THE FUNDAMENTALS OF MOLECULAR SYMMETRY

Philip R Bunker

Steacie Institute for Molecular Sciences
National Research Council
Ottawa, Canada

and

Per Jensen

Theoretische Chemie
Bergische Universität Wuppertal
Germany

February 18, 2014

Contents

Preface

In 1998 we wrote the second edition of the research level text 'Molecular Symmetry and Spectroscopy'. The present book is on the broader subject of molecular symmetry, and it is at the student level. It is designed to explain the basis for what is called 'symmetry' in chemistry, and to show how symmetry helps in the solution of problems in spectroscopy and in molecular orbital theory. A crucial part of the book is concerned with explaining the relationship between the geometrical symmetry of a molecule, as expressed using the point group symmetry of its equilibrium structure, and the true symmetry of a molecule as expressed using the *molecular symmetry* group. The elements of the molecular symmetry group involve nuclear permutations and the space fixed inversion operation called E^*. We aim at giving a balanced account of molecular symmetry using both point groups and molecular symmetry groups.

The book is organized into four parts. Part 2 introduces geometrical (point group) symmetry and true symmetry, and discusses how point group symmetry derives by approximation from true symmetry. Part 3 shows how these two symmetries are used in solving problems. These two parts could be a book in themselves, but we felt it appropriate to add the introductory part 1 in order to provide the reader with a brief account of spectroscopy, quantum mechanics and the derivation of molecular wavefunctions. In the final part 4 we develop more advanced ideas, and discuss current research on symmetry; the latter focusses on the attempts that are being made, using atomic and molecular spectroscopy experiments, to determine the extent of the breakdown of each of the symmetries that are invoked in describing matter.

> Throughout the text we introduce 'shadow boxes' such as this to focus attention on a particularly significant statement.

At the end of each chapter in parts 1, 2 and 3, we have included problems involving the application of the ideas developed in the chapter.

We are grateful to those at IOP who suggested that we write this student text, and we appreciate their encouragement in the completion of the project. PRB thanks the Alexander von Humboldt Foundation whose award allowed him to spend time at the University of Wuppertal during which part of the book was written.

Many colleagues and friends have given us advice and help for which we are very grateful, and we list their names here: O. Baum, S. Brünken, G. W. Fuchs, T. F. Giesen, S. G. Kukolich, F. Lewen, M. Litz, P. Neubauer-Guenther, S. Patchkovskii, R. D. Poshusta, A. Ruoff, A. Stolow, J. Tennyson, J. K. G. Watson, G. Winnewisser, and S. N. Yurchenko.

Line drawings were produced with xfig, figures involving numerical data were produced with idl, and figures showing 3D objects were drawn with MAPLE. Published spectra were initially digitized to a set of numerical (x, y) points which were used as input for idl. The complete text was produced using LaTeX-2ϵ, and the figures were inlined as eps files.

Philip R Bunker
Per Jensen
20 July 2004

PART 1

SPECTROSCOPY AND THE QUANTUM STATES OF MOLECULES

Chapter 1

Molecular spectroscopy

The study of the extent of the absorption, emission and scattering of electromagnetic radiation by matter, as a function of the wavelength of the radiation and of the nature of the matter, is the subject of spectroscopy. We concentrate on situations involving weak electromagnetic radiation[1] and gas phase molecular samples. In these circumstances classical theory is used to describe the radiation and quantum mechanics to describe the molecules and their interaction with the radiation.

The classical theory of electromagnetic radiation is based on Maxwell's 1860's theory of the electromagnetic field. Electromagnetic radiation consists of oscillating electric and magnetic fields by virtue of which it carries electric and magnetic energy from a source to a detector. The electric and magnetic fields that constitute the radiation oscillate at the same frequency ν [in units of cycles s^{-1} or hertz (Hz)]; these fields oscillate perpendicular to each other and to the direction of propagation of the radiation. In a vacuum, radiation propagates at the speed of light c (=299 792 458 $\mathrm{m\,s^{-1}}$), and the distance between adjacent field oscillation crests is the wavelength λ, where

$$\lambda = c/\nu. \tag{1.1}$$

1.1 Molecular spectra

Electromagnetic radiation emitted from a region of auroral activity in the upper atmosphere of Jupiter can be dispersed to yield an *emission spectrum* such as shown in figure 1.1. An emission spectrum is a plot of the intensity of the radiation emitted from a source as a function of its wavelength, frequency, or wavenumber $\tilde{\nu}$ ($\tilde{\nu} = 1/\lambda$; invariably quoted in cm^{-1} units). Figure 1.2 is part of the *absorption spectrum* of carbon monoxide CO at 300 K plotted as transmittance (see below) vs. wavenumber. Figure 1.3 is part of the Raman spectrum of methane CH_4. A Raman spectrum is obtained

---

[1] 'Weak' is defined at the end of section 1.5, where we discuss power broadening.

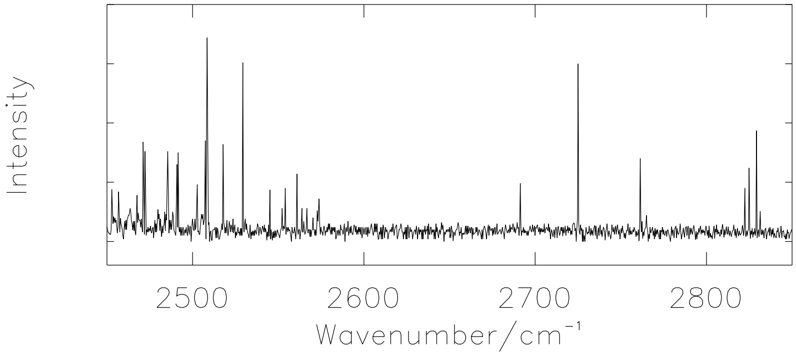

Figure 1.1. Part of the emission spectrum from a region of auroral activity in the upper atmosphere of Jupiter. Adapted from J-P. Maillard et al, Ap. J. **363**, L37 (1990).

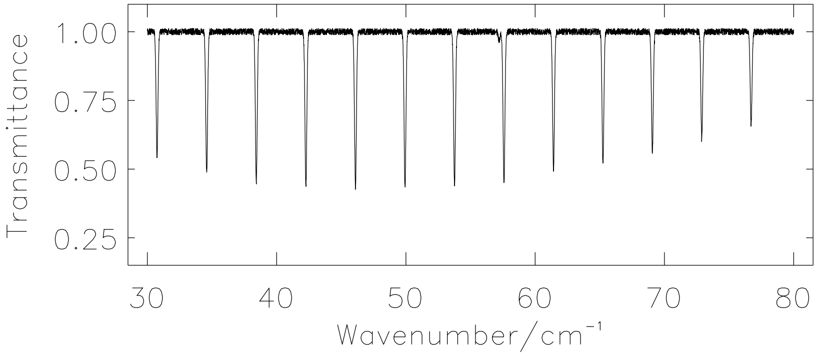

Figure 1.2. Part of the absorption spectrum of carbon monoxide at 300 K.

by illuminating a sample with monochromatic radiation (the *exciting* radiation), and measuring the intensity of the dispersed scattered radiation as a function of its difference (or shift) in frequency or wavenumber from that of the exciting radiation. These are the three most common types of molecular spectra, and they consist of spectral lines each having a position, intensity and shape.

Absorption spectra involve a measurement of transmittance as a function of frequency, wavelength or wavenumber; an example is given in figure 1.2. Transmittance is defined with the help of the Lambert-Beer law, which states: If a monochromatic and parallel beam of electromagnetic

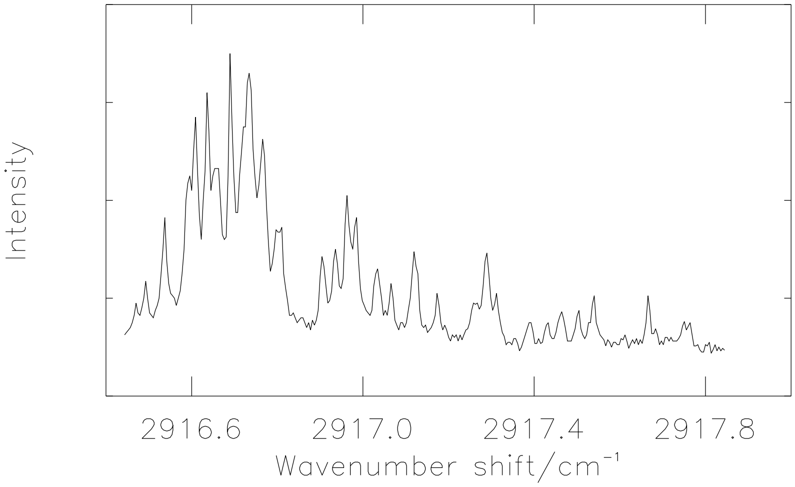

Figure 1.3. Part of the Raman spectrum of methane. Adapted from A. Owyoung et al, Chem. Phys. Lett. **59**, 156 (1978).

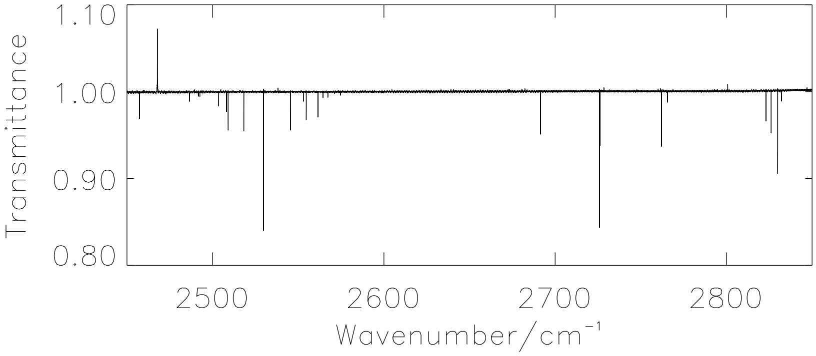

Figure 1.4. A laboratory absorption spectrum of H_3^+ in an electrical discharge through H_2. Taken from A. R. W. McKellar and J. K. G. Watson, J. Mol. Spectrosc. **191**, 215 (1998). The emission feature at 2469 cm^{-1} is caused by H atoms, and the other weaker emission features are caused by H_2.

radiation at wavenumber $\tilde{\nu}$ with intensity $I_0(\tilde{\nu})$ passes through a length l of gas at a concentration c, the transmitted radiation has intensity $I_{\rm tr}(\tilde{\nu})$ given by

$$I_{\rm tr}(\tilde{\nu}) = I_0(\tilde{\nu}) \exp[-lc\epsilon(\tilde{\nu})], \tag{1.2}$$

where the function $\epsilon(\tilde{\nu})$ is the absorption coefficient. The transmittance τ is defined as the ratio

$$\tau = \frac{I_{\rm tr}(\tilde{\nu})}{I_0(\tilde{\nu})} = \exp[-lc\epsilon(\tilde{\nu})]. \tag{1.3}$$

Figure 1.4 is a laboratory absorption spectrum of H_3^+ in an electrical discharge through hydrogen gas. Comparing the Jupiter emission spectrum in figure 1.1 with this laboratory spectrum it is clear that H_3^+ ions are present in the atmosphere of Jupiter during an aurora.[2]

> The analytical use of spectroscopy is easy to understand, and is based on the fact that each molecule has a unique spectrum that characterizes it. Molecular spectra also tell us the temperature of the sample and its concentration. Using quantum mechanics, the spectrum of a molecule can be interpreted to give the structure, bond strengths and other properties, of the molecule involved.

1.2 The energies of molecules in the gas phase

We think of a molecule in a gas sample at a particular instant in time as moving with a certain speed, and as having a certain amount of internal energy. The internal energy can be approximately separated as the sum of the rotational energy, the vibrational energy and the electronic energy. The rotational energy is the kinetic energy of the overall rotational motion of the molecule, the vibrational energy results from the relative motions of the nuclei, and the electronic energy is the energy of the electrons as they orbit the nuclear framework. The internal energy is called the rotation-vibration-electronic energy, or the *rovibronic* energy for short.

A molecule with mass M and speed v moving in an unconstrained way in free space has translational energy $Mv^2/2$; this energy can assume any value between zero and infinity. In contrast, the internal energy is *quantized*, i.e., only certain values of the internal energy occur, characteristic

---

[2] The rotational temperature of the H_3^+ that emits the spectrum shown in figure 1.1 is determined from the spectrum to be about 1000 K, whereas that of the laboratory spectrum is 287K. Because of this the line intensities below 2600 cm^{-1} in figure 1.1 are very different from what they are in the laboratory spectrum.

of finite motions. The pattern of the discrete internal energies is a unique characteristic of a molecule, and each molecule has a 'fingerprint' of internal energy levels. In figure 1.5 the lowest rotational energy levels for the CO, H_2O, CH_3D and CH_4 molecules are shown. In order to be able to relate molecular energy level separations directly to the wavenumber positions of the related spectral lines [see equation (1.7) and the discussion after it], the energies in figure 1.5 are divided by hc, where h ($=6.626\,069\,3 \times 10^{-34}$ J s) is Planck's constant, and they are quoted in cm^{-1} units.

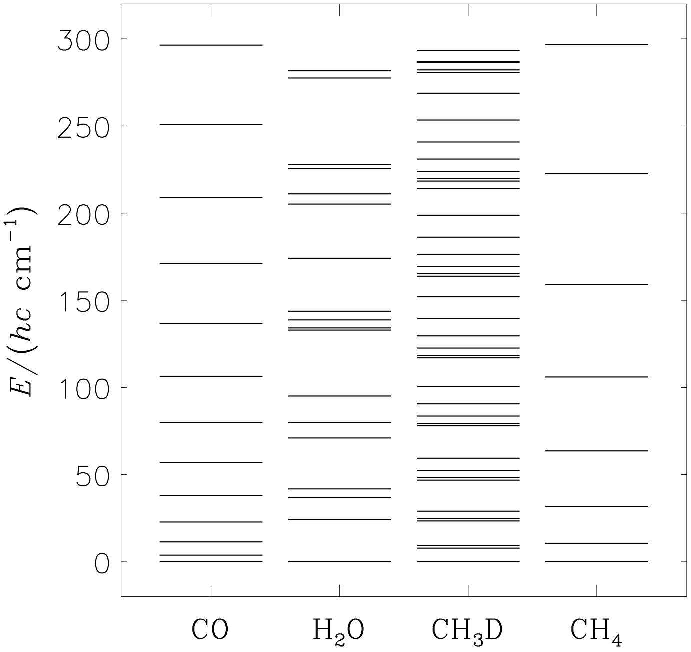

Figure 1.5. The possible rotational energy levels below 300 cm^{-1} for several simple molecules.

For small strongly bound molecules like those in figure 1.5 the rotational energy level spacings divided by hc are about 1 to 50 cm^{-1}, and the vibrational energy level spacings divided by hc are about 1 000 to 4 000 cm^{-1}. For closed shell molecules the electronic energy level spacings divided by hc are about 20 000 to 100 000 cm^{-1}. For larger, heavier, weakly bound or open shell molecules, smaller energy level spacings occur.

As an aside here, the division of the electromagnetic spectrum into three main regions roughly reflects the division of molecular energies into rotational, vibrational and electronic energies. These three regions are the microwave region (wavenumbers from 0.1 to 1 cm^{-1}), the infrared region (wavenumbers from 10^2 to 10^4 cm^{-1}), and the visible/ultraviolet region (wavenumbers from 10^4 to 10^6 cm^{-1}). Other regions are the radiofrequency region (below 0.1 cm^{-1}), the millimeterwave region (from 1 to 10^2 cm^{-1}), and the X-ray and γ-ray regions (above 10^6 cm^{-1}).

In a gas sample the speed, and hence translational energy, of each individual molecule is continually changing as a result of collisions with other molecules and with the walls of the containing vessel. However, because of the large number of molecules in a gas sample, the distribution of speeds remains constant for an isolated sample at thermal equilibrium. For example, in an isolated sample of carbon monoxide gas at thermal equilibrium at 300 K, at any instant in time, 19.3% of the molecules will have speeds between 400 and 500 m/s, whereas 1.0% of the molecules will have speeds between 0 and 100 m/s, and 1.8% of the molecules will have speeds between 900 and 1000 m/s.

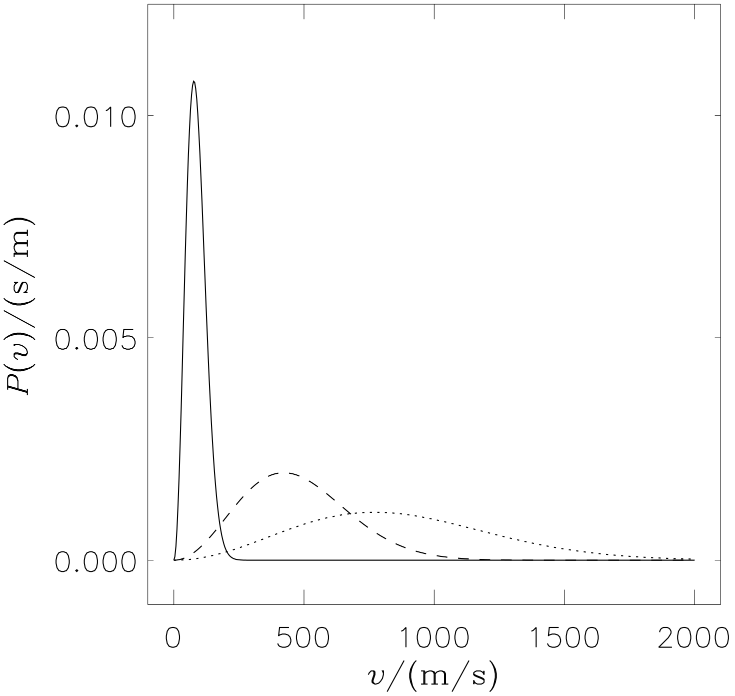

Figure 1.6. The distribution of translational speeds for the CO molecule at temperatures of 10 (——), 300 (- - - -) and 1000 K (· · · · · ·).

The expression for the distribution of speeds in an isolated ideal gas sample at thermal equilibrium can be calculated using the methods of statistical mechanics, and it is called the *Maxwell distribution of speeds.* This distribution is such that the probability of a molecule having speed between v and v+dv is given by $P(v)\mathrm{d}v$, where

$$P(v) = 4\pi(M/2\pi kT)^{3/2}v^2\mathrm{e}^{-Mv^2/2kT}. \tag{1.4}$$

In this equation k ($= 1.380\,650\,5 \times 10^{-23}$ J K^{-1}) is the Boltzmann constant, M is the mass of the molecule, and T is the absolute temperature. Equation (1.4) was used to calculate the percentages given in the preceding paragraph for the distribution of speeds of CO molecules at 300 K.

In figure 1.6 the distribution of translational speeds at temperatures of 10, 300 and 1000 K for the CO molecule is plotted. Because of the v^2 factor in equation (1.4) no molecule has zero speed, and because of the exponential factor no molecule has infinite speed. In between there is a maximum at the most probable speed given by $(2kT/M)^{1/2}$. For higher temperatures, or lower mass, the most probable speed increases, and the whole distribution spreads out and moves to higher speeds.

When a molecule suffers an *inelastic* collision it changes its internal (rovibronic) energy as well as its speed. For a large number of molecules at thermal equilibrium, the collisions between the molecules distribute the molecules among their internal energy states in a way that reflects the temperature and the Maxwell distribution of speeds so that at any instant the fraction $F(E_i)$ of the molecules in the internal energy level E_i is given by the *Maxwell-Boltzmann distribution law*:

$$F(E_i) = \frac{g_i\mathrm{e}^{-E_i/kT}}{\sum_j g_j\mathrm{e}^{-E_j/kT}}, \tag{1.5}$$

where the sum in the denominator (the denominator is called the *partition function*) runs over all the discrete possible energies E_j; each E_j is only counted once in the sum. The value of g_i is the number of states having energy E_i; it is called the *degeneracy* of the energy level E_i [see equation (2.72), and the discussion after it, for an example of a state that has $g_i>1$]. Figure 1.7 shows the fraction $F(E_i)$ of CO molecules, at thermal equilibrium, in each of its rotational states (see figure 1.5), for temperatures of 10, 300 and 1000 K. At low temperatures very few rotational energy states are populated.

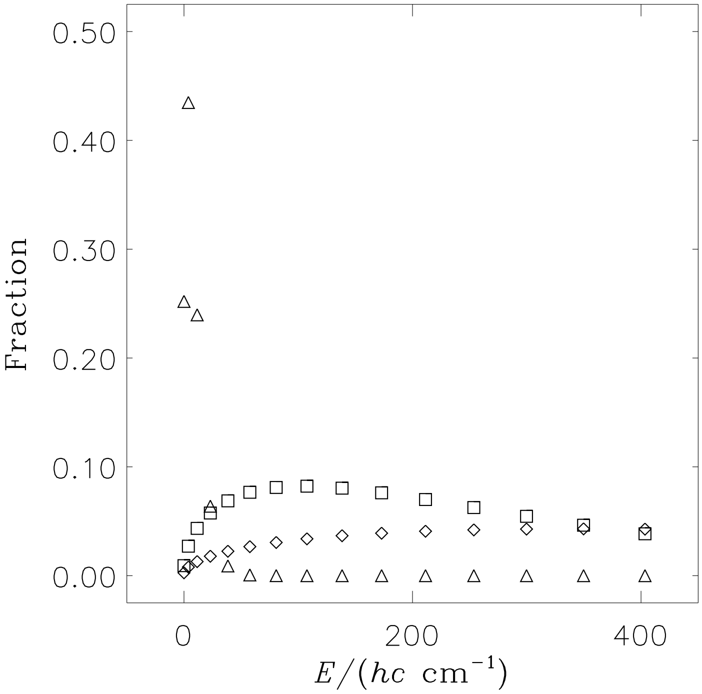

Figure 1.7. The fraction $F(E_i)$ of CO molecules in each of its rotational states for temperatures of 10 (△), 300 (□) and 1000 K (◊), at thermal equilibrium; see equation (1.5).

1.3 The positions of spectral lines

An isolated molecule in an initial internal energy state E_i can absorb energy from a weak electromagnetic radiation field and change its internal energy state to a final one with energy E_f; from the conservation of energy, the radiation absorbed has frequency ν_{if} satisfying the *Bohr frequency condition*

$$h\nu_{if} = E_f - E_i = \Delta E_{if}, \tag{1.6}$$

where h is Planck's constant. Put another way, a photon can be absorbed if the energy of the photon $h\nu$ is in *resonance* with the molecular internal energy difference ΔE concerned. Such resonant absorption causes the molecule to make a *transition* from one energy *level* to another. Dividing both sides of equation (1.6) by hc gives the wavenumber version as

$$\tilde{\nu}_{if} = \nu_{if}/c = E_f/hc - E_i/hc = \Delta E_{if}/hc, \tag{1.7}$$

where $\tilde{\nu}_{if}$ is the wavenumber of the radiation. Thus

> In an absorption spectrum the wavenumber of every spectral line gives the difference between two internal molecular energies divided by hc. Internal energies divided by hc, and quoted in cm^{-1} units, are called *term values*; their separations can be directly related to the wavenumber positions of spectral lines in cm^{-1}. For this reason spectroscopists generally quote the term values rather than the energies of molecular states.

The *assignment* of the upper and lower energy levels of each transition to their position in the ladder of energy levels of the molecule under investigation is one of the tasks of experimental molecular spectroscopy. The ultimate goal here is the determination of the term values of all internal energy levels for the molecule. The separations of the energy levels in a molecule can be analyzed to yield molecular properties such as structure and bond strengths. The discrete line structure of a spectrum shows directly that the internal energy states are quantized. If there were no restrictions on the values of the internal energy then the 'spectrum' would exhibit continuous absorption at all wavenumbers with no lines.

1.4 The intensities of spectral lines

The intensity of a spectral line in absorption is proportional to the fraction of the molecules $F(E_i)$ in the initial energy state E_i of the transition, and at thermal equilibrium this fraction can be varied, according to equation (1.5), by changing the temperature. A low temperature sample has just a few of the lowest levels populated and many molecules are in these levels, so the spectrum will consist of fewer stronger lines than that obtained for a high temperature sample. The variation of a spectrum with temperature will clearly help in its assignment since transitions originating in highly excited levels (so-called *hot* transitions) will be stronger at higher temperatures in a predictable way.

In addition to absorbing resonant radiation, molecules also undergo resonant stimulated emission. In stimulated emission, radiation of frequency ν_{if} stimulates a molecule in an excited energy level E_f to emit radiation of the same frequency ν_{if}, and to drop into a lower energy level E_i. For this to occur, the energy $h\nu_{if}$ must be in resonance with the energy difference $(E_f - E_i)$. This process competes with the absorption process and reduces the amount of absorption by the multiplicative factor

$$R_{\text{stim}}(f \to i) = 1 - \exp(-h\nu_{if}/kT). \tag{1.8}$$

At low frequencies in the GHz region this is an important cause of reduced absorption intensity.

In a process that is the complete opposite of resonant absorption, the stimulated emission process can cause the intensity of radiation at frequency ν_{if} to be amplified, and this process is used in a laser (Light Amplification by Stimulated Emission of Radiation). The successful operation of a laser requires that the excited level at E_f be continually repopulated using energy from an electrical discharge or other means, and that the nature of the molecule, and its energy level ladder, be such that the lower level at E_i be rapidly depopulated so that it does not absorb the lasing radiation.

Apart from the dependence on initial state population and extent of stimulated emission, the intensity of a line has an intrinsic value called the *line strength* $S(f \leftarrow i)$, see equation (2.87), and this depends on the specific properties of the two energy states involved. In fact some transitions have zero line strength. The absorption spectrum of CO shown in figure 1.2 only involves transitions between adjacent rotational energy levels in figure 1.5; transitions between nonadjacent rotational energy levels here have zero line strength and are said to be *forbidden.* Of all possible transitions only a selection are allowed, and symmetry is used to determine the *selection rules* that govern this behaviour. The H_3^+ spectra shown in figures 1.1 and 1.4 involve transitions between different vibrational states; transitions between its rotational energy levels are forbidden by the simplest selection rules. However, by studying the symmetry properties of the levels the possibility emerges that very weak transitions can occur between some of the rotational levels of H_3^+. Some transitions are less forbidden than others, and symmetry can help us understand whether small effects that are normally neglected can come into play to make a forbidden transition observable. Symmetry selection rules, and the spectra of CO and H_3^+ illustrated here, are discussed further in chapter 12.

We also show in chapter 12, how the quantitative value of the line strength depends on molecular properties. For example, the line strength of a transition between different rotational energy levels depends on the value of the molecular electric dipole moment [see equation (2.88)], and the line strength of a transition between different vibrational energy levels depends on how the value of the dipole moment changes with molecular deformation. All this information is important in building a complete understanding of the properties of a molecule.

By integrating the absorption coefficient over the line one obtains the expression

$$I(f \leftarrow i) = \frac{8\pi^3 N_A \nu_{if}}{(4\pi\epsilon_0)3hc^2} \frac{g_i \mathrm{e}^{-E_i/kT}}{\sum_i g_i \mathrm{e}^{-E_i/kT}} \left[1 - \exp(-h\nu_{if}/kT)\right] S(f \leftarrow i), \tag{1.9}$$

for the intensity of the absorption line for the transition from the state i with energy E_i, in thermal equilibrium at the temperature T, to the state f with energy E_f, where $h\nu_{if} = E_f - E_i$, N_A ($= 6.022\,141\,5 \times 10^{23}$ mol^{-1}) is the Avogadro constant, and ϵ_0 [$= 10^7/(4\pi c^2)$ F m^{-1}, where c is in m s^{-1}] is the permittivity of free space (also called the electric constant).

1.5 The shapes of spectral lines

Spectral lines have a finite width and a characteristic shape. Important causes of line broadening are the Doppler effect, the finite lifetime of molecular energy states, and the power of the radiation.

The molecules in a gas sample are not at rest but have a distribution of speeds, given by equation (1.4), and the frequency that a molecule 'feels' as it moves with speed v relative to the direction of propagation of radiation having frequency ν_0 is shifted by $\nu_0(v/c)$ because of the Doppler effect. Molecules moving towards the radiation source will absorb on the low frequency side of the line centre, and molecules moving away will absorb on the high frequency side. Making use of equation (1.4) one can determine that the line shape function arising from the Doppler shifts of all the molecules in a gas sample is

$$S(\nu) = S(\nu_0) \exp\Big[-\frac{Mc^2}{2kT}\Big(\frac{\nu - \nu_0}{\nu_0}\Big)^2\Big] \tag{1.10}$$

for a line centred at ν_0. The function in equation (1.10) is a Gaussian function. It has a full width at half height FWHH (the frequency width of the line at half the maximum intensity) given by

$$\begin{aligned} \mathrm{FWHH} &= \frac{2\nu_0}{c}\Big(\frac{2kT}{M}\ln 2\Big)^{1/2} \\ &\approx 7.15 \times 10^{-7}\Big(\frac{T}{M/\mathrm{u}}\Big)^{1/2}\nu_0, \end{aligned} \tag{1.11}$$

where u is the unified atomic mass unit.[3]

---

[3] 1 u = $1.660\,538\,86 \times 10^{-27}$ kg; also called the dalton or the atomic mass constant.

Around equation (1.8), the process of resonant stimulated emission was introduced. Molecules also *spontaneously* emit resonant radiation, and drop into a lower energy level; any transitions down that is allowed by the selection rules can occur. As a result, molecular energy levels have a finite *natural radiative lifetime.* This has the effect of broadening the energy levels and spectral lines; the full width at half height is related to the lifetime τ in ps by the relation

$$\mathrm{FWHH/cm^{-1}} \approx \frac{10.6}{\tau/\mathrm{ps}} \quad \text{or} \quad \mathrm{FWHH/GHz} \approx \frac{318}{\tau/\mathrm{ps}}. \qquad (1.12)$$

Spontaneous emission from an upper level having energy E_f to a lower level having energy E_i occurs with the emission of radiation having frequency ν_{if} that satisfies equation (1.6). The rate of spontaneous emission is proportional to ν_{if}^3 and so this lifetime is shorter for highly excited levels. The lifetime of a state can also be reduced by *predissociation*, which is a process whereby a molecule falls apart after a certain time. This process can occur only if the state has an energy greater than the dissociation energy of the molecule. Predissociation leads to the appearance of very broad *diffuse* lines in a spectrum.

Collisions that change the internal energy reduce the lifetime of a state. The collisional lifetime (the mean time between collisions) is reduced, and the linewidth increased, by raising the gas pressure; this cause of broadening is thus referred to as *pressure broadening.* At low pressures (less than about 10 Torr[4]), pressure broadening (or natural radiative lifetime broadening) gives rise to a Lorentzian lineshape function

$$S(\nu, \nu_0) = \frac{1}{\pi}\left[\frac{\Delta\nu}{(\nu_0 - \nu)^2 + (\Delta\nu)^2}\right] \qquad (1.13)$$

where $\Delta\nu = 1/(2\pi\tau)$, τ is the lifetime, and ν_0 is the central frequency; the full width at half height $2\Delta\nu$ is $1/(\pi\tau)$ which is given by the second of equations (1.12).

> The simultaneous occurrence of Doppler and lifetime broadening leads to a line shape that is a convolution of the two lineshape functions called a Voigt function. A detailed treatment of pressure broadening for higher pressures leads to a more complicated unsymmetrical lineshape function, and a small shift in the centre frequency, that can both be related to the nature of the intermolecular forces.

This discussion of lineshapes, and the development of equation (1.9) for the intensity of an absorption line, assume that the radiation is weak.

---

[4] 1 Torr ≈ 133.322 Pa.

By definition, the intensity of the radiation is weak if the absorption is a linear function of that intensity, i.e., if the transmittance is independent of the intensity of the radiation. As the power of the radiation is increased the molecules absorbing in the centre of the absorption line (where the absorption is the greatest) will start to absorb radiation at a greater rate than that at which they can return to the lower level of the transition to achieve thermal equilibrium. As a result the centre of the absorption line will start to saturate and the line will broaden; this is called *power broadening.*

1.6 Raman spectra

In figure 1.3 we show part of a Raman spectrum obtained by illuminating CH_4 with monochromatic radiation. In Raman spectroscopy the exciting radiation, whose wavenumber we denote $\tilde{\nu}_{\mathrm{in}}$, is normally visible laser light, and the sample absorbs and scatters photons from this light beam. As indicated in figure 1.8, we can think of the absorption as transferring molecules from an initial state with energy E_i, to a highly excited, so-called *virtual state*, with energy E_{virt}. In the vast majority of cases the molecules return from the virtual state to the initial state as shown in figure 1.8(a) and photons with wavenumber $\tilde{\nu}_{\mathrm{out}} = \tilde{\nu}_{\mathrm{in}}$ are emitted (or scattered). This process is known as *Rayleigh scattering.* However, a tiny fraction of the molecules (about 1 in 10^7) transfer from the virtual state to a final state different from the initial state. When this happens there is a *Raman shift* and the scattered radiation has wavenumber $\tilde{\nu}_{\mathrm{out}} \neq \tilde{\nu}_{\mathrm{in}}$. The energy of the final state is $E_f \neq E_i$. We can have $E_f > E_i$ [*Stokes Raman scattering*, figure 1.8(b)] so that $\tilde{\nu}_{\mathrm{out}} < \tilde{\nu}_{\mathrm{in}}$, or $E_f < E_i$ [*anti-Stokes Raman scattering*, figure 1.8(c)] with $\tilde{\nu}_{\mathrm{out}} > \tilde{\nu}_{\mathrm{in}}$. Figure 1.8 shows that the Raman shift

$$\tilde{\nu} = \tilde{\nu}_{\mathrm{in}} - \tilde{\nu}_{\mathrm{out}} = (E_f - E_i)/(hc) \tag{1.14}$$

corresponds to the energy difference between the final and initial states; such energy differences can be obtained from Raman experiments.

The intensity of Raman-scattered light is proportional to the Raman line strength $S_{\mathrm{Raman}}(f \leftarrow i)$, which is analogous to the line strength of an absorption or emission transition. The calculation of $S_{\mathrm{Raman}}(f \leftarrow i)$ is discussed in section 12.5. The Raman intensity is also proportional to the intensity of the exciting light, to the concentration of molecules in the initial state, to $\tilde{\nu}_{\mathrm{out}}^4$, and to the solid angle of observation. In addition, the intensities observed in a Raman experiment depend on the angle between the electric field vector of the exciting light and that of the scattered light; this angle is determined by the experimental set-up.

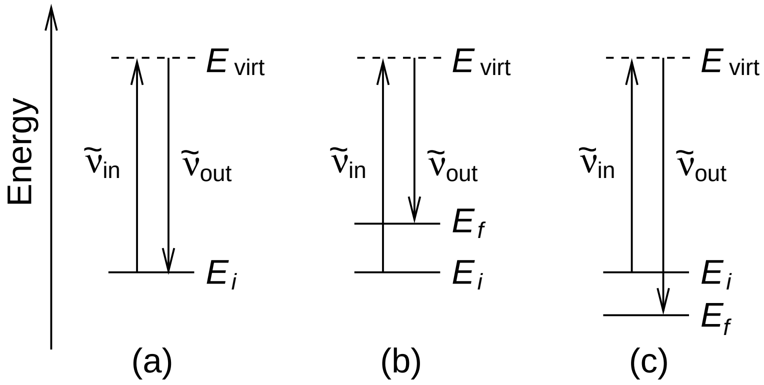

Figure 1.8. Energy-level diagrams of (a) Rayleigh scattering, (b) Stokes Raman scattering, and (c) anti-Stokes Raman scattering.

1.7 Problems

1.1 What is the wavenumber, frequency and energy per photon of (a) visible radiation having a wavelength of 500 nm, (b) infrared radiation having a wavelength of 5 μm, and (c) microwave radiation having a wavelength of 5 cm? Quote the frequency in appropriate units such as THz or GHz, and the wavenumber in cm^{-1}.

1.2 The successive rotational energy levels of the $^{12}C^{16}O$ molecule depicted in figure 1.5 are labeled $J = 0, 1, 2, \ldots$, and to three significant figures their energy divided by hc is $E_i = 1.92J(J+1)$ cm^{-1}; the degeneracy[5] of each level is $g_i = (2J{+}1)$. Calculate the numerator in the Maxwell-Boltzmann distribution function equation (1.5) for a range of values of J for temperatures T of 10, 30 and 1000 K to confirm the J-value at which the population is a maximum according to figure 1.7; in the appropriate units $k \approx 0.695$ cm^{-1}K^{-1}. By setting equal to zero the differential of the numerator with respect to J, determine an expression as a function of T for the value of J at which the population is a maximum. Check that this leads to the correct result for $T = 10$, 300 and 1000 K (J has to be an integer).

1.3 Use equation (1.11) to calculate the Doppler widths (FWHH) of infrared absorption lines of the H_3^+ molecule ($M/\mathrm{u} \approx 3$) and CH_4 molecule ($M/\mathrm{u} \approx 16$) at around 3000 cm^{-1} at 1000 K and at 10 K. What would the Doppler widths be for lines of these molecules at these temperatures at wavelengths around 1 cm (in the microwave

---

[5] This is the m-degeneracy that will be introduced in section 2.7.

region) or 100 nm (in the ultraviolet region)? The appropriate units for linewidth are cm^{-1} in the infrared and ultraviolet, and kHz in the microwave.

1.4 In a recent experiment[6] NH molecules in the excited (A) electronic state were generated by first forming ground (X) electronic state molecules using an ArF laser to photolyse NH_3, and then using a tunable dye laser to pump NH from the X-state up to the A-state. NH molecules in the A-state then emit *fluorescent* radiation as they drop back down to the X-state, and the intensity of this radiation at thermal equilibrium was found to decay according to

$$I_F(t) \propto n(t) = n(0)\mathrm{e}^{-t/\tau_{\mathrm{eff}}}, \tag{1.15}$$

where t is time. By making measurements at five different NH_3 pressures between 2-10 Pa, the decay rate was found to fit the expression

$$1/\tau_{\mathrm{eff}} = 1/\tau + k\, n_{\mathrm{NH}_3}, \tag{1.16}$$

where τ is the radiative lifetime, k is a constant, and n_{NH_3} is the number density of NH_3 molecules. It was found, for a particular rotation-vibration level of the A-state, that $\tau = 438$ ns and $k = 6.7\times10^{-10}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$. Plot this lifetime, and the linewidth of the emission line, as a function of NH_3 pressure. At room temperature, $n_{\mathrm{NH}_3} \approx 2.4\times10^{15}\ \mathrm{cm}^{-3}$ for a pressure of 10 Pa.

---

[6] A. Hake and F. Stuhl, J. Chem. Phys. 117, 2513 (2002).

Chapter 2

Quantum mechanics

2.1 The Schrödinger equation

The equation

$$\frac{\mathrm{d}}{\mathrm{d}x}\,\mathrm{e}^{a_n x} = a_n\,\mathrm{e}^{a_n x} \tag{2.1}$$

is an example of an *eigenvalue equation*; the operator $\mathrm{d}/\mathrm{d}x$ acting on the function $\mathrm{e}^{a_n x}$ gives, as result, a constant "a_n" times the function. In general, an eigenvalue equation has the form

$$\hat{O}\psi_n = O_n\psi_n, \tag{2.2}$$

where $\hat{O}$ is a differential operator, ψ_n is a function, and O_n is a constant. A function ψ_n that satisfies this equation is an *eigenfunction* of the operator $\hat{O}$, and the constant numerical factor O_n is the *eigenvalue* of the operator $\hat{O}$ appropriate for the eigenfunction ψ_n; the subscript n (= 1,2,3, etc.) labels the different solutions. Restricting the eigenfunctions of an eigenvalue equation so that they have certain properties can lead to the eigenvalues having discrete values like molecular energies.

Schrödinger postulated the way of setting up an eigenvalue equation for a molecule, and the way of interpreting and restricting the eigenfunctions, so that the eigenvalues are the molecular energies.

This special eigenvalue equation has come to be called the *Schrödinger equation.*

2.2 The postulates of quantum mechanics

Quantum mechanics is used to describe nature at the atomic and molecular level, in which there is quantization of the values of *observables* O such as energy and angular momentum. The theory of quantum mechanics leads to quantization by introducing rules or *postulates* concerning the way operators are set up to represent observables, and the way the eigenfunctions are restricted and interpreted.

Using classical mechanics for an atom or molecule that consists of l particles (electrons and nuclei), labeled $r = 1,2,\ldots,l$ with mass m_r, any observable can be written as a function of Cartesian coordinates X_r, Y_r and Z_r, and momenta $P_{\mathrm{X}r}$ $(= m_r\dot{\mathrm{X}}_r = m_r\mathrm{d}X_r/\mathrm{d}t$, where t is time), $P_{\mathrm{Y}r}$ and $P_{\mathrm{Z}r}$. The first postulate of quantum mechanics states that if one replaces the momenta $P_{\mathrm{X}r}$, $P_{\mathrm{Y}r}$ and $P_{\mathrm{Z}r}$ in the classical expression for an observable O, by the partial differential operators $\hat{P}_{\mathrm{X}r}$, $\hat{P}_{\mathrm{Y}r}$ and $\hat{P}_{\mathrm{Z}r}$ according to the rules

$$\hat{P}_{\mathrm{X}r} = -\mathrm{i}\hbar\partial/\partial\mathrm{X}_r, \tag{2.3}$$

$$\hat{P}_{\mathrm{Y}r} = -\mathrm{i}\hbar\partial/\partial\mathrm{Y}_r, \tag{2.4}$$

and

$$\hat{P}_{\mathrm{Z}r} = -\mathrm{i}\hbar\partial/\partial\mathrm{Z}_r, \tag{2.5}$$

where $\mathrm{i} = \sqrt{-1}$ and $\hbar = h/2\pi$, then the resultant differential operator $\hat{O}$ *represents* the observable O from which it was derived. If the observable depends only on coordinates, and not on momenta, then the expression for the quantum mechanical operator is identical to the classical expression for the observable. The operator that represents the energy is called *the Hamiltonian operator*, or simply *the Hamiltonian.*

The second postulate of quantum mechanics states that the only possible values for an observable are the eigenvalues of the operator that represents it when the eigenfunctions ψ_n are *restricted* to be single valued and when they are *interpreted* to be such that

$$P_n\mathrm{d}\tau = \psi_n^*\psi_n\mathrm{d}\tau = |\psi_n|^2\mathrm{d}\tau \tag{2.6}$$

is the probability that ψ_n has its coordinates in the *volume element* $\mathrm{d}\tau$. The volume element for integration, $\mathrm{d}\tau$, is a short hand notation in which, for example, if the functions ψ_n were expressed in an l-particle Cartesian coordinate space $(\mathrm{X}_1,\mathrm{Y}_1,\mathrm{Z}_1,\ldots,\mathrm{X}_l,\mathrm{Y}_l,\mathrm{Z}_l)$,

$$\mathrm{d}\tau = \mathrm{dX}_1\mathrm{dY}_1\mathrm{dZ}_1\ldots\mathrm{dX}_l\mathrm{dY}_l\mathrm{dZ}_l. \tag{2.7}$$

By appropriate transformations $\mathrm{d}\tau$ can be expressed in any coordinate system.

It is often asserted that a postulate of quantum mechanics is that the eigenfunctions be square integrable, i.e., that

$$\int |\psi_n|^2 \mathrm{d}\tau < \infty, \tag{2.8}$$

but this is only true for bound (and quantized) states; see, for example, the eigenfunctions given in equation (2.68) for a case in which there is no quantization. When there is quantization, we *normalize* the eigenfunctions so that

$$\int P_n \mathrm{d}\tau = \int \psi_n^* \psi_n \mathrm{d}\tau = \int |\psi_n|^2 \mathrm{d}\tau = 1, \tag{2.9}$$

in order that the total probability over all space be unity. When the eigenfunctions are not square integrable the ratio of $|\psi_n|^2$ at two different points is the ratio of their probabilities.

With this restriction and interpretation of the eigenfunctions, the possible values of the energy are the eigenvalues E_n of the Hamiltonian operator $\hat{H}$:

$$\hat{H}\psi_n = E_n \psi_n. \tag{2.10}$$

This equation is the (time independent) Schrödinger equation or wave equation, and the eigenfunctions ψ_n are the *wavefunctions* that represent (or simply *are*) the state of the system. The E_n are the possible *stationary state* energies of the system. The state having the lowest energy is called the *ground* state and all other states are called *excited* states.

The second postulate still allows us to multiply a wavefunction by $\exp(\mathrm{i}\theta)$, where θ is any real constant, without changing $P_n = |\psi_n|^2$, since $|\exp(\mathrm{i}\theta)|^2 = 1$. The factor $\exp(\mathrm{i}\theta)$ is called a *phase factor*, and a wavefunction multiplied by a phase factor is the same state. However, it is necessary to define the phase factor used, and to be consistent, because relative phase factors of wavefunctions can be significant.

A state ϕ_n might not be an eigenfunction of a particular operator $\hat{O}$. The third postulate of quantum mechanics concerns such a situation, and it states that the expected (or most probable) value of an observable O for a system in a state ϕ_n is the integral of the product $\phi_n^* \hat{O} \phi_n$, where $\hat{O}$ is the operator that represents O; such an integral is called an *expectation value*, and we write it as

$$O_{nn} = \langle n|\hat{O}|n\rangle = \int \phi_n^* \hat{O} \phi_n \mathrm{d}\tau. \tag{2.11}$$

The fourth postulate, concerning the time-dependence of wavefunctions, is given in section 14.1, and the fifth, concerning the symmetry of wavefunctions under the effect of the permutation of identical particles, is given in section 9.1.

2.2.1 Operators and eigenfunctions

We summarize here some important facts and definitions. An operator $\hat{O}$ is *Hermitian* if

$$\int \psi_m^* \hat{O} \psi_n \mathrm{d}\tau = \int (\hat{O}\psi_m)^* \psi_n \mathrm{d}\tau = \int (\psi_n^* \hat{O} \psi_m)^* \mathrm{d}\tau. \tag{2.12}$$

The eigenvalues of a Hermitian operator are real, and operators corresponding to real physical observables must be Hermitian. It can be proved that the eigenfunctions of a Hermitian operator that have different eigenvalues are orthogonal, i.e., they are such that

$$\int \psi_m^* \psi_n \mathrm{d}\tau = 0 \tag{2.13}$$

unless $m = n$. Equations (2.9) and (2.13) are summarized by saying that for a set of *orthonormal* functions ψ_1, ψ_2, ψ_3, etc.

$$\int \psi_m^* \psi_n \mathrm{d}\tau = \delta_{mn}, \tag{2.14}$$

where δ_{mn} is the Kronecker delta.

Acting on a function of X, $\phi(X)$ say, with the operator difference $(X\hat{P}_X - \hat{P}_X X)$ gives

$$\begin{aligned}(X\hat{P}_X - \hat{P}_X X)\phi(X) &= \big[X(-\mathrm{i}\hbar\partial/\partial X) - (-\mathrm{i}\hbar\partial/\partial X)X\big]\phi(X) \\ &= -\mathrm{i}\hbar X\frac{\partial\phi(X)}{\partial X} + \mathrm{i}\hbar\frac{\partial}{\partial X}\big[X\phi(X)\big] \\ &= -\mathrm{i}\hbar X\frac{\partial\phi(X)}{\partial X} + \mathrm{i}\hbar\Big[\phi(X) + X\frac{\partial\phi(X)}{\partial X}\Big] \\ &= \mathrm{i}\hbar\phi(X).\end{aligned} \tag{2.15}$$

We can write

$$(X\hat{P}_X - \hat{P}_X X)\phi(X) = \mathrm{i}\hbar\phi(X), \tag{2.16}$$

and formally 'cancel' out the $\phi(X)$ from each side of the equation to obtain the *operator equation*:

$$X\hat{P}_X - \hat{P}_X X = \mathrm{i}\hbar. \tag{2.17}$$

An operator equation means that each side of the equation produces the same result when it acts on a function. Two operators $\hat{O}_1$ and $\hat{O}_2$ commute if the following operator equation is true:

$$(\hat{O}_1\hat{O}_2 - \hat{O}_2\hat{O}_1) = 0. \tag{2.18}$$

We introduce the notation

$$\big[\hat{O}_1, \hat{O}_2\big] = (\hat{O}_1\hat{O}_2 - \hat{O}_2\hat{O}_1), \tag{2.19}$$

where $\left[\hat{O}_1, \hat{O}_2\right]$ is called the *commutator* of $\hat{O}_1$ and $\hat{O}_2$. Thus the commutator of X and $\hat{P}_X$ is not zero, and these two operators do not commute.

Observables are represented by Hermitian operators, and special care must sometimes be exercised when using the first postulate to set up an operator. For example, an expression such as $X\,\hat{P}_X$ is not Hermitian because X and $\hat{P}_X$ do not commute. In such a case it is necessary to properly symmetrize the classical expression before converting it to quantum mechanical form. For example, instead of XP_X one must write $(XP_X + P_XX)/2$.

If a stationary state energy level E_n is k-fold degenerate then there are k linearly independent[1] and orthogonal eigenfunctions ψ_{n1}, $\psi_{n2}, \ldots,$ ψ_{nk} having the same energy eigenvalue E_n of the Hamiltonian operator $\hat{H}$. Any other eigenfunction ψ_p having eigenvalue E_n can only be a linear combination of this *complete set* of k functions, i.e.,

$$\psi_p = \sum_{j=1}^{k} c_{pj}\psi_{nj}, \tag{2.20}$$

where the c_{pj} are constants. For the level E_n we would have $g_i = k$ in equation (1.5). Stationary states can be nondegenerate or they can be degenerate. If the level E_n is non-degenerate, and ψ_n is an eigenfunction with eigenvalue E_n, then the only other functions that can be eigenfunctions having eigenvalue E_n are of the form $c\psi_n$ where c is a constant. If ψ_1, ψ_2, … are eigenfunctions of $\hat{H}$, then linear combinations of them can be chosen that are also simultaneously the eigenfunctions of any operator that commutes with $\hat{H}$. Conversely if two operators (such as X and $\hat{P}_X$) do not commute then there are no nontrivial functions that are simultaneously the eigenfunctions of both.

2.3 Diagonalizing the Hamiltonian matrix

It frequently happens that we know a set of functions ψ_n^0 say, that are approximately the eigenfunctions of a Hamiltonian $\hat{H}$, i.e. $\hat{H}\psi_n^0 = E_n^0\psi_n^0 + X$, where $X \ll E_n^0\psi_n^0$. Such a set of known functions are called *basis functions*, and one can use them to determine the true eigenfunctions and eigenvalues by setting up and diagonalizing the Hamiltonian matrix; we now explain this procedure using some definitions and results from matrix algebra that are collected together in section 2.9.

Consider a Hamiltonian $\hat{H}$ and a set of orthonormal basis functions ψ_n^0 (where $n = 1, 2, 3, \ldots$). We introduce the integrals

$$H_{mn} = \langle m|\hat{H}|n\rangle = \int (\psi_m^0)^*\hat{H}\psi_n^0\mathrm{d}\tau, \tag{2.21}$$

---

[1] These k functions are linearly independent if there is no relation of the type $c_1\psi_{n1} + c_2\psi_{n2} + \cdots + c_k\psi_{nk} = 0$ (apart from the trivial one with all $c_i = 0$) connecting them.

which can be arranged in a matrix where m and n are the row and column indices, respectively; we call such integrals *matrix elements* of the Hamiltonian, and the entire matrix is called *the Hamiltonian matrix.* The diagonal matrix elements are the expectation values of the energy for the basis functions, and we write

$$H_{nn} = \langle n|\hat{H}|n\rangle = E_n^0. \tag{2.22}$$

For convenience, we organize the matrix so that $E_1^0 \leq E_2^0 \leq E_3^0 \ldots$.

The values of the matrix elements would change if we used different basis functions. For example, if we set up the Hamiltonian matrix using the normalized eigenfunctions ψ_n of $\hat{H}$, the diagonal matrix elements would be the eigenvalues, and the off-diagonal matrix elements would vanish. The Hamiltonian matrix would then be said to be *diagonal*.

It is the presence of nonvanishing off-diagonal matrix elements that spoils the functions ψ_n^0 as eigenfunctions. However, the degree to which the functions are spoiled does not only depend on the magnitudes of the off-diagonal matrix elements between them, but it also depends on the differences between their diagonal matrix elements. To explain this we will first show how the eigenfunctions and eigenvalues can be determined from the values of the Hamiltonian matrix elements, and then focus on a simple 2×2 example. The 2×2 example is extremely important since it is used to analyze interactions or *perturbations* between energy levels caused by a previously neglected part of the Hamiltonian which gives rise to a nonvanishing off-diagonal matrix element. In such circumstances the states ψ_n^0 would be called *zero order* states.

We wish to determine the eigenfunctions and eigenvalues, ψ_j and E_j ($j = 1,\ 2,\ 3,\ \ldots$), of the Hamiltonian $\hat{H}$, using the complete set of basis functions ψ_n^0. Since the basis set is complete, by definition we can write the unknown eigenfunctions ψ_j in terms of them as:

$$\psi_j = \sum_n C_{jn}\psi_n^0, \tag{2.23}$$

where the C_{jn} are the eigenfunction coefficients that remain to be determined. Since $\hat{H}\psi_j = E_j\psi_j$,

$$\hat{H}\Big[\sum_n C_{jn}\psi_n^0\Big] = E_j\Big[\sum_n C_{jn}\psi_n^0\Big]. \tag{2.24}$$

To determine the ψ_j and E_j we proceed as follows: Multiply each side of equation (2.24) on the left by $(\psi_m^0)^*$, make use of the fact that $\hat{H}$ and the C_{jn} commute with each other, and finally integrate each side over all space. Using equations (2.21) and (2.14) this gives

$$\sum_n C_{jn}H_{mn} = E_j \sum_n C_{jn}\delta_{mn}, \tag{2.25}$$

which can be rewritten as the matrix product

$$\sum_n (H_{mn} - \delta_{mn} E_j)\tilde{C}_{nj} = 0, \tag{2.26}$$

where $\tilde{C}$ is the transpose of C; see section 2.9. Apart from the useless solution that all elements of $\tilde{C}_{nj} = 0$, the solution obtained is the following *secular* equation for the eigenvalues E_j:

$$|H_{mn} - \delta_{mn} E| = 0, \quad \text{if} \quad E = E_j. \tag{2.27}$$

This states that the determinant[2] of the matrix $(H_{mn} - \delta_{mn} E)$ vanishes if E is an eigenvalue. This enables us to determine the eigenvalues of $\hat{H}$, and an l-dimensional Hamiltonian matrix leads to a secular equation with l eigenvalues. The E_j are the eigenvalues both of the operator $\hat{H}$ and of the matrix H that represents it using a basis set.

By substituting the eigenvalues E_j one at a time into equation (2.26) we obtain l simultaneous equations (as $m = 1$ to l) for the $\tilde{C}_{nj}$, and we obtain the elements in the jth column of the matrix $\tilde{C}$. Since $\tilde{C}_{nj} = C_{jn}$ these coefficients form the jth row of the matrix C; these are the coefficients of the basis functions ψ_n^0 in the eigenfunction ψ_j, and we can appreciate how well (or badly) ψ_j^0 represents ψ_j from their values. The orthonormality of the functions demands that the elements of C satisfy

$$\sum_n C_{jn}^* C_{kn} = \delta_{jk}, \tag{2.28}$$

which means that the matrix C is unitary; see section 2.9.

Using matrix notation it can be shown that the elements of the matrix C are such that

$$C\boldsymbol{H}C^{-1} = \Lambda \tag{2.29}$$

where $\boldsymbol{H}$ is the Hamiltonian matrix, and Λ is a matrix having non-vanishing diagonal elements $\Lambda_{jj} = E_j$ (the eigenvalues) and $\Lambda_{ij} = 0$ if $i \neq j$. We say that the *similarity transformation* of the Hamiltonian matrix $\boldsymbol{H}$ by the matrix of eigenfunction coefficients C in equation (2.29) diagonalizes $\boldsymbol{H}$ to produce the diagonal matrix Λ of eigenvalues. The process of *diagonalizing* a Hamiltonian matrix in a basis set is a routine procedure, once we have determined the elements of the Hamiltonian matrix, and standard computer routines are available.

As a simple example we consider a 2-dimensional (Hermitian) Hamiltonian matrix for the zero order states ψ_1^0 and ψ_2^0:

$$\begin{bmatrix} E_1^0 & H_{12} \\ H_{12}^* & E_2^0 \end{bmatrix} \tag{2.30}$$

---

[2] See equation (2.95) for the definition of a determinant.

Assuming, for simplicity, that H_{12} is real, equation (2.27) reduces to

$$(E_1^0 - E)(E_2^0 - E) - H_{12}^2 = 0, \tag{2.31}$$

and solving for E, one obtains the two roots:

$$E_1 = E_1^0 - S \tag{2.32}$$

and

$$E_2 = E_2^0 + S, \tag{2.33}$$

where $E_1^0 \leq E_2^0$, the energy shift

$$S = \frac{1}{2}\big(\sqrt{4H_{12}^2 + \Delta^2} - \Delta\big), \tag{2.34}$$

and $\Delta = E_2^0 - E_1^0$ is the difference between the diagonal matrix elements. Using equations (2.26) and (2.28) to obtain the eigenfunction coefficients one gets

$$\psi_1 = c^+ \psi_1^0 - c^- \psi_2^0, \tag{2.35}$$

and

$$\psi_2 = c^+ \psi_2^0 + c^- \psi_1^0, \tag{2.36}$$

where

$$c^\pm = \frac{1}{\sqrt{2}}\Big[1 \pm \frac{\Delta}{\sqrt{4H_{12}^2 + \Delta^2}}\Big]^{1/2}. \tag{2.37}$$

The expressions for S and $c^\pm$ depend on both the off-diagonal matrix element H_{12} and the diagonal matrix element difference Δ.

For situations when $|H_{12}| \ll \Delta$, the leading terms in the binomial expansion of $\sqrt{4H_{12}^2 + \Delta^2} = \Delta(1 + 4\, H_{12}^2/\Delta^2)^{1/2}$, can be used to give the approximate solution

$$S \approx \frac{H_{12}^2}{\Delta}, \tag{2.38}$$

with

$$c^+ \approx 1 - \frac{H_{12}^2}{2\Delta^2}, \tag{2.39}$$

and

$$c^- \approx \frac{H_{12}}{\Delta}. \tag{2.40}$$

Equations (2.38)-(2.40) are also obtained using second order perturbation theory (see below) for the 2×2 case.

We can now quantitatively represent the very commonly occurring phenomenon of a 2×2 energy level interaction or perturbation. The functions ψ_1^0 and ψ_2^0 would be eigenfunctions of the Hamiltonian if the off-diagonal matrix element H_{12} were zero; as H_{12} grows the two states perturb, or repel, or interact with, each other. The lower level E_1 moves down, the higher level E_2 moves up, and the wavefunctions of the two states ψ_1^0 and ψ_2^0 gradually become more and more mixed in the eigenfunctions ψ_1 and ψ_2. The extent to which the zero order functions are mixed, and the amount by which the levels repel each other, depend on the size of the off-diagonal matrix element H_{12}, and on the zero order energy separation Δ. The above equations allow us to calculate these effects for any values of H_{12} and Δ. For $\Delta = 0$ we obtain $c^+ = c^- = 1/\sqrt{2}$; we have a fifty-fifty mixing of the two zero order states and a maximal energy shift of H_{12}. On the other hand as $H_{12} \rightarrow 0$, c^+ approaches 1 while c^- approaches 0; now $\psi_1 \rightarrow \psi_1^0$ and $\psi_2 \rightarrow \psi_2^0$, with energy shifts that go to zero.

Perturbations can involve more than 2 levels interacting simultaneously, and a matrix larger than 2×2 will then have to be diagonalized. It often happens that we have to consider the complete basis set consisting of an infinite number of functions. Obviously, we can only set up and diagonalize the Hamiltonian matrix in a finite number of basis functions, so we have to *truncate* the matrix. If the size of the truncated matrix is $n^{\text{trunc}} \times n^{\text{trunc}}$ then its diagonalization will yield n^{trunc} approximate eigenvalues and eigenfunctions. If we are only interested in the lowest p states, say, then we must choose n^{trunc} to be much larger than p in order that this approximate approach leads to satisfactory results for the p states of interest. This approximate approach is called the *variational* approach. In practice, the size n^{trunc} is increased until a further increase has negligible effect on the p eigenvalues of interest; the calculation is then said to have *converged.* The lowest eigenvalue of the truncated Hamiltonian matrix $E_{\text{lowest}}^{\text{trunc}}$ will not be precisely equal to the lowest eigenvalue $E_{\text{lowest}}^{\text{exact}}$ of the Hamiltonian. The *variational theorem* states that $E_{\text{lowest}}^{\text{trunc}}$ is always above $E_{\text{lowest}}^{\text{exact}}$, i.e.,

$$E_{\text{lowest}}^{\text{trunc}} - E_{\text{lowest}}^{\text{exact}} = \Delta E > 0. \tag{2.41}$$

In a well behaved problem, increasing the number of basis functions reduces ΔE, and $E_{\text{lowest}}^{\text{trunc}}$ converges to $E_{\text{lowest}}^{\text{exact}}$ as the number of basis functions is increased. The existence of very efficient numerical computer routines for diagonalizing large matrices make the variational procedure of practical and general use.

In situations where the off-diagonal matrix elements are small compared to the differences in diagonal matrix elements an alternative procedure for determining eigenfunctions and eigenvalues called *perturbation theory* can be used. In this procedure we write the Hamiltonian operator as

$$\hat{H} = \hat{H}^0 + \lambda \hat{H}' \tag{2.42}$$

where the eigenfunctions of $\hat{H}^0$ are the known basis functions ψ_n^0, and where $\hat{H}'$ (called *the perturbation*) has nonvanishing off-diagonal matrix elements. By changing the expansion constant λ from zero to one the perturbation is switched on. In this approach analytical expressions for the eigenfunctions and eigenvalues of $\hat{H}$ are obtained as power series in λ involving matrix elements of $\hat{H}'$ in the basis functions ψ_n^0, and differences between diagonal matrix elements. Truncating these expressions at the terms quadratic in λ produces the results of *second order* perturbation theory, and this is normally where the procedure is terminated. The results obtained using perturbation theory are useful if $\hat{H}'$ has a small effect, and one can gain an understanding of the effects of $\hat{H}'$ from the analytical expressions obtained. Perturbation theory is used in the development of the *effective rotational Hamiltonian* (see section 11.5). This Hamiltonian is crucially important in the practical analysis of spectra.

2.4 The molecular Schrödinger equation

The classical expression for the total energy of a molecule consisting of l particles, nuclei and electrons, is

$$E_{\text{total}} = T + V. \tag{2.43}$$

The kinetic energy is given by

$$T = \frac{1}{2}\sum_{r=1}^{l} m_r(\dot{\mathrm{X}}_r{}^2 + \dot{\mathrm{Y}}_r{}^2 + \dot{\mathrm{Z}}_r{}^2), \tag{2.44}$$

where particle r has mass m_r (the mass of an electron being m_e), and $\dot{\mathrm{X}}_r$, $\dot{\mathrm{Y}}_r$ and $\dot{\mathrm{Z}}_r$ are the components of its velocity in a space-fixed XYZ axis system. In SI units, the electrostatic potential energy that results from the repulsions and attractions between the particles is

$$V = \sum_{r<s=1}^{l} \frac{C_r C_s e^2}{4\pi\epsilon_0 R_{rs}}, \tag{2.45}$$

where $C_r e$ is the charge[3] of particle r (the charge on an electron is $-e$), R_{rs} is the interparticle distance given by

$$R_{rs} = [(\mathrm{X}_r - \mathrm{X}_s)^2 + (\mathrm{Y}_r - \mathrm{Y}_s)^2 + (\mathrm{Z}_r - \mathrm{Z}_s)^2]^{1/2}, \tag{2.46}$$

and ϵ_0 is the permittivity of free space (introduced on page 12).

The energy expression $T + V$ can be separated into two parts: the translational energy and the internal (rovibronic) energy. In chapters 3, 4 and 5, we discuss the separation of the rovibronic energy into electronic, vibrational and rotational parts. Such separations of variables are of central importance in making the equations that occur easier to handle and to understand; they always involves making coordinate changes.

---

[3] The elementary charge $e = 1.602\,176\,53\times10^{-19}$ C; this is the charge on a proton.

2.5 The separation of translational energy

Whenever we make a change of coordinates there are two ways of proceeding: (I) First to set up the quantum mechanical molecular Hamiltonian in the initial coordinates and then to change to the new coordinates in the resultant differential equation that is the Schrödinger equation using the *chain rule*, or (II) First to change coordinates in the classical expression to obtain the classical energy expression in the new coordinates and then to set up the quantum mechanical Hamiltonian, and Schrödinger equation, in the new coordinates. We use method (II) here.

We know that the translational energy is the kinetic energy $Mv^2/2$, where $M = \sum_r m_r$ is the molecular mass and v is the speed of the molecular centre of mass through space. To change coordinates so that the molecular kinetic energy T involves this we must explicitly introduce the coordinates of the centre of mass, which we call (X_0,Y_0,Z_0). Thus the XYZ coordinates of the particles are written

$$\mathrm{X}_r = X_r + \mathrm{X}_0, \tag{2.47}$$

$$\mathrm{Y}_r = Y_r + \mathrm{Y}_0, \tag{2.48}$$

and

$$\mathrm{Z}_r = Z_r + \mathrm{Z}_0, \tag{2.49}$$

where (X_r, Y_r, Z_r) are the coordinates of particle r in an XYZ axis system that is parallel to the space-fixed XYZ axis system[4] but which has origin at the molecular centre of mass (X_0,Y_0,X_0). We must write the kinetic energy T in terms of the new set of $3l$ coordinates

$$\mathrm{X}_0, \mathrm{Y}_0, \mathrm{Z}_0, X_2, Y_2, Z_2, \ldots, X_l, Y_l, Z_l, \tag{2.50}$$

and their velocities $\dot{\mathrm{X}}_0$,. . .,$\dot{Z}_l$, where we have eliminated X_1, Y_1 and Z_1 using

$$X_1 = -\frac{1}{m_1}\sum_{r=2}^{l} m_r X_r, \tag{2.51}$$

with similar equations for Y_1 and Z_1. The $(3l{-}3)$ coordinates X_2, Y_2, Z_2,. . ., X_l, Y_l, Z_l are the *internal* coordinates; they specify the positions of the particles relative to the centre of mass of the molecule.

Using equations (2.47)-(2.49) for $r = 2$ through l gives:

$$\frac{1}{2}\sum_{r=2}^{l} m_r(\dot{\mathrm{X}}_r{}^2 + \dot{\mathrm{Y}}_r{}^2 + \dot{\mathrm{Z}}_r{}^2) = \frac{1}{2}\sum_{r=2}^{l} m_r(\dot{X}_r{}^2 + \dot{Y}_r{}^2 + \dot{Z}_r{}^2)$$

---

[4] Be careful to notice the font distinction here. We use upright font for the XYZ axes; they have space-fixed origin and space-fixed orientation. We use italic font for the XYZ axes that are parallel to them and which, therefore, have space-fixed orientation, but which have origin at the molecular centre of mass.

$$\begin{aligned} &+ \sum_{r=2}^{l} m_r(\dot{X}_r\dot{\mathrm{X}}_0 + \dot{Y}_r\dot{\mathrm{Y}}_0 + \dot{Z}_r\dot{\mathrm{Z}}_0) \\ &+ \frac{1}{2}\Big(\sum_{r=2}^{l} m_r\Big)(\dot{\mathrm{X}}_0{}^2 + \dot{\mathrm{Y}}_0{}^2 + \dot{\mathrm{Z}}_0{}^2). \end{aligned} \qquad (2.52)$$

Using equation (2.51), and the similar equations for Y_1 and Z_1, in equations (2.47)-(2.49), we obtain

$$\begin{aligned} \frac{1}{2}m_1(\dot{\mathrm{X}}_1{}^2 + \dot{\mathrm{Y}}_1{}^2 + \dot{\mathrm{Z}}_1{}^2) = {}& \frac{1}{2m_1}\sum_{r,s=2}^{l} m_r m_s(\dot{X}_r\dot{X}_s + \dot{Y}_r\dot{Y}_s + \dot{Z}_r\dot{Z}_s) \\ &- \sum_{r=2}^{l} m_r(\dot{X}_r\dot{\mathrm{X}}_0 + \dot{Y}_r\dot{\mathrm{Y}}_0 + \dot{Z}_r\dot{\mathrm{Z}}_0) \\ &+ \frac{1}{2}m_1(\dot{\mathrm{X}}_0{}^2 + \dot{\mathrm{Y}}_0{}^2 + \dot{\mathrm{Z}}_0{}^2). \end{aligned} \qquad (2.53)$$

Adding equations (2.45), (2.52) and (2.53) gives

$$E_{\text{total}} = T_{\text{trans}} + T_{\text{rve}} + V, \qquad (2.54)$$

where V is expressed in terms of the coordinates $X_2,\ldots,Z_l$. In equation (2.54) the translational kinetic energy is

$$T_{\text{trans}} = \frac{1}{2}M(\dot{\mathrm{X}}_0{}^2 + \dot{\mathrm{Y}}_0{}^2 + \dot{\mathrm{Z}}_0{}^2), \qquad (2.55)$$

and the internal (rovibronic) kinetic energy that results from the motion of the particles in the molecule relative to the molecular centre of mass is

$$\begin{aligned} T_{\text{rve}} = {}& \frac{1}{2}\sum_{r=2}^{l} m_r(\dot{X}_r{}^2 + \dot{Y}_r{}^2 + \dot{Z}_r{}^2) \\ &+ \frac{1}{2m_1}\sum_{r,s=2}^{l} m_r m_s(\dot{X}_r\dot{X}_s + \dot{Y}_r\dot{Y}_s + \dot{Z}_r\dot{Z}_s). \end{aligned} \qquad (2.56)$$

T_{rve} and V do not involve the coordinates or velocities of the centre of mass, and T_{trans} does not involve the internal coordinates or velocities.

There is a complete separation of the internal and translational degrees of freedom in the energy expression.

We can write the total energy as

$$E_{\text{total}} = E_{\text{trans}} + E_{\text{rve}} \qquad (2.57)$$

where the translational energy E_{trans} is the pure kinetic energy term T_{trans} given in equation (2.55); there is no potential energy contribution to the translational energy for a molecule moving in an unconstrained way in field free space. The rovibronic energy is

$$E_{\text{rve}} = T_{\text{rve}} + V. \tag{2.58}$$

2.5.1 The translational Schrödinger equation

To follow the procedure outlined above [see equations (2.3)-(2.10)] for obtaining the translational Schrödinger equation we begin by expressing the classical energy, given in equation (2.55), in terms of momenta P_α rather than velocities in order to obtain it in Hamiltonian form:

$$H_{\text{trans}} = \frac{1}{2M}({P_{\text{X0}}}^2 + {P_{\text{Y0}}}^2 + {P_{\text{Z0}}}^2), \tag{2.59}$$

where $P_{\text{X0}} = M\dot{\text{X}}_0$ etc. To obtain the Schrödinger equation we replace the momenta P_{X0}, P_{Y0} and P_{Z0} by the partial differential operators $\hat{P}_{\text{X0}} = -\text{i}\hbar\partial/\partial\text{X}_0$, $\hat{P}_{\text{Y0}} = -\text{i}\hbar\partial/\partial\text{Y}_0$, $\hat{P}_{\text{Z0}} = -\text{i}\hbar\partial/\partial\text{Z}_0$, in H_{trans} to yield the Hamiltonian operator for the translational motion:

$$\begin{aligned}\hat{H}_{\text{trans}} &= \frac{1}{2M}({\hat{P}_{\text{X0}}}^2 + {\hat{P}_{\text{Y0}}}^2 + {\hat{P}_{\text{Z0}}}^2)\\ &= -\frac{\hbar^2}{2M}\Big(\frac{\partial^2}{\partial{\text{X}_0}^2} + \frac{\partial^2}{\partial{\text{Y}_0}^2} + \frac{\partial^2}{\partial{\text{Z}_0}^2}\Big),\end{aligned} \tag{2.60}$$

and we set up the eigenvalue equation

$$\hat{H}_{\text{trans}}\Phi^{(n)}_{\text{trans}}(\text{X}_0, \text{Y}_0, \text{Z}_0) = E^{(n)}_{\text{trans}}\Phi^{(n)}_{\text{trans}}(\text{X}_0, \text{Y}_0, \text{Z}_0). \tag{2.61}$$

Equation (2.61) gives the translational Schrödinger equation for a molecule moving in an unconstrained way in free space. From the second quantum mechanical postulate the eigenfunctions have to be single valued, and the relative probabilities must be given by $|\Phi^{(n)}_{\text{trans}}(\text{X}_0, \text{Y}_0, \text{Z}_0)|^2$; they are then the translational wavefunctions of the molecule, and the eigenvalue $E^{(n)}_{\text{trans}}$ is the translational energy of the molecule when it is in the state $\Phi^{(n)}_{\text{trans}}(\text{X}_0, \text{Y}_0, \text{Z}_0)$.

Since $\hat{H}_{\text{trans}}$ is the sum of three independent terms in X_0, Y_0 and Z_0, we can separate the translational Schrödinger equation into three by writing

$$E_{\text{trans}} = E^{(n_X)}_{\text{transX}} + E^{(n_Y)}_{\text{transY}} + E^{(n_Z)}_{\text{transZ}}, \tag{2.62}$$

and

$$\Phi_{\text{trans}}(\text{X}_0, \text{Y}_0, \text{Z}_0) = \psi^{(n_X)}_{\text{transX}}(\text{X}_0)\psi^{(n_Y)}_{\text{transY}}(\text{Y}_0)\psi^{(n_Z)}_{\text{transZ}}(\text{Z}_0). \tag{2.63}$$

We substitute these two equations into equation (2.61). Making use of the fact that

$$\frac{\partial^2}{\partial {\mathrm{X}_0}^2}\Phi_{\mathrm{trans}}(\mathrm{X}_0,\mathrm{Y}_0,\mathrm{Z}_0)=\psi^{(n_Y)}_{\mathrm{transY}}(\mathrm{Y}_0)\psi^{(n_Z)}_{\mathrm{transZ}}(\mathrm{Z}_0)\frac{\partial^2}{\partial {\mathrm{X}_0}^2}\psi^{(n_X)}_{\mathrm{transX}}(\mathrm{X}_0), \tag{2.64}$$

with similar equations for the effects of $\partial^2/\partial {\mathrm{Y}_0}^2$ and $\partial^2/\partial {\mathrm{Z}_0}^2$, we can divide the resultant equation through by $\Phi_{\mathrm{trans}}(\mathrm{X}_0,\mathrm{Y}_0,\mathrm{Z}_0)$ to obtain the three independent equations

$$-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2}{\mathrm{d}{\mathrm{X}_0}^2}\psi^{(n_X)}_{\mathrm{transX}}(\mathrm{X}_0)=E^{(n_X)}_{\mathrm{transX}}\psi^{(n_X)}_{\mathrm{transX}}(\mathrm{X}_0), \tag{2.65}$$

$$-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2}{\mathrm{d}{\mathrm{Y}_0}^2}\psi^{(n_Y)}_{\mathrm{transY}}(\mathrm{Y}_0)=E^{(n_Y)}_{\mathrm{transY}}\psi^{(n_Y)}_{\mathrm{transY}}(\mathrm{Y}_0), \tag{2.66}$$

and

$$-\frac{\hbar^2}{2M}\frac{\mathrm{d}^2}{\mathrm{d}{\mathrm{Z}_0}^2}\psi^{(n_Z)}_{\mathrm{transZ}}(\mathrm{Z}_0)=E^{(n_Z)}_{\mathrm{transZ}}\psi^{(n_Z)}_{\mathrm{transZ}}(\mathrm{Z}_0). \tag{2.67}$$

The translational energy $E^{(n_X)}_{\mathrm{transX}}$ has to be positive and real, and the most general solution we can write for the eigenfunction of equation (2.65) is

$$\psi^{(n_X)}_{\mathrm{transX}}(\mathrm{X}_0)=A\cos(k_{\mathrm{X}}\mathrm{X}_0)+B\sin(k_{\mathrm{X}}\mathrm{X}_0) \tag{2.68}$$

or, equivalently,

$$\psi^{(n_X)}_{\mathrm{transX}}(\mathrm{X}_0)=C\exp(\mathrm{i}k_{\mathrm{X}}\mathrm{X}_0)+D\exp(-\mathrm{i}k_{\mathrm{X}}\mathrm{X}_0) \tag{2.69}$$

where $k_{\mathrm{X}}=(2ME^{(n_X)}_{\mathrm{transX}})^{1/2}/\hbar$, A and B are arbitrary constants, $C=(A-\mathrm{i}B)/2$ and $D=(A+\mathrm{i}B)/2$. Similar equations can be written for the eigenfunctions of equations (2.66) and (2.67) so that we have

$$E_{\mathrm{trans}}=\frac{\hbar^2}{2M}\left(k_{\mathrm{X}}^2+k_{\mathrm{Y}}^2+k_{\mathrm{Z}}^2\right). \tag{2.70}$$

There is no quantization of the translational states of an unconfined molecule moving in free space. The translational wavefunctions are plane waves and the eigenvalues (energies) can be any positive real number.

The above provides a very simple example of what happens when we separate the coordinates in a Hamiltonian. Here, since the Hamiltonian can be written as the sum of three independent parts, we have reduced a three dimensional Schrödinger equation (2.61) to three separate one-dimensional Schrödinger equations (2.65)-(2.67). The eigenvalues are obtained as the sum of the eigenvalues of the one-dimensional Schrödinger equations in equation (2.62), and the eigenfunctions are obtained as the product of the one-dimensional eigenfunctions in equation (2.63).

For a molecule confined to remain within a sample cell (which has finite dimensions) there is quantization of the translational states. To show how this comes about we consider the situation in which the molecule is confined within a cube shaped box with side L that has one corner at the point (X_0,Y_0,Z_0) = (0,0,0) and which lies in the positive octant of the (X_0,Y_0,Z_0) axis system. In this circumstance the eigenfunctions satisfy equations (2.63)-(2.69) within the box (i.e. when the X_0, Y_0 and Z_0 coordinates are between 0 and L). However, with the probability interpretation of the eigenfunctions they must be zero outside the box and must go smoothly to zero at the walls of the box. From equation (2.68) for $\psi^{(n_X)}_{\mathrm{transX}}(\mathrm{X}_0)$ we see that functions that go smoothly to zero at $\mathrm{X}_0 = 0$ must have A =0, and for them also to go smoothly to zero at $\mathrm{X}_0 = L$ they must also have $k_{\mathrm{X}}L = n_{\mathrm{X}}\pi$ where n_{X} is a positive integer. Thus for a molecule confined within this box the translational wavefunctions [from equations (2.63) and (2.68)] within the box are given by

$$\Phi^{(n_{\mathrm{X}},n_{\mathrm{Y}},n_{\mathrm{Z}})}_{\mathrm{trans}}(\mathrm{X}_0,\mathrm{Y}_0,\mathrm{Z}_0) = N\sin\Big(\frac{n_{\mathrm{X}}\pi}{L}\mathrm{X}_0\Big)\sin\Big(\frac{n_{\mathrm{Y}}\pi}{L}\mathrm{Y}_0\Big)\sin\Big(\frac{n_{\mathrm{Z}}\pi}{L}\mathrm{Z}_0\Big), \tag{2.71}$$

where n_{X}, n_{Y} and n_{Z} must be positive integers, and N is a constant. Outside the box the translational wavefunctions vanish. The normalizing constant N is determined to be $(8/L^3)^{1/2}$ by setting the the integral of $|\Phi_{\mathrm{trans}}|^2 d\tau$ within the box to be unity since that is the probability of finding the molecule within the box [see equation (2.9)]. Since $k_{\mathrm{X}}L = n_{\mathrm{X}}\pi$ etc., we have the result that

the translational energies of a molecule of mass M constrained to move within a cube of side L are quantized. They are given by

$$E^{(n_{\mathrm{X}},n_{\mathrm{Y}},n_{\mathrm{Z}})}_{\mathrm{trans}} = \frac{h^2}{8ML^2}(n_{\mathrm{X}}^2 + n_{\mathrm{Y}}^2 + n_{\mathrm{Z}}^2), \tag{2.72}$$

where the quantum numbers n_{X}, n_{Y} and n_{Z} are positive integers.

The lowest state has $n_{\mathrm{X}} = n_{\mathrm{Y}} = n_{\mathrm{Z}} = 1$ with energy $3h^2/(8ML^2)$, and the first excited translational state has energy $6h^2/(8ML^2)$. The energy separation is $3h^2/(8ML^2)$. This lowest excited state is actually three states with quantum numbers (n_{X},n_{Y},n_{Z}) = (2,1,1), (1,2,1) or (1,1,2) which all have the same energy; such a state is said to be three-fold degenerate or to have a degeneracy of three. The separation in energy $[3h^2/(8ML^2)]$ between the two lowest states for a $^{12}C^{16}O$ molecule (mass $M \approx 4.65\times10^{-26}$ kg) constrained to move in a cubic box with side $L = 10^{-2}$ m is 3.5×10^{-38} J. Dividing by hc, and quoting in cm^{-1}, the wavenumber separation is obtained as 1.8×10^{-15} cm^{-1}. This incredibly small energy separation shows how the quantization that results from using the rules of quantum mechanics disappears for all practical purposes for systems having macroscopic dimensions when the rules of classical mechanics are satisfactory.

We can use the above analysis of the energy levels of a particle in a box to get an approximate estimate of the energy separations involved when electrons move about within the limits of molecular dimensions, or when nuclei vibrate in bonds. For an electron (mass $M \approx 9.11\times10^{-31}$ kg) constrained to move within a cubic box of side $L = 0.3$ nm (which gives a box that has roughly the volume over which an outer electron moves in a small molecule) the above particle in a box analysis leads to a wavenumber separation between the two lowest states of 1.01×10^{5} cm^{-1}. For a particle constrained to move in one dimension within a length L the energy is given by $h^2n^2/(8ML^2)$ where $n = 1, 2, 3, ...$ (obtained by just considering the X_0 motion, for example, in the above three-dimensional analysis) and the energy separation between the two lowest states is given by $3h^2/(8ML^2)$ just as for motion within a three-dimensional box. For a proton (mass $M \approx 1.67\times10^{-27}$ kg) constrained to move in one dimension within a length of 0.03 nm (which roughly equals the stretching vibrational amplitude in a molecule) the wavenumber separation between the lowest two energy levels is 5500 cm^{-1}; a factor of about 1/20th of the electronic wavenumber (or energy) separation.

> The first excited electronic state has an energy much larger than that of the first excited vibrational state because the electron mass is so much less than any nuclear mass; this more than compensates for the fact that electronic motions are less constrained than nuclear vibrational motions in molecules.

2.6 The rovibronic Schrödinger equation

After separating translation the classical expression for the rovibronic (internal) energy of a molecule that consists of l particles (nuclei and electrons) is obtained from equations (2.45), (2.56) and (2.58) as

$$E_{\mathrm{rve}} = \frac{1}{2}\sum_{r=2}^{l} m_r(\dot{X}_r{}^2 + \dot{Y}_r{}^2 + \dot{Z}_r{}^2)$$

$$+\frac{1}{2m_1}\sum_{r,s=2}^{l} m_r m_s(\dot{X}_r\dot{X}_s+\dot{Y}_r\dot{Y}_s+\dot{Z}_r\dot{Z}_s)$$

$$+\sum_{r<s=1}^{l}\frac{C_rC_se^2}{4\pi\epsilon_0 R_{rs}}. \qquad (2.73)$$

Starting with this classical rovibronic energy expression, and using the first postulate, we obtain the rovibronic Schrödinger equation.

In the rovibronic energy expression $E_{\rm rve}$ the motion of the particles is constrained so that the centre of mass remains fixed at the origin of the XYZ axes. The general definition, allowing for constraints, of the momentum P_s *conjugate* to the coordinate Q_s is

$$P_s=\partial(T-V)/\partial\dot{Q}_s. \qquad (2.74)$$

Since the potential energy is independent of the velocities, we obtain $P_{Xr}=\partial T_{\rm rve}/\partial\dot{X}_r$, $P_{Yr}=\partial T_{\rm rve}/\partial\dot{Y}_r$, and $P_{Zr}=\partial T_{\rm rve}/\partial\dot{Z}_r$, where $T_{\rm rve}$ is given in equation (2.56); we do not obtain simple relations such as $P_{Xr}=M_r\dot{X}_r$. Inverting the equations obtained for the generalized momenta as functions of the velocities one obtains the velocities as functions of the momenta. Substituting for the velocities in equation (2.73) leads to the classical Hamiltonian $H_{\rm rve}$ as a function of the coordinates and momenta. Replacing P_{Xr} by $\hat{P}_{Xr}=-{\rm i}\hbar\partial/\partial X_r$, P_{Yr} by $\hat{P}_{Yr}=-{\rm i}\hbar\partial/\partial Y_r$ and P_{Zr} by $\hat{P}_{Zr}=-{\rm i}\hbar\partial/\partial Z_r$,

the quantum mechanical rovibronic Hamiltonian for an l-particle molecule is obtained as

$$\hat{H}_{\rm rve}=-(\hbar^2/2)\sum_{r=2}^{l}(\partial^2/\partial X_r{}^2+\partial^2/\partial Y_r{}^2+\partial^2/\partial Z_r{}^2)/m_r$$

$$+(\hbar^2/2M)\sum_{r,s=2}^{l}(\partial^2/\partial X_r\partial X_s+\partial^2/\partial Y_r\partial Y_s+\partial^2/\partial Z_r\partial Z_s)$$

$$+\sum_{r<s=1}^{l}\frac{C_rC_se^2}{4\pi\epsilon_0 R_{rs}}, \qquad (2.75)$$

where $M=\sum m_r$ is the mass of the molecule.

The rovibronic Schrödinger equation is given by

$$\hat{H}_{\rm rve}\Phi_{\rm rve}(X_2,Y_2,Z_2,\ldots,Z_l)=E_{\rm rve}\Phi_{\rm rve}(X_2,Y_2,Z_2,\ldots,Z_l). \qquad (2.76)$$

In section 3.2 we introduce *spin*, and it is explained there that because of the presence of spin, electrons and many nuclei have a magnetic dipole moment, and that some nuclei have an electric quadrupole moment as well. The internal energy of a molecule is affected by the presence of these moments. The term in the Hamiltonian that arises from the fact that each electron has a spin magnetic dipole moment is called $\hat{H}_{\rm es}$, and the term arising from the presence of the nuclear spin moments is called $\hat{H}_{\rm hfs}$. The principal terms in $\hat{H}_{\rm es}$ arise from the interaction of the electron spin magnetic moments with each other (the electron *spin-spin* interaction), and from their interaction with the magnetic moments generated by the orbital motion of the electrons (the electron *spin-orbit* interaction). $\hat{H}_{\rm hfs}$ contains similar magnetic terms involving the nuclear spin-spin and nuclear spin-orbit interactions, as well as terms for nuclear spin-electron orbit and nuclear spin-electron spin interactions. For nuclei that have an electric quadrupole moment there is an additional term involving its interaction with the electronic charge gradient at the nucleus. $\hat{H}_{\rm es}$ and $\hat{H}_{\rm hfs}$ can give rise to splittings of the energy levels called electronic fine structure splittings and nuclear hyperfine structure splittings, respectively.

Adding the sum of $\hat{H}_{\rm es}$ and $\hat{H}_{\rm hfs}$ to the electrostatic potential energy, gives the complete electromagnetic interaction energy between the particles, so that the complete quantum mechanical Hamiltonian for the internal dynamics of a molecule (that is, everything except translation) is

$$\hat{H}_{\rm int} = \hat{H}_{\rm rve} + \hat{H}_{\rm es} + \hat{H}_{\rm hfs}. \tag{2.77}$$

2.7 The angular momentum operator

The classical observable of orbital angular momentum $\boldsymbol{J}$ for a system of l particles, in the centre-of-mass axis system, has X component given by

$$J_X = \sum_{r=1}^{l} (Y_r P_{Zr} - Z_r P_{Yr}), \tag{2.78}$$

and so the operator for it is given by

$$\hat{J}_X = -\mathrm{i}\hbar \sum_{r=1}^{l} \Big(Y_r \frac{\partial}{\partial Z_r} - Z_r \frac{\partial}{\partial Y_r} \Big). \tag{2.79}$$

The operators representing $\hat{J}_Y$ and $\hat{J}_Z$ are obtained from equation (2.79) by cyclic permutation of X, Y and Z. The square of the orbital angular momentum operator is given by

$$\hat{J}^2 = \hat{J}_X^2 + \hat{J}_Y^2 + \hat{J}_Z^2. \tag{2.80}$$

The commutators $[X_r,P_{Xr}]$, $[Y_r,P_{Yr}]$ and $[Z_r,P_{Zr}]$ are each $\mathrm{i}\hbar$, from equation (2.17), but all other 'cross commutators' $[X_r,P_{Yr}]$, $[P_{Xr},P_{Yr}]$, $[X_r,P_{Xs}]$ etc. are zero. Using these results it can be shown that the operator $\hat{J}^2$ commutes with $\hat{J}_X$, $\hat{J}_Y$ or $\hat{J}_Z$, and that these four operators each commute with the rovibronic Hamiltonian $\hat{H}_{\mathrm{rve}}$ given in equation (2.75). However, the three angular momentum component operators do not commute with each other, and we have the commutation relation

$$[\hat{J}_X, \hat{J}_Y] = \mathrm{i}\hbar\hat{J}_Z, \tag{2.81}$$

with two others obtained by cyclically permuting X, Y and Z. Referring $\hat{\boldsymbol{J}}$ to molecule-fixed axes x, y and z, as we will do when we derive the rotational Hamiltonian (see section 5.5), we obtain the commutation relation

$$[\hat{J}_x, \hat{J}_y] = -\mathrm{i}\hbar\hat{J}_z, \tag{2.82}$$

with two others being obtained by cyclic permutation of x, y and z. Note the opposite signs in these two equations.

The simultaneous eigenfunctions of $\hat{H}_{\mathrm{rve}}$, $\hat{\boldsymbol{J}}^2$ and $\hat{J}_Z$ are such that

$$\hat{\boldsymbol{J}}^2\Phi_{\mathrm{rve}} = J(J+1)\hbar^2\Phi_{\mathrm{rve}}, \tag{2.83}$$

and

$$\hat{J}_Z\Phi_{\mathrm{rve}} = m\hbar\Phi_{\mathrm{rve}}, \tag{2.84}$$

where the total orbital angular momentum quantum number $J = 0$, 1, 2,…, and the projection quantum number m has one of the $2J+1$ values 0, ± 1, ± 2, …, $\pm J$. Stationary state eigenfunctions of $\hat{H}_{\mathrm{rve}}$ can be labeled using J and m, and for a given value of J the state has a $2J+1$ fold m-degeneracy.

If it is necessary to consider the magnetic interactions of the electron spin we must use $\hat{H}_{\mathrm{rve}} + \hat{H}_{\mathrm{es}}$, which commutes with the square of the sum of the total orbital angular momentum (now called $\hat{\boldsymbol{N}}$) and the total electron spin angular momentum $\hat{\boldsymbol{S}}$; this sum is called $\hat{\boldsymbol{J}}$, i.e.

$$\hat{\boldsymbol{J}}^2 = (\hat{\boldsymbol{N}} + \hat{\boldsymbol{S}})^2, \tag{2.85}$$

and the good quantum numbers J and m now refer to the sum of the orbital and electron spin angular momenta. To include the effect of the nuclear hyperfine Hamiltonian we use $\hat{H}_{\mathrm{int}}$; see equation (2.77). This Hamiltonian commutes with the square of the total angular momentum $\hat{\boldsymbol{F}}^2$, which is the square of the sum of $\hat{\boldsymbol{N}}$, $\hat{\boldsymbol{S}}$ and $\hat{\boldsymbol{I}}$, where the latter is the total nuclear spin angular momentum. Thus

$$\hat{\boldsymbol{F}}^2 = (\hat{\boldsymbol{J}} + \hat{\boldsymbol{I}})^2 = (\hat{\boldsymbol{N}} + \hat{\boldsymbol{S}} + \hat{\boldsymbol{I}})^2. \tag{2.86}$$

The eigenstates of $\hat{H}_{\mathrm{int}}$ can be labeled using the total angular momentum quantum number F, and the projection quantum number $m_F = 0$, ± 1, ± 2, ..., $\pm F$. Angular momentum is discussed further in sections 5.5.2 and 14.5, and in problems 5.7 to 5.11.

2.8 The dipole moment operator and line strengths

To calculate the intensities of the lines in an absorption spectrum we need the line strengths. Having accurate line strengths is important if one wants to use a measured spectrum to determine the concentration of the species being observed, or if one wants to know the predicted intensities in a theoretically simulated spectrum. To calculate line strengths we use the rovibronic wavefunctions in integrals that are called *transition moments.*

For a gas phase sample illuminated by a weak electromagnetic radiation field the line strength of an electric dipole transition between all possible states Φ''_{rve} having energy E''_{rve}, and all possible states Φ'_{rve} having energy E'_{rve}, is

$$S(f \leftarrow i) = \sum_{\Phi'_{\mathrm{rve}},\Phi''_{\mathrm{rve}}} \sum_{A=X,Y,Z} \left| \int \Phi'^{*}_{\mathrm{rve}} \mu_A \Phi''_{\mathrm{rve}} \mathrm{d}\tau \right|^2, \tag{2.87}$$

where $\mathrm{d}\tau = \mathrm{d}X_2\mathrm{d}Y_2\mathrm{d}Z_2 \ldots \mathrm{d}X_l\mathrm{d}Y_l\mathrm{d}Z_l$ is the volume element for integration over the internal coordinate space of the l particles.

In equation (2.87), μ_A is the component of the molecular electric dipole moment along the A axis, and it is given by

$$\mu_A = \sum_r C_r e\, A_r, \tag{2.88}$$

where $C_r e$ and A_r are the charge and A coordinate of the rth particle (nuclei or electron) in the molecule, with $A = X$, Y or Z.

The integral that is squared and summed over in equation (2.87) is a component of the electric dipole transition moment; its square is a component of the electric dipole *transition probability.* In the case of degeneracies, that is if there is more than one eigenfunction Φ''_{rve} (or Φ'_{rve}) corresponding to the eigenvalue E'_{rve}(or E''_{rve}), we obtain the line strength by adding the individual transition probabilities for all transitions between the degenerate states; this is why there is the sum over Φ''_{rve} and Φ'_{rve} in equation (2.87). Notice that translation is completely removed here. That is because the translational energy of a molecule is unaffected by a weak radiation field; a weak radiation field can only change the internal state of a molecule.

Electromagnetic radiation consists of oscillating electric and magnetic fields, both of which contribute to its energy. Above we have discussed the intensity of resonantly absorbed electric field energy, and we have expressed this in terms of the electric dipole transition moment integral in equation (2.87). A molecule can also resonantly absorb magnetic field energy, and this can be expressed in terms of a magnetic dipole transition moment integral. However, the line strength of a typical magnetic dipole transition is about 10^{-5} of a typical electric dipole transition and so we usually ignore it, just as we usually ignore the extremely weak contribution to the electric field absorption line strength from electric quadrupole absorption, but if the electric dipole intensity is low for some reason these weak contributions to the line strength may have to be considered. In electron spin resonance spectroscopy, and nuclear magnetic resonance spectroscopy, the absorption process involves changing electron or nuclear spin states for which the electric dipole transition moment is zero; they are magnetic dipole transitions. Similarly, the electric field energy absorbed in the infrared region of the spectrum by low density molecular hydrogen gas results from electric quadrupole absorption since there is no electric dipole absorption.

2.9 Matrices and matrix algebra

In this section we give a brief review of the most important definitions required when using matrices. It can be looked over cursorily on a first reading. A *matrix* is an array of numbers (called elements) arranged in rows and columns; for example

$$G = \begin{bmatrix} 2 & 4 \\ 3 & 5 \end{bmatrix} \tag{2.89}$$

is a matrix. The matrix in equation (2.89) has two rows and two columns, it is a *square matrix*, but matrices are not necessarily square. An $n \times n$ square matrix (having n rows and n columns) is said to be n-dimensional. In a general matrix, A say, the element occurring at the intersection of the ith row and jth column is called A_{ij}. Thus, from equation (2.89) we have $G_{11} = 2$, $G_{12} = 4$, $G_{21} = 3$ and $G_{22} = 5$.

The *transpose* of a matrix A, say, is obtained by interchanging each element A_{ij} with the element A_{ji}, and the matrix is written $\tilde{A}$. Thus from equation (2.89)

$$\tilde{G} = \begin{bmatrix} 2 & 3 \\ 4 & 5 \end{bmatrix}. \tag{2.90}$$

If a matrix is equal to its transpose then the matrix is said to be *symmetric.*

The *Hermitian conjugate* (or *conjugate transpose*) $A^\dagger$ of a matrix A is obtained by taking the complex conjugate of the transpose of the matrix. Thus

$$A^\dagger = (\tilde{A})^* \tag{2.91}$$

and

$$(A^\dagger)_{ij} = A^*_{ji}. \tag{2.92}$$

A matrix that is equal to its Hermitian conjugate is *Hermitian.*

The sum of the diagonal elements of a square matrix is the *trace* of the matrix; the Greek letter chi (χ) is used for it. From equations (2.89) and (2.90) we have

$$\chi(G) = \chi(\tilde{G}) = 7. \tag{2.93}$$

The *determinant* of an $n \times n$ square matrix A is written as

$$\det A = |A| = \begin{vmatrix} A_{11} & A_{12} & A_{13} & \cdots & A_{1n} \\ A_{21} & A_{22} & A_{23} & \cdots & A_{2n} \\ A_{31} & A_{32} & A_{33} & \cdots & A_{3n} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ A_{n1} & A_{n2} & A_{n3} & \cdots & A_{nn} \end{vmatrix}. \tag{2.94}$$

The value of the determinant is given by the sum

$$|A| = \sum (-1)^h A_{1r_1} A_{2r_2} A_{3r_3} \ldots A_{nr_n}, \tag{2.95}$$

where the summation is over all $n!$ possible permutations of the order of the r_i. The $(n!)/2$ terms in the sum involving an even permutation of the order of the column labels r_i from the standard numerical order $123 \ldots n$ have h even [and are hence multiplied by $(-1)^h = +1$ in the sum] and the $(n!)/2$ terms involving an odd permutation have h odd [and are hence multiplied by $(-1)^h = -1$ in the sum]. An even (odd) permutation involves the product of an even (odd) number of pair interchanges. We give two examples to show how one uses this equation.

For the matrix G in equation (2.89) the determinant involves $n! = 2! = 2$ terms: $G_{11}G_{22}$ having no permutation of the order of the r_i so that $h = 0$, i.e., h even, and $G_{12}G_{21}$ having a single permutation of 1 with 2 so that $h = 1$, i.e., h odd. Thus, in the determinant sum $G_{11}G_{22} = 2\times5$ is preceded by $+1$ (since h is even), and $G_{12}G_{21} = 4\times3$ is preceded by -1 (since h is odd). We can thus write

$$|G| = \begin{vmatrix} 2 & 4 \\ 3 & 5 \end{vmatrix} = (2 \times 5) - (4 \times 3) = -2. \tag{2.96}$$

As a further example, the determinant of the 3-dimensional matrix

$$D = \begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix} \tag{2.97}$$

involves $n! = 3! = 6$ terms:

$D_{11}D_{22}D_{33}$ having $h = 0$ (the r_i are in the standard order),
$D_{11}D_{23}D_{32}$ having $h = 1$ (2 and 3 are exchanged),
$D_{12}D_{21}D_{33}$ having $h = 1$ (1 and 2 are exchanged),
$D_{13}D_{22}D_{31}$ having $h = 1$ (1 and 3 are exchanged),
$D_{12}D_{23}D_{31}$ having $h = 2$ (1 and 2 are exchanged, and then 1 and 3),
and
$D_{13}D_{21}D_{32}$ having $h = 2$ (1 and 3 are exchanged, and then 1 and 2).

Three have h even (and their product is preceeded by $+1$ in the determinant sum), and three have h odd (and their product is preceeded by -1 in the determinant sum). Using this result, but writing out the sum in a way that shows how the determinant can be written by building it up from the determinants of 2×2 sub-matrices within the 3×3 matrix, we have

$$|D| = 1(5 \times 9 - 6 \times 8) - 2(4 \times 9 - 6 \times 7) + 3(4 \times 8 - 5 \times 7) = 0. \tag{2.98}$$

We set up electronic wavefunctions as *Slater determinants* in equation (3.28), and in this application the most significant property that follows from the definition of a determinant, given in equation (2.95), is that the determinant of a matrix will change sign if two rows are interchanged, or if two columns are interchanged. From this it follows that the determinant of a matrix will vanish if two rows are identical, or if two columns are identical.

The *product* of an $n \times m$ matrix A (having n rows and m columns) and an $m \times q$ matrix B in the order AB is an $n \times q$ matrix C where the ijth element of C is given by

$$C_{ij} = \sum_{k=1}^{m} A_{ik} B_{kj}. \tag{2.99}$$

For example, if the matrices A and B are

$$A = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \quad \text{and} \quad B = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}, \tag{2.100}$$

then equation (2.99) gives the (1,1) element of the product matrix C as:

$$\begin{aligned} C_{11} &= A_{11} \times B_{11} + A_{12} \times B_{21} \\ &= (-1/2) \times (-1/2) + \left(\sqrt{3/2}\right) \times \left(\sqrt{3/2}\right) \\ &= 1. \end{aligned} \tag{2.101}$$

The (1,2) element of the product matrix C is given by:

$$\begin{aligned} C_{12} &= A_{11} \times B_{12} + A_{12} \times B_{22} \\ &= (-1/2) \times \big(-\sqrt{3/2}\big) + \big(\sqrt{3/2}\big) \times (-1/2) \\ &= 0. \end{aligned} \tag{2.102}$$

We can use equation (2.99) to similarly determine that $C_{21} = 0$ and that $C_{22} = 1$. Thus, we can write out the product matrix C in full as

$$C = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}. \tag{2.103}$$

From equation (2.99) we see that for the multiplication between A and B to be possible the matrices A and B must be *conformable*, i.e., the number of columns in A must be equal to the number of rows in B. This means that, for example, A and B can both be m-dimensional square matrices, and their product C will be an m-dimensional square matrix. A can be a square matrix with dimension m, B can be a single column matrix with length m, and their product will be a column matrix with length m. A can be a single row matrix of length m, B can be a square matrix of dimension m, and their product will be a single row matrix of length m. A can be a single row matrix of length m, B can be a be a single column matrix with length m, and their product will be a single number. Other possibilities are obtained by choosing particular values for n and q in equation (2.99). Matrix multiplication, like quantum mechanical operator multiplication, is not necessarily commutative.

An n-dimensional square matrix E that has 1 in all diagonal positions and zero in all off-diagonal positions is called an n-dimensional *unit matrix*. The matrix C in equation (2.103) is a two-dimensional unit matrix. It is customary to use the letter E for a unit matrix. If we multiply an n-dimensional square matrix A by the n-dimensional unit matrix E the result is A. That is the matrix E plays the role in matrix multiplication that unity plays in the ordinary algebraic multiplication of numbers. Square matrices having all off-diagonal elements equal to zero are said to be *diagonal*, and the unit matrix is a special case of a diagonal matrix in which all diagonal elements are unity.

If the product of two n-dimensional square matrices A and B is the n-dimensional unit matrix E, i.e., if

$$A\,B = E, \tag{2.104}$$

then we say that one matrix is the inverse (or reciprocal) of the other, and we write

$$A^{-1} = B \quad \text{or} \quad B^{-1} = A. \tag{2.105}$$

The matrices A and B in equation (2.100) are the inverse of each other; their product is the two-dimensional unit matrix from equation (2.103). Only square matrices can have a unique inverse, and efficient computer routines exist for finding matrix inverses. However, the inverse of a matrix will not exist if the determinant of the matrix is zero; a matrix having a determinant that is zero is said to be *singular*. The matrix D in equation (2.97) is singular from equation (2.98). If the inverse of a matrix is equal to the transpose of the matrix then the matrix is *orthogonal*; the matrices A and B in equation (2.100) are orthogonal. If the inverse of a matrix is equal to the Hermitian conjugate of the matrix then the matrix is *unitary*.

2.10 Problems

2.1 Using equation (2.1), together with the fact that $\exp(2\mathrm{i}n\pi) = 1$ only if n is a positive or negative integer, determine the eigenvalues E_n and eigenfunctions $\psi_n(\alpha)$ of the operator $\mathrm{d}/\mathrm{d}\alpha$ for the situation where α is an angle, which means that the eigenfunctions are restricted to satisfy $\psi_n(\alpha + 2\pi) = \psi_n(\alpha)$. Determine also the eigenfunctions and eigenvalues of the operator $-\mathrm{i}\mathrm{d}/\mathrm{d}\alpha$. Which of the operators $\mathrm{d}/\mathrm{d}\alpha$ and $-\mathrm{i}\mathrm{d}/\mathrm{d}\alpha$ is Hermitian?

2.2 Are the eigenfunctions in problem (i) also eigenfunctions of the operator $\mathrm{d}^2/\mathrm{d}\alpha^2$?

2.3 A particle of mass M moving on a circular path of radius R has angular coordinate α. The energy of the particle is $P^2/2M$ and its angular momentum is $J = PR$. By expressing the energy in terms of the angular momentum, and then substituting the quantum mechanical operator $\hat{J} = -\mathrm{i}\hbar\mathrm{d}/\mathrm{d}\alpha$, determine the Hamiltonian, the Schrödinger equation and the quantized energies. The product MR^2 that scales the energy level spacings is called the *moment of inertia* of an orbiting particle. Determine the energy level spacings for orbiting atoms having various values of M and R.

2.4 Show how equations (2.38)-(2.40) are obtained from equations (2.34) and (2.37).

2.5 Use equations (2.34)-(2.37) for the 2×2 perturbation problem to determine S, c^+ and c^- for the situation with a constant off-diagonal matrix element H_{12} of 10 cm^{-1} but with the zero order level separation Δ being 0, 1, 10, 100 and 1000 cm^{-1}, respectively. Compare the results with the approximate values obtained using equations (2.38)-(2.40).

2.6 Prove that the ij element of the n-dimensional square matrix D that is the product of three n-dimensional square matrices A, B and C

in the order ABC is given by

$$D_{ij} = \sum_{k=1}^{n} \sum_{l=1}^{n} A_{ik} B_{kl} C_{lj}. \tag{2.106}$$

2.7* Prove that if any n-dimensional square matrix R say, is premultiplied by the nonsingular n-dimensional square matrix Q, and postmultiplied by the inverse matrix Q^{-1}, then the character of the resultant matrix $S = Q\,R\,Q^{-1}$ is the same as that of the matrix R, i.e. prove

$$\chi(S) = \chi(Q\,R\,Q^{-1}) = \chi(R) = \sum_{i=1}^{n} R_{ii}. \tag{2.107}$$

2.8 Evaluate the determinants of the matrices A and B given in equation (2.100).

Chapter 3

Electronic states

From equation (2.75) for $\hat{H}_{\mathrm{rve}}$, we see that the rovibronic Schrödinger equation (2.76) does not involve molecular parameters, such as bond lengths and angles, and that the only quantities occurring are the masses and charges of the l particles (nuclei and electrons) that make up the molecule. Thus, we can easily set up the Schrödinger equation for any molecule. One might think that we could then simply use numerical methods to solve it. However, even using the most efficient numerical methods, current computers do not have enough power for this to be possible with the required precision except for three and four particle systems such as H_2^+ and H_2. This will change as computer power increases.

For most molecules, to solve the rovibronic Schrödinger equation accurately, we are forced to make approximations and then to correct for them as best we can. The approximations introduce concepts that allow us to *understand* molecules.

Such concepts as electronic state, molecular orbital, electronic configuration, potential energy surface, equilibrium structure, force constant, electronic and vibrational angular momentum, and Coriolis coupling constant come about because of approximations that are introduced. However, these concepts are only satisfactory and useful if the approximations that lead to their introduction are reasonably valid.

3.1 The Born-Oppenheimer approximation

To solve the rovibronic Schrödinger equation we change coordinates so that it separates into simpler Schrödinger equations. Approximations have to be made, but by choosing appropriate coordinates the approximations are minimized. The first separation we make is that of the electronic motion from the nuclear motion. To do this we change coordinates in $\hat{H}_{\rm rve}$, as given in equation (2.75), from $(X_2,Y_2,Z_2,\ldots,Z_l)$ to $(\xi_2,\eta_2,\zeta_2,\ldots,\zeta_l)$, where the $\xi\eta\zeta$ axis system is parallel to the XYZ axis system but has origin at the nuclear centre of mass rather than the molecular centre of mass. This choice of origin allows us to refer the motion of the electrons to the positions of the nuclei, and it gives a kinetic energy expression that is completely separable into an electronic kinetic energy $\hat{T}_{\rm e}$ and a nuclear kinetic energy $\hat{T}_{\rm N}$. In these new coordinates the rovibronic Hamiltonian can be written:

$$\hat{H}_{\rm rve} = \hat{T}_{\rm e} + \hat{T}_{\rm N} + V_{\rm ee} + V_{\rm NN} + V_{\rm Ne}, \tag{3.1}$$

and the rovibronic Schrödinger equation is

$$\left[\hat{T}_{\rm e} + \hat{T}_{\rm N} + V_{\rm ee} + V_{\rm NN} + V_{\rm Ne}\right]\Phi_{\rm rve} = E_{\rm rve}\Phi_{\rm rve}, \tag{3.2}$$

where the electrostatic potential energy given in equation (2.75) has been written as $(V_{\rm ee} + V_{\rm NN} + V_{\rm Ne})$. $V_{\rm ee}$ is the sum of all the electron-electron electrostatic repulsions, and it only involves the coordinates of the electrons. $V_{\rm NN}$ is the sum of all the nuclear-nuclear electrostatic repulsions, and it only involves the coordinates of the nuclei. $V_{\rm Ne}$ is the sum of all the electron-nuclear electrostatic attractions, and it involves the coordinates of the nuclei and electrons.

Although the kinetic energy is completely separable into electronic and nuclear parts in these coordinates, the potential energy is not because of the presence of the electron-nuclear attraction term $V_{\rm Ne}$. This part of V is the glue that holds the molecule together and we cannot just neglect it. We cannot chose coordinates in such a way that the potential function separates into two non-interacting parts where one part just involves the nuclear coordinates and the other the electron coordinates, and we cannot follow the simple separation of variables procedure that we used to separate translational and the internal degrees of freedom in section 2.5.

All is not lost, however. We saw at the end of section 2.5.1 that

> because electrons are so much lighter than nuclei, the first excited electronic state is at a much higher energy than the first excited vibrational state. Knowledge of this leads us to treat the rovibronic Schrödinger equation in a special way, by using the Born-Oppenheimer approximation, to separate it into nuclear and electronic parts.

To understand this approximation it is helpful to view a molecule as having a nuclear framework that rotates and vibrates, while at the same time the electron cloud is continually modifying its shape so as to conform to the instantaneous nuclear geometry. It would be more appropriate to think of the electronic wavefunction as varying with the nuclear coordinates, and from it one can calculate the electronic probability distribution. Using this idea, the electronic wavefunction is obtained in the Born-Oppenheimer approximation by solving the rovibronic Schrödinger equation with the nuclei fixed at an appropriate geometry, and with only the electronic coordinates as variables. This means that in equation (3.2), we put $T_{\mathrm{N}} = 0$ (the nuclear kinetic energy is zero because the nuclei are held fixed), and neglect V_{NN} (since we are only concerned with the electron dynamics) to give:

$$\left[\hat{T}_e + V_{\mathrm{ee}} + V_{\mathrm{Ne}}\right]\Phi_{\mathrm{elec},n} = \hat{H}_{\mathrm{elec}}\Phi_{\mathrm{elec},n} = V_{\mathrm{elec},n}\Phi_{\mathrm{elec},n}, \tag{3.3}$$

where a particular nuclear geometry is chosen in V_{Ne}, and n labels the successive *electronic states* ($n = 1, 2, \ldots$). This equation is the electronic Schrödinger equation, and it is solved at many different nuclear geometries to yield the electronic wavefunctions $\Phi_{\mathrm{elec},n}$ (which are functions of the electronic coordinates), and energies $V_{\mathrm{elec},n}$; $\Phi_{\mathrm{elec},n}$ and $V_{\mathrm{elec},n}$ are each a parametric function of nuclear geometry.

The calculation of the electronic wavefunction as described above has been achieved by holding the nuclei fixed. To calculate the energies for the nuclear motion we must allow them to move under the constraint of the electrostatic nuclear-nuclear repulsion potential energy term V_{NN} in equation (3.1), but we must also include the constraint imposed by the fact that the electronic energy V_{elec} depends on the nuclear geometry. The need to include this extra constraint is easy to appreciate. Suppose the nuclei move from one geometry to another in which V_{NN} is higher and that simultaneously V_{elec} is also higher; in this case the nuclei have to work against the combined energy of ($V_{\mathrm{NN}} + V_{\mathrm{elec}}$), and this function (which depends on the nuclear geometry) provides the *potential energy surface* for the nuclear motion. For each electronic state n there will be a different potential energy surface ($V_{\mathrm{NN}} + V_{\mathrm{elec},n}$), and a different nuclear motion (rotation-vibration) Schrödinger equation given by

$$\left[\hat{T}_{\mathrm{N}} + V_{\mathrm{NN}} + V_{\mathrm{elec},n}\right]\Phi_{\mathrm{rv},nj} = E^0_{\mathrm{rve},nj}\Phi_{\mathrm{rv},nj}, \tag{3.4}$$

where j ($= 1, 2, \ldots$) labels the rotation-vibration states in the same way that n labels the electronic states from equation (3.3).

In equation (3.4) $E^0_{\mathrm{rve},nj}$ is the rovibronic energy for the j'th rotation-vibration level in the n'th electronic state, within the Born-Oppenheimer approximation. We rewrite the equation so that the zero of energy in each electronic state is the minimum value of ($V_{\mathrm{NN}} + V_{\mathrm{elec},n}$), which we call the *electronic energy* $E_{\mathrm{elec},n}$ of the electronic state n,[1] and we obtain the

---

[1] The electronic term value in cm^{-1} is called $T_{\mathrm{e}}(n)$.

rotation-vibration Schrödinger equation as

$$\left[\hat{T}_{\mathrm{N}} + V_{\mathrm{N},n}\right]\Phi_{\mathrm{rv},nj} = \hat{H}_{\mathrm{rv}}\Phi_{\mathrm{rv},nj} = E_{\mathrm{rv},nj}\Phi_{\mathrm{rv},nj}, \tag{3.5}$$

where

$$V_{\mathrm{N},n} = V_{\mathrm{NN}} + V_{\mathrm{elec},n} - E_{\mathrm{elec},n} \tag{3.6}$$

and

$$E_{\mathrm{rv},nj} = E^0_{\mathrm{rve},nj} - E_{\mathrm{elec},n}. \tag{3.7}$$

To solve the electronic and rotation-vibration Schrödinger equations, we refer the electrons and nuclei to molecule-fixed xyz axes in order to separate rotation. These axes have origin at the nuclear centre of mass, like the $\xi\eta\zeta$ axes, but they are attached to the molecule so that they rotate with it (see section 4.1).

In making a summary of the above it is helpful to represent the nuclear coordinates as $\boldsymbol{R}_{\mathrm{N}}$ and the electronic coordinates as $\boldsymbol{r}_{\mathrm{elec}}$. In the Born-Oppenheimer approximation the rovibronic eigenfunctions are the products

$$\Phi^0_{\mathrm{rve},nj}(\boldsymbol{R}_{\mathrm{N}}, \boldsymbol{r}_{\mathrm{elec}}) = \Phi_{\mathrm{elec},n}(\boldsymbol{R}_{\mathrm{N}}, \boldsymbol{r}_{\mathrm{elec}})\Phi_{\mathrm{rv},nj}(\boldsymbol{R}_{\mathrm{N}}), \tag{3.8}$$

and the rovibronic eigenvalues are the sum

$$E^0_{\mathrm{rve},nj} = E_{\mathrm{elec},n} + E_{\mathrm{rv},nj}. \tag{3.9}$$

We have reduced the problem of solving the $(3l{-}3)$-dimensional rovibronic Schrödinger equation (3.2), to one of solving two differential equations: Equation (3.3), which is the $3(l-N)$-dimensional electronic Schrödinger equation for $\Phi_{\mathrm{elec},n}(\boldsymbol{R}_{\mathrm{N}}, \boldsymbol{r}_{\mathrm{elec}})$ and $V_{\mathrm{elec},n}(\boldsymbol{R}_{\mathrm{N}})$ (and $E_{\mathrm{elec},n}$), and equation (3.5), which is the $(3N{-}3)$-dimensional rotation-vibration Schrödinger equation for $\Phi_{\mathrm{rv},nj}(\boldsymbol{R}_{\mathrm{N}})$ and $E_{\mathrm{rv},nj}$. Fortunately, it is usually the case that only the very lowest eigenstates of equation (3.3) are of interest, and efficient variational methods have been developed to obtain them even for molecules having many electrons (see section 3.3).

The Born-Oppenheimer approximation introduces the concepts of electronic state and electronic potential energy surface $V_{\mathrm{N},n}(\boldsymbol{R}_{\mathrm{N}})$. Potential energy surfaces are independent of isotopic substitution because the nuclear masses do not enter[2] equation (3.3). The nuclear geometry at the minimum of the potential energy surface of an electronic state is the *equilibrium geometry* of that state; it is the geometry at which the nuclei would naturally come to rest if they moved classically on the surface, and it is the geometry at which $V_{\mathrm{N},n}(\boldsymbol{R}_{\mathrm{N}}) = 0$. The *structure* of a molecule is its structure at the equilibrium configuration of its ground electronic state within the Born-Oppenheimer approximation.

---

[2] Within the Born-Oppenheimer approximation, a small nuclear-mass dependent electron kinetic energy term $\hat{T}'_e$ is neglected.

The exact rovibronic wavefunctions Φ_{rve} are (by definition) eigenfunctions of the rovibronic Hamiltonian $\hat{H}_{\mathrm{rve}}$ given in equation (3.2), but the functions Φ^0_{rve} are not since it can be shown that

$$\hat{H}_{\mathrm{rve}}\Phi^0_{\mathrm{rve},nj} = E^0_{\mathrm{rve},n}\Phi^0_{\mathrm{rve},nj} + H', \tag{3.10}$$

where $H' = 0$ only if

$$\hat{T}_{\mathrm{N}}\Phi_{\mathrm{elec},n}(\boldsymbol{R}_{\mathrm{N}}, \boldsymbol{r}_{\mathrm{elec}})\Phi_{\mathrm{rv},nj}(\boldsymbol{R}_{\mathrm{N}}) = \Phi_{\mathrm{elec},n}(\boldsymbol{R}_{\mathrm{N}}, \boldsymbol{r}_{\mathrm{elec}})\hat{T}_{\mathrm{N}}\Phi_{\mathrm{rv},nj}(\boldsymbol{R}_{\mathrm{N}}), \tag{3.11}$$

that is, only if $\hat{T}_{\mathrm{N}}$ and $\Phi_{\mathrm{elec},n}$ commute. Put another way, $H' = 0$ only if the effect of $\hat{T}_{\mathrm{N}}$ acting on all the $\Phi_{\mathrm{elec},n}$ is neglected. However, this is not the whole story, and the energy separation between electronic states also enters.

The separation in energy between the zero order Born-Oppenheimer states $\Phi_{\mathrm{elec},n}\Phi_{\mathrm{rv},nj}$ and $\Phi_{\mathrm{elec},m}\Phi_{\mathrm{rv},mk}$ is

$$\Delta(nj; mk) = (E_{\mathrm{elec},m} + E_{\mathrm{rv},mk}) - (E_{\mathrm{elec},n} + E_{\mathrm{rv},nj}). \tag{3.12}$$

The off-diagonal matrix element of the rovibronic Hamiltonian between these states is

$$H(nj; mk) = \int \Phi^*_{\mathrm{elec},n}\Phi^*_{\mathrm{rv},nj}\hat{T}_{\mathrm{N}}\Phi_{\mathrm{elec},m}\Phi_{\mathrm{rv},mk}\mathrm{d}\tau, \tag{3.13}$$

since the electronic off-diagonal matrix elements of $(T_e + V_{\mathrm{ee}} + V_{\mathrm{Ne}})$ and of V_{NN} vanish at all nuclear geometries. From equations (2.31)-(2.40) we see that the extent to which these two levels perturb each other depends on the ratio $H(nj; mk)/\Delta(nj; mk)$. If this ratio is small there will be little mixing of the states, i.e. little breakdown of the Born-Oppenheimer approximation.

For almost all molecules the excited electronic states are at energies well above the ground electronic state. Thus the Born-Oppenheimer approximation is almost invariably a good approximation for the levels of the ground electronic state. A significant breakdown of the Born-Oppenheimer approximation often occurs in excited electronic states if there are other excited electronic states nearby in energy.