

## Chapter 3. The Rotation-Vibration Hamiltonian

### Notes:

- *Most of the material presented in this chapter is taken from Bunker and Jensen (2005), Chaps. 4 and 5, Bunker and Jensen (1998), Chap. 10, and Wilson, Decius, and Cross, Chap. 11.*

### 3.1 Space-fixed and Molecule-fixed Axes

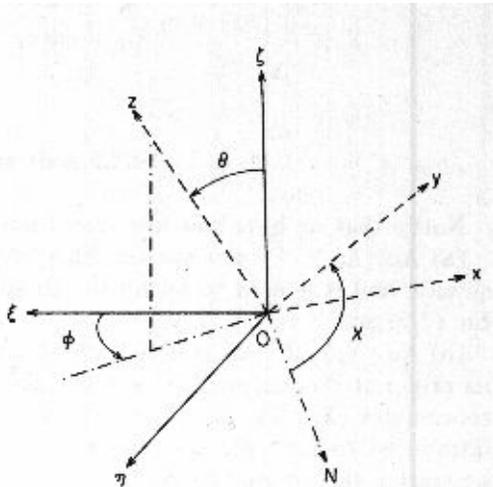
In the previous chapter we have used the Born-Oppenheimer approximation to separate the Hamiltonian into two parts: the electronic and the rotation-vibration Hamiltonians. This separation, made explicit with equations (2.21), allows for the independent analyses of electronic and rotation-vibration motions (and states). Similarly, we would like to find a way to separate rotation and vibration motions to simplify our study of the behavior and spectroscopy of molecules. In other words, we would like to introduce separate sets of rotational and vibrational coordinates.

To do so, it is necessary to define a new set of coordinates, denoted by  $(x, y, z)$ , which have their origin at the nuclear centre of mass and an orientation relative to the  $(\xi, \eta, \zeta)$  axes (defined in Section 2.1) somehow defined by the position of the nuclei only (i.e., the position of the electrons are not involved). Because of this, it is common to say that the  $(\xi, \eta, \zeta)$  axes are “space-fixed”, while the  $(x, y, z)$  axes are “molecule-fixed”. That is, the new axes rotate with the molecule while the former axes do not.

Although the origin of this new set of coordinates is unambiguously defined, there is a fair amount of freedom in defining its orientation relative to the space-fixed coordinates. We will soon discuss what conditions will be chosen for this definition, but irrespective of the way this will be done it should be clear that the relative orientation of the  $(x, y, z)$  axes to the  $(\xi, \eta, \zeta)$  axes can be expressed using the so-called **Euler angles**. We will denote the Euler angles by  $(\phi, \theta, \chi)$ , as defined in Figure 3-1. The first rotation  $0 \leq \phi \leq 2\pi$  is about the  $\zeta$ -axis, the second rotation  $0 \leq \theta \leq \pi$  is about the N-axis, which is the  $\phi$ -rotated  $\eta$ -axis, and the last rotation  $0 \leq \chi \leq 2\pi$  is about the  $z$ -axis, which is the  $\theta$ -rotated  $\zeta$ -axis. With these three rotations, any orientation for the molecule-fixed axes relative to the space-fixed axes can be unambiguously assigned a set of values for the Euler angles.

Given the space-fixed coordinates  $(\xi_i, \eta_i, \zeta_i)$  for the  $i$ th particle of the molecule, be it a nucleus or an electron, we can evaluate its corresponding molecule-fixed coordinates with

$$\begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} = \begin{bmatrix} \lambda_{x\xi} & \lambda_{x\eta} & \lambda_{x\zeta} \\ \lambda_{y\xi} & \lambda_{y\eta} & \lambda_{y\zeta} \\ \lambda_{z\xi} & \lambda_{z\eta} & \lambda_{z\zeta} \end{bmatrix} \begin{pmatrix} \xi_i \\ \eta_i \\ \zeta_i \end{pmatrix}, \quad (3.1)$$



**Figure 3-1** – Definition for the Euler angles  $(\phi, \theta, \chi)$ . The origin of both axis systems is at the nuclear centre of mass  $O$ .

where the elements of the rotation matrix are the cosine direction coefficient. More precisely, we have

$$\begin{aligned}
 \lambda_{x\xi} &= \cos(\theta)\cos(\phi)\cos(\chi) - \sin(\phi)\sin(\chi) \\
 \lambda_{y\xi} &= -\cos(\theta)\cos(\phi)\sin(\chi) - \sin(\phi)\cos(\chi) \\
 \lambda_{z\xi} &= \sin(\theta)\cos(\phi) \\
 \lambda_{x\eta} &= \cos(\theta)\sin(\phi)\cos(\chi) + \cos(\phi)\sin(\chi) \\
 \lambda_{y\eta} &= -\cos(\theta)\sin(\phi)\sin(\chi) + \cos(\phi)\cos(\chi) \\
 \lambda_{z\eta} &= \sin(\theta)\sin(\phi) \\
 \lambda_{x\zeta} &= -\sin(\theta)\cos(\chi) \\
 \lambda_{y\zeta} &= \sin(\theta)\sin(\chi) \\
 \lambda_{z\zeta} &= \cos(\theta).
 \end{aligned} \tag{3.2}$$

### 3.2 Molecule-fixed Rovibrational Coordinates

Now that we have introduced the new molecule-fixed coordinate system (although not in details, since we still have to specify the conditions that will completely determine the Euler angles), we need to transform the coordinates of each particle that form the molecule (nuclei and electrons) into this new system. We emphasize the fact that although the Euler angles do not depend on the positions of the electrons, the electrons' positions do depend on the Euler angles. This fact is important, at least in principle, because we have endeavored, and succeeded, in Chapter 2 in finding a way (through the Born-Oppenheimer approximation) to separate the kinetic energy component of the Hamiltonian into independent electronic and nuclear parts. We now need to make certain

that the change from the space-fixed to the molecule-fixed coordinates will not spoil this simplification.

To verify this, we go back to the expression for the electronic kinetic energy derived in equations (2.11), and rewrite it here for convenience

$$\hat{T}_e = -\frac{\hbar^2}{2m_e} \sum_{i=N+1}^l \nabla_i^2 + \frac{\hbar^2}{2M_N} \sum_{i,j=N+1}^l \nabla_i \cdot \nabla_j, \quad (3.3)$$

where it is understood that any derivative is taken relative to one of the  $(\xi, \eta, \zeta)$  coordinates (remember that the nuclei indices run from  $1 \leq i \leq N$ , while the electrons' run from  $N+1 \leq i \leq l$ ). We can apply the chain rule to equation (3.3) to find that in general

$$\begin{aligned} \frac{\partial}{\partial \xi_k} &= \sum_{i=2}^l \left( \frac{\partial x_i}{\partial \xi_k} \frac{\partial}{\partial x_i} + \frac{\partial y_i}{\partial \xi_k} \frac{\partial}{\partial y_i} + \frac{\partial z_i}{\partial \xi_k} \frac{\partial}{\partial z_i} \right) \\ \frac{\partial^2}{\partial \xi_j \partial \xi_k} &= \sum_{i=2}^l \frac{\partial^2 x_i}{\partial \xi_j \partial \xi_k} \frac{\partial}{\partial x_i} + \sum_{i,m=2}^l \left( \frac{\partial x_i}{\partial \xi_j} \right) \left( \frac{\partial x_m}{\partial \xi_k} \right) \frac{\partial^2}{\partial x_i \partial x_m} \\ &\quad + \sum_{i=2}^l \frac{\partial^2 y_i}{\partial \xi_j \partial \xi_k} \frac{\partial}{\partial y_i} + \sum_{i,m=2}^l \left( \frac{\partial y_i}{\partial \xi_j} \right) \left( \frac{\partial y_m}{\partial \xi_k} \right) \frac{\partial^2}{\partial y_i \partial y_m} \\ &\quad + \sum_{i=2}^l \frac{\partial^2 z_i}{\partial \xi_j \partial \xi_k} \frac{\partial}{\partial z_i} + \sum_{i,m=2}^l \left( \frac{\partial z_i}{\partial \xi_j} \right) \left( \frac{\partial z_m}{\partial \xi_k} \right) \frac{\partial^2}{\partial z_i \partial z_m}, \end{aligned} \quad (3.4)$$

and so on. But since the Euler angles do not depend on the electronic coordinates then for an electron  $j$  we have

$$\frac{\partial \lambda_{x\xi}}{\partial \xi_j} = 0, \quad N+1 \leq j \leq l, \quad (3.5)$$

and so on for the other partial derivatives of this type. Therefore, for three electrons  $j, k$  and  $m$  we simply have that

$$\begin{aligned} \frac{\partial x_k}{\partial \xi_j} &= \delta_{kj} \lambda_{x\xi} \\ \frac{\partial^2 x_k}{\partial \xi_j \partial \xi_m} &= 0, \end{aligned} \quad (3.6)$$

and so on for all other similar derivatives involving  $y, z, \eta$  and  $\zeta$ , with, of course,  $N+1 \leq j, k, m \leq l$ . It can be readily shown through the combination of equations (3.4) to (3.6) with the fact that the Euler rotation matrix is orthonormal (i.e.,  $\lambda \cdot \lambda^T = \hat{1}$ ) we obtain

$$\begin{aligned}\nabla_i^2 &= \frac{\partial^2}{\partial \xi_i^2} + \frac{\partial^2}{\partial \eta_i^2} + \frac{\partial^2}{\partial \zeta_i^2} = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \\ \nabla_i \cdot \nabla_j &= \frac{\partial^2}{\partial \xi_i \partial \xi_j} + \frac{\partial^2}{\partial \eta_i \partial \eta_j} + \frac{\partial^2}{\partial \zeta_i \partial \zeta_j} = \frac{\partial^2}{\partial x_i \partial x_j} + \frac{\partial^2}{\partial y_i \partial y_j} + \frac{\partial^2}{\partial z_i \partial z_j},\end{aligned}\quad (3.7)$$

when  $N+1 \leq i, j \leq l$ . More precisely, this result implies that the form of the electronic kinetic energy is unchanged when making the coordinate transformation discussed here. Furthermore, it still does not involve the nuclear coordinates. This is exactly what we were hoping for.

But what can be said of the nuclear kinetic energy  $\hat{T}_N$ ? Is it also unaffected by the change of coordinates? From equations (2.21), we have

$$\hat{T}_N = -\frac{\hbar^2}{2} \sum_{i=2}^N \frac{\nabla_i^2}{m_i} + \frac{\hbar^2}{2M_N} \sum_{i,j=2}^N \nabla_i \cdot \nabla_j, \quad (3.8)$$

and we see that this term involves the same types of derivatives as that for the electrons, with the important difference that the summations run from 2 to  $N$  instead of from  $N+1$  to  $l$ . To answer the question above, we first study the following partial derivative

$$\begin{aligned}\frac{\partial x_k}{\partial \xi_j} &= \delta_{kj} \lambda_{x\xi} + \frac{\partial \lambda_{x\xi}}{\partial \xi_j} \xi_k + \frac{\partial \lambda_{x\eta}}{\partial \xi_j} \eta_k + \frac{\partial \lambda_{x\zeta}}{\partial \xi_j} \zeta_k \\ &= \delta_{kj} \lambda_{x\xi} + (xk),\end{aligned}\quad (3.9)$$

where  $2 \leq j \leq N$  and  $2 \leq k \leq l$ , and  $(xk)$  stands for the last three terms of on the right hand side of the first of equations (3.9). It is clear from this that the electronic coordinates (i.e.,  $x_k$  for  $N+1 \leq k \leq l$ ) are dependent on the nuclear coordinates through the Euler angles. This dependency is contained in the  $(xk)$  term. Using similar equations for  $\partial y_k / \partial \xi_j$  and  $\partial z_k / \partial \xi_j$ , which will respectively contain  $(yk)$  and  $(zk)$  terms, and the chain rule (i.e., the first of equations (3.4)), it is easy to show that for a nucleus  $j$

$$\frac{\partial}{\partial \xi_j} = \lambda_{x\xi} \frac{\partial}{\partial x_j} + \lambda_{y\xi} \frac{\partial}{\partial y_j} + \lambda_{z\xi} \frac{\partial}{\partial z_j} + \sum_{k=2}^l \left[ (xk) \frac{\partial}{\partial x_k} + (yk) \frac{\partial}{\partial y_k} + (zk) \frac{\partial}{\partial z_k} \right]. \quad (3.10)$$

Evidently, the second derivatives (and therefore  $\nabla_i^2$  and  $\nabla_i \cdot \nabla_j$ ) will also involve the  $(xk)$ ,  $(yk)$ , and  $(zk)$  terms. It follows from this that by making the change of variables

from the space-fixed to the molecule-fixed coordinates systems we reintroduce the electronic dependency into the nuclear kinetic energy term  $\hat{T}_N$  (since it is a function of  $\nabla_i^2$  and  $\nabla_i \cdot \nabla_j$ ). This is obviously not what we wanted.

It would appear that we couldn't proceed further without spoiling the essential simplification obtained earlier with the Born-Oppenheimer approximation. Moreover, how could we ever hope to separate the vibration and rotation motions of the nuclei if the rovibrational Hamiltonian sees the electronic coordinates back in its formulation? It turns out that in most cases the electronic dependency of the rovibrational Hamiltonian is small, and can safely be neglected. This again is in line with the Born-Oppenheimer approximation that assumes that the electrons are unaffected by the motion of the nuclei. We, therefore, make the approximation that

$$\begin{aligned}\nabla_i^2 &\approx \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \\ \nabla_i \cdot \nabla_j &\approx \frac{\partial^2}{\partial x_i \partial x_j} + \frac{\partial^2}{\partial y_i \partial y_j} + \frac{\partial^2}{\partial z_i \partial z_j},\end{aligned}\tag{3.11}$$

with  $2 \leq i, j \leq N$ , when referring to equation (3.8) for the nuclear kinetic energy.

### 3.3 The Separation of Rotation and Vibration in the Hamiltonian

Within the context of the Born-Oppenheimer and every other approximations used so far, we can now write the quantum mechanical Hamiltonians as

$$\left(\hat{T}_e^0 + V_{ee} + V_{Ne}\right)\Phi_{\text{elec},n}(\mathbf{R}_N, \mathbf{r}_e) = V_{\text{elec},n}\Phi_{\text{elec},n}(\mathbf{R}_N, \mathbf{r}_e),\tag{3.12}$$

with

$$\hat{T}_e^0 = -\frac{\hbar^2}{2m_e} \sum_{i=N+1}^l \nabla_i^2,\tag{3.13}$$

for the electronic Hamiltonian and

$$\left(\hat{T}_N + V_{N,n}\right)\Phi_{\text{rv},nj}(\mathbf{R}_N) = E_{\text{rv},nj}\Phi_{\text{rv},nj}(\mathbf{R}_N),\tag{3.14}$$

with

$$\begin{aligned}\hat{T}_N &= -\frac{\hbar^2}{2} \sum_{i=2}^N \frac{\nabla_i^2}{m_i} + \frac{\hbar^2}{2M_N} \sum_{i,j=2}^N \nabla_i \cdot \nabla_j \\ V_{N,n} &= V_{NN} + V_{\text{elec},n} - E_{\text{elec},n} \\ E_{\text{rv},nj} &= E_{\text{rve},nj}^0 - E_{\text{elec},n},\end{aligned}\tag{3.15}$$

for the rovibrational Hamiltonian. The zero energy  $E_{\text{elec},n}$  is the minimum value of  $(V_{\text{NN}} + V_{\text{elec},n})$ , and the form of the different electrostatic energies appearing in equations (3.12) to (3.15) will be easily guessed from equations (2.11) and (2.13). It is also understood that we are now using the molecule-fixed coordinates  $(x,y,z)$  when evaluating positions or derivatives.

It is now established that, to a good level of precision, we can separate electronic and nuclear motions, as is attested with equations (3.12) to (3.15). As was discussed in Chapter 2, the electronic Hamiltonian of equation (3.12) can be used to determine the electronic structure of the molecule, and then the arrangement of the different atoms that form the molecule. One could therefore imagine that we could simply start with the rovibrational Hamiltonian of equation (3.14) and proceed to separate the rotation and vibration motions, and solve for their respective spectroscopy. This may seem logical, but it is not how things are usually done.

A brief inspection of the first of equations (3.15) for the nuclear kinetic energy shows that the form of this relation is somewhat awkward. For example, the nucleus of index 1 is not included in the sums. Of course, its effect is implicit to the equation and is responsible for the presence of the “cross products” in the second summation on the right hand side. This state of affair came about from our desire to remove the motion of the centre of mass of the molecule from the Hamiltonian (see Section 1.5). The analysis will be greatly simplified if we can rearrange the rovibrational Hamiltonian so it gains a mathematical form similar to that of the electronic Hamiltonian. For that reason, it is beneficial to go back to a classical expression (as opposed to the present quantum mechanical form) for the rovibrational Hamiltonian, and transform it in a manner that will help the separation and analyses of rotation and vibration motions.

One would then be justified in asking what was the purpose of the whole analysis we have performed so far. The answer is that we needed to find a way to separate the electronic and rovibrational motions, while introducing the systems of coordinate (i.e., space-fixed and molecule-fixed) that are necessary for our analysis. This we have accomplished. We now turn our attention to the classical rovibrational Hamiltonian.

### 3.3.1 The Classical Rovibrational Hamiltonian

*Note: The material of this section will closely follow that presented in Chapter 11 of Wilson, Decius, and Cross (although with a different notation). It is not essential to master the material covered here in order to understand the rest of the course. One could simply skip most of the derivations and analyses presented here, and only remember the final form of the quantum mechanical rovibrational Hamiltonian (except perhaps for the section on the Eckart conditions, which should be studied).*

We now consider only the nuclear component of the molecule (i.e., no electrons), and we use some of the same systems of axes previously introduced. It should be noted that the centre of mass of the system is now, by definition, the same as the nuclear centre of mass and we denote its position in space by

$$\mathbf{R}_N \equiv X_N \mathbf{e}_x + Y_N \mathbf{e}_y + Z_N \mathbf{e}_z. \quad (3.16)$$

The instantaneous position of nucleus  $i$  relative to the space-fixed system of axes that has its origin at the position of the centre of mass is given by  $(\xi_i, \eta_i, \zeta_i)$ , while its instantaneous position relative the molecule-fixed axes (with similar origin) is

$$\mathbf{r}_i = x_i \mathbf{e}_x + y_i \mathbf{e}_y + z_i \mathbf{e}_z, \quad (3.17)$$

where  $\mathbf{e}_x$ ,  $\mathbf{e}_y$ , and  $\mathbf{e}_z$  form the unit basis for the molecule-fixed coordinate system. We also introduce an **equilibrium position** against which the instantaneous position of the nucleus is compared; we denote this equilibrium position by

$$\mathbf{r}_i^e = x_i^e \mathbf{e}_x + y_i^e \mathbf{e}_y + z_i^e \mathbf{e}_z. \quad (3.18)$$

The difference between the instantaneous and the equilibrium positions, which we call the **displacement**, is

$$\Delta \mathbf{r}_i = \Delta x_i \mathbf{e}_x + \Delta y_i \mathbf{e}_y + \Delta z_i \mathbf{e}_z, \quad (3.19)$$

with  $\Delta x_i \equiv x_i - x_i^e$ , etc. If the molecule-fixed system is rotating with an angular velocity  $\boldsymbol{\omega}$  with respect its space-fixed counterpart, then the spatial velocity  $\mathbf{v}_i$  of the nucleus is

$$\mathbf{v}_i = \dot{\mathbf{R}}_N + \boldsymbol{\omega} \times \mathbf{r}_i + \mathbf{u}_i, \quad (3.20)$$

where

$$\mathbf{u}_i \equiv \dot{x}_i \mathbf{e}_x + \dot{y}_i \mathbf{e}_y + \dot{z}_i \mathbf{e}_z = \frac{d\Delta x_i}{dt} \mathbf{e}_x + \frac{d\Delta y_i}{dt} \mathbf{e}_y + \frac{d\Delta z_i}{dt} \mathbf{e}_z, \quad (3.21)$$

since  $\dot{x}_i^e = \dot{y}_i^e = \dot{z}_i^e = 0$ . Equation (3.21) tells us that  $\mathbf{u}_i$  is the velocity due to the vibration motion of the corresponding particle. With these definitions, the kinetic energy of the molecule is defined by

$$\begin{aligned} 2T &= \sum_{i=1}^N m_i v_i^2 \\ &= M \dot{\mathbf{R}}_N^2 + \sum_{i=1}^N m_i (\boldsymbol{\omega} \times \mathbf{r}_i) \cdot (\boldsymbol{\omega} \times \mathbf{r}_i) + \sum_{i=1}^N m_i u_i^2 \\ &\quad + 2\dot{\mathbf{R}}_N \cdot \left( \boldsymbol{\omega} \times \sum_{i=1}^N m_i \mathbf{r}_i \right) + 2\dot{\mathbf{R}}_N \cdot \sum_{i=1}^N m_i \mathbf{u}_i + 2\boldsymbol{\omega} \cdot \sum_{i=1}^N (m_i \mathbf{r}_i \times \mathbf{u}_i). \end{aligned} \quad (3.22)$$

where  $M = \sum_{i=1}^N m_i$ . But since  $\mathbf{r}_i$  is measured from the centre of mass, then we have

$$\boxed{\sum_{i=1}^N m_i \mathbf{r}_i = 0} \quad (3.23)$$

and by taking the time derivative of this last equation

$$\begin{aligned} \sum_{i=1}^N m_i \dot{\mathbf{r}}_i &= \sum_{i=1}^N m_i (\boldsymbol{\omega} \times \mathbf{r}_i + \mathbf{u}_i) \\ &= \boldsymbol{\omega} \times \sum_{i=1}^N m_i \mathbf{r}_i + \sum_{i=1}^N m_i \mathbf{u}_i = \sum_{i=1}^N m_i \mathbf{u}_i \\ &= 0. \end{aligned} \quad (3.24)$$

Equation (3.22) is then reduced to

$$2T = M\dot{\mathbf{R}}_N^2 + \sum_{i=1}^N m_i (\boldsymbol{\omega} \times \mathbf{r}_i) \cdot (\boldsymbol{\omega} \times \mathbf{r}_i) + \sum_{i=1}^N m_i u_i^2 + 2\boldsymbol{\omega} \cdot \sum_{i=1}^N (m_i \mathbf{r}_i \times \mathbf{u}_i). \quad (3.25)$$

Obviously, the first term is just the kinetic energy associated with the centre of mass, and we will omit it in everything that follows. The classical nuclear kinetic energy  $T_N$  is therefore

$$2T_N = \sum_{i=1}^N m_i (\boldsymbol{\omega} \times \mathbf{r}_i) \cdot (\boldsymbol{\omega} \times \mathbf{r}_i) + \sum_{i=1}^N m_i u_i^2 + 2\boldsymbol{\omega} \cdot \sum_{i=1}^N (m_i \mathbf{r}_i \times \mathbf{u}_i). \quad (3.26)$$

### 3.3.1.1 The Eckart Conditions

Examination of equation (3.26) will reveal that the first term on the right hand side corresponds to (twice) the energy of rotation and the second term to (twice) the energy of vibration. To understand the nature of the last term, we modify it slightly and write

$$\boldsymbol{\omega} \cdot \sum_{i=1}^N (m_i \mathbf{r}_i \times \mathbf{u}_i) = \boldsymbol{\omega} \cdot \sum_{i=1}^N (\mathbf{r}_i \times m_i \mathbf{u}_i). \quad (3.27)$$

But since the velocity  $\mathbf{u}_i$  is related to the vibration of the  $i$ th particle, it is apparent that the term under the summation can be interpreted as the total vibrational angular momentum

$$\mathbf{J}_{\text{vib}} = \sum_{i=1}^N (\mathbf{r}_i \times m_i \mathbf{u}_i), \quad (3.28)$$

and the last term on the right hand side of equation (3.26) is (twice) the amount of energy due to the coupling of the rotation and vibration motions (it can also be interpreted as a Coriolis coupling). Since our goal is to separate these two types of motions in the Hamiltonian, it would seem that this last coupling term prevents us from doing so. But all is not lost...

We must remember that we still have not specified the position of the molecule-fixed axes  $(x, y, z)$  in relation to the space-fixed positions  $(\xi_1, \eta_1, \zeta_1, \dots, \xi_N, \eta_N, \zeta_N)$  of the nuclei. To do so, we will need three equations, i.e., one for each of the Euler angles  $(\phi, \theta, \chi)$ . Since we have some freedom in choosing these three equations, one could be tempted to set as a condition that  $\mathbf{J}_{\text{vib}} = 0$ . Indeed, applying this condition would ensure the separation of rotation and vibration motions by removing any coupling between the two. However, the three available relations would not be sufficient to specify both  $\mathbf{r}_i$  and  $\mathbf{u}_i$ , which are present in equation (3.28), to satisfy  $\mathbf{J}_{\text{vib}} = 0$ .

To find out what is the next best condition we combine equations (3.17)-(3.19) and (3.28) to write

$$\begin{aligned} \mathbf{J}_{\text{vib}} &= \sum_{i=1}^N \left[ m_i (\mathbf{r}_i^e + \Delta \mathbf{r}_i) \times \mathbf{u}_i \right] \\ &= \sum_{i=1}^N (m_i \mathbf{r}_i^e \times \mathbf{u}_i) + \sum_{i=1}^N (m_i \Delta \mathbf{r}_i \times \mathbf{u}_i). \end{aligned} \quad (3.29)$$

But since we expect that the vibration of the molecule will not displace the nuclei too far from their equilibrium positions, it is therefore reasonable to set our axes-defining condition with the following approximation

$$\mathbf{J}_{\text{vib}} \approx \sum_{i=1}^N (m_i \mathbf{r}_i^e \times \mathbf{u}_i) = 0. \quad (3.30)$$

An equally adequate way of writing this condition is through the so-called **Eckart equations**

$$\boxed{\sum_{i=1}^N (m_i \mathbf{r}_i^e \times \mathbf{r}_i) = 0} \quad (3.31)$$

The problem set associated with this chapter will provide examples that will show how the Euler angles can be evaluated from equation (3.31), but we will for now use it (or rather equation (3.30)) to continue our study of the classical rovibronic Hamiltonian.

Inserting equation (3.30) into equation (3.26) we have

$$2T_N = \sum_{i=1}^N m_i (\boldsymbol{\omega} \times \mathbf{r}_i) \cdot (\boldsymbol{\omega} \times \mathbf{r}_i) + \sum_{i=1}^N m_i u_i^2 + 2\boldsymbol{\omega} \cdot \sum_{i=1}^N (m_i \Delta \mathbf{r}_i \times \mathbf{u}_i). \quad (3.32)$$

We now modify the first term on the right hand side with

$$\begin{aligned} \sum_{i=1}^N m_i (\boldsymbol{\omega} \times \mathbf{r}_i)^2 &= \sum_{i=1}^N m_i \left[ \omega^2 r_i^2 - (\boldsymbol{\omega} \cdot \mathbf{r}_i)^2 \right] \\ &= \sum_{i=1}^N m_i \left[ \omega_x^2 (y_i^2 + z_i^2) + \omega_y^2 (x_i^2 + z_i^2) + \omega_z^2 (x_i^2 + y_i^2) \right. \\ &\quad \left. - 2\omega_x \omega_y x_i y_i - 2\omega_y \omega_z y_i z_i - 2\omega_x \omega_z x_i z_i \right] \\ &= \boldsymbol{\omega}^T I \boldsymbol{\omega}, \end{aligned} \quad (3.33)$$

where

$$I_{\alpha\beta} = \sum_{i=1}^N m_i (\delta_{\alpha\beta} r_i^2 - r_{i,\alpha} r_{i,\beta}), \quad \text{for } \alpha, \beta = x, y, z \quad (3.34)$$

are the instantaneous moments of inertia ( $I$  is the inertia tensor) with respect to the molecule-fixed axes (with  $r_{i,x} = x_i$ , etc.). Inserting equation (3.33) into equation (3.32) we have for the kinetic energy

$$T_N = \frac{1}{2} \boldsymbol{\omega}^T I \boldsymbol{\omega} + \frac{1}{2} \sum_{i=1}^N m_i u_i^2 + \boldsymbol{\omega} \cdot \sum_{i=1}^N (m_i \Delta \mathbf{r}_i \times \mathbf{u}_i). \quad (3.35)$$

### 3.3.1.2 The Internal and Normal Coordinates

A molecule composed of  $N$  nuclei has  $3N$  displacement coordinates  $\Delta\alpha_i$  ( $\alpha = x, y, z$  and  $i = 1, \dots, N$ ) and corresponding velocities that enter the equation for the Hamiltonian (see equation (3.26)). On the other hand, it is well known that a  $N$ -body harmonic oscillator has only  $3N - 6$  degrees of freedom ( $3N - 5$  for a linear oscillator), which are the quantities normally used to express the Hamiltonian. For example, for a water molecule the length of the two O-H bonds and the angle subtended by these bonds are an intuitive choice for the three degrees of freedom. These lengths and angles are often called **internal coordinates**  $S_i$  ( $i = 1, \dots, 3N - 6$ ), and they are linear combinations of the displacement coordinates (a linear expansion can be used if the relationships are non-linear in nature; we then speak of **linearized internal coordinates**). To these internal coordinates we must add the six constraint relations that set the origin and the orientation of the molecule-fixed axes (i.e., equations (3.23) and (3.31)). More precisely, we introduce the six new coordinates below, each consistent with one constraint relation

$$\begin{aligned}
T_x &= M^{-1/2} \sum_{i=1}^N m_i^{1/2} (m_i^{1/2} \Delta x_i) \\
T_y &= M^{-1/2} \sum_{i=1}^N m_i^{1/2} (m_i^{1/2} \Delta y_i) \\
T_z &= M^{-1/2} \sum_{i=1}^N m_i^{1/2} (m_i^{1/2} \Delta z_i),
\end{aligned} \tag{3.36}$$

and

$$\begin{aligned}
R_x &= (I_{xx}^e)^{-1/2} \sum_{i=1}^N m_i^{1/2} [y_i^e (m_i^{1/2} \Delta z_i) - z_i^e (m_i^{1/2} \Delta y_i)] \\
R_y &= (I_{yy}^e)^{-1/2} \sum_{i=1}^N m_i^{1/2} [z_i^e (m_i^{1/2} \Delta x_i) - x_i^e (m_i^{1/2} \Delta z_i)] \\
R_z &= (I_{zz}^e)^{-1/2} \sum_{i=1}^N m_i^{1/2} [x_i^e (m_i^{1/2} \Delta y_i) - y_i^e (m_i^{1/2} \Delta x_i)].
\end{aligned} \tag{3.37}$$

The normalization factors  $M^{-1/2}$  and  $(I_{\alpha\alpha}^e)^{-1/2}$ , and the particular notation for the displacement coordinates (i.e.,  $m_i^{1/2} \Delta\alpha_i$  with  $\alpha = x, y, z$ ) are introduced for convenience, as will become clearer later on. It should be clear that

$$T_x = T_y = T_z = R_x = R_y = R_z = 0. \tag{3.38}$$

With the introduction of these three translation and three rotation coordinates, we can write an invertible matrix equation for the linear combinations linking the internal and displacement coordinates

$$\begin{pmatrix} S_1 \\ \vdots \\ S_{3N-6} \\ T_x \\ T_y \\ T_z \\ R_x \\ R_y \\ R_z \end{pmatrix} = \begin{matrix} \left[ \right. \\ \\ \\ \\ \\ \\ \\ \\ \left. \right] \end{matrix} B \begin{pmatrix} \Delta x_1 \\ \Delta y_1 \\ \Delta z_1 \\ \Delta x_2 \\ \Delta y_2 \\ \vdots \\ \Delta x_N \\ \Delta y_N \\ \Delta z_N \end{pmatrix}. \tag{3.39}$$

If we denote the column vector on the left hand side by  $\mathbf{S}$  and the one on the right hand side by  $\Delta\boldsymbol{\alpha}$ , then we can also write

$$\mathbf{S} = B\Delta\boldsymbol{\alpha}. \quad (3.40)$$

To simplify the problem further, we introduce  $3N - 6$  **normal coordinates**  $Q_i$ , which are linearly connected to the internal coordinates through

$$\mathbf{S} = L\mathbf{Q}, \quad (3.41)$$

where  $L$  is a  $3N$  by  $3N$  matrix, and  $\mathbf{Q}$  is the column vector composed of the normal coordinates augmented with the  $T_\alpha$  and  $R_\alpha$ ,  $\alpha = x, y, z$ , coordinates, just as was done for  $\mathbf{S}$  in equation (3.39) (i.e., the lower right  $6 \times 6$  block of  $L$  is a unit sub-matrix). The main reason for the introduction of the normal coordinates is that it can be shown that their introduction simplifies the kinetic energy of vibration (i.e., the second term on the right hand side of equation (3.35)) to

$$T_{\text{vib}} = \frac{1}{2} \frac{d\mathbf{Q}^T}{dt} \cdot \frac{d\mathbf{Q}}{dt}, \quad (3.42)$$

while under the assumption of small amplitude of vibrations the potential energy can be approximated to the so-called **harmonic potential energy**

$$V_{N,n}^{\text{ham}} = \frac{1}{2} \sum_{i=1}^{3N-6} \lambda_i Q_i^2, \quad (3.43)$$

where  $\lambda_i$  are constants (eigenvalues for the problem). In reality, the potential energy will not be perfectly harmonic in nature, but will contain higher-order terms that will be grouped in the so-called **anharmonic potential energy** term  $V_{N,n}^{\text{anh}}$ . The total potential energy is then expressed by

$$V_{N,n} = V_{N,n}^{\text{ham}} + V_{N,n}^{\text{anh}}. \quad (3.44)$$

However, under the restriction of small vibrations the energy of vibration takes the simple form

$$E_{\text{vib}}^0 = \frac{1}{2} \sum_{i=1}^{3N-6} \left[ \left( \frac{dQ_i}{dt} \right)^2 + \lambda_i Q_i^2 \right]. \quad (3.45)$$

There is, therefore, a great benefit in using the normal coordinates. A so-called **normal mode** is obtained when only one  $Q_i$  is allowed to be non-zero. But in order to visualize a normal mode, it is necessary to find the relationship between  $\mathbf{Q}$  and  $\Delta\boldsymbol{\alpha}$ . Using equations (3.40) and (3.41), and the fact that  $Q_j \propto m_i^{1/2} \Delta\alpha_i$  for equation (3.42) to hold, it is useful to define a new matrix  $l_{\alpha_i, j}$  that links  $\mathbf{Q}$  and  $\Delta\boldsymbol{\alpha}$  as follows



such that

$$\boldsymbol{\omega} \cdot \sum_{i=1}^N (m_i \Delta \mathbf{r}_i \times \mathbf{u}_i) = \sum_{\gamma} \omega_{\gamma} \sum_{j,k=1}^{3N-6} \zeta_{j,k}^{\gamma} Q_j \dot{Q}_k. \quad (3.52)$$

Combining equations (3.35), (3.51), and (3.52), the rovibrational kinetic energy becomes

$$T_N = \frac{1}{2} \boldsymbol{\omega}^T I \boldsymbol{\omega} + \frac{1}{2} \sum_{j=1}^{3N-6} \dot{Q}_j^2 + \sum_{\gamma} \omega_{\gamma} \sum_{j,k=1}^{3N-6} \zeta_{j,k}^{\gamma} Q_j \dot{Q}_k. \quad (3.53)$$

### 3.3.1.3 The Canonical Form of the Rovibrational Kinetic Energy

Since we want to find an expression for the Hamiltonian, it follows that we must express the kinetic energy in terms of the generalized coordinates and their corresponding momenta. Since the potential energy is not dependent on the velocities, the generalized momenta will only be a function of the kinetic energy with

$$P_k = \frac{\partial T_N}{\partial \dot{Q}_k} = \dot{Q}_k + \sum_{\gamma} \omega_{\gamma} \sum_{j=1}^{3N-6} \zeta_{j,k}^{\gamma} Q_j, \quad (3.54)$$

for the momenta associated with the normal modes and

$$M_{\alpha} = \frac{\partial T_N}{\partial \omega_{\alpha}} = \sum_{\beta} I_{\alpha\beta} \omega_{\beta} + \sum_{j,k=1}^{3N-6} \zeta_{j,k}^{\alpha} Q_j \dot{Q}_k, \quad (3.55)$$

for the components of the angular momentum. We must somehow invert equations (3.54) and (3.55) to express the generalized velocities  $\dot{Q}_k$  and  $\omega_{\alpha}$  as a function of the generalized momenta to eliminate them (that is, the velocities) from equation (3.53). As a first step, it is clear from equation (3.54) and (3.55) that

$$\sum_{k=1}^{3N-6} P_k \dot{Q}_k + \sum_{\alpha} M_{\alpha} \omega_{\alpha} = \sum_{k=1}^{3N-6} \dot{Q}_k^2 + \sum_{\alpha,\beta} I_{\alpha\beta} \omega_{\alpha} \omega_{\beta} + 2 \sum_{\alpha} \omega_{\alpha} \sum_{j,k=1}^{3N-6} \zeta_{j,k}^{\alpha} Q_j = 2T_N. \quad (3.56)$$

Next, upon substitution of equation (3.54) for  $\dot{Q}_k$  on the left hand side of equation (3.56) we have

$$2T_N = \sum_{\alpha} M_{\alpha} \omega_{\alpha} + \sum_{k=1}^{3N-6} P_k^2 - \sum_{\alpha} \omega_{\alpha} \sum_{j,k=1}^{3N-6} \zeta_{j,k}^{\alpha} Q_j P_k, \quad (3.57)$$

but upon the introduction of the **vibrational angular momentum**

$$p_\alpha = \sum_{j,k=1}^{3N-6} \zeta_{j,k}^\alpha Q_j P_k, \quad (3.58)$$

we get

$$2T_N = \sum_{\alpha} (M_{\alpha} - p_{\alpha}) \omega_{\alpha} + \sum_{k=1}^{3N-6} P_k^2. \quad (3.59)$$

We can make the same substitution for  $\dot{Q}_k$  into equation (3.55) to get

$$\begin{aligned} M_{\alpha} - p_{\alpha} &= \sum_{\beta} I_{\alpha\beta} \omega_{\beta} - \sum_{k=1}^{3N-6} \left[ \left( \sum_{j=1}^{3N-6} \zeta_{j,k}^{\alpha} Q_j \right) \left( \sum_{\gamma} \omega_{\gamma} \sum_{m=1}^{3N-6} \zeta_{m,k}^{\gamma} Q_m \right) \right] \\ &= \sum_{\beta} \left[ I_{\alpha\beta} - \sum_{k=1}^{3N-6} \left( \sum_{j=1}^{3N-6} \zeta_{j,k}^{\alpha} Q_j \cdot \sum_{m=1}^{3N-6} \zeta_{m,k}^{\beta} Q_m \right) \right] \omega_{\beta} \\ &= \sum_{\beta} [\boldsymbol{\mu}^{-1}]_{\alpha\beta} \omega_{\beta}, \end{aligned} \quad (3.60)$$

where we have introduced a new matrix  $\boldsymbol{\mu}$  whose inverse is defined by

$$[\boldsymbol{\mu}^{-1}]_{\alpha\beta} = \left[ I_{\alpha\beta} - \sum_{k=1}^{3N-6} \left( \sum_{j=1}^{3N-6} \zeta_{j,k}^{\alpha} Q_j \cdot \sum_{m=1}^{3N-6} \zeta_{m,k}^{\beta} Q_m \right) \right]. \quad (3.61)$$

Inverting equation (3.60) yields

$$\omega_{\alpha} = \sum_{\beta} \mu_{\alpha\beta} (M_{\beta} - p_{\beta}), \quad (3.62)$$

and we finally find that

$$T_N = \frac{1}{2} \sum_{\alpha,\beta} (M_{\alpha} - p_{\alpha}) \mu_{\alpha\beta} (M_{\beta} - p_{\beta}) + \frac{1}{2} \sum_{k=1}^{3N-6} P_k^2, \quad (3.63)$$

and

$$\boxed{H_N = \frac{1}{2} \sum_{\alpha,\beta} (M_{\alpha} - p_{\alpha}) \mu_{\alpha\beta} (M_{\beta} - p_{\beta}) + \frac{1}{2} \sum_{k=1}^{3N-6} P_k^2 + \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2 + V_{N,n}^{\text{anh}}} \quad (3.64)$$

for the classical rovibrational Hamiltonian. Although equation (3.64) is the result we will use in subsequent chapters, we should note that, as it stands, it is composed from a mixture of conjugate momenta ( $P_k$ ) and ordinary (angular) momenta ( $M_{\alpha} - p_{\alpha}$ , for

$\alpha = x, y, z$ ). Indeed, it will soon be necessary to use a modification to equation (3.64) where the angular momenta are expressed as conjugate momenta to the Euler angles. So, we now endeavor to accomplish just that.

From equation (3.55), we can write

$$\begin{aligned} M_\alpha &= \frac{\partial T_N}{\partial \omega_\alpha} = \frac{\partial \dot{\phi}}{\partial \omega_\alpha} \frac{\partial T_N}{\partial \dot{\phi}} + \frac{\partial \dot{\theta}}{\partial \omega_\alpha} \frac{\partial T_N}{\partial \dot{\theta}} + \frac{\partial \dot{\chi}}{\partial \omega_\alpha} \frac{\partial T_N}{\partial \dot{\chi}} \\ &= \frac{\partial \dot{\phi}}{\partial \omega_\alpha} P_\phi + \frac{\partial \dot{\theta}}{\partial \omega_\alpha} P_\theta + \frac{\partial \dot{\chi}}{\partial \omega_\alpha} P_\chi, \end{aligned} \quad (3.65)$$

with  $P_\phi \equiv \partial T_N / \partial \dot{\phi}$ , etc., and we therefore need to evaluate  $\frac{\partial \dot{\phi}}{\partial \omega_\alpha}$ , and so on. From Figure 3-1 and equations (3.2), we can write

$$\omega_\alpha = \dot{\phi}(\mathbf{e}_\alpha \cdot \mathbf{e}_\phi) + \dot{\theta}(\mathbf{e}_\alpha \cdot \mathbf{e}_\theta) + \dot{\chi}(\mathbf{e}_\alpha \cdot \mathbf{e}_\chi), \quad (3.66)$$

or more precisely

$$\begin{aligned} \omega_x &= -\dot{\phi} \sin(\theta) \cos(\chi) + \dot{\theta} \sin(\chi) \\ \omega_y &= \dot{\phi} \sin(\theta) \sin(\chi) + \dot{\theta} \cos(\chi) \\ \omega_z &= \dot{\phi} \cos(\theta) + \dot{\chi}. \end{aligned} \quad (3.67)$$

This equation can readily be written in a matrix form and inverted to yield

$$\begin{aligned} \dot{\phi} &= -\omega_x \csc(\theta) \cos(\chi) + \omega_y \csc(\theta) \sin(\chi) \\ \dot{\theta} &= \omega_x \sin(\chi) + \omega_y \cos(\chi) \\ \dot{\chi} &= \omega_x \cot(\theta) \cos(\chi) - \omega_y \cot(\theta) \sin(\chi) + \omega_z. \end{aligned} \quad (3.68)$$

If we write  $M'_\alpha \equiv M_\alpha - p_\alpha$ , then we can use equations (3.58), (3.65), and (3.68) to get

$$\begin{pmatrix} P_k \\ M'_x \\ M'_y \\ M'_z \end{pmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ -a_k & -\csc(\theta) \cos(\chi) & \sin(\chi) & \cot(\theta) \cos(\chi) \\ -b_k & \csc(\theta) \sin(\chi) & \cos(\chi) & -\cot(\theta) \sin(\chi) \\ -c_k & 0 & 0 & 1 \end{bmatrix} \begin{pmatrix} P_k \\ P_\phi \\ P_\theta \\ P_\chi \end{pmatrix}, \quad (3.69)$$

with, for  $k = 1, \dots, 3N - 6$ ,

$$\begin{aligned}
a_k &= \sum_{j=1}^{3N-6} \zeta_{j,k}^x Q_j \\
b_k &= \sum_{j=1}^{3N-6} \zeta_{j,k}^y Q_j \\
c_k &= \sum_{j=1}^{3N-6} \zeta_{j,k}^z Q_j.
\end{aligned} \tag{3.70}$$

We can use this result to replace  $M'_\alpha$  with  $P_\phi$ ,  $P_\theta$ , and  $P_\chi$  in equation (3.64) to write

$$H_N = \frac{1}{2} \sum_{j,k=1}^{3N-3} P'_j \mu'_{jk} P'_k + \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2 + V_{N,n}^{\text{anh}}, \tag{3.71}$$

with  $P'_k$  denote the elements of the vector formed with  $P_k, P_\phi, P_\theta$ , and  $P_\chi$  (see equation (3.73) below). The elements  $\mu'_{mn}$  are those of the matrix resulting from the pre- and post-multiplication of  $\mu_{\alpha\beta}$  (augmented with a  $(3N-6) \times (3N-6)$  unit sub-matrix) with the matrix (and its transposed version) of equation (3.69). That is, if we denote the matrix of equation (3.69) by  $W$ , then

$$\boldsymbol{\mu}' = W^T \left[ \begin{array}{c|c} \mathbf{1} & \mathbf{0} \\ \hline \mathbf{0} & \boldsymbol{\mu} \end{array} \right] W. \tag{3.72}$$

It is also understood from this notation that in equation (3.71) the last three indices for the conjugate momenta in the first summation correspond to  $P_\phi, P_\theta$ , and  $P_\chi$ .

The matrix of equation (3.69) can easily be inverted to yield

$$\begin{aligned}
P_k &= P_k \\
P_\phi &= -M'_x \sin(\theta) \cos(\chi) + M'_y \sin(\theta) \sin(\chi) + M'_z \cos(\theta) \\
&\quad + \sum_{k=1}^{3N-6} [-a_k \sin(\theta) \cos(\chi) + b_k \sin(\theta) \sin(\chi) + c_k \cos(\theta)] P_k \\
P_\theta &= M'_x \sin(\chi) + M'_y \cos(\chi) + \sum_{k=1}^{3N-6} [a_k \sin(\chi) + b_k \cos(\chi)] P_k \\
P_\chi &= M'_z + \sum_{k=1}^{3N-6} c_k P_k.
\end{aligned} \tag{3.73}$$

Its determinant, the reciprocal of that of matrix  $W$  of equation (3.69), is calculated to be  $\sin(\theta)$ . Therefore the determinant of  $\boldsymbol{\mu}'$  is given by

$$\mu' = \mu \csc^2(\theta), \tag{3.74}$$

with  $\mu$  the determinant of  $\boldsymbol{\mu}$ .

### 3.3.2 The Quantum Mechanical Rovibrational Hamiltonian

Now that we have obtained the classical, and canonical, form of the Hamiltonian, the only thing left to do is to transform it into the corresponding quantum mechanical expression. But as one may have already guessed, this is not as straightforward as we would hope. Accordingly, we will have to consider some mathematical intricacies before we can achieve our goal.

#### 3.3.2.1 Mathematical Considerations

Although it was mentioned in Chapter 1 that the momentum operator  $\mathbf{P}$  appearing in equations of classical mechanics is to be replaced by the operator  $-i\hbar\nabla$  to obtain corresponding quantum mechanical equations, it is important to realize that this statement can only be true in general if Cartesian coordinates are used. For example, care must be taken when dealing with the term  $P_k^2$  present in equation (3.64) for the rovibrational classical Hamiltonian. Indeed, this term involves the Laplacian  $\nabla^2$ , and this operator can take non-intuitive forms in coordinates other than Cartesian. Consider for example its representation in spherical coordinates

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial}{\partial r} \right] + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left[ \sin(\theta) \frac{\partial}{\partial \theta} \right] + \frac{1}{r^2 \sin^2(\theta)} \frac{\partial^2}{\partial \varphi^2}. \quad (3.75)$$

Obviously, this relation is more complicated in this coordinate system than it is in Cartesian coordinates, nor does it lead to the same as setting

$$\hat{\mathbf{P}} = -i\hbar \left[ \mathbf{e}_r \frac{\partial}{\partial r} + \mathbf{e}_\theta \frac{\partial}{\partial \theta} + \mathbf{e}_\varphi \frac{\partial}{\partial \varphi} \right], \quad (3.76)$$

and using  $\hat{P}^2 = \hat{\mathbf{P}} \cdot \hat{\mathbf{P}}$  in the Hamiltonian.

Another aspect that needs to be considered has to do with the normalization of the wave function appearing in Schrödinger equation. For example, if the wave function  $\psi_c$  is used when the Schrödinger equation is expressed with Cartesian coordinates, then we have

$$\int |\psi_c(x, y, z)|^2 dx dy dz = 1. \quad (3.77)$$

Accordingly, if one switches to spherical coordinates equation (3.77) becomes

$$\int |\psi_c(r, \theta, \varphi)|^2 r^2 \sin(\theta) dr d\theta d\varphi = 1. \quad (3.78)$$

Although it is perfectly correct to use equations (3.75) and (3.78) to pass from Cartesian to spherical coordinates when dealing with the Schrödinger equation, it is often the case that one desires to keep the simpler definition for the momentum operator expressed with equation (3.76). In general, given a generalized coordinate  $q_k$ , the corresponding momentum  $\hat{P}_k$  is defined as

$$\hat{P}_k = -i\hbar \frac{\partial}{\partial q_k}. \quad (3.79)$$

However, the time-independent Schrödinger equation must give the same results independently of which formalism one uses. It follows that if we are to use equation (3.79) for the definition of the generalized momenta, then we must introduce a prescription that will account for the form of the Laplacian (i.e., equation (3.75)) in the expression for the Hamiltonian. More precisely, if the Hamiltonian for a single particle of mass  $m$  in a potential  $V$  is

$$\hat{H} = -\frac{\hbar^2}{2m} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \frac{\partial}{\partial r} \right] + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left[ \sin(\theta) \frac{\partial}{\partial \theta} \right] + \frac{1}{r^2 \sin^2(\theta)} \frac{\partial^2}{\partial \varphi^2} \right\} + V(r, \theta, \varphi), \quad (3.80)$$

in spherical coordinates, then we cannot simply write that

$$\hat{H} = \frac{\hat{P}^2}{2m} + V(r, \theta, \varphi), \quad (3.81)$$

if  $\hat{\mathbf{P}}$  is given by equation (3.76).

To see how the expression for the Hamiltonian is to be modified, consider the general form of the classical Hamiltonian for a system composed of  $N$  particles of mass  $m_k$ ,  $k = 1, \dots, N$ , each bringing three generalized coordinates (for a total of  $3N$ )

$$H = \frac{1}{2} \sum_{i,j=1}^{3N} g_{ij} \dot{q}_i \dot{q}_j + V(q). \quad (3.82)$$

In equation (3.82)  $g_{ij}$  are the elements of a  $3N \times 3N$  matrix  $\mathbf{g}$ , and each element is dependent on the particle masses and generalized coordinates (i.e., not the velocities). Incidentally, this matrix is closely related to the so-called metric tensor of general relativity (and tensor calculus). One of its main properties is that it allows for the evaluation of the “length” (in a general sense) over an interval in coordinate space. More precisely, we have

$$d\ell^2 = \sum_{i,j=1}^{3N} g_{ij} dq_i dq_j. \quad (3.83)$$

This equation can be used to guess the values of  $g_{ij}$ . We want to make use of this connection to tensor calculus to push our analysis forward. To do so, we express the Hamiltonian with the momenta using

$$p_k = \frac{\partial T}{\partial \dot{q}_k} = g_{ik} \dot{q}_i, \quad (3.84)$$

and  $g^{jk} g_{ik} \equiv \delta^j_i$  (i.e.,  $g^{ij}$  are the elements of the inverse of  $\mathbf{g}$ ), to get  $\dot{q}_j = g^{jk} p_k$  and therefore

$$H = \frac{1}{2} \sum_{i,j=1}^{3N} g^{ij} p_i p_j + V(q). \quad (3.85)$$

If we now assert that in quantum mechanics we must substitute  $p_i \rightarrow -i\hbar \nabla_i$ , then as stated earlier the Laplacian enters the equation through the correspondence  $g^{ij} p_i p_j \rightarrow -\hbar^2 \nabla^2$ . But tensor calculus makes it clear as to how the Laplacian is to be calculated in any given coordinate system. More precisely, the divergence of a vector  $\mathbf{T}$  of components  $T^n$  is given by

$$\nabla \cdot \mathbf{T} = \frac{1}{\sqrt{g}} \frac{\partial}{\partial q_n} (\sqrt{g} T^n), \quad (3.86)$$

where  $g$  is the determinant of the matrix  $\mathbf{g}$  (of elements  $g_{ij}$ ). But since the Laplacian is the divergence of the gradient, we can write  $T^n = g^{mn} \frac{\partial}{\partial q_m}$  and

$$\nabla^2 = \nabla \cdot \nabla = \frac{1}{\sqrt{g}} \frac{\partial}{\partial q_n} \left( \sqrt{g} g^{mn} \frac{\partial}{\partial q_m} \right). \quad (3.87)$$

It follows that the Hamiltonian becomes

$$H = \frac{1}{2} g^{-1/2} \sum_{i,j=1}^{3N} p_i g^{1/2} g^{ij} p_j + V(q). \quad (3.88)$$

It should be noted that this relation is equally valid in classical or quantum mechanics. Of course, the quantum mechanical Hamiltonian will act on the wave function  $\psi_c$ , which is expressed using Cartesian coordinates, in such a way as to obey Schrödinger equation

$$\hat{H}\psi_c - E\psi_c = 0. \quad (3.89)$$

On the other hand, we will require that the wave function  $\psi$  associated with the generalized coordinates also obeys the usual normalization rule (but see Section 3.3.2.2 for an exception to that rule)

$$\int |\psi(q_1, \dots, q_N)|^2 d\tau = 1, \quad (3.90)$$

where  $d\tau = dq_1 \cdots dq_N$  is the “volume” element associated with the  $N$  generalized coordinates  $q_k$ , for  $k = 1, \dots, 3N$ . But tensor analysis also tells us of another connection that links the generalized coordinates  $q_k$  to the Cartesian coordinates  $x_k, y_k, z_k$ , etc., of the particles. More precisely, we have that

$$dx_1 dy_1 dz_1 \cdots dx_N dy_N dz_N = \sqrt{g} dq_1 \cdots dq_{3N}. \quad (3.91)$$

So, combining equations (3.90) and (3.91) with the similar requirement for  $\psi_c$

$$\int |\psi_c|^2 dx_1 \cdots dz_N = \int |\psi_c|^2 \sqrt{g} dq_1 \cdots dq_{3N} = \int |\psi|^2 dq_1 \cdots dq_{3N} = 1, \quad (3.92)$$

we find that

$$\psi_c = g^{-1/4} \psi. \quad (3.93)$$

Inserting this relation in equation (3.89) and multiplying on the left by  $g^{1/4}$  we get

$$\hat{H}\psi - E\psi = 0, \quad (3.94)$$

as required, and

$$\hat{H} = \frac{1}{2} g^{-1/4} \sum_{i,j=1}^{3N} \hat{p}_i g^{1/2} g^{ij} \hat{p}_j g^{-1/4} + V(q). \quad (3.95)$$

### 3.3.2.2 The Final Form of the Quantum Mechanical Rovibrational Hamiltonian

It should now be noted that equation (3.95) for the Hamiltonian can be applied to our previous result for the classical rovibrational Hamiltonian of equation (3.71), provided we make the following associations

$$\begin{aligned}
g^{ij} &\leftrightarrow \mu'_{ij} \\
\hat{p}_i &\leftrightarrow P_i \\
V(q) &\leftrightarrow \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2 + V_{N,n}^{\text{anh}}.
\end{aligned} \tag{3.96}$$

We then get

$$\hat{H}'_N = \frac{1}{2} \mu'^{1/4} \sum_{i,j=1}^{3N-3} \hat{P}'_i \mu'^{-1/2} \mu'_{ij} \hat{P}'_j \mu'^{1/4} + \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2 + V_{N,n}^{\text{anh}}. \tag{3.97}$$

However, this can be transformed as follows using equations (3.69), (3.72), (3.73), and (3.74)

$$\begin{aligned}
\hat{H}'_N &= \frac{1}{2} \csc^{1/2}(\theta) \mu^{1/4} \sum_{i,j,m,n,p=1}^{3N-3} \hat{P}'_i \sin(\theta) \mu^{-1/2} W_{mi} \mu_{mp} W_{pj} W_{jn}^{-1} \hat{P}'_n \mu^{1/4} \csc^{1/2}(\theta) \\
&\quad + \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2 + V_{N,n}^{\text{anh}} \\
&= \frac{1}{2} \csc^{1/2}(\theta) \mu^{1/4} \sum_{i,m,n=1}^{3N-3} \hat{P}'_i \sin(\theta) W_{mi} \mu^{-1/2} \mu_{mn} \hat{P}'_n \mu^{1/4} \csc^{1/2}(\theta) \\
&\quad + \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2 + V_{N,n}^{\text{anh}}.
\end{aligned} \tag{3.98}$$

It is, however, fairly straightforward to show that (using equation (3.69) for the elements  $W_{im}$ , and  $\hat{P}'_i \equiv -i\hbar\partial_i$ )

$$\sum_{i=1}^{3N-3} \hat{P}'_i \sin(\theta) W_{mi} = \sin(\theta) \sum_{n=1}^{3N-3} W_{mn} \hat{P}'_n = \sin(\theta) \hat{P}'_m, \tag{3.99}$$

where it is understood that the components  $\hat{P}'_m$  are those of the vector on the left hand side of equation (3.69). Equation (3.98) becomes

$$\begin{aligned}
\hat{H}'_N &= \frac{1}{2} \sin^{1/2}(\theta) \mu^{1/4} \sum_{\alpha,\beta} (\hat{M}_\alpha - \hat{p}_\alpha) \mu^{-1/2} \mu_{\alpha\beta} (\hat{M}_\beta - \hat{p}_\beta) \mu^{1/4} \sin^{-1/2}(\theta) \\
&\quad + \frac{1}{2} \mu^{1/4} \sum_{k=1}^{3N-6} \hat{P}'_k \mu^{-1/2} \hat{P}'_k \mu^{1/4} + \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2 + V_{N,n}^{\text{anh}}.
\end{aligned} \tag{3.100}$$

It was mentioned earlier that the wave function associated with the Hamiltonian is usually made to obey the normalization condition expressed by equation (3.90). We will here depart from that rule when considering the Euler angles. That is, equation (3.90) will be respected for the  $3N-6$  normal coordinates  $Q_k$ , but we will rather use a

normalization form similar to that of equation (3.78) for the Euler angles. We therefore write

$$\int |\psi(\phi, \theta, \chi, Q_1, \dots, Q_{3N-6})|^2 \sin(\theta) d\phi d\theta d\chi dQ_1 \cdots dQ_{3N-6} = 1. \quad (3.101)$$

Because of this prescription we must slightly modify the expression for the Hamiltonian, reflecting in effect this choice of definition for the wave function. Accordingly, we absorb the  $\sin^{-1/2}(\theta)$  factor in the first term of equation (3.100) within the wave function and multiply on the left by again  $\sin^{-1/2}(\theta)$  to get

$$\begin{aligned} \hat{H}_N = & \frac{1}{2} \mu^{1/4} \sum_{\alpha, \beta} (\hat{M}_\alpha - \hat{p}_\alpha) \mu^{-1/2} \mu_{\alpha\beta} (\hat{M}_\beta - \hat{p}_\beta) \mu^{1/4} + \frac{1}{2} \mu^{1/4} \sum_{k=1}^{3N-6} \hat{P}_k \mu^{-1/2} \hat{P}_k \mu^{1/4} \\ & + \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2 + V_{N,n}^{\text{anh}}. \end{aligned} \quad (3.102)$$

At this point, it would be reasonable to assume that we are done and that equation (3.102) is the form to be used for the molecular quantum mechanical Hamiltonian. However, J. K. G. Watson showed in a rather mind-boggling paper<sup>1</sup> that this relation can be significantly simplified by a judicious use of diverse commutation relations and sum rules. We will not study the details of Watson's analysis and only use his final result, which states that the simplified Hamiltonian is given by

$$\boxed{\begin{aligned} \hat{H}_N = & \frac{1}{2} \sum_{\alpha, \beta} (\hat{J}_\alpha - \hat{p}_\alpha - \hat{L}_\alpha) \mu_{\alpha\beta} (\hat{J}_\beta - \hat{p}_\beta - \hat{L}_\beta) + \frac{1}{2} \sum_{k=1}^{3N-6} \hat{P}_k^2 - \frac{\hbar^2}{8} \sum_{\alpha} \mu_{\alpha\alpha} \\ & + \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2 + V_{N,n}^{\text{anh}} \end{aligned}} \quad (3.103)$$

where we have used  $\hat{M}_\alpha = \hat{J}_\alpha - \hat{L}_\alpha$ , with  $\hat{J}_\alpha$  and  $\hat{L}_\alpha$  the total and electronic angular momenta, respectively. It should also be noted that on account of the following relation (also established by Watson)

$$\sum_{\alpha} \hat{P}_\alpha \mu_{\alpha\beta} = \sum_{\alpha} \mu_{\alpha\beta} \hat{P}_\alpha, \quad (3.104)$$

the order of the factors in the first term on the right hand side of equation (3.103) is irrelevant. A comparison of equations (3.64) and (3.103) shows the striking resemblance between the quantum mechanical and classical Hamiltonians, with the only difference in form due to the term

<sup>1</sup> Watson, James K. G. 1968, *Molecular Physics*, Vol. 15, No. 5, 479-490.

$$U = -\frac{\hbar^2}{8} \sum_{\alpha} \mu_{\alpha\alpha}. \quad (3.105)$$

This term can be thought of as a mass-dependent addition to the potential energy of the molecule, although *it actually originates with its kinetic energy*. In his paper, Watson also gave a prescription for expanding  $\mu_{\alpha\beta}$  with a Taylor series in the normal coordinates about the molecular equilibrium configuration. But since we don't expect the positions of the nuclei composing the molecule to deviate much from equilibrium, it will be sufficient for our purposes to approximate

$$\mu_{\alpha\beta} \approx \mu_{\alpha\beta}^e = \left\{ \left[ I^e \right]^{-1} \right\}_{\alpha\beta}. \quad (3.106)$$

These elements correspond to the normalizing factor introduced earlier in the definition of the  $R_{\alpha}$  and  $T_{\alpha}$  coordinates (see equations (3.37)). One nice consequence of this approximation is that the products of inertia vanish at equilibrium (i.e.,  $I_{\alpha\beta}^e = 0$ , for  $\alpha \neq \beta$ ; see equations (3.31) and (3.34)), and therefore the same is true for  $\mu_{\alpha\beta}^e$  (i.e.,  $\mu_{\alpha\beta}^e = 0$ , for  $\alpha \neq \beta$ ).

Finally, it is common to make further simplifications by neglecting the presence of the electronic angular momenta  $\hat{L}_{\alpha}$  (Born-Oppenheimer approximation), the vibrational angular momenta  $\hat{p}_{\alpha}$  (small because of the Eckart conditions), the anharmonicity in the potential energy  $V_{N,n}^{\text{anh}}$ , and  $U$ . Combining these simplifications we can express the approximate rovibrational Hamiltonian as

$$\hat{H}_{\text{rv}}^0 = \frac{1}{2} \sum_{\alpha} \mu_{\alpha\alpha}^e \hat{J}_{\alpha}^2 + \frac{1}{2} \sum_{k=1}^{3N-6} \left( \hat{P}_k^2 + \lambda_k Q_k^2 \right) \quad (3.107)$$

The first term on the right hand side of equation (3.107) is the so-called **rigid rotator Hamiltonian**, while the second term is the **harmonic oscillator (vibrational) Hamiltonian**.