# CHM 504 - Rotational Spectroscopy

Prof. Marissa Weichman

Spring 2022

1 A brief review of the diatomic rigid rotor

Consider a diatomic molecule with atoms of mass m_1 and m_2 and bond length r, spinning about their center of mass (COM). The center of mass is defined as the location where $m_1 r_1 = m_2 r_2$ where $r_{1,2}$ is the distance of $m_{1,2}$ from the COM. Within the rigid rotor approximation, the bond length r is fixed.
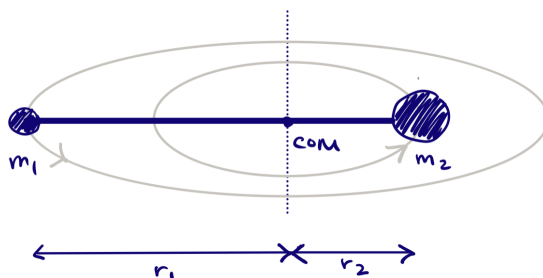
This system has:

- angular frequency ω in rad/s, analogous to linear velocity

- reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$

- moment of inertia $I = \mu r^2$, which describes how difficult it is to start the rotor spinning, the angular motion analog of mass

- angular momentum $L = I\omega$, analogous to linear momentum $(p = mv)$

- kinetic energy $KE = L^2/2I$, analogous to $KE = p^2/2m$ for linear systems

If any of these quantities are unfamiliar, McQuarrie's "Quantum Chemistry" is a good reference.

Next, we write down the time-independent Schrödinger equation for this system and consider the energy eigenstates and eigenvalues. For a free rigid rotor, we have $V(x, y, z) = 0$ and the Hamiltonian consists solely of the kinetic energy term. We can conceive of this system as a free particle constrained to explore the surface of a sphere. In three dimensions:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] + V(x, y, z) \equiv -\frac{\hbar^2}{2\mu}\nabla^2 \tag{1}$$

where ∇^2 is the Laplacian operator.

Because our "particle" (of effective reduced mass μ) is constrained to explore a rigid spherical surface of distance r from the origin, it is much simpler to solve the Schrödinger equation and express wavefunctions in terms of spherical coordinates (r, θ, ϕ) rather than Cartesian coordinates (x, y, z).
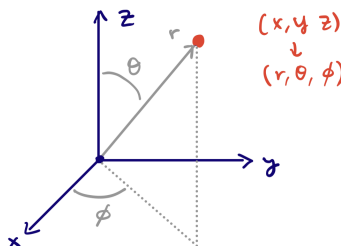
The coordinate transformation we would have to use here is:

$$r = \sqrt{x^2 + y^2 + z^2} \tag{2}$$

$$\theta = \arccos\left(\frac{z}{r}\right) \tag{3}$$

$$\phi = \arctan\left(\frac{y}{x}\right) \tag{4}$$

We will not derive the Laplacian operator in terms of spherical coordinates here, but it can be written as:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right] + \frac{1}{r^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\right] + \frac{1}{r^2}\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \tag{5}$$

For our rigid rotor, r is fixed, so we can treat it as a constant and the derivatives with respect to it disappear. We can therefore write the Hamiltonian as:

$$\hat{H} = -\frac{\hbar^2}{2I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial}{\partial\theta}\right] + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] = \frac{\hat{L}^2}{2I} \tag{6}$$

where we also have noted that $\hat{KE} = \frac{\hat{L}^2}{2I}$.

The rigid rotor solutions are found using the Hamiltonian in Eqn. 6 and solving:

$$\hat{H}\psi(\theta, \phi) = E\psi(\theta, \phi) \tag{7}$$

where the wavefunction $\psi(\theta, \phi)$ represents the probability distribution for the orientation of our rotor at any given moment in time. We won't derive the solutions to this Hamiltonian here, but the math is not too difficult. It is done out in McQuarrie Ch. 6 (see Sections 6.1 and 6.6 in particular).

The rigid rotor eigenfunctions are called *spherical harmonics*. They factor neatly into functions of θ and ϕ and are labeled with two quantum number indices J and m. By convention the

wavefunctions are referred to as $Y_J^m(\theta, \phi)$. They take the following form:

$$\psi(\theta, \phi) \equiv Y_J^m(\theta, \phi) = \Theta(\theta)\Phi(\phi) \tag{8}$$

$$\Phi(\phi) = \frac{1}{(2\pi)^{1/2}} \cdot e^{im\phi} \tag{9}$$

$$\Theta(\theta) = \left[\left(\frac{2J+1}{2} \right) \left(\frac{(J-|m|)!}{(J+|m|)!} \right) \right]^{1/2} \cdot P_J^{|m|}(\cos\theta) \tag{10}$$

$$J = \{0, 1, 2, \dots\} \tag{11}$$

$$m = \{0 \pm 1, \pm 2 \cdots \pm J\} \tag{12}$$

and where $P_J^{|m|}(\cos\theta)$ are Legendre polynomials, expressed as functions of $\cos\theta$. The Legendre polynomials are an orthogonal set of polynomial functions that are solutions to a differential equation that falls out of the rigid rotor Hamiltonian. The first few Legendre polynomials $P_J^{|m|}(x)$ are:

$$P_0^0(x) = 1 \tag{13}$$

$$P_1^0(x) = x \tag{14}$$

$$P_1^1(x) = (1 - x^2)^{1/2} \tag{15}$$

$$P_2^0(x) = \frac{1}{2}(3x^2 - 1) \tag{16}$$

$$\cdots$$

And therefore, just to be explicit about it, the functional forms of the first few rigid rotor eigenfunctions $\{Y_J^m(\theta, \phi)\}$ are:

$$Y_0^0 = \frac{1}{(4\pi)^{1/2}} \tag{17}$$

$$Y_1^0 = \left(\frac{3}{4\pi} \right)^{1/2} \cos\theta \tag{18}$$

$$Y_1^1 = -\left(\frac{3}{8\pi} \right)^{1/2} \sin\theta \cdot e^{i\phi} \tag{19}$$

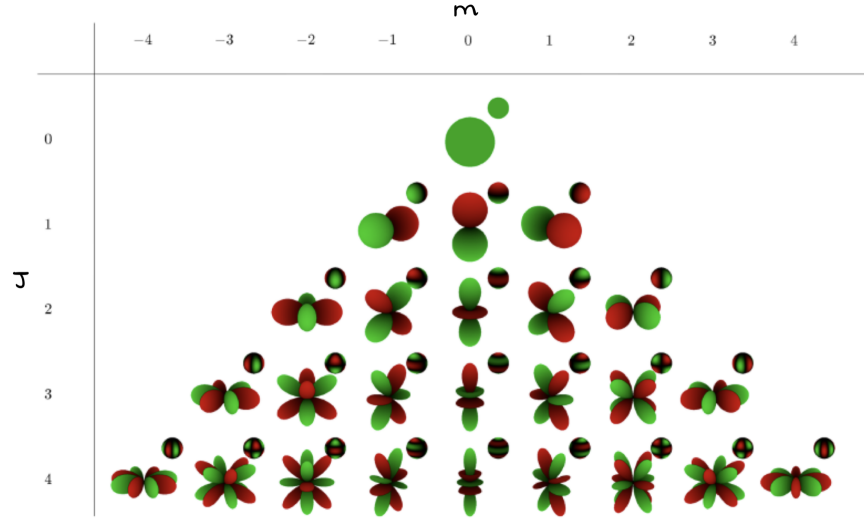$$Y_1^{-1} = \left(\frac{3}{8\pi} \right)^{1/2} \sin\theta e^{-i\phi} \tag{20}$$

$$Y_2^0 = \left(\frac{5}{16\pi} \right)^{1/2} (3\cos^2\theta - 1) \tag{21}$$

$$Y_2^1 = -\left(\frac{15}{8\pi} \right)^{1/2} \sin\theta \cos\theta e^{i\phi} \tag{22}$$

$$\cdots$$

These functions are normalized and together form a complete orthonormal basis set. They are plotted below.

A few things to note:

- J represents the total number of nodes present in a given wavefunction, while m captures the alignment of the nodes relative to the Cartesian axes of the laboratory.

- Green regions represent locations where the wavefunction has positive amplitude; red regions represent negative amplitude.

- The small spherical graphics give the actual map of how the rigid rotor is expected to be oriented in θ and ϕ. The lobed graphics give a better picture of where the angular nodes are. A particle in a given eigenstate will never be found pointing towards a node.

- Notice how the Y_0^0 eigenstate (which turns out to be the ground state) shows a uniform probability distribution on the surface of the sphere. This indicates that a rotor in state Y_0^0 is equally likely to be found pointing in any direction, since the expression for Y_0^0 given above is independent of θ and ϕ.

The spherical harmonic eigenfunctions have relatively complex forms, but they have many nice properties. The expression for their energy eigenvalues is very simple and depends only on J:

$$\hat{H}Y_J^m(\theta, \phi) = E_J Y_J^m(\theta, \phi) \tag{23}$$

$$E_J = \frac{\hbar^2}{2I}J(J+1) \equiv BJ(J+1) \tag{24}$$

where $B = \frac{\hbar^2}{2I}$ is defined as the *rotational constant* for a given system (given here in Joules).

Since the eigenenergies depend only on J, all the levels with a given J quantum number but different m have the same energy. For a given J, there are $2J + 1$ states with different $m = -J, -J + 1, \ldots J - 1, J$. The Jth energy level therefore has a *degeneracy* of $2J + 1$.

The allowed angular momenta of this system are quantized as well.

$$\hat{L}^2\, Y_J^m(\theta, \phi) = \hbar^2 J(J+1)\, Y_J^m(\theta, \phi), \quad J = 0, 1, 2, \cdots \tag{25}$$

$$\hat{L}_z\, Y_J^m(\theta, \phi) = m\hbar Y_J^m(\theta, \phi) \tag{26}$$
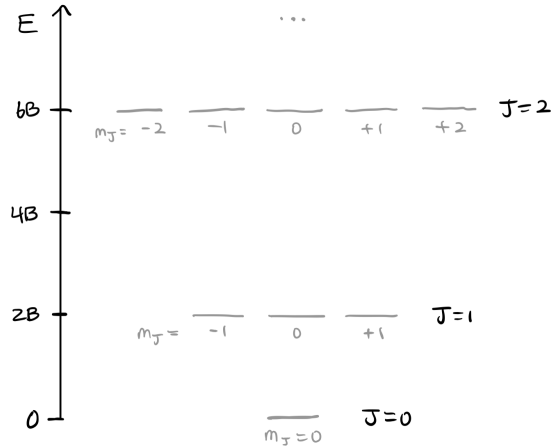
where $\hat{L}^2$ is the square of the total angular momentum and $\hat{L}_z$ is z-component of the angular momentum, e.g. its projection on the laboratory z axis.

2 The microwave spectrum and selection rules

Recall our expression for the absorption lineshape, which describes the spectrum of allowed transitions and their relative strengths:
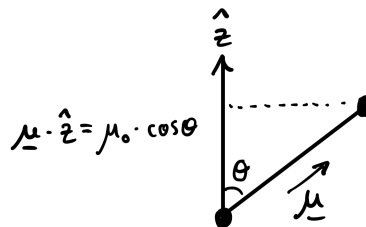
$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_i p_i \langle i | \underline{\mu} \cdot \underline{\xi} \cdot \underline{\mu}(t) \cdot \underline{\xi} | i \rangle \tag{27}$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_i p_i \langle i | \underline{\mu} \cdot \underline{\xi} \cdot e^{+i\hat{H}t/\hbar} \cdot \underline{\mu} \cdot \underline{\xi} \cdot e^{-\hat{H}t/\hbar} | i \rangle \tag{28}$$

To apply this expression to the rigid rotor, let's first note that for a linearly polarized electric field along the z axis, $\underline{\xi}$ is just the unit vector $\hat{z}$. Therefore:

$$\underline{\mu} \cdot \underline{\xi} = \underline{\mu} \cdot \hat{z} = \mu_0 \cos\theta \tag{29}$$

where within spherical coordinates θ is the angle between the axis of our rigid rotor and the z axis, and $|\mu_0|$ is the magnitude of the permanent dipole.

Re-expressing Eqn. 28 for the case of the rigid rotor, we have:

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_{J,m} p_{J,m} \langle Y_J^m | \mu_0 \cos\theta \cdot e^{+i\hat{H}_{rot}t/\hbar} \cdot \mu_0 \cos\theta \cdot e^{-\hat{H}_{rot}t/\hbar} | Y_J^m \rangle \tag{30}$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_{J,m} p_{J,m} |\mu_0|^2 \langle Y_J^m | \cos\theta \cdot e^{+i\hat{H}_{rot}t/\hbar} \cdot \cos\theta \cdot e^{-\hat{H}_{rot}t/\hbar} | Y_J^m \rangle \tag{31}$$

Some useful properties of spherical harmonic wavefunctions that we will use to evaluate this expression are:

$$\hat{H}_{rot} | Y_J^m \rangle = BJ(J+1) | Y_J^m \rangle \tag{32}$$

$$\langle Y_{J'}^{m'} | Y_J^m \rangle = \delta_{J,J'} \delta_{m,m'} \tag{33}$$

$$\cos\theta | Y_J^m \rangle = c_{J+} | Y_{J+1}^m \rangle + c_{J-} | Y_{J-1}^m \rangle \tag{34}$$

The last expression derives from the unique properties of Legendre polynomials. c_{J+} and c_{J-} are effectively Clebsch-Gordon coefficients, but we will hand-wave them away here, since they are not essential to the major features of the rotational spectrum we will derive.

Forging ahead, let's start by evaluating the quantity

$$\langle Y_J^m | \cos\theta \cdot e^{+i\hat{H}_{rot}t/\hbar} \cdot \cos\theta \cdot e^{-i\hat{H}_{rot}t/\hbar} | Y_J^m \rangle \tag{35}$$

$$= \langle Y_J^m | \cos\theta \cdot e^{+i\hat{H}_{rot}t/\hbar} \cdot \cos\theta | Y_J^m \rangle e^{-iBJ(J+1)t/\hbar} \tag{36}$$

$$= \left[c_{J+}^* \langle Y_{J+1}^m | + c_{J-}^* \langle Y_{J-1}^m | \right] e^{+i\hat{H}_{rot}t/\hbar} \left[c_{J+} | Y_{J+1}^m \rangle + c_{J-} | Y_{J-1}^m \rangle \right] e^{-iBJ(J+1)t/\hbar} \tag{37}$$

$$= \left[c_{J+}^* \langle Y_{J+1}^m | + c_{J-}^* \langle Y_{J-1}^m | \right] \left[c_{J+} | Y_{J+1}^m \rangle e^{+iB(J+1)(J+2)t/\hbar} + c_{J-} | Y_{J-1}^m \rangle e^{-iB(J-1)Jt/\hbar} \right] e^{-iBJ(J+1)t/\hbar} \tag{38}$$

$$= \left[|c_{J+}|^2 e^{+iB(J+1)(J+2)t/\hbar} + |c_{J-}|^2 e^{+iB(J-1)Jt/\hbar} \right] e^{-iBJ(J+1)t/\hbar} \tag{39}$$

$$= |c_{J+}|^2 e^{+2iB(J+1)t/\hbar} + |c_{J-}|^2 e^{-2iBJt/\hbar} \tag{40}$$

Now, moving back to the full lineshape expression:

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_{J,m} p_{J,m} |\mu_0|^2 \left[|c_{J+}|^2 e^{+2iB(J+1)t/\hbar} + |c_{J-}|^2 e^{-2iBJt/\hbar} \right] \tag{41}$$

Ignoring the m-dependence of the $c_{J\pm}$ coefficients – this is an approximation, but not a dire one – we can consider just the sum over J states. Assuming a thermal Boltzmann distribution with $\beta = 1/k_B T$ and rotational partition function Q_{rot}, the probability that a molecule is found with rotational angular momentum quantum number of J is given by:

$$p_J = \frac{(2J+1)e^{-\beta E_J}}{Q_{rot}} \tag{42}$$

where we use the fact that each J level has degeneracy $(2J+1)$ due to its m sub-levels. Therefore:

$$\sigma(\omega) = \frac{1}{2\pi}|\mu_0|^2 \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_J \frac{(2J+1)e^{-\beta E_J}}{Q_{rot}} \left[|c_{J+}|^2 e^{+2iB(J+1)t/\hbar} + |c_{J-}|^2 e^{-2iBJt/\hbar}\right] \qquad (43)$$

$$= \frac{1}{2\pi}\frac{|\mu_0|^2}{Q_{rot}} \sum_J (2J+1)e^{-\beta E_J} \int_{-\infty}^{\infty} dt \left[|c_{J+}|^2 e^{+2iB(J+1)t/\hbar - i\omega t} + |c_{J-}|^2 e^{-2iBJt/\hbar - i\omega t}\right] \qquad (44)$$

And finally, recalling that the Fourier transform of a complex sinusoid is a delta function centered at the carrier frequency:

$$\boxed{\sigma(\omega) \sim \frac{1}{2\pi}\frac{|\mu_0|^2}{Q_{rot}} \sum_J (2J+1)e^{-\beta E_J} \left[\delta(\hbar\omega - 2B(J+1)) + \delta(\hbar\omega + 2BJ)\right]} \qquad (45)$$

Eqn. 45 encodes essentially everything we need to know about rotational spectroscopy of diatomic molecules within the rigid rotor approximation! The absorption and emission spectra consist of series of evenly spaced lines – $\hbar\omega = 2B(J+1)$ in the absorption spectrum and $\hbar\omega = 2BJ$ in the emission spectrum – reflecting transitions between neighboring pairs of J states for $J = 0, 1, 2 \ldots$ The relative intensities of lines reflect the Boltzmann population in the initial J state.

$$(46)$$
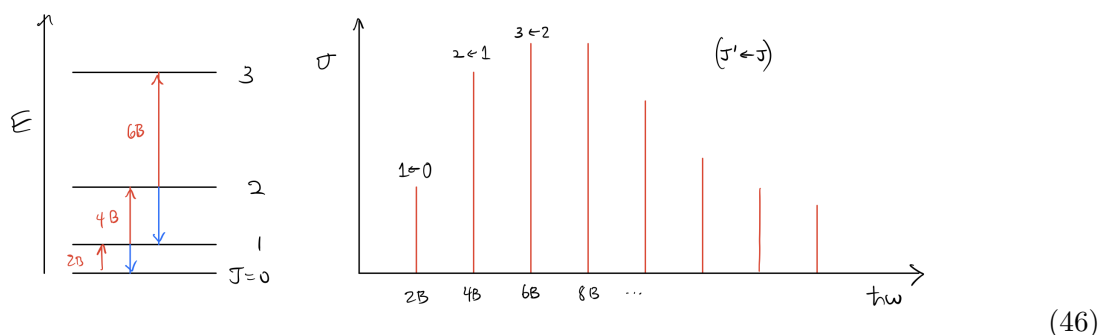
We talk about rotational transitions giving rise to a *microwave spectrum* because the transition energies spaced by $2B$ typically fall at microwave frequencies (100s of MHz to 100s of GHz). For instance, the CO molecule has a B value in the ballpark of $60\,\text{GHz}$ or $2\,\text{cm}^{-1}$.

We can also take away some information here about *selection rules*, which dictate which pairs of states feature allowed transitions. Here we glean the following rules:

- In order to have a rotational spectrum, a rigid rotor must have a finite permanent dipole moment, $\mu_0 > 0$. Homonuclear diatomic molecules like H_2 or N_2 do not have a microwave spectrum within the rigid rotor approximation.

- The only transitions which contribute to the spectrum are between states labeled J, m and $J \pm 1, m$. We therefore learn that $\Delta J = \pm 1$ and $\Delta m = 0$ during an allowed rotational transition.

Note: Our strategy here to find $\sigma(\omega)$ allowed us to solve for the entire rotational spectrum at once. Another way to find the selection rules is to evaluate the transition rate between states $|Y_J^m\rangle$ and

$Y_{J'}^{m'}\rangle$, which we know from time-dependent perturbation theory to be proportional to the square of the matrix element:

$$\Gamma_{J',m'\leftarrow J,m} \propto \left|\langle Y_J^m|\underline{\mu}\cdot\underline{\xi}|Y_{J'}^{m'}\rangle\right|^2 \tag{47}$$

This will yield the same answer. We won't work through this here, but it is done out in McQuarrie Section 6.7 for those interested.

3   Rotations of polyatomic molecules

3.1   Finding the principal axes of rotation

The rotations of nonlinear, polyatomic molecules are considerably more interesting than diatomic molecules. The moment of inertia of a nonlinear molecule depends on which axis of the *molecule* you spin it about. So there are two coordinate systems to think about: which *lab frame* axis we spin the molecule about, and which *molecular frame* axis we spin the molecule about.

The concept of principal moments of inertia will be very helpful to treat this situation. Assuming that our polyatomic molecule rotates as a rigid body, we can write down its moment of inertia I when spun through its center of mass about an arbitrary axis:

$$I = \sum_i M_i R_i^2 \tag{48}$$

where M_i is the mass of the ith atom and R_i is that atom's perpendicular distance from the axis of rotation. Using the three Cartesian axes, we can define a 3×3 moment of inertia tensor (e.g. matrix) to describe rotation about arbitrary axes. The moment of inertia tensor I has diagonal and off-diagonal elements of the form

$$I_{xx} = \sum_i M_i(y_i^2 + z_i^2) \tag{49}$$

$$I_{xy} = -\sum_i M_i x_i y_i \tag{50}$$

The moment of inertia tensor has real matrix elements and is therefore Hermitian. It can be diagonalized to find three eigenvectors with real eigenvalues. The eigenvectors represent the principal axes of the molecule, while the eigenvectors represent the principal moments of inertia about these axes. The principal axes fall along axes of symmetry of the molecule. For instance, any axis of rotational symmetry becomes a principal axis. You can also conceptualize principal axes in more familiar terms. The rotation of an airplane is described in terms of rotations about its three principal axes: pitch, roll, and yaw.

In the case of a nonlinear molecule, the three principal molecular axes are labeled a, b, c once found, with the convention that these labels are determined by

$$I_c \geq I_b \geq I_a \tag{51}$$

These principal axes make a remarkably useful coordinate system. We can decompose the total rotational angular momentum in terms of them as follows:

$$L^2 = L_a^2 + L_b^2 + L_c^2 \tag{52}$$

$$L_a = I_a\omega_a, \quad L_b = I_b\omega_b, \quad L_c = I_c\omega_c \tag{53}$$

The kinetic energy operator for this rigid rotor is therefore:

$$\hat{KE}_{rot} = \frac{\hat{L}_a^2}{2I_a} + \frac{\hat{L}_b^2}{2I_b} + \frac{\hat{L}_c^2}{2I_c} \tag{54}$$

This turns out to be much more complicated to express in any other coordinate system!

3.2 A note about coordinate systems

We are building towards finding the rotational energy eigenvalues of a polyatomic molecule. Before we do so, we should make sure that we are working with good quantum numbers. Recall that we have two sets of coordinates: the *xyz* axes are *space-fixed* coordinates set in the laboratory frame while the *abc* axes are *body-fixed* coordinates that rotate with the molecule. The relationship between these two coordinate systems is determined by three angles, called the *Euler angles* (θ, ϕ, ξ).

We can define the rotational angular momentum operators (and hence the Hamiltonian) in either coordinate system. It is possible to show that the following commutators hold in either coordinate system:

$$\left[\hat{L}^2, \hat{L}_{x,y,z}\right] = 0 \tag{55}$$

$$\left[\hat{L}^2, \hat{L}_{a,b,c}\right] = 0 \tag{56}$$

In other words, the square of the total rotational angular momentum $\hat{L}^2$ commutes with its projection on any one of the lab frame or molecular frame axes. Because both the total angular momentum and either the space-fixed and body-fixed projection on any one axis will also commute with the Hamiltonian, their J, m eigenvalues will be good quantum numbers to describe the rotational energy.

3.3 Molecular tops

A molecule is called a symmetric top when two of its three principal moments of inertia are equal and the third is non-zero. To be a symmetric top, a molecule must have a C_n $(n \geq 3)$ axis of rotational symmetry.

Prolate tops feature

$$I_c = I_b > I_a \tag{57}$$

and take on the shape of a football or a cigar. A molecular example is methyl iodide CH_3I, where the unique a axis with the smallest principal moment of inertia falls along the C_3 axis of symmetry.
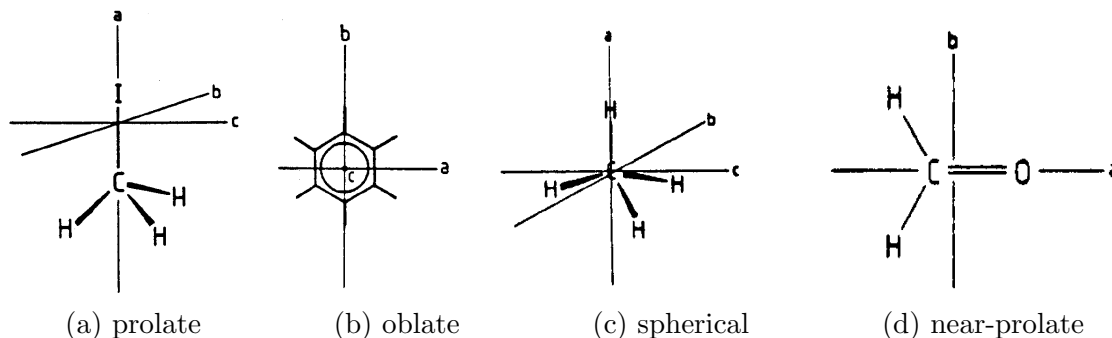
Oblate tops feature

$$I_c > I_b = I_a \tag{58}$$

and look like a hockey puck or a frisbee. Benzene is a molecular example, where the unique c axis falls along the C_6 symmetry axis.

A special type of symmetric top called a **spherical top** occurs when

$$I_c = I_b = I_a \tag{59}$$

9

(a) prolate   (b) oblate   (c) spherical   (d) near-prolate

Only molecules with very high symmetry are spherical tops. Some of the most common examples are methane (CH_4, tetrahedral symmetry), sulfur hexafluoride (SF_6, octahedral symmetry), and the C_{60} fullerene (icosahedral symmetry).

A molecule is an **asymmetric top** if it features no C_n rotational symmetry axis and all three principal moments of inertia are unique

$$I_c \neq I_b \neq I_c \tag{60}$$

Most molecules fall in this category.

Although only a small fraction of known molecules are true symmetric or spherical tops, a more sizeable group falls into the category of "near-prolate" or "near-oblate" tops with:

$$I_c \simeq I_b > I_a \tag{61}$$

$$I_c > I_b \simeq I_a \tag{62}$$

Examples of near prolate tops are C_{2v} molecules such as H_2O and H_2CO or ethylene, C_2H_4. We will discuss in a moment why this is a useful designation!

3.4   Rotational Hamiltonians for symmetric tops

In general, the rotational Hamiltonian can be written as

$$\hat{H}_{rot} = \hat{T}_{rot} = \frac{\hat{L}_a^2}{2I_a} + \frac{\hat{L}_b^2}{2I_b} + \frac{\hat{L}_c^2}{2I_c} \tag{63}$$

Let's first consider the case for a prolate top, where $I_b = I_c$. Recalling that $L^2 = L_a^2 + L_b^2 + L_c^2$ we can write:

$$\hat{H}_{rot} = \frac{\hat{L}_a^2}{2I_a} + \frac{\hat{L}_b^2}{2I_b} + \frac{\hat{L}^2 - L_a^2 - L_b^2}{2I_c} \tag{64}$$

$$= \frac{\hat{L}_a^2}{2I_a} + \frac{\hat{L}_b^2}{2I_b} + \frac{\hat{L}^2 - L_a^2 - L_b^2}{2I_b} \tag{65}$$

$$= \frac{\hat{L}^2}{2I_b} + \frac{\hat{L}_a^2}{2I_a} - \frac{\hat{L}_a^2}{2I_b} \tag{66}$$

10

We've successfully rewritten the Hamiltonian in terms of the total angular momentum and its projection on just one body-fixed axis, the molecular a axis. We know that:

$$\hat{L}^2|\psi\rangle = \hbar^2 J(J+1)|\psi\rangle \tag{67}$$

$$\hat{L}_a|\psi\rangle = \hbar J_a|\psi\rangle \equiv \hbar K|\psi\rangle \tag{68}$$

where we've labeled the projection of the total angular momentum on the unique principal axis of the molecule as K, by convention.

We're now in business to write down the resulting rotational energies:

$$\hat{H}_{rot}|\psi\rangle = E_{rot}|\psi\rangle = \left[\frac{\hbar^2 J(J+1)}{2I_b} + \frac{\hbar^2 K^2}{2}\left(\frac{1}{I_b} - \frac{1}{I_a}\right)\right]|\psi\rangle \tag{69}$$

$$\equiv \left[BJ(J+1) + (A-B)K^2\right]|\psi\rangle \tag{70}$$

where we define the three rotational constants as

$$A, B, C = \frac{\hbar^2}{2I_{a,b,c}} \tag{71}$$

For an oblate top, following a similar procedure with $I_a = I_b$ lets one obtain:

$$E_{rot} = BJ(J+1) - (B-C)K^2 \tag{72}$$

The quantum number K can take values $K = 0, \pm 1, \pm 2, \cdots \pm J$. Each J level therefore has $2J+1$ different K states, corresponding to the different quantized projections of J on the molecular body-fixed axis. Furthermore, each J, K level features an additional $2J+1$ degenerate M_J levels, corresponding to projections of J on the laboratory space-fixed axis, just like the diatomic rigid rotor. Thus, the total statistical weight for each value of J is $(2J+1)^2$. We can fully specify any rotational wavefunction with J, K, M_J quantum numbers.

The energy levels for representative prolate and oblate tops are shown below. Since $A > B > C$, tracking the energy level of a particular J state across the different K stacks reveals that the energy increases with K for a prolate top, and decreases with K for an oblate top.
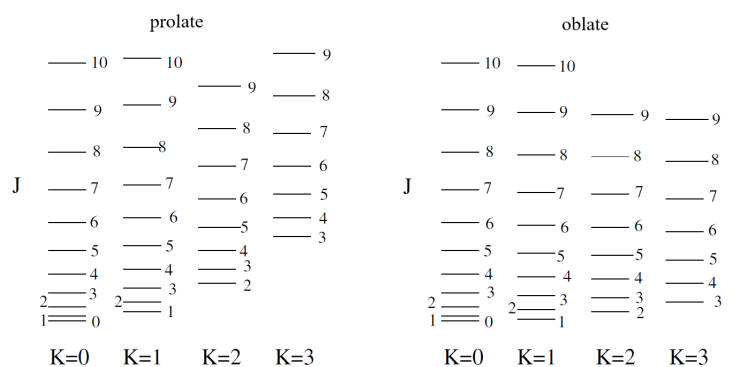
The relevant selection rules for symmetric tops are similar to those of the rigid rotor, and can be shown to be:

$$\Delta J = \pm 1 \tag{73}$$

$$\Delta K = 0 \tag{74}$$

$$\mu_0 > 0 \tag{75}$$

11

A rigorous derivation of these rules requires evaluating the transition integrals $|\langle\psi_{JKM}|\hat{\mu}\cdot\xi|\psi_{JKM}\rangle|^2$ per Fermi's golden rule. However, we can still mention conceptually why $\Delta K = 0$. Because of the high symmetry of a symmetric top, the component of the molecular dipole moment lying perpendicular to the symmetry axis is zero, and hence no torque can be applied about this axis by the radiation's electric field. Accordingly, the angular momentum about the symmetry axis cannot change due to interaction with radiation, and $\Delta K = 0$.

Because $\Delta K = 0$ during a dipole-allowed transition, allowed transitions occur between J levels within a given K-stack. The observable frequencies ΔE for a rigid symmetric top do not depend on K and we find

$$\Delta E = 2B(J+1) \tag{76}$$

for the $J \to J+1$ transition, just as for a rigid diatomic rotor.

3.5 Spherical Tops

We also note quickly that the situation is quite simple for a spherical top. With $I_a = I_b = I_c$, we find

$$\hat{H}_{rot} = \frac{\hat{L}^2}{2I_b} \tag{77}$$

$$E_{rot} = BJ(J+1) \tag{78}$$

with $\Delta J = \pm 1$. All $(2J+1)^2$ levels corresponding to different body-fixed and space-fixed projections of J are degenerate for a spherical top.

Since spherical tops are highly symmetric, they do not have a permanent dipole moment. So would we even expect to observe a microwave spectrum? Within the rigid rotor approximation, no. However, centrifugal distortion of the bonds can slightly break the symmetry, effectively converting the molecule into a symmetric rotor. This yields a very small dipole moment, and therefore a weak rotational spectrum.

3.6 Asymmetric tops

For asymmetric tops $I_a \neq I_b \neq I_c$, and the rotational Hamiltonian cannot be simplified. Approximate solutions are obtained by expanding the asymmetric top wavefunction in a basis of symmetric top wavefunctions.

The spectrum of an asymmetric rotor may therefore be extremely complex, with an irregular distribution of energy levels. The selection rules and transition probabilities between these levels are complicated. Much of the complexity arises from the fact that in an asymmetric rotor the permanent dipole moment may lie in any arbitrary direction with respect to the principal axes of inertia. This is in contrast to spherical tops, whose permanent dipole moments fall along the principal axes by symmetry.

4 Beyond the rigid rotor approximation

In reality, molecules are not rigid, and rotational motion will couple to vibrational motion of the nuclei. For instance, the simplest correction you will see to the diatomic rigid rotor approximation

is to include a *centrifugal distortion* term to the energy:

$$E(J) = BJ(J+1) - D_J J^2 (J+1)^2 \tag{79}$$

This accounts for the fact that as a real molecule rotates the bond stretches out, increasing the moment of inertia and decreasing the spacing between energy levels. This effect is amplified at higher J, as the molecule spins increasingly quickly. The centrifugal distortion constant D is typically much smaller than B. This correction means that adjacent transitions are no longer perfectly spaced in frequency space:

$$\Delta E(J) = E(J+1) - E(J) \tag{80}$$
$$= 2B(J+1) - 4D_J(J+1)^3 \tag{81}$$

In the next lecture, we will consider transitions between vibrational states and vibration-rotation interactions.