

# 1 General introduction

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## 1.1. Electromagnetic spectrum

Molecular spectroscopy involves the study of the absorption or emission of electromagnetic radiation by matter; the radiation may be detected directly, or indirectly through its effects on other molecular properties. The primary purpose of spectroscopic studies is to understand the nature of the nuclear and electronic motions within a molecule.

The different branches of spectroscopy may be classified either in terms of the wavelength, or frequency, of the electromagnetic radiation, or in terms of the type of intramolecular dynamic motion primarily involved. Historically the first method has been the most common, with different regions of the electromagnetic spectrum classified as shown in figure 1.1. In the figure we show four different ways of describing these regions. They may be classified according to the wavelength, in ångström units ( $1 \text{ \AA} = 10^{-8} \text{ cm}$ ), or the frequency in Hz; wavelength ( $\lambda$ ) and frequency ( $\nu$ ) are related by the equation,

$$\nu = c/\lambda, \quad (1.1)$$

where  $c$  is the speed of light. Very often the wavenumber unit,  $\text{cm}^{-1}$ , is used; we denote this by the symbol  $\tilde{\nu}$ . Clearly the wavelength and wavenumber are related in the simple way

$$\tilde{\nu} = 1/\lambda, \quad (1.2)$$

with  $\lambda$  expressed in cm. Although offensive to the purist, the wavenumber is often taken as a unit of energy, according to the Planck relationship

$$E = h\nu = hc\tilde{\nu}, \quad (1.3)$$

where  $h$  is Planck's constant. From the values of the fundamental constants given in General Appendix A, we find that  $1 \text{ cm}^{-1}$  corresponds to  $1.986445 \times 10^{-23} \text{ J molecule}^{-1}$ . A further unit of energy which is often used, and which will appear in this book, is the electronvolt, eV; this is the kinetic energy of an electron which has been accelerated through a potential difference of 1 V; 1 eV is equal to  $8065.545 \text{ cm}^{-1}$ .

In the classical theory of electrodynamics, electromagnetic radiation is emitted when an electron moves in its orbit but, according to the Bohr theory of the atom,

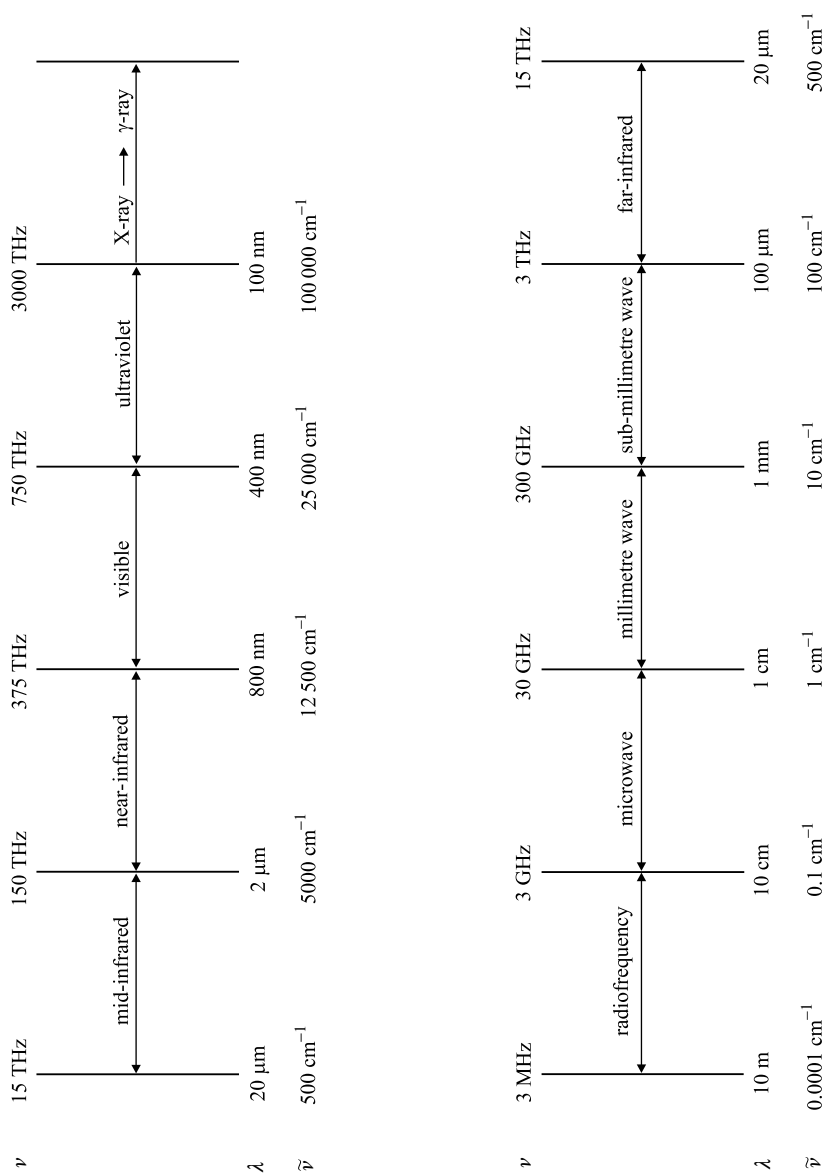


Figure 1.1. The electromagnetic spectrum, classified according to frequency ( $\nu$ ), wavelength ( $\lambda$ ), and wavenumber units ( $\tilde{\nu}$ ). There is no established convention for the division of the spectrum into different regions; we show our convention.

emission of radiation occurs only when an electron goes from a higher energy orbit  $E_2$  to an orbit of lower energy  $E_1$ . The emitted energy is a photon of energy  $h\nu$ , given by

$$h\nu = E_2 - E_1, \quad (1.4)$$

an equation known as the Bohr frequency condition. The reverse process, a transition from  $E_1$  to  $E_2$ , requires the absorption of a quantum of energy  $h\nu$ . The range of frequencies (or energies) which constitutes the electromagnetic spectrum is shown in figure 1.1. Molecular spectroscopy covers a nominal energy range from  $0.0001 \text{ cm}^{-1}$  to  $100\,000 \text{ cm}^{-1}$ , that is, nine decades in energy, frequency or wavelength. The spectroscopy described in this book, which we term *rotational* spectroscopy for reasons to be given later, is concerned with the range  $0.0001 \text{ cm}^{-1}$  to  $100 \text{ cm}^{-1}$ . Surprisingly, therefore, it covers six of the nine decades shown in figure 1.1, very much the major portion of the molecular spectrum! Indeed our low frequency cut-off at 3 MHz is somewhat arbitrary, since molecular beam magnetic resonance studies at even lower frequencies have been described. As we shall see, the experimental techniques employed over the full range given in figure 1.1 vary a great deal. We also note here that the spectroscopy discussed in this book is concerned solely with molecules in the gas phase. Again the reasons for this discrimination will become apparent later in this chapter.

So far as the classification of the type of spectroscopy performed is concerned, the characterisation of the dynamical motions of the nuclei and electrons within a molecule is more important than the region of the electromagnetic spectrum in which the corresponding transitions occur. However, before we come to this in more detail, a brief discussion of the nature of electromagnetic radiation is necessary. This is actually a huge subject which, if tackled properly, takes us deeply into the details of classical and semiclassical electromagnetism, and even further into quantum electrodynamics. The basic foundations of the subject are Maxwell's equations, which we describe in appendix 1.1. We will make use of the results of these equations in the next section, referring the reader to the appendix if more detail is required.

## 1.2. Electromagnetic radiation

Electromagnetic radiation consists of both an electric and a magnetic component, which for plane-polarised (or linearly-polarised) radiation, travelling along the  $Y$  axis, may be represented as shown in figure 1.2. Each of the three diagrams represents the electric and magnetic fields at different instants of time as indicated. The electric field ( $\mathbf{E}$ ) is in the  $YZ$  plane parallel to the  $Z$  axis, and the magnetic field ( $\mathbf{B}$ ) is everywhere perpendicular to the electric field, and therefore in the  $XY$  plane. Consideration of Maxwell's equations [1] shows that, as time progresses, the entire field pattern shifts to the right along the  $Y$  axis, with a velocity  $c$ . The wavelength of the radiation,  $\lambda$ , shown in the figure, is related to the frequency  $\nu$  by the simple expression  $\nu = c/\lambda$ . At every point in the wave at any instant of time, the electric and magnetic field strengths

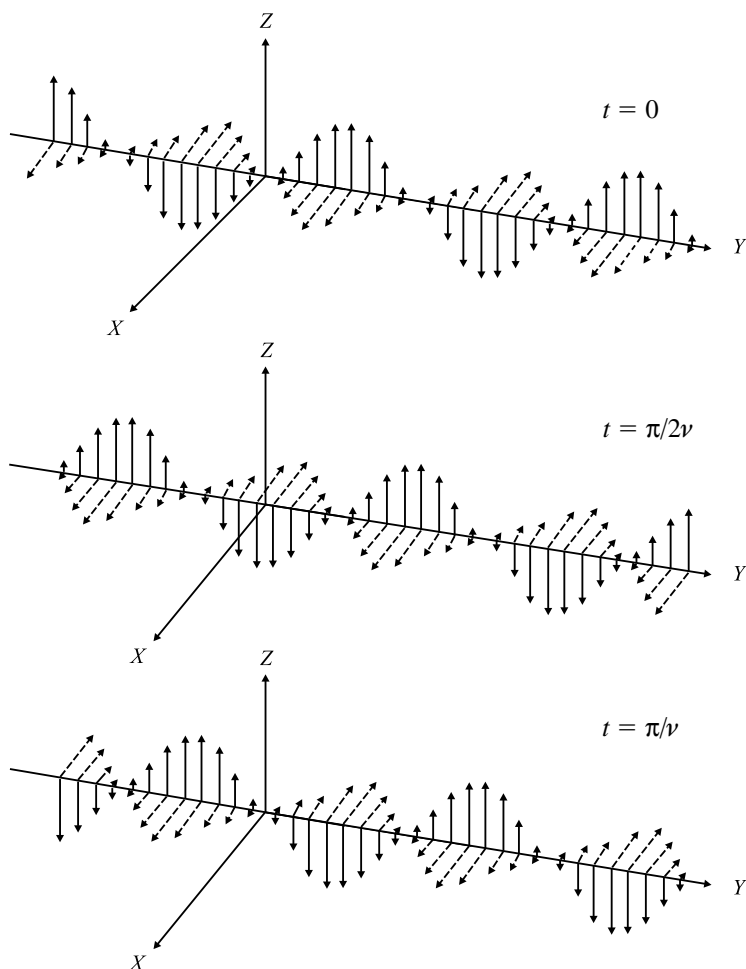


Figure 1.2. Schematic representation of plane-polarised radiation projected along the  $Y$  axis at three different instants of time. The solid arrows denote the amplitude of the electric field ( $\mathbf{E}$ ), and the dashed arrows denote the perpendicular magnetic field ( $\mathbf{B}$ ).

are equal; this means that, in cgs units, if the electric field strength is  $10 \text{ V cm}^{-1}$  the magnetic field strength is  $10 \text{ G}$ .

Although it is simplest to describe and represent graphically the example of plane polarised radiation, it is also instructive to consider the more general case [2]. For propagation of the radiation along the  $Y$  axis, the electric field  $\mathbf{E}$  can be decomposed into components along the  $Z$  and  $X$  axes. The electric field vector in the  $XZ$  plane is then given by

$$\mathbf{E} = i' E_X + k' E_Z \quad (1.5)$$

where  $i'$  and  $k'$  are unit vectors along the  $X$  and  $Z$  axes. The components in

equation (1.5) are given by

$$\begin{aligned} E_X &= E_X^0 \cos(k^*Y - \omega t + \alpha_X), \\ E_Z &= E_Z^0 \cos(k^*Y - \omega t + \alpha_Z), \\ \alpha &= \alpha_X - \alpha_Z. \end{aligned} \quad (1.6)$$

Here  $\omega = 2\pi\nu$ ,  $\omega$  is the angular frequency in units of  $\text{rad s}^{-1}$ ,  $\nu$  is the frequency in Hz, and  $k^*$  is called the propagation vector with units of inverse length. In a vacuum  $k^*$  has a magnitude equal to  $2\pi/\lambda_0$  where  $\lambda_0$  is the vacuum wavelength of the radiation. Finally,  $\alpha$  is the difference in phase between the  $X$  and  $Z$  components of  $\mathbf{E}$ .

Plane-polarised radiation is obtained when the phase factor  $\alpha$  is equal to 0 or  $\pi$  and  $E_X^0 = E_Z^0$ . When  $\alpha = 0$ ,  $E_X$  and  $E_Z$  are in phase, whilst for  $\alpha = \pi$  they are out-of-phase by  $\pi$ . The special case illustrated in figure 1.2 corresponds to  $E_X^0 = 0$ . Other forms of polarisation can be obtained from equations (1.6). For elliptically-polarised radiation we set  $\alpha = \pm\pi/2$  so that equations (1.6) become

$$\begin{aligned} E_X &= E_X^0 \cos(k^*Y - \omega t), \\ E_Z &= E_Z^0 \cos(k^*Y - \omega t \pm \pi/2) = \pm E_Z^0 \sin(k^*Y - \omega t), \\ \mathbf{E}_\pm &= \mathbf{i}' E_X \pm \mathbf{k}' E_Z \\ &= \mathbf{i}' E_X^0 \cos(k^*Y - \omega t) \pm \mathbf{k}' E_Z^0 \sin(k^*Y - \omega t). \end{aligned} \quad (1.7)$$

If  $E_X^0 = E_Z^0 = \mathfrak{E}$  for  $\alpha = \pm\pi/2$ , we have circularly-polarised radiation given by the expression

$$E_\pm = \mathfrak{E}[\mathbf{i}' \cos(k^*Y - \omega t) \pm \mathbf{k}' \sin(k^*Y - \omega t)]. \quad (1.8)$$

When viewed looking back along the  $Y$  axis towards the radiation source, the field rotates clockwise or counter clockwise about the  $Y$  axis. When  $\alpha = +\pi/2$  which corresponds to  $E_+$ , the field appears to rotate counter clockwise about  $Y$ .

Conventional sources of electromagnetic radiation are incoherent, which means that the waves associated with any two photons of the same wavelength are, in general, out-of-phase and have a random phase relation with each other. Laser radiation, however, has both spatial and temporal coherence, which gives it special importance for many applications.

### 1.3. Intramolecular nuclear and electronic dynamics

In order to understand molecular energy levels, it is helpful to partition the kinetic energies of the nuclei and electrons in a molecule into parts which, if possible, separately represent the electronic, vibrational and rotational motions of the molecule. The details of the processes by which this partitioning is achieved are presented in chapter 2. Here we give a summary of the main procedures and results.

We start by writing a general expression which represents the kinetic energies of the nuclei ( $\alpha$ ) and electrons ( $i$ ) in a molecule:

$$T = \sum_{\alpha} \frac{1}{2M_{\alpha}} \mathbf{P}_{\alpha}^2 + \sum_i \frac{1}{2m} \mathbf{P}_i^2, \quad (1.9)$$

where  $M_{\alpha}$  and  $m$  are the masses of the nuclei and electrons respectively. The momenta  $\mathbf{P}_{\alpha}$  and  $\mathbf{P}_i$  are vector quantities, which are defined by

$$\begin{aligned} \mathbf{P}_i &= -i\hbar \frac{\partial}{\partial \mathbf{R}_i}, \\ \mathbf{P}_{\alpha} &= -i\hbar \frac{\partial}{\partial \mathbf{R}_{\alpha}}, \end{aligned} \quad (1.10)$$

expressed in a space-fixed axis system ( $X, Y, Z$ ) of arbitrary origin.  $\mathbf{R}_{\alpha}$  gives the position of nucleus  $\alpha$  within this coordinate system. The partial derivative ( $\partial/\partial \mathbf{R}_{\alpha}$ ) is a shorthand notation for the three components of the gradient operator,

$$\frac{\partial}{\partial \mathbf{R}_{\alpha}} \equiv \left( \frac{\partial}{\partial R_X} \right)_{\alpha} \mathbf{i}' + \left( \frac{\partial}{\partial R_Y} \right)_{\alpha} \mathbf{j}' + \left( \frac{\partial}{\partial R_Z} \right)_{\alpha} \mathbf{k}', \quad (1.11)$$

where  $\mathbf{i}'$ ,  $\mathbf{j}'$ ,  $\mathbf{k}'$  are unit vectors along the space-fixed axes  $X, Y, Z$ .

It is by no means obvious that (1.9) contains the vibrational and rotational motion of the nuclei, as well as the electron kinetic energies, but a series of origin and axis transformations shows that this is the case. First, we transform from the arbitrary origin to an origin at the centre of mass of the molecule, and then to the centre of mass of the nuclei. As we show in chapter 2, these transformations convert (1.9) into the expression

$$T = \frac{1}{2M} \mathbf{P}_O^2 + \frac{1}{2\mu} \mathbf{P}_R^2 + \frac{1}{2m} \sum_i \mathbf{P}_i'^2 + \frac{1}{2(M_1 + M_2)} \sum_{i,j} \mathbf{P}_i'' \cdot \mathbf{P}_j''. \quad (1.12)$$

The first term in (1.12) represents the kinetic energy due to translation of the whole molecule through space; this motion can be separated off rigorously in the absence of external fields. In the second term,  $\mu$  is the reduced nuclear mass,  $M_1 M_2 / (M_1 + M_2)$ , and this term represents the kinetic energy of the nuclei. The third term describes the kinetic energy of the electrons and the last term is a correction term, known as the mass polarisation term. The transformation is described in detail in chapter 2 and appendix 2.1. An alternative expression equivalent to (1.12) is obtained by writing the momentum operators in terms of the Laplace operators,

$$T = -\frac{\hbar^2}{2M} \nabla^2 - \frac{\hbar^2}{2\mu} \nabla_R^2 - \frac{\hbar^2}{2m} \sum_i \nabla_i'^2 - \frac{\hbar^2}{2(M_1 + M_2)} \sum_{i,j} \nabla_i'' \cdot \nabla_j''. \quad (1.13)$$

The next step is to add terms representing the potential energy, the electron spin interactions and the nuclear spin interactions. The total Hamiltonian  $\mathfrak{H}_T$  can then be subdivided into electronic and nuclear Hamiltonians,

$$\mathfrak{H}_T = \mathfrak{H}_{el} + \mathfrak{H}_{nucl}, \quad (1.14)$$

where

$$\bar{\mathcal{H}}_{\text{el}} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 - \frac{\hbar^2}{2M_N} \sum_{i,j} \nabla_i \cdot \nabla_j + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 R_{ij}} - \sum_{\alpha,i} \frac{Z_\alpha e^2}{4\pi\epsilon_0 R_{i\alpha}} + \bar{\mathcal{H}}(\mathbf{S}_i) + \bar{\mathcal{H}}(\mathbf{I}_\alpha), \quad (1.15)$$

$$\bar{\mathcal{H}}_{\text{nucl}} = -\frac{\hbar^2}{2\mu} \nabla_R^2 + \sum_{\alpha,\beta} \frac{Z_\alpha Z_\beta e^2}{4\pi\epsilon_0 R}. \quad (1.16)$$

The third and fourth terms in (1.15) represent the potential energy contributions (in SI units, see General Appendix E) arising from the electron–electron and electron–nuclear interactions, whilst the second term in (1.16) describes the nuclear repulsion term between nuclei with charges  $Z_\alpha e$  and  $Z_\beta e$ . The electron and nuclear spin Hamiltonians introduced into (1.15) are described in detail later.

The total nuclear kinetic energy is contained within the first term in equation (1.16) and we now introduce a further transformation from the axes translating with the molecule but with fixed orientation to molecule-fixed axes gyrating with the nuclei. In chapter 2 the two axis systems are related by Euler angles,  $\phi$ ,  $\theta$  and  $\chi$ , although for diatomic molecules the angle  $\chi$  is redundant. We may use a simpler transformation to spherical polar coordinates  $R$ ,  $\theta$ ,  $\phi$  as defined in figure 1.3. With this transformation the space-fixed coordinates are given by

$$\begin{aligned} X &= R \sin \theta \cos \phi, \\ Y &= R \sin \theta \sin \phi, \\ Z &= R \cos \theta. \end{aligned} \quad (1.17)$$

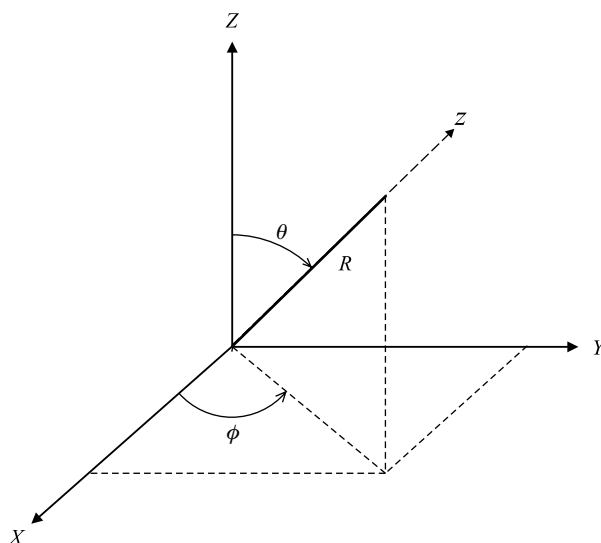


Figure 1.3. Transformation from space-fixed axes  $X$ ,  $Y$ ,  $Z$  to molecule-fixed axes using the spherical polar coordinates  $R$ ,  $\theta$ ,  $\phi$ , defined in the figure.

We proceed to show, in chapter 2, that this transformation of the axes leads to the nuclear kinetic energy term being converted into a new expression:

$$\begin{aligned} \frac{1}{2\mu} \mathbf{P}_R^2 &= -\frac{\hbar^2}{2\mu} \nabla_R^2 \\ &= -\frac{\hbar^2}{2\mu} \left\{ \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{1}{R^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{R^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right\}. \end{aligned} \quad (1.18)$$

This is a very important result because the first term describes the vibrational kinetic energy of the nuclei, whilst the second and third terms represent the rotational kinetic energy. The transformation is straightforward provided one takes proper note of the non-commutation of the operator products which arise.

The transformation of terms representing the kinetic energies of all the particles into terms representing, separately, the electronic, vibrational and rotational kinetic energies is clearly very important. The nuclear kinetic energy Hamiltonian, (1.18), is relatively simple when the spherical polar coordinate transformation (1.17) is used. When the Euler angle transformation is used, it is a little more complicated, containing terms which include the third angle  $\chi$ :

$$\begin{aligned} \bar{\mathcal{H}}_{\text{nucl}} &= -\frac{\hbar^2}{2\mu R^2} \left\{ \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \text{cosec} \theta \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) \right. \\ &\quad \left. + \text{cosec}^2 \theta \left[ \frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial \chi^2} - 2 \cos \theta \frac{\partial^2}{\partial \phi \partial \chi} \right] \right\} + V_{\text{nucl}}(R). \end{aligned} \quad (1.19)$$

We show in chapter 2 that when the transformation of the electronic coordinates, including electron spin, into the rotating molecule-fixed axes system is taken into account, equation (1.19) takes the much simpler form

$$\bar{\mathcal{H}}_{\text{nucl}} = -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + \frac{\hbar^2}{2\mu R^2} (\mathbf{J} - \mathbf{P})^2 + V_{\text{nucl}}(R), \quad (1.20)$$

where  $\mathbf{J}$  is the total angular momentum and  $\mathbf{P}$  is the total electronic angular momentum, equal to  $\mathbf{L} + \mathbf{S}$ . Hence although the electronic Hamiltonian is free of terms involving the motion of the nuclei, the nuclear Hamiltonian (1.20) contains terms involving the operators  $P_x$ ,  $P_y$  and  $P_z$  which operate on the electronic part of the total wave function. The Schrödinger equation for the total wave function is written as

$$(\bar{\mathcal{H}}_{\text{el}} + \bar{\mathcal{H}}_{\text{nucl}}) \Psi_{\text{rve}} = E_{\text{rve}} \Psi_{\text{rve}}, \quad (1.21)$$

and, as we show in chapter 2, the Born approximation allows us to assume total wave functions of the form

$$\Psi_{\text{rve}}^0 = \psi_{\text{e}}^n(\mathbf{r}_i) \phi_{\text{rv}}^n(R, \phi, \theta). \quad (1.22)$$

The matrix elements of the nuclear Hamiltonian that mix different electronic states are then neglected; the electronic wave function is taken to be dependent upon nuclear coordinates, but not nuclear momenta. If the first-order contributions of the nuclear



kinetic energy are taken into account, we have the Born adiabatic approximation; if they are neglected, we have the Born–Oppenheimer approximation. This approximation occupies a central position in molecular quantum mechanics; in most situations it is a good approximation, and allows us to proceed with concepts like the potential energy curve or surface, molecular shapes and geometry, etc. Those special cases, usually involving electronic orbital degeneracy, where the Born–Oppenheimer approximation breaks down, can often be treated by perturbation methods.

In chapter 2 we show how a separation of the vibrational and rotational wave functions can be achieved by using the product functions

$$\phi_{rv}^n = \chi^n(R) e^{iM_J\phi} \Theta^n(\theta) e^{ik\chi}, \quad (1.23)$$

where  $M_J$  and  $k$  are constants taking integral or half-odd values. We show that in the Born approximation, the wave equation for the nuclear wave functions can be expressed in terms of two equations describing the vibrational and rotational motion separately. Ultimately we obtain the wave equation of the vibrating rotator,

$$\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} R^2 \frac{\partial \chi^n(R)}{\partial R} + \left\{ E_{rve} - V - \frac{\hbar^2}{2\mu R^2} J(J+1) \right\} \chi^n(R) = 0. \quad (1.24)$$

The main problem with this equation is the description of the potential energy term ( $V$ ). As we shall see, insertion of a restricted form of the potential allows one to express data on the ro-vibrational levels in terms of semi-empirical constants. If the Morse potential is used, the ro-vibrational energies are given by the expression

$$E_{v,J} = \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 + B_e J(J+1) - D_e J^2(J+1)^2 - \alpha_e(v+1/2)J(J+1). \quad (1.25)$$

The first two terms describe the vibrational energy, the next two the rotational energy, and the final term describes the vibration–rotation interaction.

#### 1.4. Rotational levels

This book is concerned primarily with the rotational levels of diatomic molecules. The spectroscopic transitions described arise either from transitions between different rotational levels, usually adjacent rotational levels, or from transitions between the fine or hyperfine components of a single rotational level. The electronic and vibrational quantum numbers play a different role. In the majority of cases the rotational levels studied belong to the lowest vibrational level of the ground electronic state. The detailed nature of the rotational levels, and the transitions between them, depends critically upon the type of electronic state involved. Consequently we will be deeply concerned with the many different types of electronic state which arise for diatomic molecules, and the molecular interactions which determine the nature and structure of the rotational levels. We will not, in general, be concerned with transitions between different electronic states, except for the double resonance studies described in the final chapter. The vibrational states of diatomic molecules are, in a sense, relatively uninteresting.

The detailed rotational structure and sub-structure does not usually depend upon the vibrational quantum number, except for the magnitudes of the molecular parameters. Furthermore, we will not be concerned with transitions between different vibrational levels.

Rotational level spacings, and hence the frequencies of transitions between rotational levels, depend upon the values of the rotational constant,  $B_v$ , and the rotational quantum number  $J$ , according to equation (1.25). The largest known rotational constant, for the lightest molecule ( $\text{H}_2$ ), is about  $60 \text{ cm}^{-1}$ , so that rotational transitions in this and similar molecules will occur in the far-infrared region of the spectrum. As the molecular mass increases, rotational transition frequencies decrease, and rotational spectroscopy for most molecules occurs in the millimetre wave and microwave regions of the electromagnetic spectrum.

The fine and hyperfine splittings within a rotational level, and the transition frequencies between components, depend largely on whether the molecular species has a closed or open shell electronic structure. We will discuss these matters in more detail in section 1.6. For a closed shell molecule, that is, one in a  $^1\Sigma^+$  state, intramolecular interactions are in general very small. They depend almost entirely on the presence of nuclei with spin magnetic moments, or with electric quadrupole moments. If both nuclei in a diatomic molecule have spin magnetic moments, there will be a magnetic interaction between them which leads to splitting of a rotational level. The interaction may occur as a through-space dipolar interaction, or it may arise through an isotropic scalar coupling brought about by the electrons. Dipolar interactions are much larger than the scalar spin–spin couplings, but even so only produce splittings of a few kHz in the most favourable cases. A molecule also possesses a magnetic moment by virtue of its rotational motion, which can interact with any nuclear spin magnetic moments present in the molecule. Nuclear and rotational magnetic moments interact with an applied magnetic field, and these interactions are at the heart of the molecular beam magnetic resonance studies described in chapter 8. The pioneering experiments in this field were carried out in the period 1935 to 1955; they are capable of exceptionally high spectroscopic resolution, with line widths sometimes only a fraction of a kHz, and they form the foundations of what came to be known as nuclear magnetic resonance [3]. Nuclear electric quadrupole moments, where present, interact with the electric field gradient caused by the other charges (nuclei and electrons) in a molecule and the resulting interaction, called the nuclear electric quadrupole interaction, can in certain cases be quite large (i.e. several GHz). This interaction may be studied through molecular beam magnetic resonance experiments, but it can also be important in conventional microwave absorption studies, as we describe in chapter 10. Magnetic resonance studies require the presence of a magnetic moment, but in the closely related technique of molecular beam electric resonance, the interaction between a molecular electric dipole moment and an applied electric field is used. These experiments are also described in detail in chapter 8. The magnetic resonance studies of closed shell molecules almost always involve transitions between components of a rotational level, and usually occur in the radiofrequency region of the spectrum. Electric resonance experiments, on the other hand, often deal with electric dipole transitions between rotational levels,