

## 8 Wavefunctions - Schrödinger's Equation

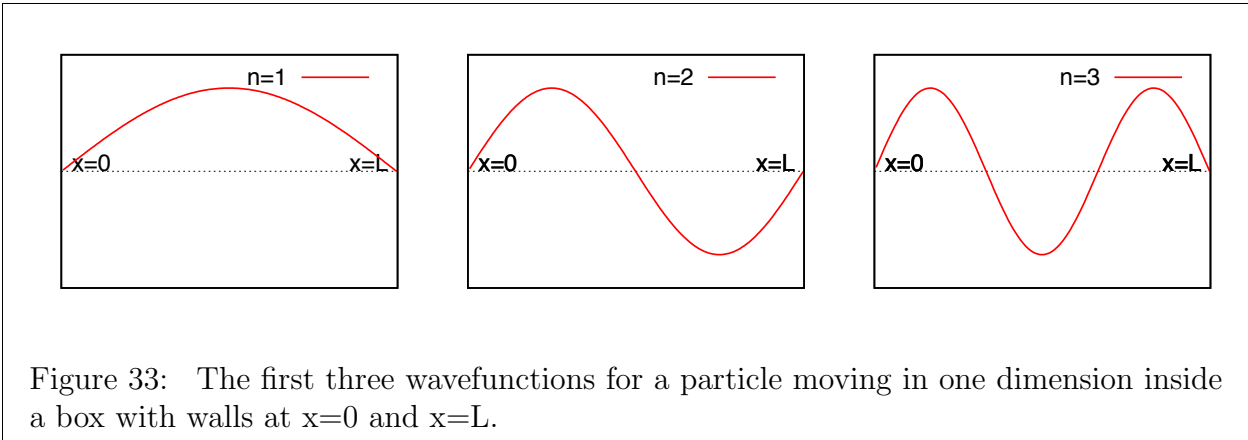
So far we have considered only free particles - i.e. particles whose energy consists entirely of its kinetic energy. In general, however, a particle moves under the influence of a force and possesses both kinetic energy, due to its motion, and potential energy, due to its position in the force field. Such particles are also described by a wavefunction, whose interpretation is, as before, that the square of the amplitude at position,  $\mathbf{x}$ , is the probability to find the particle at that position. The wavefunction is more complicated than in the case for a free particle and it is given by the solution to the most important equation in Quantum Physics - Schrödinger's wave equation. This is not a simple equation for the wavefunction,  $\Psi(\mathbf{x}, t)$ , which is a function of position,  $\mathbf{x}$ , and time  $t$ . It is a "differential equation" which relates the way in which the wavefunction,  $\Psi(\mathbf{x}, t)$ , varies with a change in position to the way in which it varies with a change in time. Such differential equations do not always have a solution - this is not a statement about our inability to solve the equation if it's too hard, but a mathematical theorem stating that such differential equations only possess unique solutions under certain circumstances. There are therefore only limited force fields for which we know the solution to Schrödinger's equation and can therefore derive the wavefunction for a particle moving in that field of force. For other systems of forces there are often very good approximations which can be made so that the wavefunction can still be obtained up to a certain accuracy.

### 8.1 Discrete Energy Levels

When the force is attractive i.e. it pulls the particle towards some point, the particle can form a bound state in which the magnitude of its potential energy exceeds its kinetic energy and a quantity of energy known as the binding energy has to be injected to order to free the particle. Examples are a particle on a spring or any other **harmonic oscillator** such as the ions in a crystal lattice, or a charged particle moving in the electrostatic field of an oppositely charged particle. Classically, such bound states can have any energy, but in Quantum Physics it turns out that the Schrödinger equation only allows solutions for which the system has one of a discrete set of allowed energies. These are called **energy levels**. The energy is said to be "quantized". The fact that the Schrödinger equation, when applied to certain systems, only has solutions for a discrete set of energy levels is the mathematical justification for Planck's original postulate that whereas classically oscillators and other systems can have any energy, in Quantum Physics this energy is quantized. We look at three examples of systems with discrete energy levels.

#### 8.1.1 Particle in a Box (in one dimension)

The simplest example of discrete energy levels is the case of a particle moving in one dimension (this can easily be extended to the more realistic case of a particle moving in three dimensions) in a "box" with impenetrable walls at  $x = 0$  and  $x = L$ , so that the



particle must remain inside the box, whose length is  $L$ . This means that there is zero probability of finding the particle outside the box - or even at the edge of the box, so we need a wavefunction which is zero at  $x = 0$  and at  $x = L$ .

We have already discussed this case under the section on standing waves. The waves that obey this condition have wavelengths given by

$$\lambda_n = \frac{2L}{n} \quad (n = 1, 2, 3 \dots) \quad (8.1)$$

The first three wavefunctions are shown in Fig. 33. From the de Broglie wave relation, the particle with these allowed wavelengths, has momentum

$$p_n = \frac{h}{\lambda_n} = \frac{nh}{2L}. \quad (8.2)$$

For a particle of mass  $m$ , the kinetic energy,  $T$  ( $= \frac{1}{2}mv^2$ ), is related to the momentum,  $p$ , ( $p = mv$ ) by

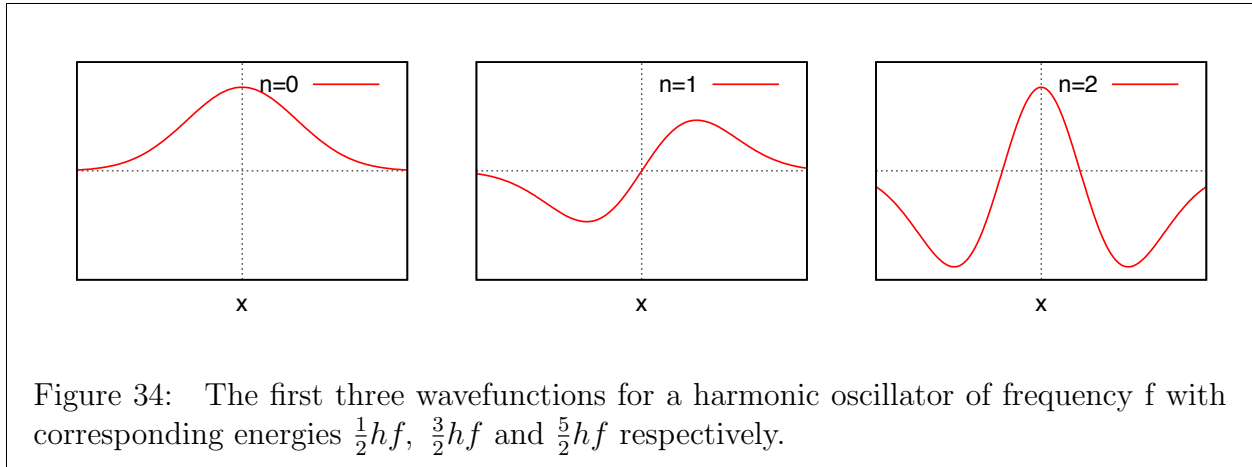
$$T = \frac{1}{2}mv^2 = \frac{p^2}{2m}. \quad (8.3)$$

There is no force on the particle except at the wall, so that between the walls there is no potential energy and the energy consists entirely of the kinetic energy. This means that the energy of the particle is given by

$$E_n = \frac{n^2 h^2}{8mL^2} \quad (8.4)$$

The only energies permitted are these values where  $n$  is a positive integer number. This differs from our classical picture for which a particle can have any energy whether it is confined to a box or not. We do not have any visual experience of this “quantization” since for any macroscopic system the size,  $L$ , of the box is so large that the energy levels are far too closely packed together to be identified as discrete as opposed to continuous.

Examination of the wavefunctions in Fig. 33 shows us that the wavefunction for  $n = 1$ , the lowest allowed energy, known as the “ground state”, does not cross the axis - it is never zero between  $x = 0$  and  $x = L$ . The wavefunction for the next lowest energy level,  $n = 2$ ,



(the “first excited state”) crosses the axis once i.e. there is one point where it is zero between  $x = 0$  and  $x = L$ . For the next excited state there are two zeros etc. This is a feature of all sets of discrete wavefunctions - the wavefunction for the ground state does not cross the axis, whereas the wavefunction for the  $n^{\text{th}}$  excited state crossed the axis  $n$  times.

### 8.1.2 Harmonic Oscillator

For a harmonic oscillator such as a particle attached to a spring, there is a force which is proportional to the displacement of the particle from its equilibrium position and is directed in the opposite direction from the displacement - hence it is called a “restoring” force. At the sub-microscopic level, an example would be an ion in a crystal which experiences a restoring force proportional to its displacement from its lattice site. Such particles oscillate around their equilibrium position with some frequency,  $f$ , that depends on the strength of the restoring force and the mass of the particle. To find the wavefunctions for such a system we need to solve the Schrödinger equation appropriate for such a restoring force. The equation can only be solved for a discrete set of energies (energy levels). The wavefunctions for the first three such energy levels are shown in Fig. 34) these are actually labelled  $n = 0$ ,  $n = 1$ ,  $n = 2 \dots$  (the ground state has the label  $n = 0$ , unlike the previous example where it was labelled  $n = 1$  but this is merely a convention) and again we see that they cross the axis  $n$  times.

The corresponding energies,  $E_n$ , are given by

$$E_n = \left( n + \frac{1}{2} \right) hf. \quad (8.5)$$

This is almost in agreement with the postulate made by Planck to solve the problem of the ultraviolet catastrophe - with the exception of the offset of  $\frac{1}{2}hf$ . In other words a harmonic oscillator in its lowest allowed energy level (ground state) does not have zero energy but a very small energy  $E_0 = \frac{1}{2}hf$ . For macroscopic oscillators this energy is so small that it may be neglected. However, for sub-microscopic systems it is not possible to have an oscillator

with zero energy. In order to have zero energy, the momentum of the particle has to be zero (zero kinetic energy) and the displacement of the particle from its equilibrium position has to be zero (zero potential energy). This would mean that the momentum and position of the particle were known exactly, thereby violating the Heisenberg uncertainty principle. The energy  $\frac{1}{2}hf$  turns out to be the minimum energy that an oscillator can possess without violating the Heisenberg uncertainty principle. Note that all of the wavefunctions tend to zero for large (positive or negative)  $x$  indicating that the probability of finding the particle with very large (positive or negative) displacement position is very small.

### 8.1.3 The Hydrogen Atom

The classical picture of the hydrogen atom was that of an electron orbiting around a proton. Such an electron can have any energy, depending only on the radius of the orbit. There is an internal inconsistency with this picture. An electric charge in orbit emits electromagnetic radiation with a frequency equal to the frequency of the electron's rotation. As it does so it would lose energy so that it would move into an orbit of smaller radius and the electron would very quickly spiral into the nucleus. The classical picture of the atom is unstable !!

There is also an experimental inconsistency. The (classical) electron would have an orbit of any radius with a corresponding frequency of rotation - like planets moving around the sun. Classically, a charged particle radiates at a frequency equal to its frequency of rotation which depends on the radius of orbit. If all orbit radii are permitted then the atom would radiate at all possible frequencies. However, experimentally it is found that atoms emit electromagnetic radiation only with certain fixed frequencies (these are called “**spectral lines**”).

So the classical picture in which an electron has a well-defined orbit is not viable. Motion in an orbit implies that the electron has a well-defined position in an orbit and a well-defined velocity (and hence well-defined momentum) as it moves around the orbit. This is not consistent with the Heisenberg uncertainty principle. In Quantum Physics the best we can do is to calculate the wavefunction which tells us what the probability is that the electron is at a particular point and also the probability that it has a given momentum - but since the electron actually does not possess a well-defined position or a well-defined momentum, so it is not meaningful to talk about “orbits”.

The wavefunctions are found by solving the Schrödinger equation which is appropriate for an electron with an attractive force toward the proton. Such a force decreases as the square of the distance between the electron and the proton. The first three allowed wavefunctions, which depend only on the distance,  $r$ , between the proton and the electron are shown in Fig. 35. In this case we once again have the lowest energy, (ground state) wavefunction labelled as  $n = 1$ . Again we see that the number of times the wavefunction crosses the axis is  $n - 1$ . We also note that all of the wavefunctions tend asymptotically to zero for large  $r$ , indicating that the probability of finding the electron at a distance  $r$  from the proton is very small for very large distance,  $r$ , between the electron and the nucleus. This is an expected result - we would not expect to find an electron of a hydrogen atom a very long way away

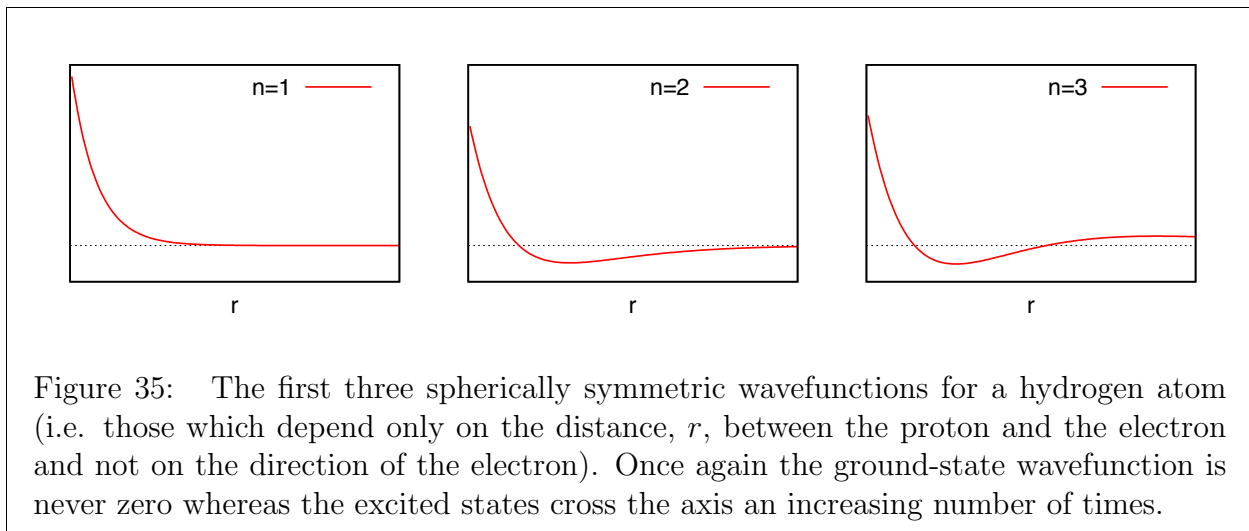


Figure 35: The first three spherically symmetric wavefunctions for a hydrogen atom (i.e. those which depend only on the distance,  $r$ , between the proton and the electron and not on the direction of the electron). Once again the ground-state wavefunction is never zero whereas the excited states cross the axis an increasing number of times.

from its nucleus.

The corresponding energies for a given value of (integer)  $n$  are given by the simple formula

$$E_n = \frac{R_H h c}{n^2}. \quad (8.6)$$

$R_H$  is a constant called the “**Rydberg constant**”. It is constructed out of the electric charge of the electron,  $e$ , the mass of the electron,  $m_e$ , Planck’s constant,  $h$ , and the speed of light,  $c$ . Its value is 0.011 per nm.

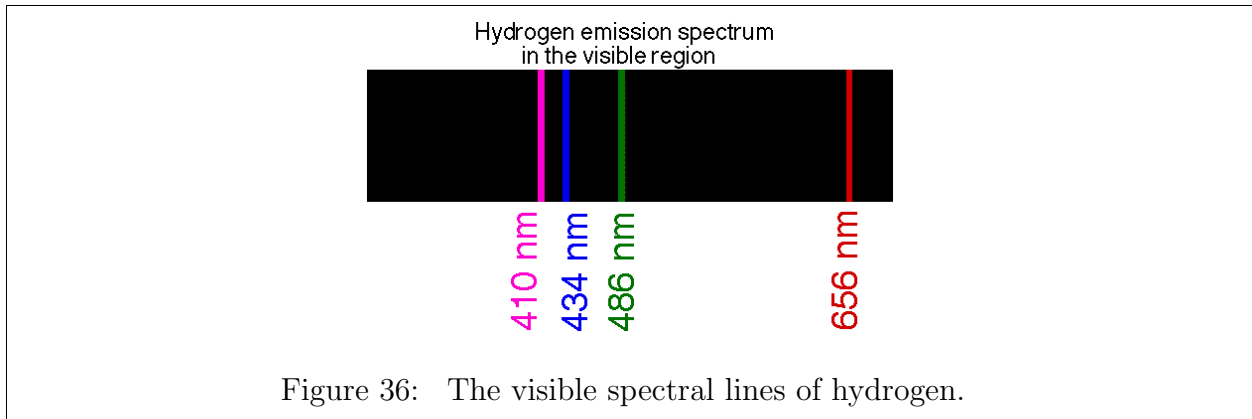
When an atom makes a transition from a higher (lower) energy level to a lower (higher) energy level it emits (absorbs) a photon whose energy is equal to the difference in energies of the initial and final energy level. Since the energy levels are known, the allowed energies of the photon emitted or absorbed when a hydrogen makes such a transition can be calculated. Furthermore, since the energy of a photon is proportional to the frequency of the light, the allowed radiation frequencies (and hence the wavelengths) can therefore be determined.

For those of you who are not afraid of a little algebra, we can go through the steps from the expression for the energy levels of a hydrogen atom (eq.(8.6)) and the wavelengths of the spectrum - otherwise skip to eq.(8.9). From the expression (8.6) for the energy levels of hydrogen, the energy difference,  $\Delta E$ , between the state state  $n = n_i$  to a state  $n = n_f$  is given by (using eq.(8.6) for  $n = n_i$  and  $n = n_f$ )

$$\Delta E = R_H h c \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (8.7)$$

The photon energy is related to the wavelength by

$$\Delta E = h f = \frac{h c}{\lambda} \quad (8.8)$$



Therefore (substituting eq.(8.8) into eq.(8.7) and dividing both sides by  $h c$ ) the wavelengths,  $\lambda$ , of the spectrum of hydrogen are given by

$$\frac{1}{\lambda} = R_H \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (8.9)$$

This simple formula reproduces the observed wavelengths of the hydrogen spectrum with spectacular accuracy as can be seen from Fig. 36 which shows the wavelengths of the visible lines of the hydrogen spectrum, for the case  $n_f = 2$ . The above formula gives the following values:

$$n_i = 3 : \frac{1}{\lambda} = 0.011 \left( \frac{1}{2^2} - \frac{1}{3^2} \right) = 0.00153, \text{ so that } \lambda = 655 \text{ nm.}$$

$$n_i = 4 : \frac{1}{\lambda} = 0.011 \left( \frac{1}{2^2} - \frac{1}{4^2} \right) = 0.00206, \text{ so that } \lambda = 485 \text{ nm.}$$

$$n_i = 5 : \frac{1}{\lambda} = 0.011 \left( \frac{1}{2^2} - \frac{1}{5^2} \right) = 0.00231, \text{ so that } \lambda = 433 \text{ nm.}$$

$$n_i = 6 : \frac{1}{\lambda} = 0.011 \left( \frac{1}{2^2} - \frac{1}{6^2} \right) = 0.00244, \text{ so that } \lambda = 409 \text{ nm.}$$

Comparing these theoretical predictions for the wavelengths with the measured values shown in Fig. 36 is a remarkable success for Quantum Physics.

The next simplest atom is the **helium atom** which has two electrons. This has an added complication that as well as the electrons experiencing a force which attracts them towards the nucleus, there is a **repulsive force** between the two electrons. This is sufficient to render the Schrödinger equation for the helium atom impossible, even in principle, to solve exactly. Fortunately there are several very effective approximate methods that can be used to obtain very accurate approximations to the solution. Needless to say the situation for atoms with more electrons is even worse! Finding good approximations to such wavefunctions and determining the allowed energy levels (and consequently the wavelengths of the atomic spectra) is the subject of Atomic Physics and also the basis of chemistry.