

## Chapter 14

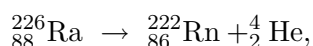
# Solving Schrödinger's Wave Equation - (2)

### Topics

*Examples of quantum mechanical tunnelling: radioactive  $\alpha$ -decay, the ammonia molecule, tunnel diodes, the scanning tunnelling microscope. The quantisation of angular momentum, the rotational spectra of diatomic molecules. The quantum harmonic oscillator. Vibrations of a diatomic molecule.*

### 14.1 Radioactive $\alpha$ -Decay

The most famous application of quantum mechanical tunnelling is to the process of radioactive  $\alpha$ -decay of heavy nuclei, first described by George Gamow in 1928. An  $\alpha$ -particle is a helium nucleus consisting of two protons and two neutrons. In such a radioactive decay, the parent nucleus decays into a lighter nucleus with two fewer protons and two fewer neutrons, ejecting an  $\alpha$ -particle in the process. Perhaps the most famous  $\alpha$ -decay is the decay of radium into radon discovered by Marie Curie,



where the superscripts are the mass numbers and the subscripts the atomic numbers of the nuclei. The half-life of this isotope of radium is 1,602 years.

In general, in the process of  $\alpha$ -decay, the kinetic energies of the ejected  $\alpha$ -particles range from  $E_\alpha = 1.9$  MeV to 9.2 MeV.

One of the features of  $\alpha$ -decay is that, although there is a relatively narrow range in the kinetic energies of the  $\alpha$ -particles, the range of their half-lives  $t_{1/2}$  is enormous, from about  $3 \times 10^{-7}$  seconds to  $2 \times 10^{17}$  years. There is a relation between  $E_\alpha$  and  $t_{1/2}$  which is known as the *Geiger-Nuttall law*,

$$\log t_{1/2} = AE_\alpha^{-1/2} - \text{constant}. \quad (14.1)$$

Let us see if we can account for this relation in terms of quantum mechanical tunnelling.

The de Broglie wavelength of a 5 MeV  $\alpha$ -particle is  $\lambda = h/p = h/\sqrt{2mE} = 7 \times 10^{-15}$  m. This is of the same order as the size of the nucleus and suggests a model in which the  $\alpha$ -particle is trapped within the potential well of the nucleus, which can be approximated as a square well potential. Outside the sphere of influence of the strong nuclear forces, the potential experienced by the  $\alpha$ -particle is just the repulsive electrostatic force of the remaining positive charge of the nucleus, as demonstrated by Rutherford's  $\alpha$ -particle scattering experiments. If the nuclear charge is initially  $Z$ , then outside the nucleus the electrostatic potential energy of the  $\alpha$ -particle is

$$V = \frac{2 \times (Z - 2)e^2}{4\pi\epsilon_0 r}$$

A simple model for the potential experienced by the  $\alpha$ -particle is shown in Figure 14.1, where  $r_0$  is the radius of the nuclear potential well, which we can think of as the radius of the nucleus. Within  $r_0$ , the nucleus is held together by the strong nuclear force which is represented by the negative potential at  $r \leq r_0$ .

We can imagine that the protons and neutrons moving within the nuclear potential are continually assembling themselves into loose associations of  $\alpha$ -particles which rapidly dissociate. If the energy of the  $\alpha$ -particle association in the nucleus is negative, as represented, for example, by the line X in Figure 14.1, it cannot escape from the nucleus. If, however, it has positive energy, for example, the

These energetic particles are important in cancer therapy – on passing through the cancerous cells, the  $\alpha$ -particles are decelerated and their kinetic energies are deposited as heat which kills the cells.

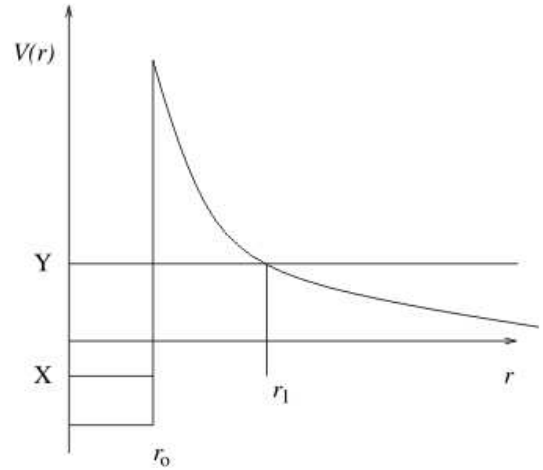


Figure 14.1. Model potential for  $\alpha$  decay

line Y in Figure 14.1, it can escape by quantum mechanical tunnelling. By the same types of random collision processes which we discussed in connection with the Boltzmann and Maxwell distributions,  $\alpha$ -particles can acquire a significant amount of kinetic energy and so can have positive energy, as illustrated by the line Y.

We can develop a simple model to work out the rate at which such  $\alpha$ -decays should take place. We suppose that the  $\alpha$ -particle associations in the nucleus have speed  $v$  and, every time one of these crosses the nucleus, there is a probability  $p$  that it will tunnel through the potential barrier. The number of attempted tunnelling events per second is  $\sim Nv/2r_0$ , where  $N$  is the average number of  $\alpha$ -particle associations present in the nucleus. If the kinetic energy of the particle is  $E_\alpha$ , the width of the potential barrier is from  $r_0$  to  $r_1$ , where the value of  $r_1$  is found from the condition that the kinetic energy of the  $\alpha$ -particles is equal to the electrostatic potential energy at  $r_1$ ,

$$r_1 = \frac{2(Z-2)e^2}{4\pi\epsilon_0 E_\alpha}. \quad (14.2)$$

The probability of successful tunnelling is

$$p = \frac{|\psi(r > r_1)|^2}{|\psi(r < r_0)|^2},$$

and hence the rate of decay, that is, the probability  $\lambda$  that the particle decays in one second is

$$\lambda \approx \frac{Nv}{2r_0} \frac{|\psi(r > r_1)|^2}{|\psi(r < r_0)|^2}. \quad (14.3)$$

**The following mathematical details are non-examinable**

The only problem is that, unlike our previous analysis, the barrier is no longer of constant height. We can take account of this approximately by treating the barrier as the sum of many small barriers of width  $\Delta r$ , across each of which the amplitude of the wavefunction decreases by  $\exp[-\sqrt{2m(V-E)} \Delta r/\hbar] =$

$\exp(-\alpha \Delta r)$  (Figure 14.2). Therefore the decrease in amplitude of the wavefunction is

$$\begin{aligned} \frac{\psi(r > r_1)}{\psi(r < r_0)} &\approx \prod_i \exp(-\alpha \Delta r_i) \\ &= \exp \left( - \sum_i \alpha \Delta r_i \right), \end{aligned}$$

noting that  $\alpha$  is a function of  $r$ .

In the limit, we can replace the sum by an integration and then,

$$\begin{aligned} \frac{\psi(r > r_1)}{\psi(r < r_0)} &\approx \exp \left( - \int_{r_0}^{r_1} \alpha dr \right) \\ &= \exp \left\{ - \int_{r_0}^{r_1} \frac{\sqrt{2m}}{\hbar} \left[ \frac{2(Z-2)e^2}{4\pi\epsilon_0 r} - E \right]^{1/2} dr \right\}. \end{aligned}$$

and the probability is the square of this ratio.

The details of how to carry out this integral are given in the margin note. The result is

$$\lambda \approx \frac{Nv}{2r_0} \exp \left\{ -2 \left[ \frac{mr_1(Z-2)e^2}{\pi\epsilon_0 \hbar^2} \right]^{1/2} \left[ \cos^{-1} \left( \frac{r_0}{r_1} \right)^{1/2} - \left( \frac{r_0}{r_1} \right)^{1/2} \left( 1 - \frac{r_0}{r_1} \right)^{1/2} \right] \right\}. \quad (14.4)$$

Let us assume that the potential barrier is thick so that  $r_1 \gg r_0$ . Then, inspecting the second term in square brackets, the term in  $\cos^{-1}$  becomes  $\pi/2$  and the second term becomes very small. Therefore, from (14.4), we find

$$\begin{aligned} \lambda &\approx \frac{Nv}{2r_0} \exp \left\{ -2 \left[ \frac{mr_1(Z-2)e^2}{\pi\epsilon_0 \hbar^2} \right]^{1/2} \times \frac{\pi}{2} \right\}, \\ &= \frac{Nv}{2r_0} \exp \left\{ - \left[ \frac{2(Z-2)e^2\pi}{4\pi\epsilon_0 \hbar} \right] \left( \frac{2m}{E_\alpha} \right)^{1/2} \right\}. \end{aligned} \quad (14.5)$$

Therefore, the typical half-life of the parent nucleus for  $\alpha$ -decay is  $t_{1/2} \approx \lambda^{-1}$ , that is

$$t_{1/2} \approx \frac{2r_0}{Nv} \exp \left\{ \left[ \frac{2(Z-2)e^2\pi}{4\pi\epsilon_0 \hbar} \right] \left( \frac{2m}{E_\alpha} \right)^{1/2} \right\}. \quad (14.6)$$

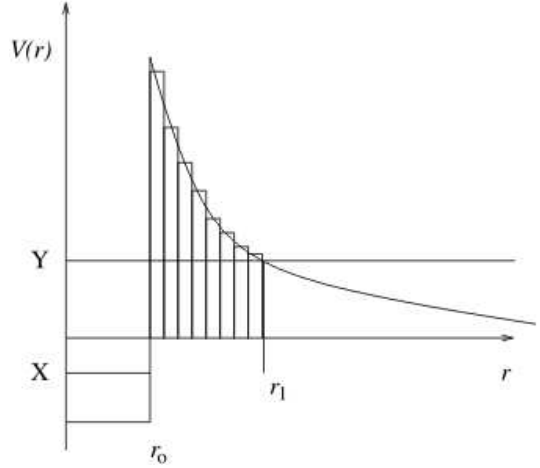


Figure 14.2. Model potential for  $\alpha$  decay

approximated by a series of constant potential steps of width  $\Delta r_i$ .

#### Performing the integral

The first thing to do is to simplify the integral so that it has the form

$$\int_{r_0}^{r_1} \text{constant} \left( \frac{1}{r} - \frac{1}{r_1} \right)^{1/2} dr.$$

Substituting  $y = (r/r_1)^{1/2}$ , the integral becomes

$$2r_1^{1/2} \int_{y_0}^{y_1} (1 - y^2)^{1/2} dy.$$

Then, using  $y = \sin \theta$ , or  $y = \cos \theta$ , the solution

$$r_1^{1/2} [\sin \theta \cos \theta - \theta]_{\theta_0}^{\theta_1}$$

is found. Substituting the limits of the integral and rearranging the result, we find

$$r_1^{1/2} \left[ \cos^{-1} \left( \frac{r_0}{r_1} \right)^{1/2} - \left( \frac{r_0}{r_1} \right)^{1/2} \left( 1 - \frac{r_0}{r_1} \right)^{1/2} \right]$$

Taking logarithms and substituting for the values of the constants, we find

$$\log_{10} t_{1/2} = \log_{10} \left( \frac{2r_0}{Nv} \right) + 1.71(Z - 2)E_\alpha^{-1/2}, \quad (14.7)$$

where the energy of the particle  $E_\alpha$  is in MeV.

This is the *Geiger-Nuttall law* and it has a number of important features. Notice that the quantities which we do not know very well,  $N$  and  $v$ , appear inside the logarithm and so we do not need to know them very accurately. The half-life is, however, very sensitive to the values of  $Z$  and  $E_\alpha$ . For isotopes with  $Z \approx 90$ , a change of a factor of four in  $E_\alpha$  results in a change in  $t_{1/2}$  by a factor of about  $10^{77}$ ! Although this is a bit on the large side, it does show that a very wide range of half-lives is obtained for a small change in the energy of the  $\alpha$ -particle.

The importance of this result, first derived by Gamow, was that it was the first successful application of quantum mechanics to the physics of the nucleus.

## 14.2 Other examples

### 14.2.1 The Ammonia Molecule

The ammonia molecule  $\text{NH}_3$  has the form of a tetrahedron and is shown in Figure 14.3 with the nitrogen atom at the top. If the nitrogen atom were to try to move downwards towards the plane of the triangle of hydrogen atoms, it would be repelled by the hydrogen atoms and so classically cannot pass through the triangle to the other side. This barrier is represented in Figure 14.4.

According to quantum mechanics, however, the nitrogen atom can penetrate the barrier and, in fact, does so with a frequency of about  $10^{10}$  oscillations per second.

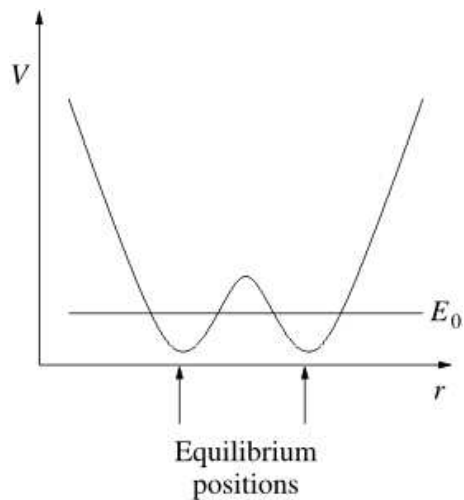
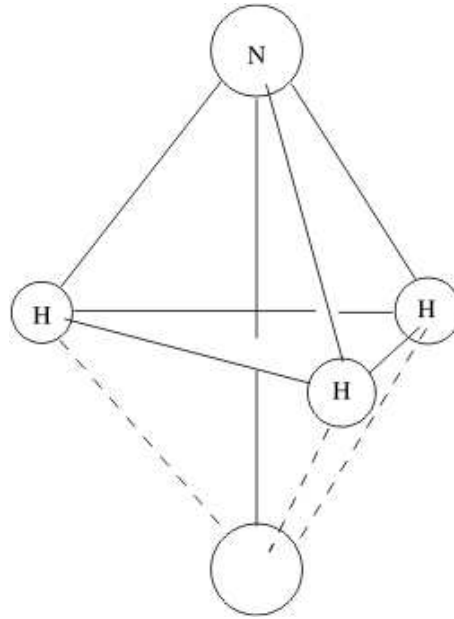


Figure 14.4. Illustrating the potential barrier between the two states of the ammonia molecule.

### 14.2.2 The Tunnel Diode

Tunnel diodes are semiconductor devices in which the conduction electrons encounter a potential barrier of the type shown in the diagram. Classically, the electrons cannot penetrate the barrier but they can pass through quantum mechanically. The important feature of the tunnel diode is that the rate at which electrons pass through the potential barrier can be regulated by varying the height of the voltage barrier. This can be done very rapidly and so switching frequencies of  $10^9$  Hz or more can be achieved.

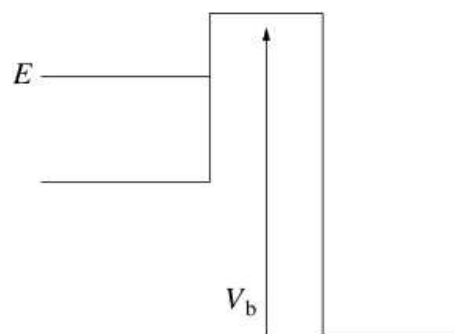


Figure 14.5. The potential barrier for a tunnel diode. The height of the barrier potential can be altered by changing the bias voltage  $V_b$ .

### 14.2.3 Scanning Tunneling Microscope

This device was invented by Gerd Binnig and Heinrich Rohrer in 1982 and enables surfaces to be imaged with atomic precision. An extremely sharp conducting needle is scanned across the surface and a small bias voltage is applied between the tip and the surface. As a result of quantum mechanical tunnelling, a current flows. The height of the needle is continually adjusted to keep the current constant and as a result the contours of the surface of the material can be measured with an accuracy of better than 0.01 nm.

In Figure 14.6, a scanning tunnel microscope image is shown of a ring of 36 cobalt atoms which have been placed in an elliptical ring on a copper surface. Within the ring, a series of concentric ellipses can be seen which represent the total probabilities associated with the wave functions of all the cobalt atoms adding coherently within the ring.

An ellipse has the property that the sum of the distances from a point on the ellipse to the two foci is a constant. In the experiment shown in the left hand images of Figure 14.6, a cobalt atom is placed at one focus of the ellipse and a 'mirage' of that atom is observed in the other focus. The wave functions from the atom at one focus add coherently at the other focus, since all paths from the one focus to the other are the same for the 'reflection' of the wave functions by the ellipse. The intensity of the

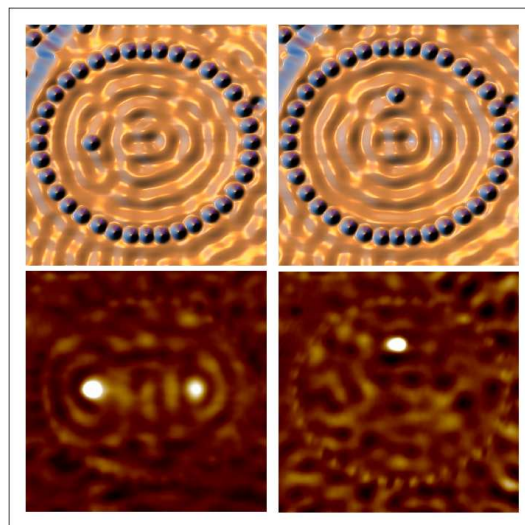


Figure 14.6. A scanning tunnel microscope image of an ellipse of 36 cobalt atoms. If a cobalt atom is placed at one focus, a 'mirage' atom is observed at the other focus. If the atoms is not at a focus, no mirage is observed.

mirage is about one third of that of the real atom. The same image is shown in Figure 14.7.

If the cobalt atom is not placed at the focus, as in the right hand panels in Figure 14.6, no mirage is observed.

### 14.3 The quantisation of angular momentum and the rotational spectra of diatomic molecules

In our development of the Bohr model of the hydrogen atom, we noted the central role which the quantisation of angular momentum plays in determining the energy levels in the hydrogen atom.

$$J = m_e v r = n \hbar$$

or, in vector form,

$$\mathbf{J}^2 = n^2 \hbar^2 \quad \text{with } n = 1, 2, 3, \dots \quad (14.8)$$

The quantisation of angular momentum carries over into the full quantum theory, but with some important differences. For motion about a single axis, say the  $z$ -axis, the result has the same form as we met for the hydrogen atom

$$J_z = m_j \hbar \quad \text{with } m_j = 1, 2, 3, \dots \quad (14.9)$$

The explanation of this result is very similar to the argument we developed for the Bohr atom – the wave function must form a standing wave pattern in the angular direction about the  $z$  axis.

When we consider the *total angular momentum*, the result is however more complicated and takes the form

$$\mathbf{J}^2 = j(j+1)\hbar^2 \quad \text{with } j = 0, 1, 2, 3, \dots \quad (14.10)$$

One of the  $j$ s in Bohr's formula (14.8) has been replaced by  $j+1$ . There are all sorts of other rules about angular momentum in quantum mechanics, some of which we will describe later in this section.

We can understand qualitatively why the expression for the total angular momentum should be

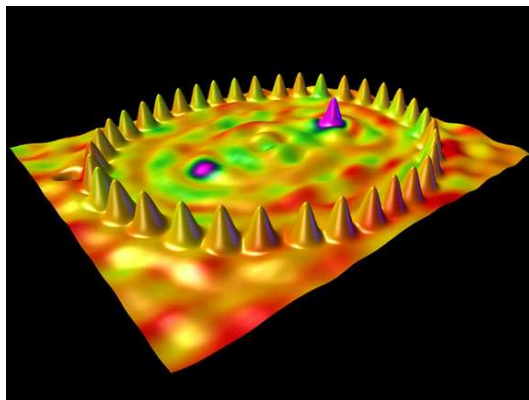


Figure 14.7. A prettier version of Figure 14.6, showing the ellipse of cobalt atoms, as well as the real and 'mirage' cobalt atoms at the foci.

#### Quantisation of a component of angular momentum

$$J_z = m_j \hbar \quad \text{with } m_j = 1, 2, 3, \dots$$

#### Quantisation of the total angular momentum

$$\mathbf{J}^2 = j(j+1)\hbar^2 \quad \text{with } j = 0, 1, 2, 3, \dots$$

somewhat more complicated than the simple Bohr picture from the uncertainty principle and the equivalences which we developed between linear and rotational motion in Section 8.4. We recall that the laws of classical dynamics result in correspondences between linear displacement  $d\mathbf{r}$  and the angular displacement  $d\boldsymbol{\theta}$  and between the linear momentum  $d\mathbf{p}$  and the angular momentum  $d\mathbf{L}$ . In quantum mechanics, the uncertainty principle sets a lower limit to the uncertainty with which we can determine  $\mathbf{p}$  and  $\mathbf{x}$ ,  $\Delta p \Delta x \geq \hbar/2$ . In exactly the same way, we cannot know simultaneously both  $\mathbf{L}$  and  $\boldsymbol{\theta}$ . Thus, the term 1 in  $(j+1)$  can be thought of as an expression of uncertainty principle as applied to rotational motion. The combination of (14.9) and (14.10) tells us that we cannot project the total angular momentum onto a given axis, essentially because of the uncertainty principle.

There is one very pleasant example of the application of the expression for the quantisation of angular momentum. Consider the simplest case of a diatomic molecule such as carbon monoxide CO or hydrogen chloride HCl. We can treat the molecule as a classical rigid body and work out the relation between its kinetic energy of rotation and its angular momentum. We recall that the rotational kinetic energy  $E_{\text{rot}}$  and angular momentum  $J$  are

$$E_{\text{rot}} = \frac{1}{2} I \omega^2 \quad \text{and} \quad J = I \omega, \quad (14.11)$$

where  $I$  is the moment of inertia of the molecule about its centre of mass. Therefore, the classical relation between energy and angular momentum is

$$E_{\text{rot}} = \frac{J^2}{2I}. \quad (14.12)$$

We suppose that the masses of the atoms are  $m_1$  and  $m_2$ . Then, if  $r_1$  and  $r_2$  are the distances of the two atoms from their centre of mass, the distance between the atoms is  $R = r_1 + r_2$  and, from the definition of the centre of mass,  $m_1 r_1 = m_2 r_2$ . Consequently, we can express  $r_1$  and  $r_2$  in terms of  $R$ ,  $m_1$  and  $m_2$ .

$$r_1 = \frac{m_2}{m_1 + m_2} R \quad r_2 = \frac{m_1}{m_1 + m_2} R.$$



Therefore, the moment of inertia  $I$  of the molecule about its centre of mass is

$$\begin{aligned} I &= m_1 r_1^2 + m_2 r_2^2 = \frac{(m_1 m_2^2 + m_1^2 m_2) R^2}{(m_1 + m_2)^2}, \\ &= \frac{m_1 m_2}{m_1 + m_2} R^2, \\ I &= \mu R^2, \end{aligned} \quad (14.13)$$

where  $\mu = m_1 m_2 / (m_1 + m_2)$  is the *reduced mass* of the molecule.

In the same way as we identified the quantum mechanical energy with the kinetic energy  $E = p^2/2m$ , we identify the quantum mechanical rotational kinetic energy as

$$E = \frac{J^2}{2I}. \quad (14.14)$$

Inserting (14.10) for the quantisation of angular momentum into (14.14),

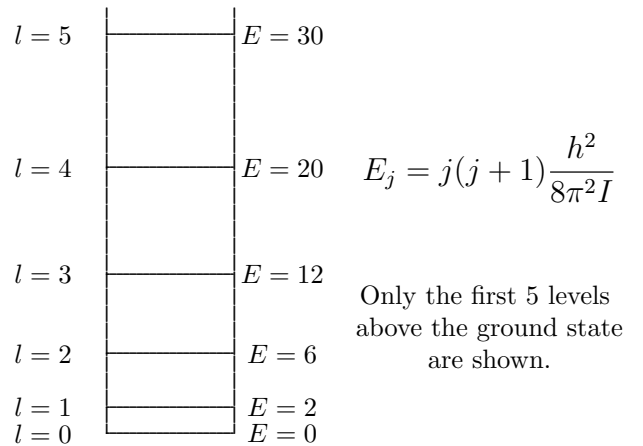
$$E_j = \frac{J^2}{2\mu R^2} = \frac{j(j+1)\hbar^2}{2\mu R^2}, \quad (14.15)$$

where  $j = 0, 1, 2, \dots$ . These quantised rotational energy levels of the molecule are illustrated in Figure 14.8, in which the energies are shown in units of  $\hbar^2/2\mu R^2$ .

Now, just as in the case of the hydrogen atom, the molecule emits a photon of energy  $h\nu$  when it changes from one rotational state to another. We need, however, rules which tell us which of all the possible transitions are allowed. For the simplest transitions, which are known as *electric dipole transitions*, the rule is that the *angular momentum quantum number  $j$  should change by only one unit*, that is, for the case of emission of radiation  $j \rightarrow j-1$  while in the case of absorption of a photon  $j \rightarrow j+1$ . We can therefore work out the energy of the photons emitted in the rotational transition  $j \rightarrow j-1$ .

$$\begin{aligned} \Delta E_{j \rightarrow j-1} &= h\nu = [j(j+1) - (j-1)j] \frac{\hbar^2}{2\mu R^2}, \\ &= \frac{j\hbar^2}{\mu R^2}. \end{aligned} \quad (14.16)$$

Figure 14.8. Energy Level Diagram for a Quantum Rotator



Hence,

$$\nu = \frac{\Delta E_{j \rightarrow j-1}}{h} = \frac{j\hbar}{4\pi^2\mu R^2} = \frac{j\hbar}{2\pi\mu R^2}$$

where  $j = 0, 1, 2, \dots$

Thus, the transitions are equally spaced in frequency and this results in the characteristic *rotational ladder* for the rotational spectra of diatomic molecules. This finds application in many different fields. Many of the transitions fall in the far infrared region and millimetre regions of the spectrum. A beautiful example is the carbon monoxide molecule which is the next most abundant molecule in interstellar space after molecular hydrogen. In the problem sheet, we ask you to show that the  $j = 1 \rightarrow 0$  transition occurs at 115 GHz, or a wavelength of 2.6 mm,  $j = 2 \rightarrow 1$  at 230 GHz, or a wavelength of 1.3 mm,  $j = 3 \rightarrow 2$  at 345 GHz, or a wavelength of 0.87 mm and so on. The giant molecular clouds which are the birth places of the stars are most readily identified by their CO line emission.

Notice also that we can carry out the calculation backwards to understand the structure of the diatomic molecules. If we measure the rotational ladder of a diatomic molecule, we are able to work out the separation between the atoms in the molecule. For example, in the case of hydrogen chloride molecules, the separation between the spectral lines is  $\Delta\nu = 6.234 \times 10^{11}$  Hz and, since  $\Delta\nu = \hbar/2\pi\mu R^2$ , we can show that the separation of the atoms is about  $10^{-10}$  m.

## 14.4 The Harmonic Oscillator

You have spent a great deal of time this year investigating the classical harmonic oscillator and have seen how important it is in a variety of contexts. The same is true in quantum mechanics. The harmonic oscillator, or more strictly the *harmonic potential*, is a good model for many physical systems, for example, a chemical bond. We shall therefore develop the quantum theory of the harmonic oscillator in some detail. We start by using the approximate methods developed in Chapter 13 and then

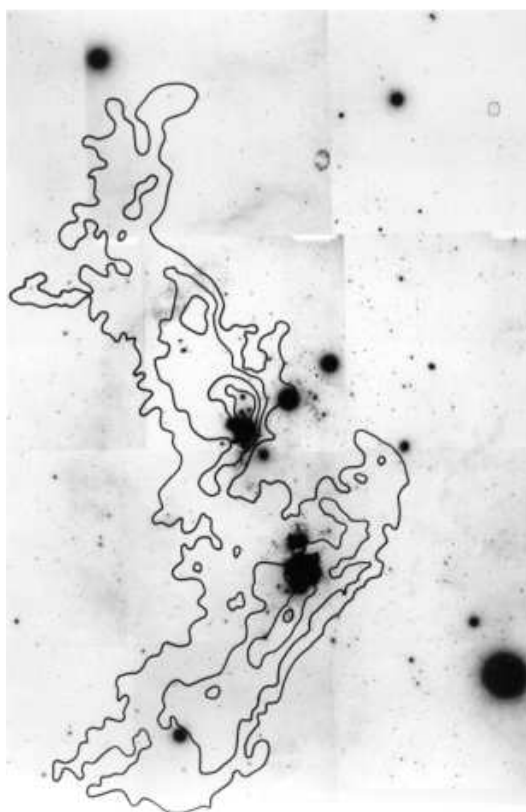


Figure 14.9. An image of the distribution of CO molecules in the constellation of Orion from observations of the CO molecular line at 2.6 mm.

use this insight to find a formal (non-examinable) solution and derive the energy levels.

#### 14.4.1 Approximate Solution

The potential has the form  $V = \frac{1}{2}ax^2$ . Now consider the ground state of the system and apply the ideas of section 13.1 to obtain an approximate form for the wave function.

- The ground state must minimise the curvature of the wave function and as before we do not expect any nodes in the function.
- If the ground state energy is  $E$ , then classically the particle cannot enter the region with  $E \geq \frac{1}{2}ax^2$ , that is, the regions  $|x| > (2E/a)^{1/2}$ . However, just as in the case of the finite depth potential well, we expect the wavefunction to fall off roughly exponentially in this region. For large  $x$ ,  $E \ll \frac{1}{2}ax^2$  and Schrödinger's equation becomes:

$$\frac{d^2\psi}{dx^2} \approx \frac{2m}{\hbar^2} \frac{1}{2}ax^2\psi = \frac{am}{\hbar^2}x^2\psi \quad (14.17)$$

To find an approximate solution, we guess a trial solution of the form  $\psi = A \exp(-\frac{1}{2}\beta x^2)$ . Then,

$$\begin{aligned} \frac{d\psi}{dx} &= A \exp(-\frac{1}{2}\beta x^2) \times (-\beta x), \\ &= (-\beta x)\psi. \\ \frac{d^2\psi}{dx^2} &= -\beta\psi + (-\beta x)\frac{d\psi}{dx}, \\ &= -\beta\psi + \beta^2 x^2\psi, \\ &\approx \beta^2 x^2\psi, \end{aligned}$$

where the last approximation holds good when  $x^2$  is large. Therefore, from (14.17), the solution is approximately  $A \exp(-\frac{1}{2}\beta x^2)$  with  $\beta^2 = am/\hbar^2$ .

- For  $|x| \leq (2E/a)^{1/2}$  the wavefunction has its greatest curvature near  $x = 0$  where  $E - V$  is a maximum and decreases systematically until at  $|x| = (2E/a)^{1/2}$  the curvature is zero and so there is a *point of inflection*.

#### The time-independent Schrödinger wave equation

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi = E\psi.$$

#### Remember

The curvature of the wavefunction is found from the rate of change of the gradient of  $\psi$ ,

$$\frac{d}{dx} \left( \frac{d\psi}{dx} \right) = -\frac{2m}{\hbar^2} [E - V(x)]\psi.$$

The solution is shown in Figures 14.10 and 14.11.

The higher energy states can be found by an analogous procedure to that used in the analysis of the finite potential well. Assuming the energy is quantised and the energy of the  $n$ th level is  $E_n$ , the ground state corresponds to  $n = 0$ .

- The first excited state has one node and, since the potential is symmetric, the node must be at the origin; the second will have two nodes and so on. Clearly for even  $n$  the wave function is even and for odd  $n$  it is an odd, anti-symmetric function.
- The point at which we enter the classically forbidden region depends on the energy, for the  $n$ th state,  $|x| > (2E_n/a)^{1/2}$ . At this point the wave function has a point of inflection.
- As we approach the point of inflection the kinetic energy  $(E - V)$  decreases – we have already argued that this corresponds to decreasing curvature of the wave function and to increasing wavelength. This corresponds classically to decreasing kinetic energy and hence to a decreasing speed as the oscillator reaches the limits of its motion. The quantum analogy of this is that we expect an increased probability of finding the particle in these regions compared to those locations in which  $(E - V)$  is large – in other words the amplitude of the wave function increases in regions of small  $(E - V)$ .

Figures 14.10 and 14.11 show some of the excited states of the harmonic oscillator. These are in fact the exact solutions, but it is clear that our qualitative analysis has described all the main features.

Our qualitative arguments are not sufficient to prove that the energy levels are quantised, and of course we cannot obtain expressions for the energy. In fact, the answers are very simple. If we introduce, by analogy with the classical harmonic oscillator, the frequency,  $\omega$

$$\omega = \sqrt{\frac{a}{m}},$$

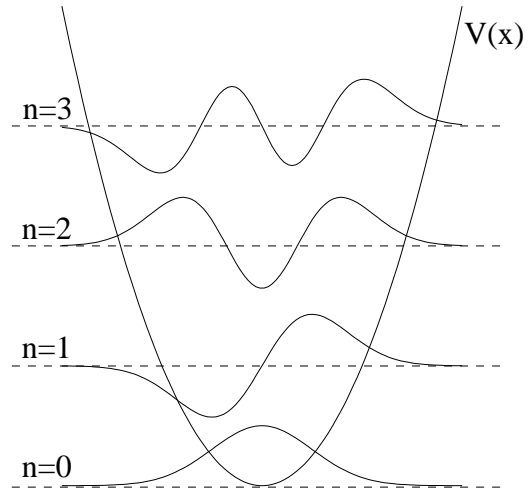


Figure 14.10. Wave functions for the harmonic oscillator

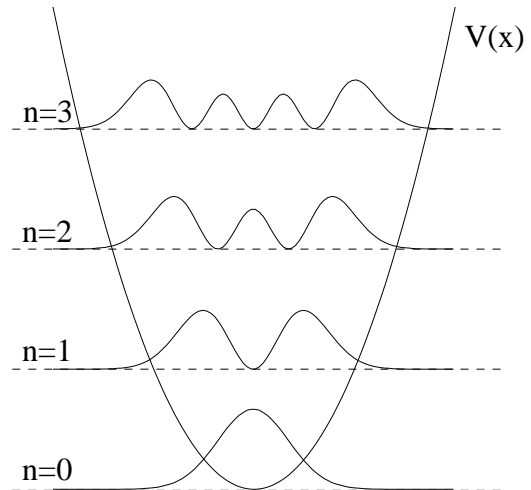


Figure 14.11. Probability densities for the harmonic oscillator.

then the energy levels are given by

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega. \quad (14.18)$$

(see Figure 14.12).

Note that for  $n = 0$  the energy is  $E_0 = \frac{1}{2}\hbar\omega$  – this is a further example of a zero-point energy and arises for the same physical reasons as we discussed for the infinitely deep potential well. In the next section we shall go through the formal solution of the harmonic oscillator and derive the energy levels – the next section is, however, *strictly non examinable*.

#### 14.4.2 Formal Derivation

**The material of this section is strictly non examinable**

We can use the qualitative arguments of the previous section as the starting point for the solution of Schrödinger's equation for a harmonic oscillator.

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2}ax^2\right) \psi = 0.$$

In the previous section, we showed that, at large  $x$ , an approximate solution is  $A \exp(-\frac{1}{2}\beta x^2)$ , where  $\beta^2 = am/\hbar^2$ . First of all, we change variables to  $\xi = \sqrt{\beta}x$  and it is easy to show that Schrödinger's equation becomes

$$\frac{d^2\psi}{d\xi^2} + (\Lambda - \xi^2) \psi = 0,$$

where  $\Lambda = 2E/(\hbar\omega)$  and  $\omega = \sqrt{a/m}$ . Using our knowledge of the limiting behaviour as a guide, we adopt a trial solution of the form

$$\psi = H(\xi) \exp(-\frac{1}{2}\xi^2).$$

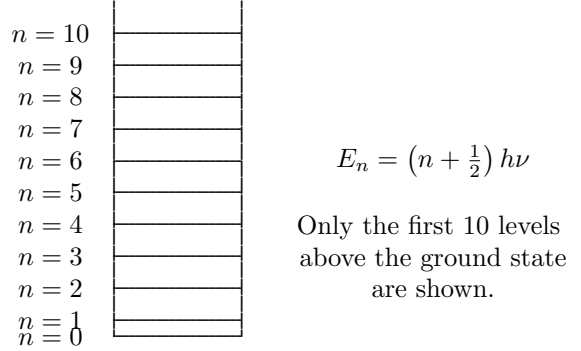
Substituting this expression into the above equation we obtain a new differential equation for  $H(\xi)$ :

$$\frac{d^2H}{d\xi^2} - 2\xi \frac{dH}{d\xi} + (\Lambda - 1)H = 0.$$

#### Energy levels of the quantum harmonic oscillator

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

Figure 14.12. Energy Level Diagram for a Quantum Harmonic Oscillator



To solve this equation we use a trial solution in the form of a series

$$H(\xi) = \sum_{n=0} a_n \xi^n.$$

We then find that the terms in the differential equation with the same powers of  $\xi$  are

$$\begin{aligned} \frac{d^2 H}{d\xi^2} &= \sum_n a_{2+n} (n+2)(n+1) \xi^n \\ -2\xi \frac{dH}{d\xi} &= -\sum_n a_n 2n \xi^n \\ (\Lambda - 1)H &= (\Lambda - 1) \sum_n a_n \xi^n \end{aligned}$$

We now substitute these back into the differential equation. For this to be a solution for all values of  $\xi$ , the coefficients of each power of  $\xi$  must be equal. Therefore, we find that

$$a_{2+n}(n+2)(n+1) = a_n(2n - \Lambda + 1) \quad (14.19)$$

- An equation of this form is called a *recurrence relation*; given say  $a_0$  we can find  $a_2$  and so on. Note however that we only find the even terms in this way – we find the odd terms by starting with  $a_1$  and then find  $a_3$  and so on.
- We therefore have two types of solution – even solutions  $a_0 + a_2 \xi^2 + a_4 \xi^4 + \dots$  or odd solutions  $a_1 \xi + a_3 \xi^3 + a_5 \xi^5 + \dots$  – these correspond to the odd and even solutions we found from our qualitative analysis.
- For the wave function to go to zero at  $\pm\infty$  we have to make sure the series is truncated at some point. From (14.19), this will be the case if, for a particular value of  $n$ ,

$$2n - \Lambda + 1 = 0.$$

Therefore, from the definition  $\Lambda = 2E/\hbar\omega$ ,

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

The series defined in this way,  $H_n(\xi)$  are called *Hermite polynomials*.

## 14.5 Vibrational Energies of Diatomic Molecules

A simple model of a diatomic molecule is of two masses  $m_1$  and  $m_2$  interacting via a force which gives rise to a harmonic potential (the classical model is two masses joined by a spring) of the form  $V = \frac{1}{2}ax^2$  where  $x$  is the interatomic separation. We can easily write down the total energy of this system:

$$E = \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 + \frac{1}{2}ax^2.$$

In the zero of momentum frame this expression takes on a particularly simple form since we can re-write the energy expression in terms of the momenta which are equal and opposite:

$$E = \frac{p^2}{2m_1} + \frac{p^2}{2m_2} + \frac{1}{2}ax^2.$$

We now introduce the reduced mass

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2},$$

and the energy expression is just

$$E = \frac{p^2}{2\mu} + \frac{1}{2}ax^2.$$

This has exactly the same form as the energy of a harmonic oscillator but with the mass replaced by the reduced mass. The quantum solution to this problem must therefore be precisely that of the quantum harmonic oscillator we have just discussed with energy levels given by

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega,$$

where in this case  $\omega = \sqrt{a/\mu}$ . The constant  $a$  we interpret as a *force constant*.