Rigid Rotor, Harmonic Oscillator form of Hamiltonian for polyatomic molecules.

a) Rotational part of the problem

The derivation of the rotational part of the Hamiltonian is complicated, and I will not attempt to give a derivation, but only list the pertinent points. Even classically, rotational motion is most easily described in a molecule-fixed (or body-fixed) frame, rather than a laboratory-fixed frame. If we assume a molecule having 3N atoms, we can list the coordinates as \( R_j, j = 1..N, \alpha = x, y, z \), and each of the nuclei having mass \( m_j \). The center of mass is defined as

\[
R_{cm} = \frac{\sum_j m_j R_j}{\sum_j m_j}
\]

and the moment of inertia tensor is defined as

\[
I_{\alpha\beta} = \delta_{\alpha\beta} \sum_j m_j (R^2_{j\alpha} + R^2_{j\beta}) - \sum_j m_j R_{j\alpha} R_{j\beta}
\]

This symmetric matrix can be diagonalized, yielding eigenvalues \( I_a, I_b, I_c \), and a set of so-called principal axis \( a, b, c \). These axes, the eigenvectors of the moment of inertia tensor, rotate with the molecule. In terms of these (instantaneous) axes the kinetic energy operator due to rotations can be written as

\[
\hat{T}_r = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}
\]

where \( J \) is the angular momentum operator \( \mathbf{J} = \mathbf{r} \times \mathbf{p} \), with respect to the molecule-fixed frame. To describe the eigenfunctions of the angular momentum operator, one uses both the space-fixed angular momentum operators \( J_x, J_y, J_z \), \( J_\pm = J_x \pm iJ_y \), and molecule fixed angular momentum operators \( J_a, J_b, J_c, J_\pm = J_a \mp iJ_b \). Please note that the ladder operators for the molecule fixed frame differ in sign from the space-fixed operators, and is distinguished by the superscript \( \pm \). The total angular momentum operator is independent of the axis of
rotation, and is given by $J^2 = J_x^2 + J_y^2 + J_z^2 = J_a^2 + J_b^2 + J_c^2$. The basis functions used to solve the rigid rotor problem are defined as

$$\Psi_{j,k,m}(\theta, \varphi, \chi) = \left| j, k, m \right\rangle = P_{jkm}(\theta)e^{ik\varphi}e^{im\chi}$$

and the angles $\varphi, \theta, \chi$ are the so-called Euler angles that describe the general rotation of a point (or axis system) in space. The following relations are useful to solve the problem.

$$J_x|j,k,m\rangle = j,j+1|j,k,m\rangle$$
$$J_y|j,k,m\rangle = m|j,k,m\rangle$$
$$J_z|j,k,m\rangle = k|j,k,m\rangle$$
$$J_x|j,k,m\rangle = (J_x \pm iJ_y)|j,k,m\rangle = |j,k,m \pm 1\rangle \sqrt{(j \mp m)(j \pm m + 1)}$$
$$J^z|j,k,m\rangle = (J_a \mp iJ_b)|j,k,m\rangle = |j,k, \pm 1\rangle \sqrt{(j \mp k)(j \pm k + 1)}$$

In rotational spectra the eigenvalues are the same always for all $m = -j \ldots j$, and the rotational levels are hence $(2j + 1)$-fold degenerate (the same as for a diatomic molecule). The eigenvalues of the rotational Hamiltonian can be obtained by diagonalizing the matrix over the basis functions $|j,k,m\rangle, k = -j \ldots j$, for a fixed $j$ and $m$.

The rotational Hamiltonian can be written as

$$H_r = \alpha J_x^2 + \beta J_y^2 + \gamma J_z^2$$

$$= \alpha(J_a^2 + J_b^2 + J_c^2) + \beta J_c^2 + 2\gamma(J_a^2 - J_b^2)$$

$$= (\alpha + 2\gamma)J_a^2 + (\alpha - 2\gamma)J_b^2 + (\alpha + \beta)J_c^2$$

$$\equiv \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}$$

We hence choose

$$\alpha = \frac{1}{4}\left(\frac{1}{I_a} + \frac{1}{I_b}\right), \; \gamma = \frac{1}{8}\left(\frac{1}{I_a} - \frac{1}{I_b}\right), \; \beta = \frac{1}{2}\left(\frac{1}{I_a} - \frac{1}{2}\left(\frac{1}{I_a} + \frac{1}{I_b}\right)\right)$$

The most complicated term in the Hamiltonian is the third one, involving $\gamma$, and if two moments of inertia are equal (symmetric top molecules), we would choose them as the $a$ and $b$ axis, such that $\gamma = 0$. In that case the functions $|j,k,m\rangle$ are eigenfunctions themselves with eigenvalues $\alpha j(j+1) + \beta k^2$. If the moments of inertia are all equal (spherical top), also $\beta = 0$, and the eigenvalues are simply $\alpha j(j+1)$. For the general asymmetric top the Hamiltonian has to explicitly diagonalized. Using the ladder operators
it is easy to construct the Hamiltonian, for a particular $j$ and $m$, but over all $k = -j \ldots j$, and perform the diagonalization. This would allow one to explicitly calculate the partition functions in thermodynamics without having to use the high temperature limit. For the general rotational problem, there is no closed from solution and one needs to diagonalize (small) matrices of dimension $(2j+1)$ to calculate the rotational eigenvalues and wave functions.

b) Vibrational part of the problem

If we denote the coordinates of all the nuclei as the $3N$ components of a vector

$$
\vec{R} = (x_1, y_1, z_1, \ldots, x_N, y_N, z_N)
$$

we can expand the electronic energy (including nuclear repulsion) around the equilibrium conformation $\vec{R}^e$ as (Taylor series expansion):

$$
E(\vec{R}) = E(\vec{R}^e) + \sum_i \frac{\partial E}{\partial R_i} (\vec{R} - \vec{R}^e)_i + \frac{1}{2} \sum_{i,j} \frac{\partial^2 E}{\partial R_i \partial R_j} (\vec{R} - \vec{R}^e)_i (\vec{R} - \vec{R}^e)_j + \ldots
$$

and note that at $\vec{R}^e$ where the energy is minimal, the first derivative vanishes. The second derivative is called the Hessian and is a generalization of the force-constant of the one-dimensional Harmonic oscillator. Let us denote it $K_{ij} = \frac{\partial^2 E}{\partial R_i \partial R_j}$, evaluated at $\vec{R}^e$. The Hamiltonian for the nuclear problem then takes the form

$$
\hat{H} = E(\vec{R}^e) - \frac{\hbar^2}{2} \sum_i \frac{1}{M_i} \frac{\partial^2}{\partial R_i^2} + \frac{1}{2} \sum_{i,j} (\vec{R} - \vec{R}^e)_i K_{ij} (\vec{R} - \vec{R}^e)_j
$$

The energy $E(\vec{R}^e)$ is a constant and does not play a role, unless one considers electronic transitions. The aim of this write up is to show that by a suitable choice of coordinates the Hamiltonian reduces to

$$
\hat{H} = \sum_a \left( -\frac{\hbar^2}{2} \frac{\partial^2}{\partial q_a^2} + \frac{1}{2} \lambda_a q_a^2 \right)
$$
6 (5 for a linear molecule) of the $\lambda_\alpha$ will be zero, corresponding to coordinates $q_\alpha$ that describe the center of mass motion and the overall rotation of the molecule. The underlying assumption of the Taylor series expansion is that one examines only small amplitude motion. The above Hamiltonian does not provide a proper treatment of rotations, which are large amplitude motions. In particular the “rotational normal modes” only describe infinitesimal rotations, but would distort the molecule under larger displacements. Hence the potential energy function, which is independent of the rotational normal modes ($\lambda_\alpha=0$) is not accurate at all in this limit. A fully proper derivation of the molecular Hamiltonian is really quite involved, and I will not pursue it. The remaining 3N-6 (3N-5) coordinates are so-called normal modes corresponding to nuclear vibrations. These normal modes can be pictured classically and correspond to stretches, bending, twisting and so forth. All of these motions are occurring simultaneously in a molecule but they can be decomposed into elementary harmonic motions that all have their own frequency. This underlying simplicity allows us to understand vibrational spectra fairly easily. Because in the new coordinate system the Hamiltonian separates completely the construction of nuclear eigenfunctions and eigenvalues is easy (although the rotational part is actually fairly complicated).

$$\Psi(R_1, R_2, \ldots, R_N) \rightarrow \phi_1(q_1) \phi_2(q_2) \ldots \phi_{3N-6}(q_{3N-6}) \Phi^R(\alpha, \beta, \gamma) X^T(X^{cm}, Y^{cm}, Z^{cm})$$

where the $\phi_i(q_i)$ are eigenfunctions of the one-dimensional H.O. The total energy would be

$$E = E^{\text{Trans}} + E^{\text{Rot}} + (v_1 + \frac{1}{2})\hbar \omega_1 + (v_2 + \frac{1}{2})\hbar \omega_2 + \ldots (v_{3N-6} + \frac{1}{2})\hbar \omega_{3N-6}$$

Translational motion is little discussed in spectroscopy (but probed for example in scattering experiments, and it plays a vital role in statistical mechanics) while rotational motion has been treated above. Here we are concerned with the derivation of Eqn. 4 starting from Eqn. 3.

Define mass weighted coordinates

$$y_i = \sqrt{M_i} (\bar{R} - \bar{R}^e)_i \rightarrow \bar{R}_i = \frac{1}{\sqrt{M_i}} y_i + \bar{R}^e_i$$

and, using the chain rule,
(8)

\[ \frac{\partial}{\partial y_k} = \sum_i \frac{\partial R_i}{\partial y_k} \frac{\partial}{\partial R_i} = \sum_i \frac{1}{\sqrt{M_i}} \frac{\partial y_i}{\partial y_k} \frac{\partial}{\partial R_i} = \sum_i \frac{1}{\sqrt{M_i}} \delta_{ik} \frac{\partial}{\partial R_i} = \frac{1}{\sqrt{M_k}} \frac{\partial}{\partial R_k} \]

(take the steps one by one, as it shows you how to manipulate summations and indices).

It follows that the kinetic energy operator in terms of the \( y_k \) becomes

\[ -\frac{\hbar^2}{2} \sum_k \frac{1}{M_k} \frac{\partial^2}{\partial y_k^2} = -\frac{\hbar^2}{2} \sum_k \frac{\partial^2}{\partial y_k^2} \]

which looks more like eqn. 4. The potential energy term in terms of the coordinates \( y_k \) becomes

\[ \frac{1}{2} \sum_{i,j} y_i \frac{1}{\sqrt{M_i}} K_{ij} \frac{1}{\sqrt{M_j}} y_j = \frac{1}{2} \sum_{i,j} y_i G_{ij} y_j \]

such that the Hamiltonian expressed in the mass-weighted coordinates \( y_j \) becomes

\[ \hat{H} = -\frac{\hbar^2}{2} \sum_j \frac{\partial^2}{\partial y_j^2} + \frac{1}{2} \sum_{i,j} y_i G_{ij} y_j \]

This is not quite Eqn. 4 yet because of the coupling terms for \( i \neq j \). For this reason we next obtain the eigenvectors \( U \) of the matrix \( G \) with elements \( G_{ij} \) (this is done in actual computations)

\[ \sum_j G_{ij} U_{jk} = U_{ik} \lambda_k \]

where \( U_{jk}, j = 1, \ldots, 3N \) are the components of the \( k^{th} \) eigenvector that has eigenvalue \( \lambda_k \).

The eigenvectors of a symmetric matrix \((G_{ij} = G_{ji})\) can be chosen orthonormal (proof is analogous to orthogonality of eigenfunctions of hermitean operators), and this is expressed as

\[ \sum_k U_{ik} U_{kj} = \delta_{ij} \]

The normal modes in terms of the eigenvectors \( U \) are defined as

\[ \sum_k U_{jk} q_k = y_j \]

It may appear that the definition of the normal coordinates in Eqn. (14) is backwards. We will see that everything works out properly. Using relation (13), we easily obtain the inverse relationship

\[ \sum_j U_{ji} \left( \sum_k U_{jk} q_k \right) = \sum_j U_{ji} y_j \rightarrow \sum_k \delta_{ik} q_k = \sum_j U_{ji} y_j \]
i.e.  

\[ q_i = \sum_j U_{ji} y_j \]  

Using the above information Eqn. (10) becomes  

\[ \frac{1}{2} \sum_{i,j} y_i G_{ij} y_j = \frac{1}{2} \sum_{i,j,k} y_i G_{ij} U_{jk} q_k = \frac{1}{2} \sum_{i,k} y_i U_{ik} \lambda_k q_k = \frac{1}{2} \sum_k q_k \lambda_k q_k \]  

Hence the potential energy term has become a sum of diagonal terms with 'force constants' \( \lambda_k \).

To complete the derivation we have to show that the kinetic energy operator satisfies

\[ -\frac{\hbar^2}{2} \sum_j \frac{\partial^2}{\partial y_j^2} = -\frac{\hbar^2}{2} \sum_k \frac{\partial^2}{\partial q_k^2} \]  

Using the definition (14) and the chain rule we see that  

\[ \frac{\partial}{\partial q_k} = \sum_j \frac{\partial y_j}{\partial q_k} \frac{\partial}{\partial y_j} = \sum_j U_{jk} \frac{\partial}{\partial y_j} \]  

Hence  

\[ \sum_k \frac{\partial^2}{\partial q_k^2} = \sum_{i,j,k} U_{jk} \frac{\partial}{\partial y_j} U_{ik} \frac{\partial}{\partial y_i} = \sum_i \delta_{ij} \frac{\partial^2}{\partial y_i \partial y_j} = \sum_i \frac{\partial^2}{\partial y_i^2} \]  

It then follows that the Hamiltonian takes the final form of eqn. 4.

Some important techniques involving summations are used here. The derivation is non-trivial and going through it will give you excellent practice. For example: The names of summation labels are irrelevant; \( i, j \), it does not matter. Each independent summation uses a different summation label. Moreover, the order in which you sum terms in principle doesn't matter, but simplifications in derivations only occur if you do it in the right order!

Finally the Hamiltonian can be expressed in terms of dimensionless reduced normal mode coordinates by defining  

\[ q_i = \tilde{q}_i \sqrt{\frac{\hbar}{\omega_i}}; \quad \omega_i = \sqrt{\lambda_i}. \]  

The Hamiltonian then takes on a sum of familiar harmonic oscillators
\[ \hat{H} = \sum_i \hbar \omega_i \left( \frac{1}{2} \frac{\partial^2}{\partial q_i^2} + \frac{1}{2} \dot{q}_i^2 \right) \] (21)

which can be written immediately in second quantization

\[ \hat{H} = \sum_i \hbar \omega_i (\hat{b}_i^\dagger \hat{b}_i + \frac{1}{2}) \] (22)

and we can find the solutions following the procedure in the hand-written notes.