SESSION 3: The Schrödinger Wave Equation and the Ground & Excited States of Hydrogen

Overview: In this session we will be looking at:

- the basic form of the Schrödinger Wave Equation and information derived from it
- the wavefunctions for the ground and some excited states of hydrogen

After the introduction to waves and wavefunctions in the previous session, and now, with a better understanding of the interaction of waves, we can now return to the ground state hydrogen atom and resume our investigation of the behaviour of the electron.

What we can conclude here is that since the electron in the hydrogen atom exhibits wave-like characteristics, then its motion must therefore be described by a wavefunction, ψ. This wavefunction must contain (or must allow us to determine) all the information about the electron in the **ground state** hydrogen atom. The atom is three-dimensional. The electron is free to move about in this three-dimensional space. In space, the position of a particle can be located by the three Cartesian Coordinates x, y and z. The wavefunction ψ can therefore be described as a function of x, y and z.

The probability of locating the electron in the ground state hydrogen atom is given by the probability function P. The probability function P is given by the square of the wavefunction,

i.e. $P = \psi^2$.

The probability of finding the electron in a region of space with volume $d\tau$ (= dx.dy.dz), is

$$P = \int \psi^2 d\tau$$

or

$$P = \int \psi^2 \, dx.dy.dz$$

where $d\tau$ is a small cube of dimensions dx, dy and dz.

The wavefunction ψ is determined by solving the Schrödinger Wave Equation (SWE).

The Schrödinger Wave Equation (SWE)

The (time-independent) Schrödinger Wave Equation is of the general form

$$H\psi = E\psi \ .$$

In this course you will not be required to solve this equation but at least you should understand its significance and its mode of operation. It is solved by applying a special kind of algebra known as **operator algebra** (i.e. the method of wave mechanics is operator algebra).

H is the **Hamiltonian or energy Operator**, which prescribes a series of mathematical operations associated with kinetic and potential energy to be performed on the wavefunction ψ.

The **wavefunction ψ**, is a mathematical expression that describes or defines the electron in terms of its wave properties. So for the electron in the lowest energy (ground) state hydrogen atom, the specific wavefunction would describe the wave properties of the electron under these specific conditions.

The wavefunction appears on both sides of the SWE, and this is for a very special reason. In order to solve the SWE, the wavefunction must also come out of (be a part of) the solution. This implies that for a specific state of a system (in this case the ground state hydrogen atom) the wavefunction is specific and unique.

The Energy Function E (the total energy), is the net energy of the system under investigation. Again, for the ground state hydrogen atom, E in this case would represent the energy of the electron in the field of the proton. For the wavefunction to be solvable ,E cannot have just any arbitrary value but only one of a series of discrete, possible, energy values. (i.e. Quantum Theory).

For the hydrogen atom in the ground state H, E and ψ are specific, thus:

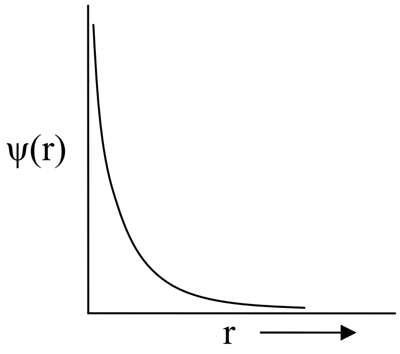
$$H\ \psi_1 = E_1\psi_1$$

where the subscript ‘1’ denotes the ground state (or first allowed energy state) of the hydrogen atom.

Classical mechanics states that the energy of any object should be continuous.

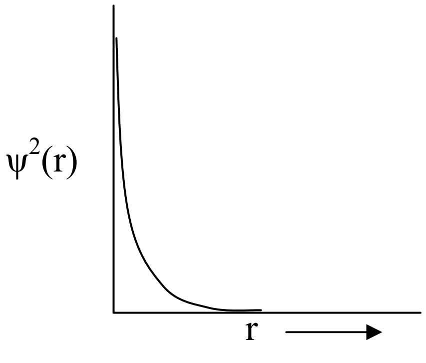
Solution of the SWE, and therefore Wave Mechanics, predicts that there is a definite state of minimum (and non-zero) energy of the hydrogen atom for which **ψ is spherically symmetric**. Having spherical symmetry, means that, if determinations of **ψ** are made at the same distance in all directions around the H-nucleus, the wavefunction is found to be the same. It is different for a different distance, but is the same for a given distance.

The following figure depicts the variation of the wavefunction with distance, r ($r = [x^2 + y^2 + z^2]^{1/2}$), from the nucleus for the ground state H-atom.



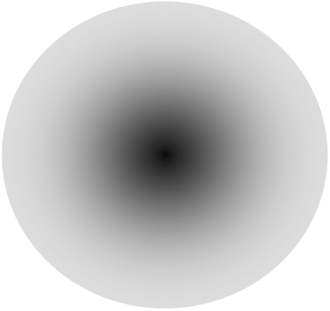
This figure shows that the wavefunction has larger values for small electron – nucleus separations, and smaller values as the separation increases. The notation $\psi(r)$, means that ψ is a function of r. In other words, the value of ψ depends only on the value of r.

We will now recall that the probability of finding the electron at a distance r from the nucleus is given by the square of ψ at r. A plot of the square of $\psi(r)$ against r is shown below.



This figure suggests that, in the ground state H-atom, the probability of finding the electron increases the closer the nucleus is approached. In simple words: on average, the electron spends most of its time closer to the nucleus.

If several photographs are taken of the H-atom, and if it were possible to see the electron in these pictures, the electron would be in different places each time. However, if a long-time exposure photograph is taken, then the resulting picture would show a blur, with the blur being most dense at the centre of the atom, as shown below:



The density of the blur in any small volume element, dV, is representative of the probability of finding the electron in that volume element.

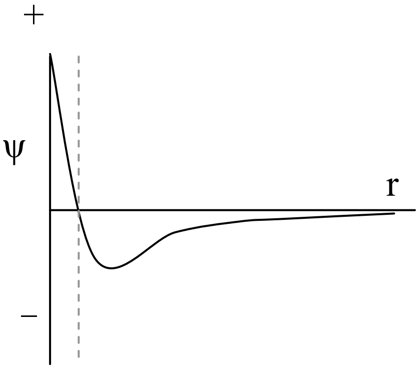
Excited States of Hydrogen Atom

The H-atom can be excited by the absorption of discrete amounts of radiation energy, to higher energy states, each described by its own characteristic wavefunction. Because of the obvious analogy between the classical orbits and the wave mechanical wavefunctions, the latter are referred to as **orbitals**.

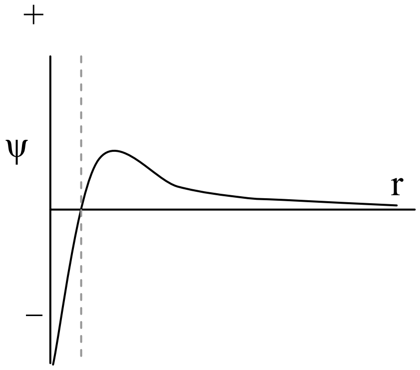
In the H-atom the ground state orbital has the same sign everywhere. This implies that the sign of the ground state H-atomic orbital must be either all positive or all negative. Inspection of the SWE reveals that if $\boldsymbol{\psi}$ is a solution, then $\boldsymbol{-\psi}$ is also a solution. The important thing however is that, whether the orbital is all positive or all negative, the square gives the same result.

Other orbitals consist of parts with opposite signs. Where the orbital changes sign, $\psi = 0$, and it must of course pass through zero. Regions where $\psi = 0$ are called nodes. Therefore, the probability of finding the electron there is zero.

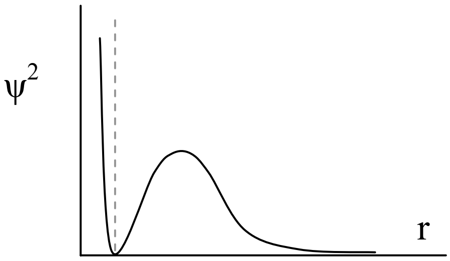
The first available excited state of the hydrogen atom, has a wavefunction of spherical symmetry and changes sign once in going from the nucleus outwards. This is shown in the following figure:



(a)

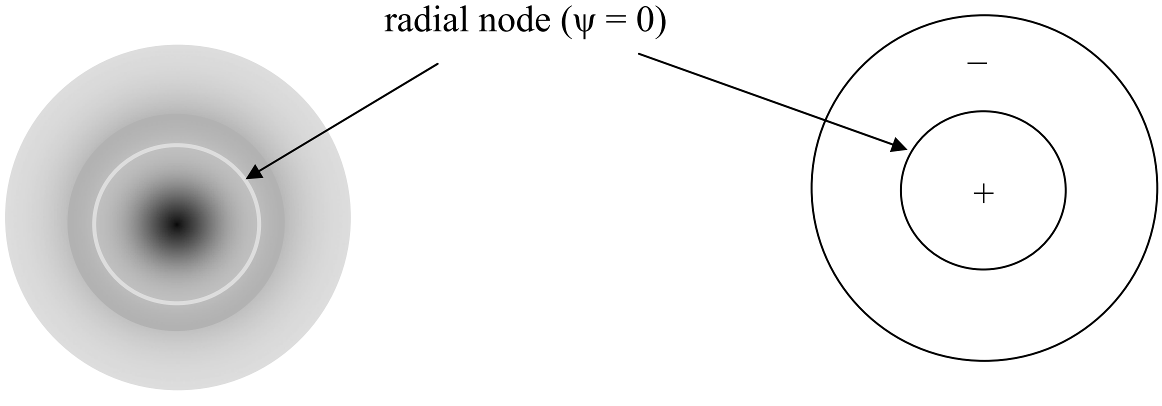


(b)



(c)

These figures show that the absolute sign (phase) of the wavefunction is insignificant. The square of both gives the same result, which represents the probability function P (= ψ^2 = $(-\psi)^2$). The electron-density profile and a diagram for the above wavefunction can be represented as:

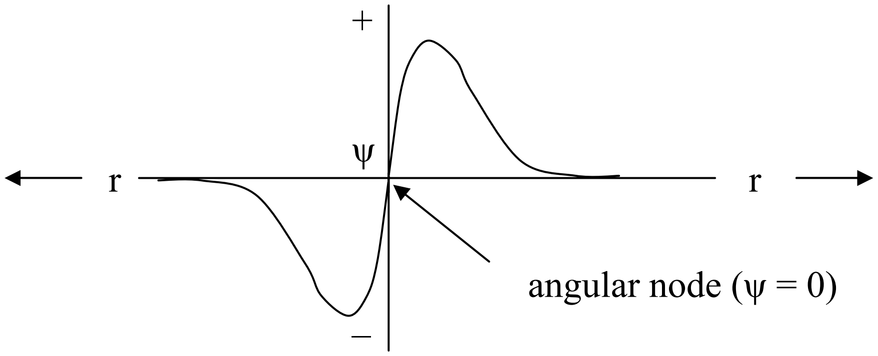


electron density profile

wavefunction, ψ (for (a))

respectively, where the the electron density is high at the centre, falls off to zero at the radial node ($\psi = 0$), increases to a maximum and then falls off as the electron-nucleus distance increases.

Another of the excited states of the H-atom has a wavefunction that is depicted in the following figure:



The figure shows that this specific wavefunction has opposite signs on opposite sides of the nucleus. The square of this wavefunction however is identical on opposite sides, representing equal distribution of electron density on both sides of the nucleus. (See following figure)