1.2: Some Important Experiments with Electrons and Light

Certainly the early experiments on the properties of electrons did not suggest that any unusual behaviour was to be expected. Everything pointed to the electron being a particle of very small mass. The trajectory of the electron can be followed in a device such as a Wilson cloud chamber. Similarly, a beam of electrons generated by passing a current between two electrodes in a glass tube from which the air has been partially evacuated will cast the shadow of an obstacle placed in the path of the beam. Finally, the particle nature of the electron was further evidenced by the determination of its mass and charge.

Just as classical considerations placed electrons in the realm of particles, the same classical considerations placed light in the realm of waves with equal certainty. How can one explain diffraction effects without invoking wave motion?

In the years from 1905 to 1928 a number of experiments were performed which could be ***interpreted by classical mechanics*** only if it was assumed that electrons possessed a wave motion, and light was composed of a stream of particles! Such dualistic descriptions, ascribing both wave and particle characteristics to electrons or light, are impossible in a physical sense. The electron must behave either as a particle or a wave, but not both (assuming it is either). "Particle" and "wave" are both concepts used by ordinary or classical mechanics and we see the paradox which results when classical concepts are used in an attempt to describe events on an atomic scale. We shall consider just a few of the important experiments which gave rise to the classical explanation of dual behaviour for the description of electrons and light, a description which must ultimately be abandoned.

The Photoelectric Effect

Certain metals emit electrons when they are exposed to a source of light. This is called the photoelectric effect. The pertinent results of this experiment are

i. The number of electrons released from the surface increases as the intensity of he light is increased, but the energies of the emitted electrons are independent of the intensity of the light.
ii. No electrons are emitted from the surface of the metal unless the frequency of the light is greater than a certain minimum value. When electrons are ejected from the surface they exhibit a range of velocities, from zero up to some maximum value. The energy of the electrons with the maximum velocity is found to increase linearly with an increase in the frequency of the incident light.

The first result shows that light cannot be a wave motion in the classical sense. As an analogy, consider waves of water striking a beach and hitting a ball (in place of an electron) at the water's edge. The intensity of a wave is proportional to the square of the amplitude (or height) of the wave. Certainly, even when the frequency with which the waves strike the beach remains constant, an increase in the amplitude of the waves will cause much more energy to be released when they strike the beach and hit the ball. Yet when light "waves" strike a substance only the number of emitted electrons increases as the intensity is increased; the energy of the most energetic electrons remains constant. This can be explained only if it is assumed that the energy in a beam of light is not transmitted in the manner characteristic of a wave, but rather that the energy comes in bundles or packets and that the size of the packet is determined by the frequency of the light. This explanation put forward by Einstein in 1905 relates the energy to the frequency - and not to the intensity of the light - as required by the experimental results. A packet of light energy is called a photon. The results of the photoelectric experiment show that the energy e of a photon is directly proportional to the frequency n of the light, or, calling the constant of proportionality h, we have:

$$\varepsilon = hv \tag{1.2.1}$$

Since the electron is bound to the surface of the metal, the photon must possess a certain minimum amount of energy, i.e., possess a certain minimum frequency n_o, just sufficient to free the electron from the metal. When an electron is ejected from the surface by a photon with a frequency greater than this minimum value, the energy of the photon in excess of the minimum amount appears as kinetic energy of the electron. Thus:

$$kinetic\ energy\ of\ electron = hv - hv_0 \tag{1.2.2}$$

where hn is the energy of the photon with frequency n, and hn_o is the energy of the photon which is just sufficient to free the electron from the metal. Experimentally we can measure the kinetic energy of the electrons as a function of the frequency n. A plot of the kinetic energy versus the frequency gives a straight line whose slope is equal to the value of h, the proportionality constant. The value of h is found to be 6.6 ´ 10^{-27} erg sec.

Equation 1.2.1 is revolutionary. It states that the energy of a given frequency of light cannot be varied continuously, (Click here for note.) as would be the case classically, but rather that it is fixed and comes in packets of a discrete size. The energy of light is said to be quantized and a photon is one quantum (or bundle) of energy.

It is tempting at this point, if we desire a classical picture of what is happening, to consider each bundle of light energy, that is, each photon, to be an actual particle. Then one photon, on striking an individual electron, scatters the electron from the surface of the metal. The energy originally in the photon is converted into the kinetic energy of the electron (minus the energy required for the electron to escape from the surface). This picture must not be taken literally, for then the diffraction of light is inexplicable. Nor, however, can the wave picture for diffraction be taken literally, for then the photoelectric effect is left unexplained. In other words, light behaves in a different way from ordinary particles and waves and requires a special description.

The constant *h* determines the size of the light quantum. It is termed Planck's constant in honour of the man who first postulated that energy is not a continuously variable quantity, but occurs only in packets of a discrete size. Planck proposed this postulate in 1901 as a result of a study of the manner in which energy is distributed as a function of the frequency of the light emitted by an incandescent body. Planck was forced to assume that the energies of the oscillations of the electrons in the incandescent matter, which are responsible for the emission of the light, were quantized. Only in this way could he provide a theoretical explanation of the experimental results. There was a great reluctance on the part of scientists at that time to believe that Planck's revolutionary postulate was anything more than a mathematical device, or that it represented a result of general applicability in atomic physics. Einstein's discovery that Planck's hypothesis provided an explanation of the photoelectric effect as well indicated that the quantization of energy was indeed a concept of great physical significance. Further examples of the quantization of energy were soon forthcoming, some of which are discussed below.

The Diffraction of Electrons

Just as we have found dualistic properties for light when its properties are considered in terms of classical mechanics, so we find the same dualism for electrons. From the early experiments on electrons it was concluded that they were particles. However, a beam of electrons, when passed through a suitable grating, gives a diffraction pattern entirely analogous to that obtained in diffraction experiments with light. In other words, not only do electrons and light both appear to behave in completely different and strange ways when considered in terms of our everyday physics, they both appear to behave in the same way! Actually, the same strange behaviour can be observed for protons and neutrons. All the fundamental particles and light exhibit behaviour which leads to conflicting conclusions when classical mechanics is used to interpret the experimental findings.

The diffraction experiment with electrons was carried out at the suggestion of de Broglie. In 1923 de Broglie reasoned that a relationship should exist between the "particle" and "wave" properties for light. If light is a stream of particles, they must possess momentum. He applied to the energy of the photon Einstein's equation for the equivalence between mass and energy:

$$\varepsilon = mc^2$$

where *c* is the velocity of light and *m* is the mass of the photon. Thus the momentum of the photon is *mc* and:

$$\varepsilon = momentum \times c$$

If light is a wave motion, then of course it possesses a characteristic frequency *n* and wavelength l which are related by the equation:

$$v = \frac{c}{\lambda}$$

The frequency and wavelength may be related to the energy of the photon by using Einstein's famous relationship:

$$\varepsilon = hv = \frac{hc}{\lambda}$$

By equating the two expressions for the energy:

$$\frac{hc}{\lambda} = momentum \times c$$

de Broglie obtained the following relationship which bears his name:

$$\lambda = \frac{h}{momentum} \tag{1.2.3}$$

However, de Broglie did not stop here. It was he who reasoned that light and electrons might behave in the same way. Thus a beam of electrons, each of mass *m* and with a velocity *u* (and hence a momentum *mu*) should exhibit diffraction effects with an apparent wavelength:

$$\lambda = \frac{h}{mv}$$

Using de Broglie's relationship, we can calculate that an electron with a velocity of 1 ´ 10^9 cm/sec should have a wavelength of approximately 1 x 10^{-8} cm. This is just the order of magnitude of the spacings between atoms in a crystal lattice. Thus a crystal can be used as a diffraction grating for electrons. In 1927 Davisson and Germer carried out this very experiment and verified de Broglie's prediction. (See Problem 1 at the end of this section.)

Line Spectra

A gas will emit light when an electrical discharge is passed through it. The light may be produced by applying a large voltage across a glass tube containing a gas at a low pressure and fitted with electrodes at each end. A neon sign is an example of such a "discharge tube." The electrons flowing through the tube transfer some of their energy to the electrons of the gaseous atoms. When the atomic electrons lose this extra energy and return to their normal state in the atom the excess energy is emitted in the form of light. Thus the gaseous atoms serve to transform electrical energy into the energy of light. The puzzling feature of the emitted light is that when it is passed through a diffraction grating (or a prism) to separate the light according to its wavelength, only certain wavelengths appear in the spectrum. Each wavelength appears in the spectrum as a single narrow line of coloured light, the line resulting from the fact that the emitted light is passed through a narrow slit (thus producing a thin "line" of light) before striking the grating or the prism and being diffracted. Thus a "line" spectrum rather than a continuous spectrum is obtained when atomic electrons are excited by an electrical discharge.

An example of such a spectrum is given in Fig. 1-1, which illustrates the visible spectrum observed for the hydrogen atom. This spectrum should be contrasted with the more usual continuous spectrum obtained from a source of white light which consists of a continuous band of colours ranging from red at the long wavelength end to violet at short wavelengths.

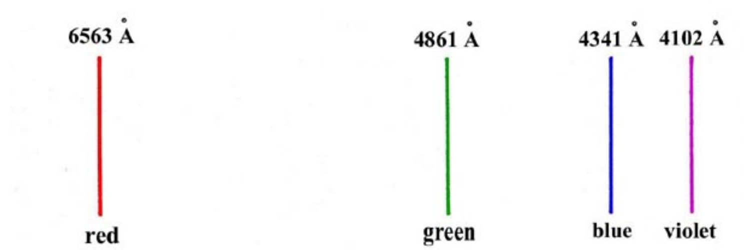

Fig. 1-1. The visible spectrum for hydrogen atoms (1Å = 1 Ångstrom = 1 ´ 10^{-8} cm)

The energy lost by an electron as it is attracted by the nucleus appears in the form of light. If all energies were possible for an electron when bound to an atom, all wavelengths or frequencies should appear in its emission spectrum, i.e., a continuous spectrum should be observed. The fact that only certain lines appear implies that only certain values for the energy of the electron are possible or allowed. We could describe this by assuming that the energy of an electron bound to an atom is quantized. The electron can then lose energy only in fixed amounts corresponding to the difference in value between two of the allowed or quantized energy values of the atom. Since the energy of a photon is given by

$\varepsilon = hv$

and e must correspond to the difference between two of the allowed energy values for the electron, say *E* and *E*' {*E*' > *E*), then the value of the corresponding frequency for the photon will be given by

$$\frac{E' - E}{h} = v = \frac{\varepsilon}{h} \tag{1.2.4}$$

Obviously, if only certain values of *E* are allowed, only certain values of e or *n* will be observed, and a line spectrum rather than a continuous spectrum (which contains all values of *n*) will be observed.

Equation 1.2.4 was put forward by Bohr in 1913 and is known as Bohr's frequency condition. It was Bohr who first suggested that atomic line spectra could be accounted for if we assume that the energy of the electron bound to an atom is quantized. Thus the parallelism between the properties of light and electrons is complete. Both exhibit the wave-particle dualism and the energies of both are quantized.

The Compton Effect

The results of one more experiment will play an important role in our discussions of the nature of electrons bound to an atom. The experiment concerns the direct interaction of a photon and an electron.

In order to determine the position of an object we must somehow "see" it. This is done by reflecting or scattering light from the object to the observer's eyes. However, when observing an object as small as the electron we must consider the interaction of an individual photon with an individual electron. It is found experimentally and this is the Compton effect that when a photon is scattered by an electron, the frequency of the emergent photon is lower than it was before the scattering. Since e = *hn*, and *n*is observed to decrease, some of the photon's energy has been transmitted to the electron. If the electron was initially free, the loss in the energy of the photon would appear as kinetic energy of the electron. From the law of conservation of energy,

$$hv - hv' = \frac{1}{2}mv^2 = kinetic\ energy\ of\ electron$$

where *n*' is the frequency of the photon after collision with the electron. This experiment brings forth a very important effect in the making of observations on the atomic level. We cannot make an observation on an object without at the same time disturbing the object. Obviously, the electron receives a kick from the photon during the observation. While it is possible to determine the amount of energy given to the electron by measuring *n* and *n*', we cannot however, predict in advance the final momentum of the electron. A knowledge of the momentum requires a knowledge of the direction in which the electron is scattered after the collision and while this can be measured experimentally one cannot predict the outcome of any given encounter. We shall illustrate later, with the aid of a definite example, that information regarding both the position and the momentum of an electron cannot be obtained with unlimited accuracy. For the moment, all we wish to draw from this experiment is that we must be prepared to accept a degree of uncertainty in the events we observe on the atomic level. The interaction of the observer with the system he is observing can be ignored in classical mechanics where the masses are relatively large. This is not true on the atomic level as here the "tools" employed to make the observation necessarily have masses and energies comparable to those of the system we are observing.

In 1926 Schrödinger, inspired by the concept of de Broglie's "matter waves," formulated an equation whose role in solving problems in atomic physic's corresponds to that played by Newton's equation of motion in classical physics. This single equation will correctly predict all physical behaviour, including, for example, the experiments with electrons and light discussed above. Quantization follows automatically from this equation, now called Schrödinger's equation, and its solution yields all of the physical information which can be known about a given system. Schrödinger's equation forms the basis of quantum mechanics and as far as is known today the solutions to all of the problems of chemistry are contained within the framework of this new mechanics. We shall in the remainder of this site concern ourselves with the behaviour of electrons in atoms and molecules as predicted and interpreted by quantum mechanics.
