

SESSION 2: Behaviour Of The Electron In The Constant Energy Hydrogen Atom

Overview: In this session we will be:

- looking at the regularities in the behaviour of the electron in the hydrogen atom
- doing a short introduction to waves and their interaction
- looking at matter in terms of both wave and particulate properties

The first part of the discussion will be focusing on the hydrogen atom in its lowest possible energy state, referred to as the *ground state*.

A very important regularity appears in measurements of the position of the electron in the H atom. What is found, is that we can give a definite estimate of the likelihood that the electron will be found in some specified region of space.

Suppose the electron and the proton are separated by a distance r , and r is measured a large number of times with the H atom in the same state (same total energy). The value of r will vary (as suggested by the uncertainty principle), and the probability of r having some value a is always the same. **In other words** the probability of getting some value of r between a and $a + \delta a$ is always the same. We can express this by saying that the probability is given by $P(a)\delta r$, where $P(r)$ is a function of r that we can determine from our measurements. This would suggest that we could specify a given state of the atom by specifying the corresponding function P , which can be determined by experiment and which does in fact vary with the energy of the atom.

This is some achievement, but is not enough since it does not take into account that very small particles exhibit wavelike behaviour. In fact, electrons undergo diffraction and interference just like light.

This takes us to the concept of **Wave-Particle Duality**, where waves are seen to exhibit particle-like properties and particles exhibit wave-like properties, i.e. matter has a dual nature.

Matter Waves

It was put forward, by Louis de Broglie in 1924, that any particle travelling with linear momentum p ($= mv$) should have a wavelength λ given by the relation:

$$\lambda = \frac{h}{p}. \quad (7)$$

Since $p = mv$, then it is expected that for a given value of the velocity v , smaller particles will have a larger wavelength. The display of wave property by a particle occurs when the particle is bounded in a region which has dimensions that are comparable to the natural wavelength of the particle. The diameter of a ground state hydrogen atom is about 1 \AA ($= 10^{-10} \text{ m} = 100 \text{ pm}$). An electron traveling with a speed of one-third the speed of light has a natural wavelength of about 7 pm . This therefore suggests that an electron bounded within the hydrogen atom (or other atoms) will display wavelike properties. This observation is crucial in that it suggests that wave properties should become more important for smaller particles. This therefore means that classical mechanics is not able to explain the motion of very small particles. To account for the wave-like nature exhibited by these small particles, Wave Mechanics is the tool of choice.

Exercise 4. Calculate the de Broglie wavelength of a 50.0-kg man running at a velocity of 10.0 m s^{-1} .

Solution

$$\lambda = h/p = h/mv = 6.626 \times 10^{-34} \text{ J s} / (50.0 \text{ kg} \times 10.0 \text{ m s}^{-1}) = 1.33 \times 10^{-36} \text{ m}.$$

The value of this wavelength (which **aids us in the prediction** of wave-like characteristics) is extremely small, and confirms that the wave properties of the man can be ignored.

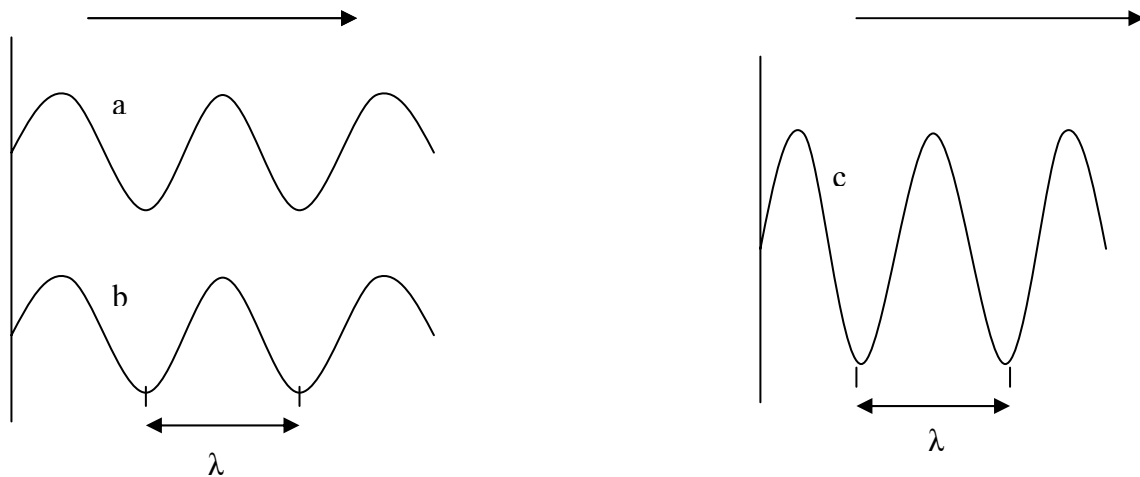
Self Test. *Calculate the de Broglie wavelength of the electron mentioned above.*

Waves, Waveforms and Wavefunctions

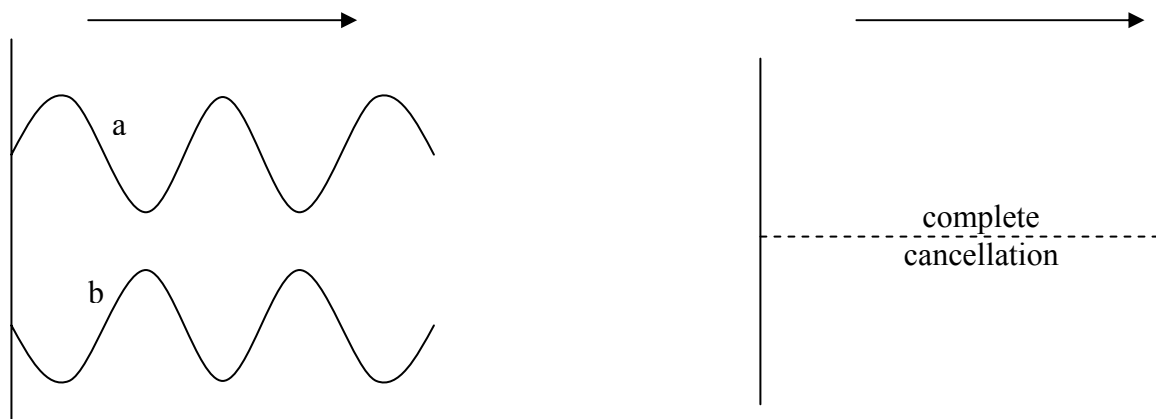
Not every student will have done physics, and so might not have met the topic on waves. Before we move on, we must have, at least, a basic understanding of the behaviour and interaction of waves. This basic understanding of waves should help you to appreciate the wave concept. Waves can be considered simply:

The waves (or waveforms) depicted by a and b below (left) are generated at the same time and are doing exactly the same thing at any point in time, and are said to be ***in phase***. The interaction of waves is called **interference**. If these two

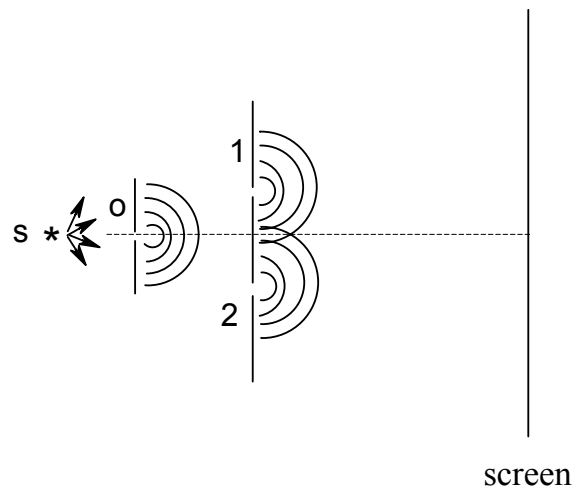
waveforms interact then a new waveform c, is produced with twice the amplitude of the original waveforms, but with the same wavelength λ . This type of interaction where a waveform is produced with greater amplitude is called *constructive interference*. This compares to a brighter light or louder sound.



The waves (or waveforms) depicted by a and b below are generated at the same time and are doing exactly the opposite thing at the same time, and are said to be (completely) *out of phase*. The interaction of these two waveforms leads to complete cancellation. This type of interaction is called *destructive interference*. This would result in darkness if they were light waves.



This forms the basis for wave interaction. It must be noted, however, that completely constructive or destructive interference does not occur in every case of interaction of two waves. An intermediate phase difference will lead to intermediate interaction intensity. This is demonstrated by the *Young's Double Slit* experiment:



S is a monochromatic (single wavelength) light source. Slits 1 and 2 are equidistant from the slit O, which means that points on the same wave front will arrive at slits 1 and 2 simultaneously, and 1 and 2 will now become two new identical monochromatic sources of light. What is observed on the screen is a very bright spot (or line) where it intersects the dashed line, with a series of symmetrical light and dark spots going up and down from the centre, with the light spots becoming progressively less intense. These bright spots occur when the waves from the two sources (slits 1 and 2) reach a spot on the screen and are in phase. Similarly the dark spots occur when they reach a spot and are (exactly) out of phase. This display of light and dark spots is known as a **diffraction** pattern, which is as a consequence of the wave nature of light.

If this experiment is repeated (as done by Davisson & Germer) with a source of monoenergetic electrons with the same wavelength, a similar diffraction pattern is observed. Not that you would see bright and dark spots but, regions of high and low electron density would be seen. This confirms that electrons do have wave properties.

One cannot tell where a given electron will hit the screen because of the HUP, but if one uses a many electron beam then the proportion hitting some particular area will have a definite value given by the corresponding probability function P. The analogy with light indicates that electronic behaviour cannot

only be explained by P but with a wave function ψ (psi – pronounced “sigh”), of which P is the square.

This does not mean that electrons are waves, but that their behaviour is governed by mathematical equations similar to those for wave motion. A mathematical representation describing a given wave motion is called a **wavefunction**, ψ . This wavefunction can be positive or negative. The intensity of the wave motion (e.g. the brightness of light or the loudness of sound) at some point in space is a function of ψ^2 at that point.

For two interacting wave forms with respective wavefunctions ψ_1 and ψ_2 , the wavefunction describing the new wave form in the region of space where they interact is given by, $\psi_{12} = \psi_1 + \psi_2$. The resulting intensity is therefore given by

$$\psi_{12}^2 = (\psi_1 + \psi_2)^2 = \psi_1^2 + \psi_2^2 + 2\psi_1\psi_2. \quad (8)$$

This result shows us that the intensity of the new waveform is different from that of the sum of the intensities of the two separate waveforms, i.e.

$$(\psi_1 + \psi_2)^2 \neq \psi_1^2 + \psi_2^2 \quad (9)$$

Since ψ_1 and ψ_2 can be positive or negative, so can be their product $\psi_1\psi_2$. It can therefore be seen that when both ψ_1 and ψ_2 have the same sign then,

$$(\psi_1 + \psi_2)^2 > \psi_1^2 + \psi_2^2$$

and when they are of opposite signs then,

$$(\psi_1 + \psi_2)^2 < \psi_1^2 + \psi_2^2.$$

It can be reasoned as follows:

if ψ_2 is negative, then $\psi_1 + \psi_2$ becomes $\psi_1 + -\psi_2$ which is equal to $\psi_1 - \psi_2$. Therefore,

$$(\psi_1 - \psi_2)^2 = \psi_1^2 + \psi_2^2 - 2\psi_1\psi_2$$

which is less than $(\psi_1 + \psi_2)^2$ by $4\psi_1\psi_2$.

You will find this very useful when studying hybridization of orbitals and the formation of bonds between atoms to form molecules, since both of these concepts involve the interaction of orbitals which can be on the same atom (as in hybridization) or on different atoms (as in bond formation).

Exercise 5. Two hydrogen (H) atoms are interacting to form a molecule (H₂). If the wavefunction for each atom is given as ψ_a , which is allowed to be positive or negative, derive the intensities associated with the resulting wavefunctions. Comment on the solutions.

Solution

When the wavefunctions are both positive and both negative the resulting wavefunctions are:

$$\psi_a + \psi_a = \psi_a + \psi_a = 2\psi_a, \text{ and } (-\psi_a) + (-\psi_a) = -(\psi_a + \psi_a) = -2\psi_a, \text{ respectively}$$

The intensities are given by the square of the wavefunctions, and give the same solution of $4\psi_a^2$ in both cases, i.e. $(2\psi_a)^2 = (-2\psi_a)^2 = 4\psi_a^2$.

When one is positive and the other is negative, the new wavefunction is:

$\psi_a + (-\psi_a) = \psi_a - \psi_a = 0!$ The wavefunctions cancel and thus the intensity is also zero.

The first result signifies constructive interference between the atoms and leads to increased (shared) electron density between the nuclei and results in bond formation, (i.e. *bonding*) and the second result shows destructive interference, or no shared electron density and results in *anti-bonding*. (You will meet this topic in the Inorganic part of the course under the topic of *Structure and Bonding*, and in the Organic Chemistry part under Hybridization).