

## Chapter 1. The harmonic oscillator

### 1.1 An oscillating dipole moment leads to infrared absorption

The permanent dipole moment of a molecule oscillates about an equilibrium value as the molecule vibrates. Thus, the dipole moment depends on the nuclear coordinate  $Q$ , where  $\mu$  is the dipole operator.

$$\mu(Q) = \mu_0 + \left(\frac{\partial\mu}{\partial Q}\right)Q + \dots \quad (1.1.1)$$

Rotational transitions arise from the rotation of the permanent dipole moment that can interact with an electromagnetic field in the microwave region of the spectrum. Here the transition moment interacts with electromagnetic radiation because of the oscillation in the dipole itself as shown in Figure 1.1.

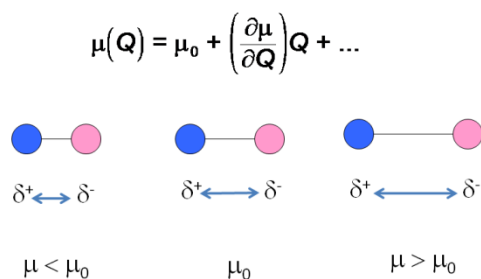


Figure 1.1 Depiction of oscillating dipole moment.

The series expansion is used since it represents the change in the dipole moment. We have only used the first term since that suffices to express the main effect of the change in dipole moment as the molecules vibrate. Although Figure 1.1 shows a diatomic molecule the same principle applies to the normal modes of polyatomic molecules. An oscillating dipole moment can lead to absorption of infrared radiation. However, for absorption to occur there must be a dipole moment.

### 1.2 Classical description of vibration

In classical physics vibration is treated as harmonic motion. The model of a mass on a spring. Figure 1.2A shows the model of a mass attached to a wall (or object of large mass). Here only the mass of the object affects the frequency. Figure 1.2B shows the situation for a diatomic molecule or any spring with two masses attached. In this case, it is the reduced mass that affects the frequency. In the classical picture the assumption of a Hooke's law spring gives a linear restoring force:

$$F = -kQ \tag{1.2.1}$$

Since the potential is related to the force as

$$F = -\frac{dV}{dQ} \tag{1.2.2}$$

We can see that the classical potential energy is:

$$V(Q) = \frac{k}{2}Q^2 \tag{1.2.3}$$

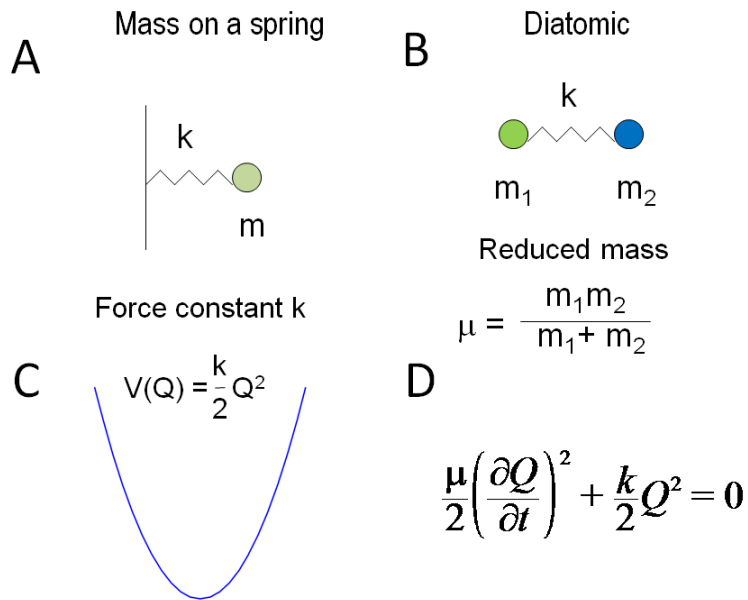


Figure 1.2. Classical depiction of harmonic motion.

A solution to the classical equation of motion in Figure 1.2 is:

$$Q(t) = Q_0 \cos(\omega t) \tag{1.2.4}$$

$$-\frac{\mu}{2}\omega^2 Q_0 \cos(\omega t) = -\frac{k}{2}Q_0 \cos(\omega t)$$

Therefore,

$$\omega = \sqrt{\frac{k}{\mu}} \quad (1.2.5)$$

The quantity,  $\omega$ , is the angular frequency. The frequency in Hertz,  $\nu$ , is more useful. The relationship between them is:

$$\omega = 2\pi\nu \quad (1.2.6)$$

Thus, we can write

$$\nu(s^{-1}) = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (1.2.7)$$

We can write the result in  $\text{cm}^{-1}$  by dividing by  $c$  (in units of  $\text{cm/s}$ ).

$$\tilde{\nu}(\text{cm}^{-1}) = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (1.2.8)$$

### 1.3 Quantum mechanical model of vibrational motion

Molecular bonds have a potential energy surface (PES) such as that shown in Figure 1.3.

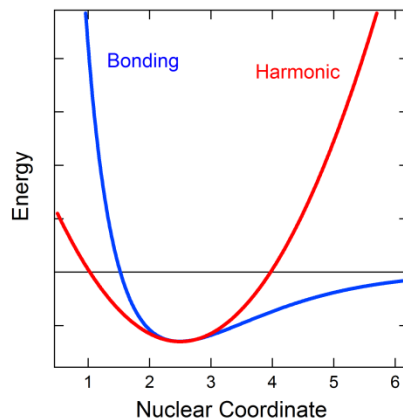


Figure 1.3. Comparison of a realistic bonding potential energy surface calculated for the hydrogen molecule ion and a harmonic potential energy surface approximation.

The potential energy surface has asymmetric form and is not readily adapted to quantum chemical calculation of the vibrational frequency. To obtain a model that can readily be calculated we employ the harmonic approximation. The inspiration for this approach from the

classical harmonic oscillator where the potential is rigorously harmonic (in the limit of small displacements where Hooke's law is valid). We expand the true potential  $V(Q)$  in a series expansion as follows:

$$V(Q) = V(Q_0) + \left(\frac{\partial V}{\partial Q}\right)(Q - Q_0) + \frac{1}{2}\left(\frac{\partial^2 V}{\partial Q^2}\right)(Q - Q_0)^2 + \dots \quad (1.3.1)$$

The first term,  $V(Q_0)$  is an offset in energy and does not affect either the shape of the PES. We can also simplify this expression by shifting the coordinate system so that  $Q_0 = 0$ . The second term is zero at the equilibrium position where we are most interested in expanding the potential energy. The first term that has information regarding the potential energy is the quadratic term. The second derivative ( $d^2V/dQ^2$ ) is the curvature of the potential energy surface at the equilibrium position. This is equivalent to the force constant,  $k$ , in the classical model.

$$k = \left(\frac{\partial^2 V}{\partial Q^2}\right) \quad (1.3.2)$$

Therefore, we can use a harmonic potential in the Schrödinger equation to calculate the wave functions and energies of the vibrations of molecules.

$$-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial Q^2} \chi + \frac{k}{2} Q^2 \chi = E \chi \quad (1.3.3)$$

Making the definitions,

$$y = \sqrt{\alpha} Q \quad \text{where } \alpha = \frac{\mu\omega}{\hbar} \quad \text{and } \epsilon = \frac{2E}{\hbar\omega} \quad (1.3.4)$$

Noting that

$$\frac{\partial^2}{\partial Q^2} = \frac{\mu\omega}{\hbar} \frac{\partial^2}{\partial y^2} \quad (1.3.5)$$

we can write Eqn. 1.3.3 as

$$-\frac{\partial^2}{\partial y^2} \chi + y^2 \chi = \epsilon \chi \quad (1.3.6)$$

One approach to solving such an equation is to find an asymptotic solution,  $g(y)$  by assuming that  $\epsilon \approx 0$ . Then, we can assume that the true solution is the product of  $g(y)$  and a function,

$f(y)$ , which can be a series expansion that will give different solutions for various values of  $\epsilon$ . The asymptotic equation is,

$$\frac{\partial^2}{\partial y^2} \chi \approx y^2 \chi \quad (1.3.7)$$

A Gaussian function is an appropriate trial solution for this equation,

$$\chi_{trial} = e^{-y^2/2} \quad (1.3.8)$$

$$\frac{\partial^2}{\partial y^2} \chi_{trial} = (y^2 - 1)e^{-y^2/2} \quad (1.3.9)$$

For large values of  $y$  we have

$$\frac{\partial^2}{\partial y^2} e^{-y^2/2} \approx y^2 e^{-y^2/2} \quad (1.3.10)$$

which solves Eqn. 1.3.7. Thus, our trial solution for the general equation is

$$\chi_{trial} = f(y)e^{-y^2/2} \quad (1.3.11)$$

In order to substitute this equation into Eqn. 1.3.6 we need the derivatives. We have

$$\frac{\partial \chi_{trial}}{\partial y} = \left( \frac{\partial f}{\partial y} - fy \right) e^{-y^2/2}$$

and

$$\frac{\partial^2 \chi_{trial}}{\partial y^2} = \left( \frac{\partial^2 f}{\partial y^2} - 2y \frac{\partial f}{\partial y} + (y^2 - 1)f \right) e^{-y^2/2} \quad (1.3.12)$$

Substituting this into Eqn. 1.3.6 gives us

$$\frac{\partial^2 f}{\partial y^2} - 2y \frac{\partial f}{\partial y} + (\epsilon - 1)f = 0 \quad (1.3.13)$$

If we assume that  $f(y)$  has the form of a series,

$$f(y) = \sum_{n=0}^{\infty} a_n y^n \quad (1.3.14)$$

Then the derivatives of  $f(y)$  are given by

$$\begin{aligned} \frac{\partial f}{\partial y} &= \sum_{n=0}^{\infty} n a_n y^{n-1} \\ \frac{\partial^2 f}{\partial y^2} &= \sum_{n=0}^{\infty} n(n-1) a_n y^{n-2} \\ &= \sum_{n=0}^{\infty} (n+1)(n+2) a_{n+2} y^n \end{aligned} \quad (1.3.15)$$

Substituting these series into Eqn. 1.3.13

$$\sum_{n=0}^{\infty} (n+1)(n+2) a_{n+2} y^n - 2y \sum_{n=0}^{\infty} n a_n y^{n-1} + (\epsilon - 1) \sum_{n=0}^{\infty} a_n y^n = 0 \quad (1.3.16)$$

$$\sum_{n=0}^{\infty} ((n+1)(n+2) a_{n+2} + (\epsilon - 1 - 2n) a_n) y^n = 0 \quad (1.3.17)$$

Once we choose a value for  $\epsilon$  there is one and only one sequence of coefficients,  $a_n$ , that defines the function  $f(y)$ . Therefore, the sum can be zero for all values of  $y$  if and only if the coefficient of each power of  $y$  vanishes separately. Thus,

$$(n+1)(n+2) a_{n+2} + (\epsilon - 1 - 2n) a_n = 0 \quad (1.3.18)$$

and

$$a_{n+2} = \frac{1 + 2n - \epsilon}{(n+1)(n+2)} a_n \quad (1.3.19)$$

Rather than finding an infinite series (which would actually be divergent in this case!) we will assume that the solution is a polynomial that terminates after a finite number of terms,  $n$ . The condition for the series to terminate is

$$a_{n+2} = 0 \tag{1.3.20}$$

which implies

$$1 + 2n - \epsilon = 0$$

or

$$\epsilon = 2n + 1 \tag{1.3.21}$$

Therefore, from Eqn. 1.3.4 we have

$$E = \frac{1}{2}(2n + 1)\hbar\omega = \left(n + \frac{1}{2}\right)\hbar\omega \tag{1.3.22}$$

Using the definition of  $\alpha$  in Eqn. 1.3.4, the solutions have the form:

$$\chi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha Q^2/2}$$

$$\chi_1 = \left(\frac{\alpha}{\pi}\right)^{1/4} \sqrt{2\alpha} Q e^{-\frac{\alpha Q^2}{2}}$$

$$\chi_2 = \left(\frac{\alpha}{\pi}\right)^{1/4} \frac{(4\alpha Q^2 - 2)}{2\sqrt{2}} e^{-\alpha Q^2/2}$$

(1.3.23)

in which the polynomials are known as Hermite polynomials. We can obtain the Hermite polynomials using a generating function,

$$H_n(y) = (-1)^n e^{y^2/2} \frac{d^n}{dy^n} e^{-y^2/2} \tag{1.3.24}$$

We will use the quantum number  $v$  for the quantum harmonic oscillator. Thus, the definitions of the energy become,

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega \tag{1.3.25}$$

The energy levels are evenly spaced starting a  $1/2\hbar\nu$ . The significance of the offset from zero is a consequence of the Uncertainty principle. Vibrations are present even at absolute zero in crystalline substances. The nuclear motion in crystals can never cease since that would mean that the positions would be precisely located and the momentum would be precisely known because it would be zero. For this reason  $1/2\hbar\nu$  is known as the zero-point energy and the motion in that state is the zero-point motion. Note that the energy levels are evenly spaced above the zero-point level, so that there is only one observed vibrational transition even if higher vibrational states are thermally occupied.

The form of the wave functions is Gaussian, but with a polynomial factor that gives rise to the nodes in the wave functions that can be seen in Figure 1.4..

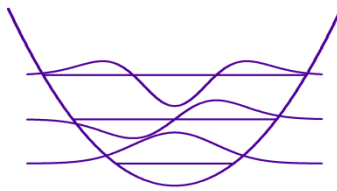


Figure 1.4. Graphical representation of the first three wave functions of the solution to the harmonic oscillator.

While we have not derived the solutions (Eqns. 1.3.4), we can test them for consistency by substituting into the Schrödinger equation, Eqn. 1.3.3. We will use  $\chi_0$  as an example. Leaving out the normalization constant, the second derivative is

$$\frac{\partial}{\partial Q} e^{-\frac{\alpha Q^2}{2}} = -\alpha Q e^{-\frac{\alpha Q^2}{2}}$$

$$\frac{\partial}{\partial Q} -\alpha Q e^{-\alpha Q^2/2} = -\alpha e^{-\alpha Q^2/2} + \alpha^2 Q^2 e^{-\frac{\alpha Q^2}{2}} = (\alpha^2 Q^2 - \alpha) e^{-\alpha Q^2/2}$$

Now we substitute that result into the Schrödinger equation. We do not include the normalization constant here since it cancels out in each term.

$$-\frac{\hbar^2}{2\mu} (\alpha^2 Q^2 - \alpha) e^{-\alpha Q^2/2} + \frac{k}{2} Q^2 e^{-\alpha Q^2/2} = E e^{-\alpha Q^2/2}$$

So

$$-\frac{\hbar^2}{2\mu} \left( \frac{\mu k}{\hbar^2} Q^2 - \frac{\sqrt{\mu k}}{\hbar} \right) + \frac{k}{2} Q^2 = E$$

and



$$E = \frac{\hbar}{2} \sqrt{\frac{k}{\mu}} = \frac{1}{2} \hbar \omega \quad (1.3.26)$$

We can see that  $\chi_0$  is a solution and gives the zero-point energy as the eigenvalue. As we have seen for other quantum mechanical solutions, the harmonic oscillator wave functions are orthogonal. They have been normalized using the properties of Gaussian integrals.

#### 1.4. Orthonormality of harmonic oscillator wave functions

Since the harmonic oscillator basis functions are orthogonal, integrals of the type,

$$\int_{-\infty}^{\infty} \chi_{v'} \chi_v dQ = \delta_{vv'} \quad (1.4.1)$$

Are zero unless  $v = v'$ . That is the meaning of the Kroenecker delta.

$$\delta_{vv'} = \begin{cases} 0 & \text{if } v \neq v' \\ 1 & \text{if } v = v' \end{cases} \quad (1.4.2)$$

### 1.5 Normal modes of vibration

#### 1.1.1 Vibrational degrees of freedom

In a non-linear polyatomic molecule with N atoms, there are  $3N - 6$  vibrational modes. Each normal mode has an associated solution to the harmonic oscillator model. By definition, the normal modes themselves are orthogonal so each one contributes independently to motion and each vibrational frequency can be observed by infrared spectroscopy, if the difference dipole moment is sufficiently large.

A normal mode is a collective motion of the molecule. At the minimum of the motion all of the nuclei pass in each mode through the equilibrium position of the molecule. The extent of motion may be different for different nuclei, but they are still in-phase. The importance of normal modes is that this method of calculation permits application of the harmonic oscillator model to all of the modes of a polyatomic molecule. This means that the method is generally applicable.

We shall illustrate the normal mode concept with two examples,  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .  $\text{H}_2\text{O}$  has 3 atoms and 9 total degrees freedom.  $\text{H}_2\text{O}$  is a non-linear molecule so it has 3 translations and 3 rotations leaving 3 vibrational modes. These are shown in Figure 1.5A. Since  $\text{CO}_2$  is linear molecule, it has only 2 rotational degrees of freedom. Thus, it has two orthogonal bending modes shown in Figure 1.5B.

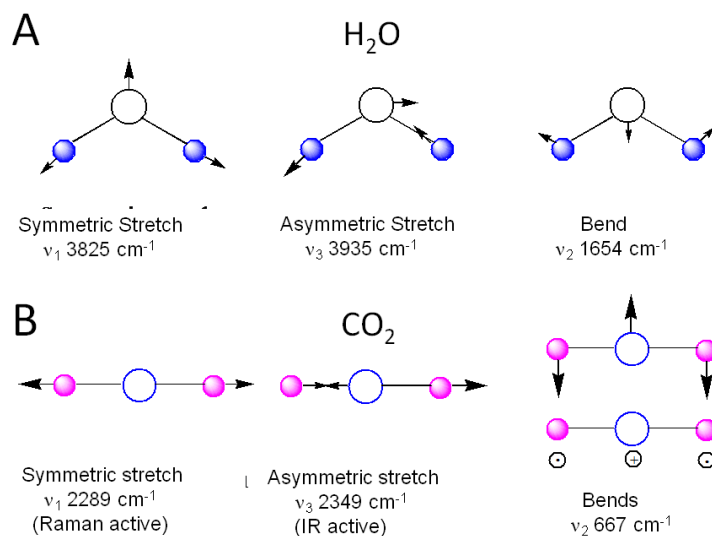


Figure 1.5. Normal modes of vibration

A.) the 3 modes of vibration for  $\text{H}_2\text{O}$  are shown.

B.) the 4 modes of vibration for  $\text{CO}_2$  are shown.

### 1.1.2 The eigenvalue approach to normal modes

Polyatomic molecules can be considered as a set of coupled harmonic oscillators. Although this is a classical model we shall see that it can be used to interpret spectra using the quantum-mechanical harmonic oscillator wave functions. The collective motions of the atoms in a molecule are decomposed into normal modes of vibration within the harmonic approximation. The normal modes are mutually orthogonal. That is they represent linearly independent motions of the nuclei about the center-of-mass of the molecule.

#### 1.1.2.1 Kinetic and potential energy in Cartesian coordinates

Our starting point is to consider the potential and kinetic energy in Cartesian coordinates:

$$T = \frac{1}{2} \sum_{i=1}^N m_i \left\{ \left( \frac{\partial x_i}{\partial t} \right)^2 + \left( \frac{\partial y_i}{\partial t} \right)^2 + \left( \frac{\partial z_i}{\partial t} \right)^2 \right\}$$

$$V = V_0 + \sum_{i=1}^N \left\{ \left( \frac{\partial V}{\partial x_i} \right) x_i + \left( \frac{\partial V}{\partial y_i} \right) y_i + \left( \frac{\partial V}{\partial z_i} \right) z_i \right\}$$

$$+ \frac{1}{2} \sum_{i=1}^N \left\{ \left( \frac{\partial^2 V}{\partial x_i^2} \right) x_i^2 + \left( \frac{\partial^2 V}{\partial y_i^2} \right) y_i^2 + \left( \frac{\partial^2 V}{\partial z_i^2} \right) z_i^2 \right\}$$

$$+ \frac{1}{2} \sum_{i,j=1}^N \left\{ \left( \frac{\partial^2 V}{\partial x_i \partial y_j} \right) x_i y_j + \left( \frac{\partial^2 V}{\partial y_i \partial z_j} \right) y_i z_j + \left( \frac{\partial^2 V}{\partial z_i \partial x_j} \right) z_i x_j \right\}$$

We will assume that the potential energy is expanded about the equilibrium position and thus the first derivative terms are equal to zero. The term  $V_0$  is an arbitrary energy offset and it will also be set equal to zero.

### 1.1.2.2 Kinetic and potential energy in mass-weighted Cartesian coordinates

These expressions can be greatly simplified using mass-weighted coordinates:

$$T = \frac{1}{2} \sum_{i=1}^{3N} \left( \frac{\partial \eta_i}{\partial t} \right)^2$$

$$V = \frac{1}{2} \sum_{i,j=1}^{3N} a_{ij} \eta_i \eta_j$$

where

$$\eta_i = \sqrt{m_i} x_i$$

$$a_{ij} = \left( \frac{\partial^2 V}{\partial \eta_i \partial \eta_j} \right)$$

The equations of motion for the collection of atoms in the molecule are:

$$\frac{\partial^2 \eta_i}{\partial t^2} + \sum_{j=1}^{3N} a_{ij} \eta_j = 0$$

The trial solutions have the form:

$$\eta_i = \eta_i^0 \sin(\sqrt{\lambda} t + \delta)$$

$$\frac{\partial \eta_i}{\partial t} = \sqrt{\lambda} \eta_i^0 \cos(\sqrt{\lambda} t + \delta)$$

$$\frac{\partial^2 \eta_i}{\partial t^2} = -\lambda \eta_i^0 \sin(\sqrt{\lambda} t + \delta)$$

When substituted into the equations of motion we have:

$$-\lambda \eta_i^0 + \sum_{j=1}^{3N} a_{ij} \eta_j^0 = 0$$

for  $i = 1$  to  $3N$ . This equation is a matrix equation

$$(\mathbf{A} - \lambda \mathbf{I})\boldsymbol{\eta}^0 = 0$$

where  $\mathbf{I}$  is the identity matrix. The general form of the matrix equations is:

$$\left( \begin{array}{ccc|ccc} a_{11} & a_{12} & a_{13} & \dots & \lambda_1 & 0 & 0 & \dots \\ a_{21} & a_{22} & a_{23} & \dots & 0 & \lambda_2 & 0 & \dots \\ a_{31} & a_{32} & a_{33} & \dots & 0 & 0 & \lambda_3 & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \end{array} \right) \begin{pmatrix} \eta_1^0 \\ \eta_2^0 \\ \eta_3^0 \\ \dots \end{pmatrix} = 0$$

There is a trivial solution in which all of the terms in the  $\boldsymbol{\eta}^0$  column vector are zero. The interesting solution, however, is the solution for which the determinant of the matrix  $|\mathbf{A} - \lambda \mathbf{I}|$  is equal to zero.

### 1.1.2.3 Transformation to normal coordinates

The potential energy is written in the general form:

$$V = \frac{1}{2} \begin{pmatrix} \eta_1 & \eta_2 & \eta_3 & \dots \end{pmatrix} \begin{pmatrix} a_{11} & a_{12} & a_{13} & \dots \\ a_{21} & a_{22} & a_{23} & \dots \\ a_{31} & a_{32} & a_{33} & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} \eta_1 \\ \eta_2 \\ \eta_3 \\ \dots \end{pmatrix}$$

or in matrix form as

$$V = \frac{1}{2} \boldsymbol{\eta}^T \mathbf{A} \boldsymbol{\eta}$$

where  $\boldsymbol{\eta}^T$  is the transpose of  $\boldsymbol{\eta}$ .  $\mathbf{A}$  is a symmetric matrix, but it is not diagonal. In fact, the procedure of finding  $\det |\mathbf{A} - \lambda \mathbf{I}|$  is a matrix diagonalization of  $\mathbf{A}$ . To perform this diagonalization we transform to normal coordinates  $Q_i$  where:

$$Q_i = \sum_{k=1}^{3N} \ell_{ik} \eta_k$$

for  $i = 1 \dots 3N$ . Although the sum extends to include all  $3N$  degrees of freedom, only  $3N-6$  or  $3N-5$  of these are vibrational modes for non-linear or linear molecules, respectively. In matrix form  $\mathbf{Q} = \mathbf{L}^T \boldsymbol{\eta}$ . We can write this in matrix form as follows.

$$\begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \\ \dots \end{pmatrix} = \begin{pmatrix} \ell_{11} & \ell_{12} & \ell_{13} & \dots \\ \ell_{21} & \ell_{22} & \ell_{23} & \dots \\ \ell_{31} & \ell_{32} & \ell_{33} & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} \eta_1 \\ \eta_2 \\ \eta_3 \\ \dots \end{pmatrix}$$

where  $\mathbf{L}^T$  is the transpose of  $\mathbf{L}$ .  $\mathbf{L}$  is a unitary matrix; its inverse is equal to its transpose  $\mathbf{L}^{-1} = \mathbf{L}^T$ . Because  $\mathbf{L}$  is unitary  $\mathbf{Q} = \mathbf{L}^T \boldsymbol{\eta} = \mathbf{L}^{-1} \boldsymbol{\eta}$  and  $\boldsymbol{\eta} = \mathbf{L} \mathbf{Q}$ . The inverse transformation is:

$$\begin{pmatrix} \eta_1 \\ \eta_2 \\ \eta_3 \\ \dots \end{pmatrix} = \begin{pmatrix} \ell_{11} & \ell_{21} & \ell_{31} & \dots \\ \ell_{12} & \ell_{22} & \ell_{32} & \dots \\ \ell_{13} & \ell_{23} & \ell_{33} & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix} \begin{pmatrix} Q_1 \\ Q_2 \\ Q_3 \\ \dots \end{pmatrix}$$

This means that we can calculate the total displacements in Cartesian coordinates from

$$\eta_k = \sum_{i=1}^{3N} \ell'_{ik} Q_i$$

Where  $\ell'$  refers to the elements of the transposed (i.e. inverse) matrix. Using a similarity transform, the matrices  $\mathbf{L}^T$  and  $\mathbf{L}$  can be used to diagonalize  $\mathbf{A}$ , as follows.

$$\mathbf{L}^T \mathbf{A} \mathbf{L} = \mathbf{\Lambda} = \begin{pmatrix} \lambda_1 & 0 & 0 & \dots \\ 0 & \lambda_2 & 0 & \dots \\ 0 & 0 & \lambda_3 & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix}$$

Thus, the eigenvalues are related to the mode frequencies as

$$\sqrt{\lambda_i} = \omega_i = 2\pi\nu_i$$

The collection of elements,  $\ell_{ki}$ , are called an eigenvector. The eigenvectors are normalized such that

$$\sum_{k=1}^{3N} \ell_{ki}^2 = 1$$

for each of the  $i$  modes. The kinetic energy is:

$$T = \frac{1}{2} \frac{\partial \mathbf{Q}^T}{\partial t} \mathbf{L}^T \mathbf{L} \frac{\partial \mathbf{Q}}{\partial t} = \frac{1}{2} \frac{\partial \mathbf{Q}^T}{\partial t} \frac{\partial \mathbf{Q}}{\partial t} = \frac{1}{2} \sum_{i=1}^{3N} \left( \frac{\partial Q_i}{\partial t} \right)^2$$

$$V = \frac{1}{2} \mathbf{Q}^T \mathbf{L}^T \mathbf{A} \mathbf{L} \mathbf{Q} = \frac{1}{2} \mathbf{Q}^T \mathbf{\Lambda} \mathbf{Q} = \frac{1}{2} \sum_{i=1}^{3N} \lambda_i Q_i^2$$

The uncoupled equations of motion are now represented by

$$Q_i = Q_i^0 \sin(\sqrt{\lambda_i} t + \delta)$$

Each normal mode oscillates independently about the center-of-mass of the molecule.

## 1.6 Anharmonic corrections

The harmonic approximation works remarkably well in a general sense. It permits one to calculate infrared and Raman spectra from first principles as will be discussed in future chapters. However, a more realistic picture of the vibrational motions in molecules should include anharmonic corrections. We can accomplish this in theory by including higher order terms in the expansion in Eqn. 1.3.1.

$$V(Q) = V(0) + \frac{1}{2}kQ^2 + \frac{\beta}{6}Q^3 + \frac{\gamma}{24}Q^4 \dots \quad (1.7.1)$$

The cubic anharmonicity given the term  $\beta Q^3/6$  is applicable asymmetric bonds. The X-H bond (X= C, N, O) is an excellent example. Quartic anharmonicity,  $\gamma Q^4/24$ , arises in cases where there are symmetric out-of-plane displacements. The exocyclic amino group is a good example. Ammonia has a pyramidal shape. We think of the amino group in aniline as planar, but in reality is oscillating very rapidly between two pyramidal distortions away from planarity. The potential energy surface has the form shown in 1.7.

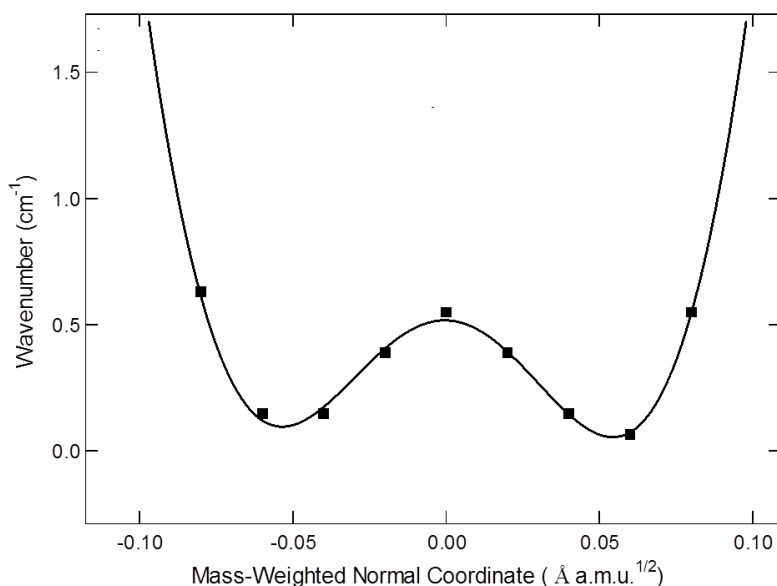


Figure 1.7. Quartic potential energy surface representing symmetric out-of-plane distortions such as the amino group out-of-plane motion in aromatic compounds that have an exocyclic amino group.

Cubic and quartic anharmonicities can be treated using perturbation theory.

The Morse oscillator is a widely used model for potential energy surfaces. It has a realistic look as shown in Figure 1.8.

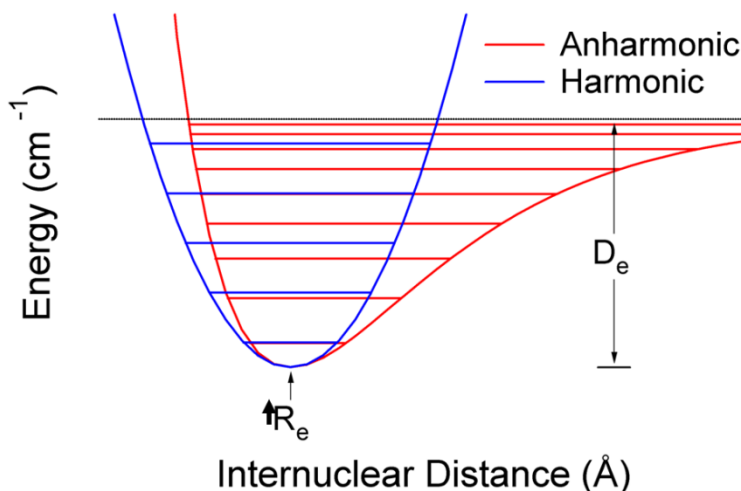


Figure 1.8. Morse potential energy surface compared to a harmonic potential surface. The dissociation energy ( $D_e$ ) and equilibrium bond length ( $R_e$ ) are shown in the figure.

The Morse function is:

$$V(x) = D_e(1 - \exp\{-a(r - r_0)\})^2 - D_e \quad (1.7.2)$$

Where  $D_e$  is the dissociation energy and the parameter,

$$a = \sqrt{\frac{k}{2D_e}} \quad (1.7.3)$$

Which also implies that the Morse model can be expressed in terms of the harmonic frequency,

$\omega$

$$\omega = a \sqrt{\frac{2D_e}{\mu}} \quad (1.7.4)$$

The Morse model correctly predicts that there will be decrease in the spacing of the frequency as the quantum number  $v$  increases.

$$E_v = \hbar\omega \left(v + \frac{1}{2}\right) + \frac{(\hbar\omega)^2}{4D_e} \left(v + \frac{1}{2}\right)^2$$

(1.7.5)

Such that the energy spacing decreases as,

$$\Delta E = \hbar\omega - \frac{(\hbar\omega)^2}{2D_e} \left( v + \frac{1}{2} \right)$$

(1.7.6)

These expressions can be compared to the anharmonicity,

$$E_v = \hbar\omega \left( v + \frac{1}{2} \right) - \hbar\omega x_e \left( v + \frac{1}{2} \right)^2$$

(1.7.7)

Which can also written the following form,

$$\frac{\Delta E}{hc} = \tilde{\nu} \left( v + \frac{1}{2} \right) - \tilde{\nu} x_e \left( v + \frac{1}{2} \right)^2$$

(1.7.8)

So that the anharmonicity constant is

$$x_e = \frac{\hbar\omega}{4D_e}$$

(1.7.9)

$$\omega = a \sqrt{\frac{2D_e}{\mu}}$$

## Chapter 2. The rotational wave function: molecular rotation

### 2.1 The moment of inertia

We have seen that rotation in two-dimensions is a problem that is easily solved. The “particle-on-a-circle” equation is nothing less than the Schrödinger equation for rotational motion in two dimensions. Of course, in that case the value of R (the radius) is fixed and the only variable is  $\phi$ , the rotation angle about the z axis. In the three dimensional case, which is the general treatment of molecular rotation, we will need two angles,  $\theta$  and  $\phi$ . Once again the radius is fixed since the molecular rotation can be specified in terms of a moment of inertia. For a diatomic molecule the moment of inertia is:

$$I = \mu R^2 \tag{2.1.1}$$

Where R is the intermolecular bond length and  $\mu$  is the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$



(2.1.2)

For a single mass rotating around an axis the moment of inertia is:

$$I = mR^2 \quad (2.1.3)$$

where R is the radius of rotation and m is the mass. This definition can be extended to an arbitrary number of masses rotating about their center of mass.

$$I = \sum_{i=1}^N m_i R_i^2 \quad (2.1.4)$$

where N is the number of atoms.

## 2.1 The oscillating dipole

The permanent dipole moment of a molecule oscillates about an equilibrium value as the molecule vibrates. Thus, the dipole moment depends on the nuclear coordinate Q, where  $\mu$  is the dipole operator.

$$\mu(Q) = \mu_0 + \left(\frac{\partial\mu}{\partial Q}\right)Q + \dots \quad (2.2.1)$$

We will ignore higher terms than linear. We can separate rotational transitions from vibrational transitions by applying a rigid rotor approximation. If the nuclei are rigid, then  $(\partial\mu/\partial Q) = 0$ , and the second term in Eqn. 2.2.1 vanishes. Rotational transitions arise from the rotation of the permanent dipole moment that can interact with an electromagnetic field in the microwave region of the spectrum. In this approximation the dipole moment is just  $\mu_0$ .

$$\mu(Q) = \mu_0 \quad (2.2.2)$$

Thus, it is the interaction of electromagnetic radiation with this rotating dipole moment that gives rise to pure rotational (microwave) spectra and to side-bands in infrared spectra of molecules.

Another way to consider the origin of the dipole moment is to consider the fact that a molecule is described by a total wave function that consists of an electronic, vibrational and rotational part.

$$\Psi = \psi_{elec}\chi_{vib}Y_{rot} \quad (2.2.3)$$

The dipole operator is  $\mu = er$ , where e is the charge on an electron and r is a displacement. The dipole operator has units of charge displaced through distance, which corresponds to the classical picture. For example, a diatomic such as HF with charge  $\delta^+$  and  $\delta^-$  on H and F, respectively, has a dipole moment of  $\delta eR$ , where R is the bond length and  $\delta$  is the fraction of a charge displaced from atom to the other. However, quantum mechanically we would calculate the dipole moment from the operator as:

$$\vec{\mu} = e \int \psi_{elec}^* r \psi_{elec} d\tau \quad (2.2.4)$$

The wave function gives the charge distribution over the basis. Both definitions of dipole moment have units of Cm or Debye, D, where

$$1 D = 2.33 \times 10^{-30} Cm$$

If we apply the dipole operator to the entire basis we have:

$$\vec{\mu} = e \int \int \chi_{vib}^* Y_{rot}^* r (\psi_{elec}^* r \psi_{elec} d\tau) \chi_{vib} Y_{rot} dQ \sin\theta d\theta d\phi \quad (2.2.5)$$

or

$$\vec{\mu} = \mu_0 \int \chi_{vib}^* \chi_{vib} dQ \int Y_{rot}^* Y_{rot} \sin\theta d\theta d\phi$$

where

$$\int \chi_{vib}^* \chi_{vib} dQ = 1$$

since the vibrational wave functions are normalized. Thus, the rotational transition moment is,

$$\vec{\mu} = \mu_0 \int \int Y_{j'}^{M'*} Y_j^M \sin\theta d\theta d\phi \quad (2.2.6)$$

where the integral is equal to one if  $J = J'$  and  $M = M'$ . There must be a different in quantum number in order for a transition to occur. If we assume that there is an electric field polarized along x, y or z then we have the following possible terms that can interact with the rotational transition moment:

$$\begin{aligned} \vec{E}_x &= \vec{E}_0 \sin\theta \cos\phi \\ \vec{E}_y &= \vec{E}_0 \sin\theta \sin\phi \\ \vec{E}_z &= \vec{E}_0 \cos\theta \end{aligned} \quad (2.2.7)$$

The interaction energy of the transition dipole with the electric field is:

$$H' = -\vec{\mu} \cdot \vec{E} \quad (2.2.8)$$

This is the contribution to the Hamiltonian that gives rise to spectroscopic transitions. Note that the dot product means that the interaction energy depends on the cosine of the angle between  $\vec{\mu}$  and  $\vec{E}$ . In a sample where molecules have many orientations one will need to take this into account. However, our discussion will usually ignore this point and assume that the electric field

is aligned along the transition dipole for simplicity ( $\cos(0) = 1$ ). In that case we may write the interaction Hamiltonian as,

$$H' = -\mu E \quad (2.2.9)$$

where  $\mu$  and  $E$  are scalars (i.e. just numbers).

### 2.3 Spherical polar coordinates

In order to proceed with any quantitative work related to solutions of the spherical harmonics and the transitions between them, we need to define the angles  $\theta$  and  $\phi$  in spherical polar coordinates.

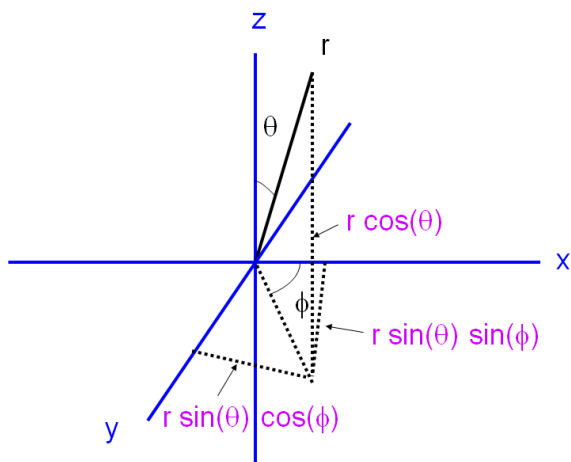


Figure 2.1. The spherical polar coordinate system. The radius vector,  $r$ , has the projections shown on each of the axes,  $z = r\cos\theta$ ,  $y = r\sin\theta\sin\phi$ , and  $x = r\sin\theta\cos\phi$ .

### 2.4 Rotation in a two-dimension coordinate system: the rigid rotator

The quantum mechanical treatment of rotation in a two coordinate system is mathematically identical to the particle on a circle model treated in Chapter 2. Here we assume that there is no vibration, and thereby separate the rotational problem treated in this Chapter from the vibrational problem, which will be discussed in Chapter 6.

The simplest model for a rotation is a two-dimensional model that refers to the angular momentum of a mass traveling in a circle as shown in Figure 2.2

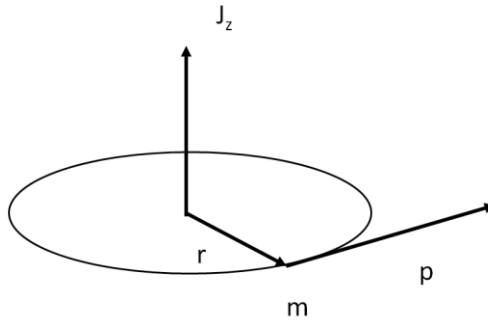


Figure 2.2. Illustration of two-dimensional rotation. The angular momentum  $J_z = r \times p$ . Since  $r$  is perpendicular to  $p$  this can simply be written as  $J_z = rp$ .

As shown in the figure, the angular momentum is  $J_z = rp$ . Applying the DeBroglie relation for the linear momentum,  $p$ , we see that

$$J_z = rp = \frac{rh}{\lambda} \quad (2.2.1)$$

Since  $\lambda$  must have an integral number of wavelengths around a circle, this is also a condition for quantization. The condition is:

$$2\pi r = M\lambda \quad (6.2.2)$$

where  $M$  is an integer. Thus,

$$\frac{1}{\lambda} = \frac{M}{2\pi r}$$

which leads to

$$J_z = M\hbar \quad (6.2.3)$$

The energy of rotation is:

$$E = \frac{J_z^2}{2I} = \frac{M^2\hbar^2}{2I} \quad (6.2.4)$$

where  $I$  is the moment of inertia. Using the definition of the moment of inertia,  $I = mr^2$ , This is precisely the result we obtained using the particle on a circle, which shows the correspondence for two-dimensional rotation.

## 2.5 Rotation in a three-dimensional coordinate system

The full quantum mechanical treatment of rotation requires the use of spherical polar coordinates described in section 2.6. The Hamiltonian is:

$$-\frac{\hbar^2}{2I} \left( \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} Y + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left( \sin\theta \frac{\partial}{\partial\theta} Y \right) \right) = EY \quad (6.1.1)$$

The solutions to this equation are functions of both  $\theta$  and  $\phi$  that are known as spherical harmonics. Spherical harmonics are standing waves on a sphere. The number of nodes is given the quantum number  $J$ , which is also the total angular momentum quantum number. The quantum number  $M$ , which was also derived in the previous section, is known as the azimuthal quantum number. It is the projection of the angular momentum along the  $z$ -axis.. The first three spherical harmonics are:

$$Y_0^0(\theta, \phi) = \left( \frac{1}{4\pi} \right)^{\frac{1}{2}}$$

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

$$Y_1^{\pm 1}(\theta, \phi) = \left( \frac{3}{8\pi} \right)^{\frac{1}{2}} \sin\theta e^{\pm i\phi}$$

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

$$Y_2^{\pm 1}(\theta, \phi) = \left( \frac{5}{8\pi} \right)^{\frac{1}{2}} \sin\theta \cos\theta e^{\pm i\phi}$$

$$Y_2^{\pm 2}(\theta, \phi) = \left( \frac{5}{32\pi} \right)^{\frac{1}{2}} \sin^2\theta e^{\pm i2\phi} \quad (6.1.2)$$

These have the appearance of the  $s$ ,  $p$  and  $d$ -orbitals for quantum numbers,  $J = 0$ , 1 and 2, respectively. Examples of the first three spherical harmonics are represented in Figure 2.6.

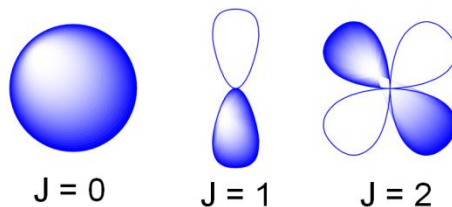


Figure 2.6. Representation of the first three spherical harmonics

with zero, one and two planar nodes, respectively.

These wave functions form an orthonormal set. The normalization can be seen by taking  $Y_1^0$  as an example. The normalization for  $Y_1^0(\theta, \phi)$  is:

$$\int_0^{2\pi} \int_0^\pi Y_1^{0*}(\theta, \phi) Y_1^0(\theta, \phi) \sin\theta d\theta d\phi = \left(\frac{3}{4\pi}\right) \int_0^{2\pi} \int_0^\pi \cos\theta \cos\theta \sin\theta d\theta d\phi =$$

$$\left(\frac{3}{4\pi}\right) \int_0^{2\pi} d\phi \int_{-1}^1 x^2 dx = \left(\frac{3}{4\pi}\right) (2\pi) \left(\frac{1}{3} - \frac{-1}{3}\right) = 1$$

Note that we used the substitution  $x = \cos\theta$ , which is the easiest way to solve the  $\theta$ -integral. Orthogonality means that the integrals of any two different wave functions in the basis should be zero. For example,  $Y_1^{-1}(\theta, \phi)$  and  $Y_1^1(\theta, \phi)$

$$\int_0^{2\pi} \int_0^\pi Y_1^{-1*}(\theta, \phi) Y_1^1(\theta, \phi) \sin\theta d\theta d\phi = \left(\frac{3}{8\pi}\right) \int_0^{2\pi} \int_0^\pi \sin\theta e^{i\phi} \sin\theta e^{i\phi} \sin\theta d\theta d\phi =$$

$$\left(\frac{3}{8\pi}\right) \int_0^{2\pi} e^{i2\phi} d\phi \int_0^\pi \sin^3\theta d\theta = 0$$

The integral vanishes because of the  $\phi$  integral. Recall that

$$e^{i2\phi} = \cos(2\phi) + i\sin(2\phi)$$

You could prove mathematically that the  $\cos(2\phi)$  integral is zero or you can examine a plot of  $\cos(2\phi)$  and realize that this is an integral over 2 cycles of the wave. The positive and negative parts cancel so that the integral is zero. Similar comments apply to the  $\sin(2\phi)$  integrated from 0 to  $2\pi$ .

The solutions represented in Figure 2.3 are only a subset of the possible solutions. Quantum number  $J$  has  $g_J = 2J + 1$  solutions, we therefore say that the degeneracy of the quantum levels is  $2J + 1$ . The different solutions have different values of quantum number  $M$  such that  $|M| \leq J$ . This is shown for  $J = 2$ , which has 5 different projections on the  $z$ -axis.

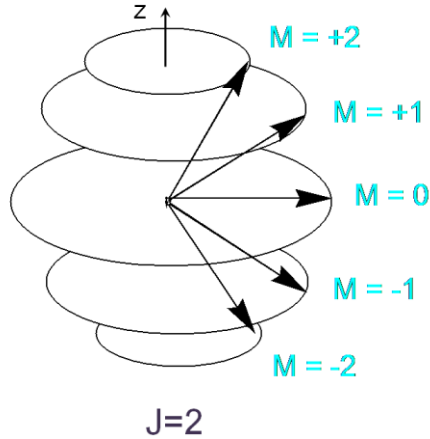


Figure 2.6. Spatial quantization of the azimuthal angular momentum.

The energy of the wave functions depends only on  $J$ . We say that the 5 sublevels in  $J = 2$  are degenerate. These wave functions correspond to the energies,

$$E_J = \frac{\hbar^2}{2I} J(J + 1) \quad (6.1.3)$$

## 2.6 Pure rotational spectra

Transitions can occur as a result of interaction with electromagnetic radiation. In pure rotational spectra, it is the rotation of the permanent dipole,  $\mu_0$ , that leads to interaction with radiation of the appropriate frequency. There are two requirements for the absorption of radiation. These are the conservation of energy and angular momentum. Here we will not prove the conservation of angular momentum. However, since the  $Y_J^M$  form an orthonormal set of wave functions we know that there must be an additional term that leads to a transition. Such a term is given by the oscillating electric field in Eqn. 2.2.7. We can consider the transition from  $J = 1 \rightarrow J = 2$ . The product of the transition moment and electric field is:

$$M \vec{E}_0 = \vec{E}_0 \vec{\mu}_0 \int_0^{2\pi} \int_0^\pi Y_{J+1}^M * \cos\theta Y_J^M \sin\theta d\theta d\phi \quad (2.2.1)$$

For z-polarized light we must use  $Y_1^0$ . Then we must choose the spherical harmonic for  $J+1$  that also has the appropriate symmetry. We can guess that it is the function that corresponds to  $d_{z2}$  (i.e.  $Y_2^0$ ). This spherical harmonic is,

$$Y_2^0(\theta, \phi) = \left( \frac{5}{16\pi} \right)^{\frac{1}{2}} (3\cos^2\theta - 1) \quad (6.2.2)$$

Thus we have

$$M\vec{E}_0 = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \left(\frac{5}{16\pi}\right)^{\frac{1}{2}} \vec{E}_0 \vec{\mu}_0 \int_0^{2\pi} \int_0^{\pi} (3\cos^2\theta - 1) \cos\theta \sin\theta d\theta d\phi$$

$$M\vec{E}_0 = \left(\frac{15}{64}\right)^{\frac{1}{2}} \frac{1}{\pi} \vec{E}_0 \vec{\mu}_0 \int_0^{2\pi} d\phi \int_{-1}^1 (3x^2 - 1) x^2 dx$$

We solve the  $\cos\theta$  (i.e.  $x$ ) integral separately.

$$\int_{-1}^1 (2 - 3x^2) x^2 dx = \int_{-1}^1 x^2 dx - 3 \int_{-1}^1 x^4 dx = \left(\frac{1}{3} - \frac{-1}{3}\right) - 3\left(\frac{1}{5} - \frac{-1}{5}\right) = \frac{2}{3} - \frac{6}{5} = \frac{10}{15} - \frac{18}{15} = -\frac{8}{15}$$

Therefore,

$$M\vec{E}_0 = -\left(\frac{15}{64}\right)^{\frac{1}{2}} \frac{1}{\pi} \vec{E}_0 (2\pi) \left(\frac{8}{15}\right) \vec{\mu}_0 = -\frac{2\vec{E}_0 \vec{\mu}_0}{\sqrt{15}} \quad (6.2.3)$$

It is all right that this value is negative. It is the square of this value that is proportional to the transition probability. Given that this is the method applied to z-polarized light, we leave it as an exercise to determine which of the spherical harmonics give allowed transitions for x polarized light. Hint: it may be necessary to form linear combinations of the spherical harmonics within a given angular momentum level. You may consider the polarization of the electric field in terms of imaginary components, e.g.  $\cos(\phi) = \frac{1}{2}(e^{i\phi} + e^{-i\phi})$ .

The general case for transitions gives rise to the selection rule  $\Delta J = \pm 1$ .  $\Delta J = 1$  for absorption and  $\Delta J = -1$  for emission. This selection rule is a consequence of the requirement for conservation of angular momentum. In addition to conservation of angular momentum, we must have conservation of energy. The energy for transition between any two states  $J$  and  $J + 1$  is,

$$\Delta E = E_{J+1} - E_J = \frac{\hbar^2}{2I} [(J+1)(J+2) - J(J+1)] = \frac{\hbar^2}{2I} [2(J+1)] \quad (6.2.4)$$

We call  $\frac{\hbar^2}{2I}$  the rotational constant, and give it the name  $B$ . The rotational constant can be expressed in  $\text{cm}^{-1}$ , by dividing the above value in Joules by  $hc$ .

$$\tilde{B} = \frac{\hbar^2}{2I hc} = \frac{\hbar}{4\pi c \mu R^2} = \frac{h}{8\pi^2 c \mu R^2} \quad (6.2.5)$$

Note that the spacing of the energy levels increases as  $2(J+1)$ , where  $J = 0, 1, 2, 3, \dots$  as shown in Figure 2.5. The pattern is that the transitions are observed at  $2J, 4J, 6J$ , etc. and thus, every  $2J$ .



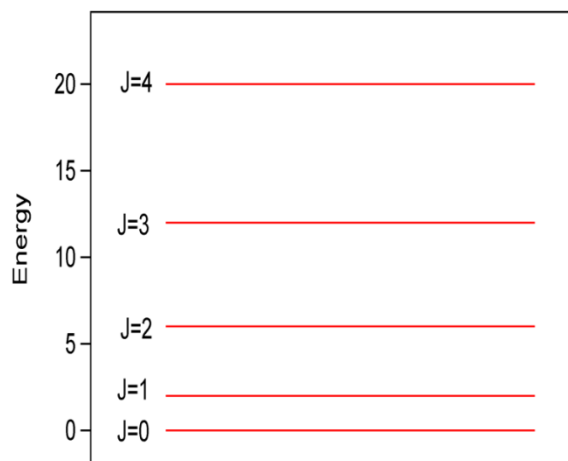


Figure 2.5. Difference energy level spacing for rotational transitions.

The result is that the pure rotational spectra are a progression of lines with spacing equal to  $2B$ , the rotational constant. Pure rotational spectra are microwave spectra. Rotational constants range from  $< 1\text{cm}^{-1}$  to as large as  $60\text{cm}^{-1}$  for  $\text{H}_2$ . By definition  $\text{H}_2$  has the largest rotational constant since it has the smallest moment of inertia. The appearance of a typical pure rotational spectrum is a set of lines spaced at  $2B$  that peaks at some point and then decreases. A typical spectrum is shown in Figure 2.6. Note that the energy value is given in gigahertz (GHz), which corresponds to a unit of  $10^9\text{s}^{-1}$ . This is a unit of frequency,  $\nu$  and is obtained from wavenumber,  $\tilde{\nu}$ , by the equation,  $\nu = \tilde{\nu}c$ .

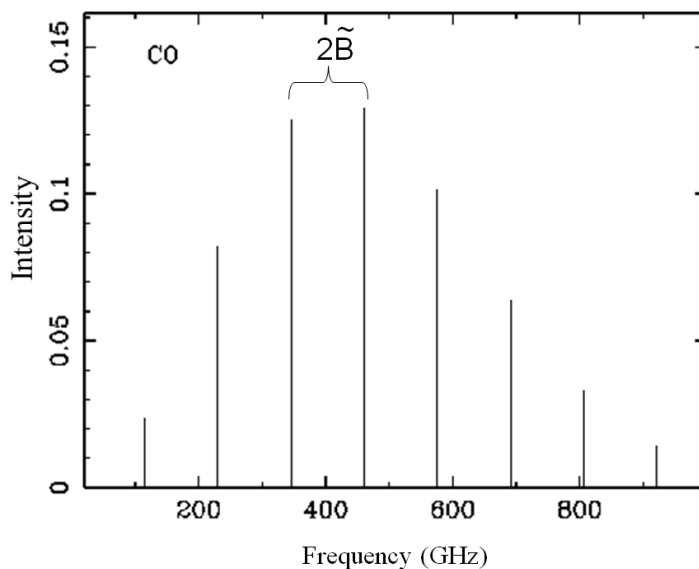


Figure 2.6. Pure rotational (microwave) spectrum for CO. Note that the frequencies are given in GHz (gigahertz).

## 2.7 The rotational partition function

The solutions to the rotational Hamiltonian provide energy levels that can be used to determine the rotational partition function. The sum over all of the energy levels weighted by their Boltzmann population gives the rotational partition function,

$$q_{rot} = \sum_{J=0}^{\infty} (2J + 1) \exp \left\{ -\frac{\hbar^2}{2Ik_B T} J(J + 1) \right\} \quad (2.7.1)$$

When the rotational energy level spacing is considerably less than thermal energy, i.e.

$$\frac{\hbar^2}{2I} \ll k_B T \quad (2.7.2)$$

We can approximate the sum by an integral,

$$q_{rot} = \int_0^{\infty} (2J + 1) \exp \left\{ -\frac{\hbar^2}{2Ik_B T} J(J + 1) \right\} dJ \quad (2.7.3)$$

It is quite fortuitous that this integral can be simplified by the substitution,

$$u = -\frac{\hbar^2}{2Ik_B T} J(J + 1)$$

Then

$$du = -\frac{\hbar^2}{2Ik_B T} (2J + 1) dJ$$

So that we can write

$$q_{rot} = -\frac{2Ik_B T}{\hbar^2} \int_0^{-\infty} e^u du = \frac{2Ik_B T}{\hbar^2} \quad (2.7.4)$$

The rotational partition function can include a symmetry number if the axis of rotation is also an axis of symmetry of the molecule. The symmetry is  $\sigma$ , where  $\sigma$  is equal to the order of the symmetry axis,

$$q_{rot} = \frac{2Ik_B T}{\sigma \hbar^2} \quad (2.7.5)$$

One consequence of the population of rotational energy levels is that pure rotational spectra have a temperature dependent profile. One can summarize this dependence by calculating the maximum value of the quantum number  $J$  as a function of temperature. To determine  $J_{\max}$  we take the derivative of the individual terms of the partition function with respect to  $J$ . Those terms are

$$p_J = C(2J + 1) \exp \left\{ -\frac{\hbar^2}{2Ik_B T} J(J + 1) \right\}$$

where  $C = 1/q_{\text{rot}}$ . Therefore,

$$\frac{\partial p_J}{\partial J} = 0 = \left( 2 - (2J + 1)^2 \frac{\hbar^2}{2Ik_B T} \right) \exp \left\{ -\frac{\hbar^2}{2Ik_B T} J(J + 1) \right\}$$

Solving for J we first write

$$2 = (2J + 1)^2 \frac{\hbar^2}{2Ik_B T}$$

$$(2J + 1) = \frac{\sqrt{4Ik_B T}}{\hbar}$$

To finally yield

$$J_{\text{max}} = \frac{\sqrt{Ik_B T}}{\hbar} - \frac{1}{2}$$

## Chapter 4 Summary

### Rotational energy levels and transitions

Pure rotational spectra or microwave are only observed for molecules that have a permanent dipole moment. The rotational selection rule is  $\Delta J = \pm 1$ . Pure rotational spectra have energies,

$$\Delta E = \frac{\hbar^2}{I} (J + 1)$$

The spacing of lines in the pure rotational spectrum is  $2B$ , where

$$B = \frac{\hbar^2}{2I}$$

### Extracting bond lengths from rotational spectra

The moment of inertia is

$$I = \mu R^2$$

for a diatomic molecule so that the bond length,  $R$ , of the molecule can be obtained from the rotational line spacing. In units of  $\text{cm}^{-1}$  we can write,

$$\tilde{B} = \frac{h}{8\pi^2 c \mu R^2}$$

or

$$R = \sqrt{\frac{h}{8\pi^2 c \mu \tilde{B}}}$$

### The rotational partition function

The rotational partition function can be treated in a classical limit since the rotational line spacing  $\tilde{B} \ll k_B T$ . The partition function is,

$$q_{rot} = \frac{2Ik_B T}{\sigma \hbar^2}$$

where  $\sigma$  is equal to the order of the symmetry axis of the molecule.

### Exercises

**2.1.** The spectrum in Figure 2.6 is called a pure rotational spectrum. The transitions are a direct measure of the solutions to the rotational Schrödinger equation. The x-axis is given in gigahertz (GHz), where  $1 \text{ GHz} = 10^9 \text{ s}^{-1}$ .

A. How many GHz are in one  $\text{cm}^{-1}$ ?

B. Estimate the rotational constant for CO in wavelength from Figure 2.6. In what region of the electromagnetic spectrum is it found?

C. Estimate the value of J that is maximum at  $T = 40 \text{ K}$ . How will this change at  $100 \text{ K}$ ?

**2.2.** The spectrum in Figure 2.7 represents a combination of rotation and vibration. The central line, which is missing because of the selection rule for rotation, is the vibrational transition frequency, given in units of electron volts (eV). When multiplied by the charge of one electron  $1\text{eV}$  is equivalent to 1 Joule,

$$(1\text{eV})(1.62 \times 10^{-19} \text{ C}) = 1.62 \times 10^{-19} \text{ Joule}$$

A. How many  $\text{cm}^{-1}$  are there per eV?

B. Sketch a vibrational potential energy surface with two vibrational energy levels. Add rotational sublevels above each vibrational energy level. Draw arrows to show the P and R branches on the diagram.

**2.6.** The rotational constant is directly related to the bond length of a diatomic molecule through the moment of inertia for rotation. We can use the rotational constant measured from spectroscopy to calculate the bond length as follows. We begin with Eqn. 6.2.5,

$$\tilde{B} = \frac{h}{8\pi^2 c \mu R^2}$$

and then solve for R,

$$R = \sqrt{\frac{h}{8\pi^2 c \mu \tilde{B}}}$$

The speed of light should be given in  $\text{cm/s}$  in order to convert  $\tilde{B}$  from  $\text{cm}^{-1}$  to MKS units. From the data in Figure 2.6 we can estimate the line spacing is  $\sim 120 \text{ GHz}$ . Use that information to calculate a bond length for CO.