# Advanced Quantum Mechanics \& Spectroscopy (CHEM 7520) 

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## Week 2-3: Rotations of polyatomic molecules

## III. QUANTUM MECHANICS OF RIGID ROTATIONS

## A. The rotational Hamiltonian operator

1) The classical Hamiltonian function involves the angular momentum vectors $\mathbf{J}$ with components (in the principal molecule-fixed coordinate system) $\mathbf{J}=$ $\left(J_{a}, J_{b}, J_{c}\right)$. In quantum mechanical description, we replace $J_{a}, J_{b}, J_{c}$ by the corresponding differential operators $\hat{J}$ that involve coordinates describing rotations. The appropriate coordinates are those that describe the orientation of the molecule relative to a nonrotating space-fixed coordinate system with origin located at the center of mass of the molecule. We will denote this coordinate system as $(X, Y, Z)$. To specify the orientation of the molecule-fixed principal axes $a, b, c$ with respect to the space-fixed axes $X, Y, Z$, we must specify three angles. These angles are known as the Euler angles.
2) To define the Euler angles we assume that coordinate systems ( $a, b, c$ ) and $(X, Y, Z)$ share the same origin $O$, which is also the center of mass (see Levine "Molecular spectroscopy" Figure 5.2). The three angles $\theta, \phi, \chi$ are defined as follows:
(a) $\theta$ is the angle between $O Z$ and $O c(0 \leq \theta \leq \pi)$
(b) $\phi$ is the angle between $O X$ and the projection of $O c$ in the $X Y$ plane $(0 \leq \phi \leq 2 \pi)$
(c) $\chi$ is the angle of rotation about the $O c$ axis in the $a b$ plane $(0 \leq \chi \leq 2 \pi)$

The angles $\theta$ and $\phi$ specify the orientation of the $c$ axis, while $\chi$ specifies the orientation of $a$ and $b$. The line of intersection of the $X Y$ and $a b$ planes is called the line of nodes ( $O N$ ).
3) We need to express the components of the angular momentum operator $\hat{J}$ in terms of the Euler angles. We use the following fact from the theory of the orbital angular momentum: the component of the angular momentum operator along some axis is $-i \hbar \frac{\partial}{\partial \beta}$, where $\beta$ is the angle of rotation about that axis. The angles
$\phi, \chi$, and $\theta$ are the angles of rotation about the $O Z, O c$, and $O N$ axes, respectively. Thus, we obtain:

$$
\begin{equation*}
\hat{J}_{Z}=-i \hbar \frac{\partial}{\partial \phi} \quad \hat{J}_{c}=-i \hbar \frac{\partial}{\partial \chi} \quad \hat{J}_{N}=-i \hbar \frac{\partial}{\partial \theta} \tag{1}
\end{equation*}
$$

The operators $\hat{J}_{Z}, \hat{J}_{c}, \hat{J}_{N}$ are simple, but they do not belong to the same coordinate system $[(X, Y, Z)$ or $(a, b, c)]$. To derive expressions for $\hat{J}_{a}$ and $\hat{J_{b}}$, we study the relationship between different components of the angular momentum vector $\mathbf{J}$ in classical mechanics. We can express $\mathbf{J}$ in terms of the unit vectors $\mathbf{e}_{\mathbf{i}}$ along axes $a, b, c$ :

$$
\begin{equation*}
\mathbf{J}=\mathbf{e}_{\mathbf{a}} J_{a}+\mathbf{e}_{\mathbf{b}} J_{b}+\mathbf{e}_{\mathbf{c}} J_{c} \tag{2}
\end{equation*}
$$

The component $J_{N}$ can thus be written by projecting the vector $\mathbf{J}$ by the unit vector $\mathbf{e}_{\mathrm{N}}$ :

$$
\begin{equation*}
J_{N}=\left(\mathbf{e}_{\mathbf{N}} \cdot \mathbf{e}_{\mathbf{a}}\right) J_{a}+\left(\mathbf{e}_{\mathbf{N}} \cdot \mathbf{e}_{\mathbf{b}}\right) J_{b}+\left(\mathbf{e}_{\mathbf{N}} \cdot \mathbf{e}_{\mathbf{c}}\right) J_{c} \tag{3}
\end{equation*}
$$

Similarly, for $J_{Z}$ we obtain:

$$
\begin{equation*}
J_{Z}=\left(\mathbf{e}_{\mathbf{Z}} \cdot \mathbf{e}_{\mathbf{a}}\right) J_{a}+\left(\mathbf{e}_{\mathbf{Z}} \cdot \mathbf{e}_{\mathbf{b}}\right) J_{b}+\left(\mathbf{e}_{\mathbf{Z}} \cdot \mathbf{e}_{\mathbf{c}}\right) J_{c} \tag{4}
\end{equation*}
$$

The dot products that appear in Eqs. (3) and (4) can be expressed in terms of the trigonometric functions of $\phi, \chi$, and $\theta$. Since expression for $J_{c}$ is known, we can regard $J_{a}$ and $J_{b}$ as two unknowns and obtain expressions for them from Eqs. (3) and (4). We obtain:

$$
\begin{align*}
& J_{a}=-\cos \chi \csc \theta J_{Z}+\cos \chi \cot \theta J_{c}+\sin \chi J_{N}  \tag{5}\\
& J_{b}=\sin \chi \csc \theta J_{Z}-\sin \chi \cot \theta J_{c}+\cos \chi J_{N} \tag{6}
\end{align*}
$$

Replacing classical quantities by operators we can write expressions for the components of the angular momentum operator in the molecule-fixed coordinate system:

$$
\begin{align*}
& \hat{J}_{a}=i \hbar\left[\cos \chi \csc \theta \frac{\partial}{\partial \phi}-\cos \chi \cot \theta \frac{\partial}{\partial \chi}-\sin \chi \frac{\partial}{\partial \theta}\right]  \tag{7}\\
& \hat{J}_{b}=i \hbar\left[-\sin \chi \csc \theta \frac{\partial}{\partial \phi}+\sin \chi \cot \theta \frac{\partial}{\partial \chi}-\cos \chi \frac{\partial}{\partial \theta}\right]  \tag{8}\\
& \hat{J}_{c}=-i \hbar \frac{\partial}{\partial \chi} \tag{9}
\end{align*}
$$

In a similar way, we can obtain expressions for the components of the angular momentum operator in the space-fixed coordinate system:

$$
\begin{align*}
& \hat{J}_{X}=i \hbar\left[\cos \phi \cot \theta \frac{\partial}{\partial \phi}-\cos \phi \csc \theta \frac{\partial}{\partial \chi}+\sin \phi \frac{\partial}{\partial \theta}\right]  \tag{10}\\
& \hat{J}_{Y}=i \hbar\left[\sin \phi \cot \theta \frac{\partial}{\partial \phi}-\sin \phi \csc \theta \frac{\partial}{\partial \chi}-\cos \phi \frac{\partial}{\partial \theta}\right]  \tag{11}\\
& \hat{J}_{Z}=-i \hbar \frac{\partial}{\partial \phi} \tag{12}
\end{align*}
$$

4) We have previously derived the expression for the Hamiltonian function in classical mechanics. Replacing the classical quantities by the corresponding operators, we can write the quantum-mechanical Hamiltonian of molecular rotation as:

$$
\begin{equation*}
\hat{H}_{r o t}=\frac{\hat{J}_{a}^{2}}{2 I_{a}}+\frac{\hat{J}_{b}^{2}}{2 I_{b}}+\frac{\hat{J}_{c}^{2}}{2 I_{c}} \tag{13}
\end{equation*}
$$

We can use this Hamiltonian to solve the rotational Schrödinger equation. Instead of solving it directly, we are going to find the eigenvalues of $\hat{H}_{\text {rot }}$ using the commutation properties of the angular momentum operators.
5) The total angular momentum operator is given by:

$$
\begin{gather*}
\hat{J}^{2}=\hat{J}_{a}^{2}+\hat{J}_{b}^{2}+\hat{J}_{c}^{2}=\hat{J}_{X}^{2}+\hat{J}_{Y}^{2}+\hat{J}_{Z}^{2}  \tag{14}\\
\hat{J}^{2}=-\hbar^{2}\left[\csc ^{2} \theta \frac{\partial^{2}}{\partial \phi^{2}}+\csc ^{2} \theta \frac{\partial^{2}}{\partial \chi^{2}}-2 \cot \theta \csc \theta \frac{\partial^{2}}{\partial \phi \partial \chi}+\frac{\partial^{2}}{\partial \theta^{2}}+\cot \theta \frac{\partial}{\partial \theta}\right] \tag{15}
\end{gather*}
$$

The angular momentum operators have the following commutation relations:

$$
\begin{array}{rll}
{\left[\hat{J}_{X}, \hat{J}_{Y}\right]=i \hbar \hat{J}_{Z}} & {\left[\hat{J}_{Y}, \hat{J}_{Z}\right]=i \hbar \hat{J}_{X}} & {\left[\hat{J}_{Z}, \hat{J}_{X}\right]=i \hbar \hat{J}_{Y}} \\
{\left[\hat{J}_{a}, \hat{J}_{b}\right]=-i \hbar \hat{J}_{c}} & {\left[\hat{J}_{b}, \hat{J}_{c}\right]=-i \hbar \hat{J}_{a}} & {\left[\hat{J}_{c}, \hat{J}_{a}\right]=-i \hbar \hat{J}_{b}} \\
{\left[\hat{J}^{2}, \hat{J}_{F}\right]=0} & {\left[\hat{J}^{2}, \hat{J}_{g}\right]=0} & {\left[\hat{J}_{F}, \hat{J}_{g}\right]=0} \tag{18}
\end{array}
$$

where $F \in\{X, Y, Z\}$ and $g \in\{a, b, c\}$.
6) Using the properties of the angular momentum operators, we can derive the commutators of the Hamiltonian:

$$
\begin{equation*}
\left[\hat{H}_{r o t}, \hat{J}^{2}\right]=0 \quad\left[\hat{H}_{r o t}, \hat{J}_{Z}\right]=0 \tag{19}
\end{equation*}
$$

Thus, $\hat{H}_{\text {rot }}$ commutes with the total angular momentum operator $\hat{J}^{2}$ and one of its space-fixed components $\hat{J}_{Z}$. This is, however, not the case for the angular momentum component in the molecule-fixed coordinate system:

$$
\begin{equation*}
\left[\hat{H}_{r o t}, \hat{J}_{c}\right]=i \hbar\left(\frac{1}{2 I_{a}}-\frac{1}{2 I_{b}}\right)\left(\hat{J}_{a} \hat{J}_{b}+\hat{J}_{b} \hat{J}_{a}\right) \tag{20}
\end{equation*}
$$

## B. Solutions of the rotational Schrödinger equation

1) The rotational Schrödinger equation can be written as

$$
\begin{equation*}
\hat{H}_{r o t}\left|\Psi_{r o t}\right\rangle=E_{r o t}\left|\Psi_{r o t}\right\rangle \tag{21}
\end{equation*}
$$

Since $\hat{H}_{\text {rot }}$ commutes with $\hat{J}^{2}$ and $\hat{J}_{Z}$, the rotational eigenfunctions $\left|\Psi_{\text {rot }}\right\rangle$ can be chosen as eigenfunctions of these two operators. From the theory of angular momentum operators we obtain:

$$
\begin{align*}
\hat{J}^{2}\left|\Psi_{r o t}\right\rangle & =J(J+1) \hbar^{2}\left|\Psi_{r o t}\right\rangle, \quad J=0,1,2, \ldots  \tag{22}\\
\hat{J}_{Z}\left|\Psi_{r o t}\right\rangle & =M \hbar\left|\Psi_{r o t}\right\rangle, \quad M=0, \pm 1, \ldots, \pm J \tag{23}
\end{align*}
$$

where $\sqrt{J(J+1)} \hbar$ is the magnitude of the total rotational angular momentum and $M \hbar$ is its component along a space-fixed axis. Since the eigenfunctions of $\hat{J}_{Z}=-i \hbar \frac{\partial}{\partial \phi}$ are $\frac{e^{i M \phi}}{(2 \pi)^{1 / 2}}$, the rotor eigenfunctions have the general form:

$$
\begin{equation*}
\left|\Psi_{r o t}\right\rangle=\frac{1}{(2 \pi)^{1 / 2}} F(\theta, \chi) e^{i M \phi} \tag{24}
\end{equation*}
$$

The above equations apply to molecules that belong to any rotational type. Let's consider special cases for different types of rotors.

## 2) Spherical top:

The Hamiltonian takes the form:

$$
\begin{equation*}
\hat{H}_{\text {rot }}=\frac{\hat{J}_{a}^{2}}{2 I_{b}}+\frac{\hat{J}_{b}^{2}}{2 I_{b}}+\frac{\hat{J}_{c}^{2}}{2 I_{b}}=\frac{\hat{J}^{2}}{2 I_{b}} \tag{25}
\end{equation*}
$$

The Schrödinger equation becomes:

$$
\begin{align*}
\frac{\hat{J}^{2}}{2 I_{b}}\left|\Psi_{r o t}\right\rangle & =E_{r o t}\left|\Psi_{r o t}\right\rangle  \tag{26}\\
E_{r o t} & =\frac{J(J+1) \hbar^{2}}{2 I_{b}} \tag{27}
\end{align*}
$$

Note that the spherical top energy depends only on quantum number $J$. We can express the rotational energy in $\mathrm{cm}^{-1}$ as follows:

$$
\begin{equation*}
F_{r o t}=\frac{E_{r o t}}{h c}=B J(J+1) \tag{28}
\end{equation*}
$$

where $B$ is the rotational constant that we defined in the classical theory of molecular rotations. While $\hat{H}_{\text {rot }}$ in general does not commute with $\hat{J}_{c}$, for the spherical top $\hat{H}_{r o t}$ involves only $\hat{J}^{2}$, which commutes with $\hat{J}_{c}$. Hence, we obtain:

$$
\begin{equation*}
\left[\hat{H}_{r o t}, \hat{J}_{c}\right]=0 \tag{29}
\end{equation*}
$$

Thus, in addition to $\hat{J}^{2}$ and $\hat{J}_{Z}$, for the spherical top $\left|\Psi_{\text {rot }}\right\rangle$ is also an eigenfunction of $\hat{J}_{c}$. Since $\hat{J}_{c}=-i \hbar \frac{\partial}{\partial \chi}$ has a very similar form to that of $\hat{J}_{Z}$, we conclude that the corresponding eigenvalue equation should be similar to that of Eq. (23), i.e.:

$$
\begin{equation*}
\hat{J}_{c}\left|\Psi_{r o t}\right\rangle=K \hbar\left|\Psi_{r o t}\right\rangle, \quad K=0, \pm 1, \ldots, \pm J \tag{30}
\end{equation*}
$$

where we assign a new quantum number $K$ that labels the eigenfunctions of $\hat{J}_{c}$ and describes the rotational angular momentum component along a molecule-fixed axis of the spherical top. Similarly, the $\hat{J}_{c}$ eigenfunctions should have the form: $\frac{e^{i K x}}{(2 \pi)^{1 / 2}}$. Taking into account results obtained in Eqs. (22) to (24), we conclude that the spherical top eigenfunctions should have the form:

$$
\begin{equation*}
\left|\Psi_{r o t}\right\rangle=\frac{1}{2 \pi} H_{J K M}(\theta) e^{i M \phi} e^{i K \chi} \tag{31}
\end{equation*}
$$

We therefore have three quantum numbers $J, K$, and $M$, but the energy depends only on $J$. Each $K$ and $M$ can have $2 J+1$ different values for each value of $J$. Thus, the spherical top rotational levels are $(2 J+1)^{2}$-fold degenerate.

## 3) Linear molecule:

In linear molecules, the Hamiltonian only depends on angles $\theta$ and $\phi$, not on $\chi$.

It has a similar form to that of the spherical top

$$
\begin{equation*}
\hat{H}_{r o t}=\frac{\hat{J}^{2}}{2 I_{b}} \tag{32}
\end{equation*}
$$

but we should remember that for a linear molecule $I_{a}=0$. The expression for the total angular momentum operator simplifies:

$$
\begin{equation*}
\hat{J}^{2}=-\hbar^{2}\left[\csc ^{2} \theta \frac{\partial^{2}}{\partial \phi^{2}}+\frac{\partial^{2}}{\partial \theta^{2}}+\cot \theta \frac{\partial}{\partial \theta}\right] \tag{33}
\end{equation*}
$$

This turns out to be exactly the expression for the total orbital angular momentum that can be found in many introductory books on quantum mechanics. Thus, the eigenfunctions of $\hat{J}^{2}$ for linear or diatomic molecules are spherical harmonics:

$$
\begin{align*}
\left|\Psi_{r o t}\right\rangle & =\left|Y_{J M}(\theta, \phi)\right\rangle  \tag{34}\\
\hat{J}^{2}\left|Y_{J M}(\theta, \phi)\right\rangle & =J(J+1) \hbar^{2}\left|Y_{J M}(\theta, \phi)\right\rangle  \tag{35}\\
\hat{J}_{Z}\left|Y_{J M}(\theta, \phi)\right\rangle & =M \hbar\left|Y_{J M}(\theta, \phi)\right\rangle \tag{36}
\end{align*}
$$

The energy expression has the form:

$$
\begin{equation*}
F_{r o t}=\frac{E_{r o t}}{h c}=B J(J+1) \tag{37}
\end{equation*}
$$

In this case, each rotational energy level depends only on $J$ and is $(2 J+1)$-fold degenerate in $M$.

## 4) Symmetric top:

For the symmetric top only two principal moments of inertia are the same. Assuming we have oblate top ( $I_{a}=I_{b}$ ) so that $c$ principal axis is the symmetry axis, we can write the Hamiltonian as:

$$
\begin{equation*}
\hat{H}_{\text {rot }}=\frac{\hat{J}_{a}^{2}+\hat{J}_{b}^{2}}{2 I_{b}}+\frac{\hat{J}_{c}^{2}}{2 I_{c}}=\frac{\hat{J}^{2}-\hat{J}_{c}^{2}}{2 I_{b}}+\frac{\hat{J}_{c}^{2}}{2 I_{c}} \tag{38}
\end{equation*}
$$

Since $\hat{J}_{c}$ commutes with $\hat{J}^{2}$ and $\hat{J}_{c}^{2}$, we conclude that $\left[\hat{H}_{r o t}, \hat{J}_{c}\right]=0$. Thus, the oblate symmetric top wavefunction $\left|\Psi_{\text {rot }}\right\rangle$ is an eigenfunction of $\hat{J}_{c}$ :

$$
\begin{equation*}
\hat{J}_{c}\left|\Psi_{r o t}\right\rangle=K \hbar\left|\Psi_{r o t}\right\rangle, \quad K=0, \pm 1, \ldots, \pm J \tag{39}
\end{equation*}
$$

Using this result, we can obtain the oblate top energy expression following the derivation:

$$
\begin{align*}
\hat{J}_{c}^{2}\left|\Psi_{r o t}\right\rangle & =K^{2} \hbar^{2}\left|\Psi_{r o t}\right\rangle  \tag{40}\\
\left(\frac{\hat{J}^{2}-\hat{J}_{c}^{2}}{2 I_{b}}+\frac{\hat{J}_{c}^{2}}{2 I_{c}}\right)\left|\Psi_{r o t}\right\rangle & =E_{r o t}\left|\Psi_{r o t}\right\rangle  \tag{41}\\
\left(\frac{J(J+1) \hbar^{2}-K^{2} \hbar^{2}}{2 I_{b}}+\frac{K^{2} \hbar^{2}}{2 I_{c}}\right)\left|\Psi_{r o t}\right\rangle & =E_{r o t}\left|\Psi_{r o t}\right\rangle  \tag{42}\\
\frac{J(J+1) \hbar^{2}}{2 I_{b}}+K^{2} \hbar^{2}\left(\frac{1}{2 I_{c}}-\frac{1}{2 I_{b}}\right) & =E_{r o t} \tag{43}
\end{align*}
$$

Expressing the rotational energy in $\mathrm{cm}^{-1}$, we get for the oblate top:

$$
\begin{equation*}
\left.F_{\text {rot }}=\frac{E_{\text {rot }}}{h c}=B J(J+1)+(C-B) K^{2} \quad \text { (oblate }\right) \tag{44}
\end{equation*}
$$

We note that $(C-B)$ is negative, therefore the oblate top energy will decrease with increasing $K$. For the prolate top, a similar derivation can be performed with the only difference that we must interchange axes $a$ and $c$. The resulting energy expression is:

$$
\begin{equation*}
F_{\text {rot }}=\frac{E_{\text {rot }}}{h c}=B J(J+1)+(A-B) K^{2} \quad(\text { prolate }) \tag{45}
\end{equation*}
$$

Here, $A-B$ is positive, thus the prolate top energy will increase with increasing $K$. We also note that for $A=B=C$, the symmetric top energy expression will reduce to that of the spherical top. Since the symmetric top $\left|\Psi_{\text {rot }}\right\rangle$ is an eigenfunction of $\hat{J}^{2}, \hat{J}_{Z}$, and $\hat{J}_{c}$, it has the following form:

$$
\begin{equation*}
\left|\Psi_{r o t}\right\rangle=\frac{1}{2 \pi} G_{J K M}(\theta) e^{i M \phi} e^{i K \chi} \tag{46}
\end{equation*}
$$

This form is identical to that of the spherical top. The symmetric top eigenfunctions can be expressed using the so-called Wigner rotation matrices. More explicitly, the $G_{J K M}(\theta)$ factor has the form:

$$
\begin{equation*}
G_{J K M}(\theta)=\sqrt{\frac{2 J+1}{2}} d_{M K}^{J}(\theta) \tag{47}
\end{equation*}
$$

where

$$
\begin{equation*}
d_{M K}^{J}(\theta)=\sqrt{(J+M)!(J-M)!(J+K)!(J-K)!} \times \tag{48}
\end{equation*}
$$

$$
\begin{equation*}
\sum_{\sigma=\max \{0,-(K+M)\}}^{\min \{J-M, J-K\}} \frac{(-1)^{J-K-\sigma}[\cos (\theta / 2)]^{K+M+2 \sigma}[\sin (\theta / 2)]^{2 J-K-M-2 \sigma}}{\sigma!(K+M+\sigma)!(J-M-\sigma)!(J-K-\sigma)!} \tag{49}
\end{equation*}
$$

These expressions allow to calculate the symmetric top wavefunctions analytically as a function of $\theta, \phi$, and $\chi$.
As we can see from Eqs. (44) and (45), the symmetric top energy depends on $J$ and $K^{2}$. There is a $(2 J+1)$-fold degeneracy associated with $M$. In addition, for $K \neq 0$ there is a two-fold degeneracy associated with $+|K|$ and $-|K|$. Thus, the symmetric top degeneracy is $4 J+2$ for $K \neq 0$ and $2 J+1$ for $K=0$.

## 5) Asymmetric top:

The asymmetric top Hamiltonian is

$$
\begin{equation*}
\hat{H}_{\text {rot }}=\frac{\hat{J}_{a}^{2}}{2 I_{a}}+\frac{\hat{J}_{b}^{2}}{2 I_{b}}+\frac{\hat{J}_{c}^{2}}{2 I_{c}} \tag{50}
\end{equation*}
$$

Since all moments of inertia are different, there is no simplification. The rotational wavefunctions have the general form that we obtained before:

$$
\begin{equation*}
\left|\Psi_{\text {rot }}\right\rangle=\frac{1}{(2 \pi)^{1 / 2}} F(\theta, \chi) e^{i M \phi} \tag{51}
\end{equation*}
$$

Because $\hat{H}_{\text {rot }}$ does not commute with $\hat{J}_{c}$, for the asymmetric top $K$ is no longer a good quantum number.
The asymmetric top energy expression cannot be obtained in closed form for arbitrary values of $J$. To solve the Schrödinger equation, we expand $\left|\Psi_{\text {rot }}\right\rangle$ in terms of some known complete orthonormal basis set. A convenient choice is to use a set of the symmetric top wavefunctions, which are functions of the same coordinates (the Euler angles) that satisfy the same boundary conditions as the asymmetric top functions. Since for the asymmetric top $\hat{H}_{\text {rot }}$ commutes with $\hat{J}^{2}$ and $\hat{J}_{Z}$, each wavefunction is labelled with $J$ and $M$ quantum numbers and can be expanded as follows:

$$
\begin{equation*}
\left|\Psi_{r o t}\right\rangle=\left|\psi_{J M \tau}\right\rangle=\sum_{K=-J}^{J} C_{J M K \tau}\left|\phi_{J M K}\right\rangle \tag{52}
\end{equation*}
$$

where $C_{J M K \tau}$ are the expansion coefficients and $\left|\phi_{J M K}\right\rangle$ are the symmetric top
wavefunctions that we discussed earlier

$$
\begin{equation*}
\left|\phi_{J M K}\right\rangle=\frac{1}{2 \pi} G_{J K M}(\theta) e^{i M \phi} e^{i K \chi} \tag{53}
\end{equation*}
$$

In Eq. (52), $\tau$ is an index (not a quantum number) that labels the asymmetric top wavefunctions in the order with increasing energy. The convention is that $\tau$ runs from $-J$ to $J$ as the energy increases. There is a total of $2 J+1$ terms in the expansion on the right-hand side of Eq. (52) and, thus, there are $2 J+1$ wavefunctions $\left|\psi_{J M \tau}\right\rangle$ for specfic values of $J$ and $M$.
We can now write the Schrödinger equation using the expansion in Eq. (52) and express it in the matrix form projecting by $\left|\phi_{J^{\prime} M^{\prime} K^{\prime}}\right\rangle$ on the left:

$$
\begin{align*}
\hat{H}_{r o t}\left|\psi_{J M \tau}\right\rangle & =E_{\tau}\left|\psi_{J M \tau}\right\rangle  \tag{54}\\
\hat{H}_{r o t} \sum_{K=-J}^{J} C_{J M K \tau}\left|\phi_{J M K}\right\rangle & =E_{\tau} \sum_{K=-J}^{J} C_{J M K \tau}\left|\phi_{J M K}\right\rangle  \tag{55}\\
\sum_{K=-J}^{J}\left\langle\phi_{J^{\prime} M^{\prime} K^{\prime}}\right| \hat{H}_{r o t}\left|\phi_{J M K}\right\rangle C_{J M K \tau} & =E_{\tau} \sum_{K=-J}^{J} C_{J M K \tau}\left\langle\phi_{J^{\prime} M^{\prime} K^{\prime}} \mid \phi_{J M K}\right\rangle  \tag{56}\\
\sum_{K=-J}^{J}\left\langle\phi_{J^{\prime} M^{\prime} K^{\prime}}\right| \hat{H}_{r o t}\left|\phi_{J M K}\right\rangle C_{J M K \tau} & =\delta_{J^{\prime} J} \delta_{M^{\prime} M} C_{J M K^{\prime} \tau} E_{\tau} \tag{57}
\end{align*}
$$

where we used the fact that the symmetric top wavefunctions are orthogonal. We see that the right-hand side of Eq. (57) is zero unless $J=J^{\prime}$ and $M=M^{\prime}$. This indicates that the asymmetric top Hamiltonian matrix elements $\left\langle\phi_{J^{\prime} M^{\prime} K^{\prime}}\right| \hat{H}_{\text {rot }}\left|\phi_{J M K}\right\rangle=0$ if $J \neq J^{\prime}$ and $M \neq M^{\prime}$ (this is a consequence of $\hat{H}_{\text {rot }}$ commuting with $\hat{J}^{2}$ and $\hat{J}_{Z}$ ). We then obtain a simplified form of the Schrödinger equation

$$
\begin{align*}
\sum_{K=-J}^{J}\left\langle\phi_{J M K^{\prime}}\right| \hat{H}_{\text {rot }}\left|\phi_{J M K}\right\rangle C_{J M K \tau} & =C_{J M K^{\prime} \tau} E_{\tau}  \tag{58}\\
\sum_{K=-J}^{J} H_{K^{\prime} K}^{J M} C_{K}^{J M \tau} & =C_{K^{\prime}}^{J M \tau} E_{\tau}  \tag{59}\\
\mathbf{H}^{\mathbf{J M}} \mathbf{C}^{\mathbf{J M}} & =\mathbf{C}^{\mathbf{J M}} \mathbf{E} \tag{60}
\end{align*}
$$

where we defined $H_{K^{\prime} K}^{J M} \equiv\left\langle\phi_{J M K^{\prime}}\right| \hat{H}_{\text {rot }}\left|\phi_{J M K}\right\rangle$ and $C_{K}^{J M \tau} \equiv C_{J M K \tau}$. For a specific value of $J, \mathbf{H}^{\mathbf{J M}}$ is a matrix with dimensions $2 J+1$ by $2 J+1$. Eq. (60) can be solved by diagonalizing $\mathbf{H}^{\mathbf{J M}}$ for each value of $J$ and $M$ to find the energy levels $E_{\tau}$ (eigenvalues) and the mixing coefficients $C_{K^{\prime}}^{J M \tau}$ (eigenvectors).

If we choose the oblate-top wavefunctions as the basis set $\left|\phi_{J M K}\right\rangle$, the matrix elements $H_{K^{\prime} K}^{J M}$ have the form:

$$
\begin{align*}
H_{K^{\prime} K}^{J M} & =\frac{h c}{2} \delta_{K K^{\prime}}\left[(2 C-A-B)\left(K^{\prime}\right)^{2}+(A+B) J(J+1)\right] \\
& +\frac{h c}{4} \delta_{K\left(K^{\prime}+2\right)}(B-A) \sqrt{\left[J(J+1)-K^{\prime}\left(K^{\prime}+1\right)\right]\left[J(J+1)-\left(K^{\prime}+1\right)\left(K^{\prime}+2\right)\right]} \\
& +\frac{h c}{4} \delta_{K\left(K^{\prime}-2\right)}(B-A) \sqrt{\left[J(J+1)-K^{\prime}\left(K^{\prime}-1\right)\right]\left[J(J+1)-\left(K^{\prime}-1\right)\left(K^{\prime}-2\right)\right]} \tag{61}
\end{align*}
$$

Note that even and odd values of $K$ do not mix. Prolate-top wavefunctions constitute another satisfactory choice of the basis set.
For $J=0$, the matrix $\mathbf{H}^{\mathbf{J M}}$ contains only one element $H_{00}$. In this case, $E=H_{00}=0$, and the $J=0$ asymmetric top wavefunction is identical to the symmetric-top $J=0$ wavefunction. For $J=1$, we have $K=-1,0,+1$. The Hamiltonian matrix has the form:

$$
\mathbf{H}^{\mathbf{1 M}}=\left[\begin{array}{ccc}
\frac{h c}{2}(2 C+A+B) & 0 & \frac{h c}{2}(B-A)  \tag{62}\\
0 & h c(A+B) & 0 \\
\frac{h c}{2}(B-A) & 0 & \frac{h c}{2}(2 C+A+B)
\end{array}\right]
$$

The eigenvalues can be calculated either by diagonalizing the $3 \times 3$ matrix $\mathbf{H}^{\mathbf{1 M}}$ or by solving the $3 \times 3$ secular determinant equation $\operatorname{det}\left(\mathbf{H}^{\mathbf{1 M}}-\mathbf{1} \mathbf{E}\right)=0$. We obtain in the order of increasing energy:

$$
\begin{equation*}
F_{1}=\frac{E_{1}}{h c}=(B+C), \quad F_{2}=(A+C), \quad F_{3}=(A+B) \tag{63}
\end{equation*}
$$

For large $J$ values, $\mathbf{H}^{\mathbf{J M}}$ can be diagonalized numerically.
In asymmetric tops, the rotational constant $B$ can take any value between $A$ and $C$. In the limit $B=A$, we have an oblate symmetric top; for $B=C$, we have a prolate symmetric top. We can introduce the so-called Ray's asymmetry parameter

$$
\begin{equation*}
\kappa=\frac{2 B-A-C}{A-C} \tag{64}
\end{equation*}
$$

For the oblate symmetric top, $\kappa=1$, while for the prolate symmetric top $\kappa=-1$. For the asymmetric tops, $\kappa$ takes a value between 1 and -1 . If we vary $B$ while keeping $A$ and $C$ fixed, we can draw a correlation diagram showing the energy of the asymmetric top as a function of $\kappa$ (see Levine "Molecular spectroscopy"

Figure 5.4). Instead of using the index $\tau$ to label the asymmetric top energies and wavefunctions, we can use the values of $|K|$ for the prolate- and oblate-top levels that correlate with the asymmetric top levels. These values are usually written as subscripts to the $J$ value: $J_{K_{\mathrm{pr}} K_{\mathrm{ob}}}$ (sometimes labeled as $J_{K_{\mathrm{a}} K_{\mathrm{c}}}$ ).

