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# Rigid Rotators: Molecular Rotational Spectra

## A The Diatomic Molecule Rigid Rotator

For a rotating molecule the angular momentum, associated with the rotation of this "nearly rigid" body can be expressed in terms of Euler angles and their partial derivatives. Hence, this may be a good first example. Consider the simplest case: a diatomic molecule, e.g., the HCl molecule with one hydrogen and one Chlorine nucleus and 1 + 17 electrons. The full 20-body problem is extremely complicated, but at very low energies no excitations associated with the electron degrees of freedom will come into play. The electron cloud binds the two atomic nuclei into a nearly rigid structure. The position of the diatomic molecule in 3-D space can be described by a radial coordinate, $r$, giving the distance between the H and Cl nuclei, and two angles, $\theta$, and $\phi$, giving the orientation in space of the molecule axis, or H–Cl line. The wave function can be written as $\psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi)$. The electron cloud gives rise to a potential, $V(r)$, with a deep (nearly parabolic) well with a minimum ar $r = r_e$, where this is the equilibrium distance between the two atomic nuclei. The radial problem is associated with the vibrational motion of the molecule, a nearly harmonic oscillator motion to good first approximation. The energy associated with this vibration, $\hbar\omega_0$, is approximately 30 times that associated with the lower rotational excitations. Thus, at sufficiently low energies, we can replace the radial coordinate with its constant equilibrium value, $r_e$, and the Hamiltonian collapses to

$$H = -\frac{\hbar^2}{2\mathcal{I}_e}\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) = \frac{\hbar^2}{2\mu r_e^2}\vec{L}^2, \qquad (1)$$

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with corresponding Schrödinger equation

$$\frac{\hbar^2}{2\mu r_e^2}\vec{L}^2 Y_{lm}(\theta,\phi) = EY_{lm}(\theta,\phi) = \frac{\hbar^2}{2\mu r_e^2} l(l+1) Y_{lm}(\theta,\phi). \tag{2}$$

Here, $\mu$ is the H-Cl reduced mass, and $\mathcal{I}_e$ is the moment of inertia about an axis perpendicular to the molecular axis, through the center of mass of the system. The energies are

$$E_l = \frac{\hbar^2}{2\mu r_e^2} l(l+1). \tag{3}$$

The eigenfunctions are the standard spherical harmonics. Each level is $(2l+1)$-fold degenerate, because the energy does not depend on $m$.

## B The Polyatomic Molecule Rigid Rotator

For a polyatomic molecule, such as $H_2O$, with an isosceles triangle equilibrium structure, the rotational Hamiltonian is more complicated. We now need three Euler angles to specify the orientation in space of the nearly rigid molecule: two angles, $\theta$ and $\phi$, to give the direction of the triangle's symmetry axis, and a third angle, $\chi$, to describe the "spinning" of the two H atoms about this symmetry axis. Again, assuming the energies to be considered are so low vibrational excitations can be neglected, we can replace the coordinates of the atomic nuclei by their (constant) equilibrium values and are led to the rigid rotator Hamiltonian

$$H = \frac{1}{2A}P_{x'}^2 + \frac{1}{2B}P_{y'}^2 + \frac{1}{2C}P_{z'}^2, \tag{4}$$

where $P_{z'}$ is the component of the rotational angular momentum vector along the $z'$, body-fixed principal axis, the $H_2O$ symmetry axis; similarly, the $x'$ and $y'$ axes can be taken as the remaining principal axes, one perpendicular to the plane of the triangle, the other lying in the triangle plane, all going through the center of mass of the molecule. The constants $A$, $B$, $C$ are the three principal moments of inertia in the equilibrium configuration: $I_{xx} = A$, $I_{yy} = B$, $I_{zz} = C$. The principal or primed axes components of the rotational angular momentum vector, $\vec{P}$, must be translated to operator form to write the above Hamiltonian in quantum-mechanical form. Using the techniques of problem 5, these components are [converting from the physical angular momentum components of eq. (4) to dimensionless ones, e.g., $(P_{z'})_{\text{phys.}} = \hbar P_{z'}$],

$$\begin{aligned}
P_{x'} &= \frac{1}{i}\left(\frac{\sin\chi}{\sin\theta}\frac{\partial}{\partial\phi} + \cos\chi\frac{\partial}{\partial\theta} - \sin\chi\cot\theta\frac{\partial}{\partial\chi}\right),\\
P_{y'} &= \frac{1}{i}\left(\frac{\cos\chi}{\sin\theta}\frac{\partial}{\partial\phi} - \sin\chi\frac{\partial}{\partial\theta} - \cos\chi\cot\theta\frac{\partial}{\partial\chi}\right),\\
P_{z'} &= \frac{1}{i}\frac{\partial}{\partial\chi},
\end{aligned} \tag{5}$$

with

$$\vec{P}^2 = -\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\left[\frac{\partial^2}{\partial\phi^2} - 2\cos\theta\frac{\partial^2}{\partial\phi\partial\chi} + \cos^2\theta\frac{\partial^2}{\partial\chi^2}\right] + \frac{\partial^2}{\partial\chi^2}\right). \tag{6}$$

We can of course also write the space-fixed, $x$, $y$, and $z$ components of the rotational angular momentum in this operator form. The component of greatest interest to us is the space-fixed $z$-component

$$P_z = \frac{1}{i}\frac{\partial}{\partial\phi}. \tag{7}$$

The three operators $P_z$, $P_{z'}$, and $\vec{P}^2$, form a set of three commuting operators. In addition, straightforward calculation gives the commutator algebra of the three body-fixed or principal axis components of the rotational angular momentum operator

$$[P_{x'}, P_{y'}] = -iP_{z'}, \qquad [P_{y'}, P_{z'}] = -iP_{x'}, \qquad [P_{z'}, P_{x'}] = -iP_{y'}. \tag{8}$$

Note the minus signs! These signs are the complex conjugates of the standard angular momentum commutators. If we had taken the space-fixed components $P_x$, $P_y$, and $P_z$, we would have been led to the standard angular momentum commutator algebra. In translating the standard results to their complex conjugates (needed for the primed components), we must merely interchange $P'_+$ and $P'_-$, where now

$$P'_+ = (P_{x'} + iP_{y'}), \qquad P'_- = (P_{x'} - iP_{y'}). \tag{9}$$

Now

$$[P_{z'}, P'_+] = -P'_+, \qquad [P_{z'}, P'_-] = +P'_-. \tag{10}$$

(Note the difference in sign compared with the standard angular momentum algebra!) Also, now, the simultaneous eigenvectors of the three commuting operators, $P_z$, $P_{z'}$, and $\vec{P}^2$, will yield a complete basis of the subspace of our Hilbert space, corresponding to the three rotational degrees of freedom. (We need three quantum numbers, and three commuting, hermitian operators.) The needed eigenvector equations are

$$\begin{aligned}\vec{P}^2|JMK\rangle &= \lambda|JMK\rangle = J(J+1)|JMK\rangle,\\ P_z|JMK\rangle &= M|JMK\rangle,\\ P_{z'}|JMK\rangle &= K|JMK\rangle,\end{aligned} \tag{11}$$

where the commutator algebra of the unprimed angular momentum components leads to $M_{\text{max}} = -M_{\text{min}} = J$, and the commutator algebra of the primed angular momentum components leads to $K_{\text{max}} = -K_{\text{min}} = J$, where $\lambda = J(J+1)$. Because we are dealing with orbital degrees of freedom of a many-body system, the quantum numbers, $J, M, K$ must all be integers, with $M = J, (J-1), \ldots, -J$, and, similarly, $K = J, (J-1), \ldots, -J$. (We use capital letters for the $J$, $M$, $K$ quantum numbers according to the usual convention by which capital letters are used for many-body systems.)

We will now write the rigid rotator Hamiltonian for the asymmetric top with $A \neq B \neq C$ (valid for the $H_2O$ molecule), by first introducing the energy constants

$$a = \frac{\hbar^2}{2A}, \qquad b = \frac{\hbar^2}{2B}, \qquad c = \frac{\hbar^2}{2C}. \tag{12}$$

$$\begin{aligned} H &= aP_{x'}^2 + bP_{y'}^2 + cP_{z'}^2 = \frac{1}{2}(a+b)(P_{x'}^2 + P_{y'}^2) + \frac{1}{2}(a-b)(P_{x'}^2 - P_{y'}^2) + cP_{z'}^2 \\ &= \frac{1}{2}(a+b)(\vec{P}^2 - P_{z'}^2) + \frac{1}{4}(a-b)(P'_+P'_+ + P'_-P'_-) + cP_{z'}^2. \end{aligned} \tag{13}$$

In the $|JMK\rangle$ basis, the nonzero matrix elements of the primed components of $\vec{P}$ are

$$\begin{aligned} \langle JM(K+1)|P'_-|JMK\rangle &= \sqrt{(J-K)(J+K+1)}, \\ \langle JM(K-1)|P'_+|JMK\rangle &= \sqrt{(J+K)(J-K+1)}, \\ \langle JMK|P_{z'}|JMK\rangle &= K. \end{aligned} \tag{14}$$

($P'_-$ is now a $K$ step-up operator, and $P'_+$ is a $K$ step-down operator. This results because the commutation relations of the primed components of the rotational angular-momentum operators are the complex conjugates of the standard ones.) The Hamiltonian is not diagonal in the $|JMK\rangle$ basis. In this basis, the diagonal matrix elements of the Hamiltonian are

$$\langle JMK|H|JMK\rangle = \frac{1}{2}(a+b)(J(J+1) - K^2) + cK^2. \tag{15}$$

With $a \neq b$, off-diagonal terms exist. For the special case of a symmetric rotator, with $a = b$, however, these terms vanish, and the $|JMK\rangle$ are eigenstates of this symmetric rotator. The rotational energies are

$$E_{JK} = \frac{1}{2}(a+b)(J(J+1) - K^2) + cK^2. \tag{16}$$

For the asymmetric rotator, with $a \neq b$, we need the matrix elements

$$\begin{aligned} &\langle JMK'|P'_-P'_-|JMK\rangle \\ &= \delta_{K'(K+2)}\sqrt{(J-K)(J-K-1)(J+K+1)(J+K+2)}, \\ &\langle JMK'|P'_+P'_+|JMK\rangle \\ &= \delta_{K'(K-2)}\sqrt{(J+K)(J+K-1)(J-K+1)(J-K+2)}. \end{aligned} \tag{17}$$

When multiplied by (a-b)/4, these give the nonzero off-diagonal matrix elements. To get the energy eigenvectors, we now need to make a transformation from the $|JMK\rangle$ basis to a basis of the type $|JME_\alpha\rangle$, where these base vectors are simultaneously eigenvectors of the three commuting operators, $\vec{P}^2$, $P_z$, and $H$, with

$$\begin{aligned} \vec{P}^2|JME_\alpha\rangle &= J(J+1)|JME_\alpha\rangle, \\ P_z|JME_\alpha\rangle &= M|JME_\alpha\rangle, \\ H|JME_\alpha\rangle &= E_\alpha|JME_\alpha\rangle, \end{aligned} \tag{18}$$

where $\alpha$ is a label that simply orders the energy eigenvalues for a particular $J\ M$. To find the energy eigenvalues and eigenvectors, we need to make a transformation from the $|JMK\rangle$ basis to the $|JME_\alpha\rangle$ basis:

$$|JME_\alpha\rangle = \sum_{K=-J}^{K=+J} |JMK\rangle\langle JMK|JME_\alpha\rangle = \sum_{K=-J}^{K=+J} c_K(E_\alpha)|JMK\rangle. \tag{19}$$

If we substitute this linear combination of the $|JMK\rangle$ into the energy eigenequation

$$H|JME_\alpha\rangle = E_\alpha|JME_\alpha\rangle, \tag{20}$$

we get

$$\sum_K H|JMK\rangle\langle JMK|JME_\alpha\rangle = E_\alpha|JME_\alpha\rangle. \tag{21}$$

Taking the scalar product of this with a particular $\langle JMK'|$, i.e., with left-multiplication by the bra for a particular value of $K'$, we get

$$\sum_K \langle JMK'|H|JMK\rangle\langle JMK|JME_\alpha\rangle = E_\alpha\langle JMK'|JME_\alpha\rangle. \tag{22}$$

If we use the shorthand notation

$$\langle JMK'|H|JMK\rangle = H_{K'K}, \qquad c_K = \langle JMK|JME_\alpha\rangle, \tag{23}$$

the above equation can be written as

$$\sum_K H_{K'K}c_K = E_\alpha c_{K'}, \qquad \text{or} \qquad \sum_K \big(H_{K'K} - E_\alpha\delta_{K'K}\big)c_K = 0. \tag{24}$$

The $H$ submatrix for a particular $J$, and some fixed $M$, has been abbreviated by its matrix elements $H_{K'K}$, where the common quantum numbers, $J$ and $M$, have been suppressed. [From eqs. (15) and (17), these matrix elements are functions only of $J$ and $K$ and are completely independent of $M$.] Eq. (24) is a set of $(2J+1)$ linear equations in the unknown coefficients, $c_K$, with $K' = +J, +(J-1), \ldots, -J$. These linear equations have solutions for the $c_K$ if/only if the determinant of the coefficients is zero:

$$\det|H_{K'K} - E_\alpha\delta_{K'K}| = 0. \tag{25}$$

This determinantal relation leads to a polynomial in the unknown $E_\alpha$ of degree $(2J+1)$, which must be set equal to zero, leading to (2J+1) roots $E_\alpha$, with $\alpha = 1, 2, \ldots, (2J+1)$.

For example, for $J = 1$, the linear equations are

$$\begin{aligned} (H_{+1+1} - E)c_{+1} + H_{+10}c_0 + H_{+1-1}c_{-1} &= 0,\\ H_{0+1}c_{+1} + (H_{00} - E)c_0 + H_{0-1}c_{-1} &= 0,\\ H_{-1+1}c_{+1} + H_{-10}c_0 + (H_{-1-1} - E)c_{-1} &= 0, \end{aligned} \tag{26}$$

with the determinantal relation

$$\begin{vmatrix} (H_{+1+1} - E) & H_{+10} & H_{+1-1}, \\ H_{0+1} & (H_{00} - E) & H_{0-1}, \\ H_{-1+1} & H_{-10} & (H_{-1-1} - E) \end{vmatrix} = 0.$$

The Hamiltonian matrix for $J = 1$ follows from eqs. (15) and (17). The $J = 1$ matrix is

$$\langle JMK'|(H-E)|JMK\rangle =$$

$$\begin{array}{cc} & \begin{array}{ccc} K=+1 & \quad K=0 \quad & K=-1 \end{array} \\ \begin{array}{c} K=+1 \\ K=0 \\ K=-1 \end{array} & \begin{pmatrix} (\frac{a+b}{2}+c-E) & 0 & \frac{a-b}{2} \\ 0 & (a+b-E) & 0 \\ \frac{a-b}{2} & 0 & (\frac{a+b}{2}+c-E), \end{pmatrix} \end{array}$$

where it would have been advantageous to rearrange the columns and rows (taking first all even $K$ values, followed by all odd $K$ values), because the matrix elements of $H$ are nonzero only for $\Delta K = \pm 2$. The determinant of the $(H - E)$ matrix will then always factor into two subdeterminants. For $J = 1$, the determinantal relation leads to the requirement

$$\Big[(a+b-E)\Big]\Big[(\frac{a+b}{2}+c-E)^2 - (\frac{a-b}{2})^2\Big] = 0, \qquad (27)$$

with the three roots

$$\begin{aligned} E_1 &= (a+b), \\ E_2 &= (\frac{a+b}{2}+c) + (\frac{a-b}{2}) = (a+c), \\ E_3 &= (\frac{a+b}{2}+c) - (\frac{a-b}{2}) = (b+c). \end{aligned} \qquad (28)$$

For $E = E_1 = (a + b)$, the allowed c's are given by $c_{+1} = c_{-1} = 0$, $c_0 = 1$. For $E = E_2$ or $E = E_3$, we must have $c_0 = 0$, and the remaining $c$'s follow from the equations

$$\begin{aligned} (\frac{a+b}{2}+c-E)c_{-1} + (\frac{a-b}{2})c_{+1} &= 0 \\ (\frac{a-b}{2})c_{-1} + (\frac{a+b}{2}+c-E)c_{+1} &= 0 \end{aligned} \qquad (29)$$

For $E = E_2 = (a + c)$, these equations have the solution $c_{-1} = c_{+1} = \sqrt{\frac{1}{2}}$. Conversely, for $E = E_3 = (b + c)$, these equations lead to $-c_{-1} = c_{+1} = \sqrt{\frac{1}{2}}$. We have normalized the solutions such that $\sum_K |c_K|^2 = 1$.

Thus, the energy eigenvalues and eigenvectors of the asymmetric rotator, with $J = 1$ are

$$\begin{aligned} &E_1 = (a+b), \qquad |J=1\,M\,E_1\rangle = |J=1\,M\,K=0\rangle, \\ &\text{and for} \\ &E_2 = (a+c), \qquad \text{and} \quad E_3 = (b+c), \\ &|J=1\,M\,E_2\rangle = \frac{1}{\sqrt{2}}\big(|J=1\,M\,K=+1\rangle + |J=1\,M\,K=-1\rangle\big), \\ &|J=1ME_3\rangle = \frac{1}{\sqrt{2}}\big(|J=1MK=+1\rangle - |J=1MK=-1\rangle\big). \end{aligned} \qquad (30)$$

For arbitrary $J$, we are led to a $(2J+1) \times (2J+1)$ determinantal problem. The $(2J+1)$ roots of eq. (24) will give us the eigenvalues $E_\alpha$ and the eigenvectors for arbitrary $J$. The energies are independent of $M$. All states are therefore still $(2J+1)$-fold degenerate. This degeneracy can be lifted only by an external field. For the $H_2O$ molecule, which has a permanent electric dipole moment directed along its symmetry axis, the degeneracy could be removed if the molecule is placed in an external electric field (Stark effect).

In condensed-matter physics, effective Hamiltonians of the type of eq. (13) are often useful. These may be functions, e.g., of the spin operators of an impurity ion and have the general form

$$H = aS_x^2 + bS_y^2 + cS_z^2 + d(S_xS_y + S_yS_x) + e(S_xS_z + S_zS_x) + f(S_yS_z + S_zS_y). \quad (31)$$

The combinations, such as $(S_xS_y + S_yS_x)$, are hermitian. Problems of this type can be solved by the techniques illustrated in this section by the asymmetric rotator.

## Problems

**20.** Find the allowed energies for the $J = 2$ states of the asymmetric rigid rotator with Hamiltonian

$$H = aP_{x'}^2 + bP_{y'}^2 + cP_{z'}^2 = \tfrac{1}{2}(a+b)(\vec{P}^2 - P_{z'}^2) + \tfrac{1}{4}(a-b)(P'_+P'_+ + P'_-P'_-) + cP_{z'}^2$$

as functions of $a$, $b$, $c$. Find the eigenvectors of these states as linear combinations of the $|JMK\rangle$; i.e., find the coefficients, $c_K$, for the allowed $J = 2$ states in the expansions

$$|JME_\alpha\rangle = \sum_K c_K^{(\alpha)} |JMK\rangle.$$

**21.** For the asymmetric rigid rotator of problem 20, show from the symmetry of the Hamiltonian, $H$, the eigenvectors split into four classes of the form

$$|JME_\alpha\rangle_{\pm,e(o)} = \sum_K \frac{1}{\sqrt{2}}(|JMK\rangle \pm |JM-K\rangle),$$

where the $e(o)$ states involve a sum over even or odd $K$ values only. Using this $e+$, $e-$, $o+$, $o-$ basis, show the $7 \times 7$ matrix of the Hamiltonian matrix for $J = 3$ factors into three $2 \times 2$ submatrices and one $1 \times 1$ submatrix, and find the allowed energies for $J = 3$ as functions of $a$, $b$, $c$.

**22.** An impurity ion with a spin, $S = \frac{3}{2}$, is imbedded in a magnetic crystal and is subject to the local effective Hamiltonian

$$H = a(S_xS_y + S_yS_x) + bS_z^2,$$

where $S_x$, $S_y$, $S_z$ are the three components of the spin operator and $a$ and $b$ are constants. Find the Hamiltonian matrix in the basis, $|SM_S\rangle$, where $M_S$ is the eigenvalue of $S_z$. Find the energy eigenvalues, $E_\alpha$, and the energy eigenvectors as linear combinations of the $|SM_S\rangle$.