mu} \left[\frac{1}{R^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \left(\frac{1}{R^2 \sin^2 \theta} \right) \frac{\partial^2}{\partial \phi^2} \right] \psi = E\psi$$

or more succinctly in terms of the angular momentum operator as

$$\frac{L^2 \psi}{2\mu R^2} = E\psi$$

The Hamiltonian in this problem contains only the kinetic energy of rotation; no potential energy is present because the molecule is undergoing unhindered "free rotation". The angles θ and ϕ describe the orientation of the diatomic molecule's axis relative to a laboratory-fixed coordinate system, and μ is the reduced mass of the diatomic molecule

$$\mu = \frac{m_1 m_2}{m_1 + m_2}.$$

The Eigenfunctions and Eigenvalues

The eigenvalues corresponding to each eigenfunction are straightforward to find because H_{rot} is proportional to the L^2 operator whose eigenvalues have already been determined. The resultant rotational energies are given as:

$$E_J = \hbar^2 \frac{J(J+1)}{(2\mu R^2)} = BJ(J+1)$$

and are *independent* of M . Thus each energy level is labeled by J and is $2J+1$ -fold degenerate (because M ranges from $-J$ to J). The rotational constant B (defined as $\hbar^2/2\mu R^2$) depends on the molecule's bond length and reduced mass. Spacings between successive rotational levels (which are of spectroscopic relevance because angular momentum selection rules often restrict ΔJ to 1, 0, and -1) are given by

$$\Delta E = B(J+1)(J+2) - BJ(J+1) = 2B(J+1).$$

Within this "rigid rotor" model, the absorption spectrum of a rigid diatomic molecule should display a series of peaks, each of which corresponds to a specific $J \rightarrow J+1$ transition. The energies at which these peaks occur should grow linearly with J . An example of such a progression of rotational lines is shown in the figure below.

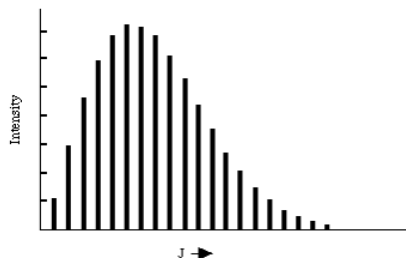


Figure 13.1.1: Insert caption here!

The energies at which the rotational transitions occur appear to fit the $\Delta E = 2B(J+1)$ formula rather well. The intensities of transitions from level J to level $J+1$ vary strongly with J primarily because the population of molecules in the absorbing level varies with J . These populations P_J are given, when the system is at equilibrium at temperature T , in terms of the degeneracy $(2J+1)$ of the J^{th} level and the energy of this level $B J(J+1)$:

$$P_J = Q^{-1} (2J+1) e^{\frac{-BJ(J+1)}{kT}},$$

where Q is the [rotational partition function](#):

$$Q = \sum_J (2J+1) e^{\frac{-BJ(J+1)}{kT}}.$$

For low values of J , the degeneracy is low and the $e^{\frac{-BJ(J+1)}{kT}}$ factor is near unity. As J increases, the degeneracy grows linearly but the $e^{\frac{-BJ(J+1)}{kT}}$ factor decreases more rapidly. As a result, there is a value of J , given by taking the derivative of $(2J+1)e^{\frac{-BJ(J+1)}{kT}}$ with respect to J and setting it equal to zero,

$$2J_m a x + 1 = \sqrt{\frac{2kT}{B}}$$

at which the intensity of the rotational transition is expected to reach its maximum.

The eigenfunctions belonging to these energy levels are the spherical harmonics $Y_{L,M}(\theta, \phi)$ which are normalized according to

$$\int_0^\pi \int_0^{2\pi} Y_{L,M}^*(\theta, \phi) Y_{L',M'}(\theta, \phi) \sin\theta d\theta d\phi = \delta_{L,L'} \delta_{M,M'}.$$

These functions are identical to those that appear in the solution of the angular part of Hydrogen-like atoms. The above energy levels and eigenfunctions also apply to the rotation of rigid linear polyatomic molecules; the only difference is that the moment of inertia I entering into the rotational energy expression is given by

$$I = \sum_a m_a R_a^2$$

where m_a is the mass of the a^{th} atom and R_a is its distance from the center of mass of the molecule. This moment of inertia replaces mR^2 in the earlier rotational energy level expressions.

Non-Linear Molecules

The rotational kinetic energy operator for a rigid polyatomic molecule is shown in Appendix G to be

$$H_{rot} = \frac{J_b^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}$$

where the I_k ($k = a, b, c$) are the three principal moments of inertia of the molecule (the eigenvalues of the moment of inertia tensor). This tensor has elements in a Cartesian coordinate system ($K, K' = X, Y, Z$) whose origin is located at the center of mass of the molecule that are computed as:

$$I_{K,K} = \sum_j m_j (R_j^2 - R_{K,j}^2) \text{ (for } K = K')$$

$$I_{K,K'} = - \sum_j m_j R_{K,j} R_{K',j} \text{ (for } K \neq K').$$

The components of the quantum mechanical angular momentum operators along the three principal axes are:

$$J_a = -i\hbar \cos\chi \left[\cot\theta \frac{\partial}{\partial\chi} - \frac{1}{\sin\theta} \frac{\partial}{\partial\phi} \right] - i\hbar \sin\chi \frac{\partial}{\partial\theta}$$

$$J_b = i\hbar \sin\chi \left[\cot\theta \frac{\partial}{\partial\chi} - \frac{1}{\sin\theta} \frac{\partial}{\partial\phi} \right] - i\hbar \cos\chi \frac{\partial}{\partial\theta}$$

$$J_c = -i\hbar \frac{\partial}{\partial\chi}.$$

The angles θ , ϕ , and χ are the Euler angles needed to specify the orientation of the rigid molecule relative to a laboratory-fixed coordinate system. The corresponding square of the total angular momentum operator J^2 can be obtained as

$$J^2 = J_a^2 + J_b^2 + J_c^2 = -\frac{\partial^2}{\partial \theta^2} - \cot \theta \frac{\partial}{\partial \theta} - \frac{1}{\sin \theta} \left(\frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial \chi^2} - 2 \cos \theta \frac{\partial^2}{\partial \phi \partial \chi} \right),$$

and the component along the lab-fixed Z axis J_Z is $-i\hbar \frac{\partial}{\partial \phi}$.

The Eigenfunctions and Eigenvalues for Special Cases

Spherical Tops

When the three principal moment of inertia values are identical, the molecule is termed a **spherical top**. In this case, the total rotational energy can be expressed in terms of the total angular momentum operator J^2

$$H_{rot} = \frac{J^2}{2I}$$

As a result, the eigenfunctions of H_{rot} are those of J^2 (and J_a as well as J_Z both of which commute with J^2 and with one another; J_Z is the component of \mathbf{J} along the lab-fixed Z-axis and commutes with J_a because $J_Z = -i\hbar \frac{\partial}{\partial \phi}$ and $J_a = -i\hbar \frac{\partial}{\partial \chi}$ act on different angles). The energies associated with such eigenfunctions are

$$E(J, M, K) = \hbar^2 \frac{J(J+1)}{2I^2},$$

for all K (i.e., J_a quantum numbers) ranging from -J to J in unit steps and for all M (i.e., J_Z quantum numbers) ranging from -J to J. Each energy level is therefore $(2J+1)^2$ degenerate because there are $2J+1$ possible K values and $2J+1$ possible M values for each J.

The eigenfunctions of J^2 , J_Z and J_a , $|J, M, K\rangle$ are given in terms of the set of rotation matrices $D_{J,M,K}$:

$$|J, M, K\rangle = \sqrt{\frac{2J+1}{8\pi^2}} D_{J,M,K}^*(\theta, \phi, \chi)$$

which obey

$$J^2 |J, M, K\rangle = \hbar^2 J(J+1) |J, M, K\rangle,$$

$$J_a |J, M, K\rangle = \hbar K |J, M, K\rangle,$$

$$J_Z |J, M, K\rangle = \hbar M |J, M, K\rangle.$$

Symmetric Tops

Molecules for which two of the three principal moments of inertia are equal are called **symmetric tops**. Those for which the unique moment of inertia is smaller than the other two are termed **prolate** symmetric tops; if the unique moment of inertia is larger than the others, the molecule is an **oblate** symmetric top. Again, the rotational kinetic energy, which is the full rotational Hamiltonian, can be written in terms of the total rotational angular momentum operator J^2 and the component of angular momentum along the axis with the unique principal moment of inertia:

$$H_{rot} = \frac{J^2}{2I} + J_a^2 \left[\frac{1}{2I_a} - \frac{1}{2I} \right]$$

for prolate tops and

$$H_{rot} = \frac{J^2}{2I} + J_c^2 \left[\frac{1}{2I_c} - \frac{1}{2I} \right]$$

for oblate tops.

As a result, the eigenfunctions of H_{rot} are those of J^2 and J_a or J_c (and of J_Z), and the corresponding energy levels are:

$$E(J, K, M) = \hbar^2 \frac{J(J+1)}{2I^2} + \hbar^2 K^2 \left[\frac{1}{2I_a} - \frac{1}{2I} \right],$$

for prolate tops

$$E(J, K, M) = \hbar^2 \frac{J(J+1)}{2I^2} + \hbar^2 K^2 \left[\frac{1}{2I_a} - \frac{1}{2I} \right],$$

for oblate tops, again for K and M (i.e., J_a or J_c and J_z quantum numbers, respectively) ranging from -J to J in unit steps. Since the energy now depends on K, these levels are only $2J + 1$ degenerate due to the $2J + 1$ different M values that arise for each J value. The eigenfunctions $|J, M, K\rangle$ are the same rotation matrix functions as arise for the spherical-top case.

Asymmetric Tops

The rotational eigenfunctions and energy levels of a molecule for which all three principal moments of inertia are distinct (a so-called **asymmetric top**) can not easily be expressed in terms of the angular momentum eigenstates and the J, M, and K quantum numbers. However, given the three principal moments of inertia I_a, I_b , and I_c , a matrix representation of each of the three contributions to the rotational Hamiltonian

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

can be formed within a basis set of the $\{|J, M, K\rangle\}$ rotation matrix functions. This matrix will not be diagonal because the $|J, M, K\rangle$ functions are not eigenfunctions of the asymmetric top H_{rot} . However, the matrix can be formed in this basis and subsequently brought to diagonal form by finding its eigenvectors $\{C_{n,J,M,K}\}$ and its eigenvalues $\{E_n\}$. The vector coefficients express the asymmetric top eigenstates as

$$\Psi_n(\theta, \phi, \chi) = \sum_{J,M,K} C_{n,J,M,K} |J, M, K\rangle.$$

Because the total angular momentum J^2 still commutes with H_{rot} , each such eigenstate will contain only one J-value, and hence Ψ_n can also be labeled by a J quantum number:

$$\Psi_{n,J}(\theta, \phi, \chi) = \sum_{M,K} C_{n,J,M,K} |J, M, K\rangle.$$

To form the only non-zero matrix elements of H_{rot} within the $|J, M, K\rangle$ basis, one can use the following properties of the rotation-matrix functions:

$$\langle J, M, K | J_a^2 | J, M, K \rangle = \langle J, M, K | J_b^2 | J, M, K \rangle = \frac{1}{2} \langle J, M, K | J^2 - J_c^2 | J, M, K \rangle = \hbar^2 [J(J+1) - K^2],$$

$$\langle J, M, K | J_c^2 | J, M, K \rangle = \hbar^2 K^2,$$

$$\begin{aligned} \langle J, M, K | J_a^2 | J, M, K \pm 2 \rangle &= -\langle J, M, K | J_b^2 | J, M, K \pm 2 \rangle \\ &= \hbar^2 \sqrt{J(J+1) - K(K \pm 1)} \sqrt{J(J+1) - (K \pm 1)(K \pm 2)} \end{aligned}$$

$$\langle J, M, K | J_c^2 | J, M, K \pm 2 \rangle = 0.$$

Each of the elements of J_c^2 , J_a^2 , and J_b^2 must, of course, be multiplied, respectively, by $\frac{1}{2I_c}$, $\frac{1}{2I_a}$ and $\frac{1}{2I_b}$ summed together to form the matrix representation of H_{rot} . The diagonalization of this matrix then provides the asymmetric top energies and wavefunctions.

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