CHAPTER I

§ 1. Nowadays when a physicist wishes to investigate a molecular or atomic problem, often the first thing he does is to draw an energy diagram. He draws a graph, plotting the potential energy of the system as ordinate against some co-ordinate as abscissa. For example, it may be the energy of mutual attraction or repulsion of two atoms plotted against their distance apart, or it may be the potential energy of an electron in a molecular electrostatic field. This way of tackling problems is characteristic of quantum mechanics, and is due to the fact that the potential energy V of the system, as a function of the co-ordinates, occurs in every form of the Schroedinger wave equation.

Facility in the rapid construction and rapid interpretation of these energy diagrams is easily acquired, and is of great help in understanding the innovations of quantum mechanics. We will therefore first consider energy diagrams according to classical laws, beginning with the simplest problem. The reader who is already familiar with these graphical methods may prefer to pass on to § 2.

If we throw a mass m vertically upwards with an initial velocity v, it will rise to a height equal to $v^2/2g$, where g is the acceleration due to gravity. During its flight, the total energy of the body, W, neglecting air-resistance, will be constant. If then we plot W as ordinate against h as abscissa, we obtain a horizontal straight line, such as AQ, fig. 1. As the body rises, it acquires potential energy V, at any height h equal to mgh. Plotting this on the same diagram, we obtain a straight line BD, whose slope is mg. The vertical distance at any point between the two lines, such as AB, gives of course the kinetic energy of the body at the corresponding height. As the body rises, the potential

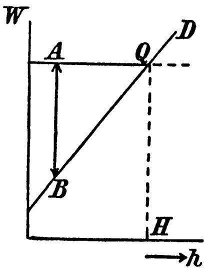

Fig. 1

energy goes on increasing until it becomes equal to the total energy W, when the two lines intersect; the kinetic energy has obviously fallen to zero, i.e. the particle has come to rest at a certain height H corresponding to the vertical dotted line through Q. And according to classical mechanics the particle will return from this point. The suggestion that the particle might rise to a height beyond H is absurd, because its potential energy would be greater than its total energy, and its kinetic energy would need to be negative, which is meaningless. The region beyond H is therefore a forbidden region into which particles of energy W cannot enter.

The process of retardation and stoppage, illustrated in fig. 1, is at the basis of the stability of the material universe. When in the nineteenth century the idea was developed by Clausius and Maxwell that all heat was due to the unceasing rapid motion of molecules, there was no difficulty as regards gases; on the contrary, the hypothesis accounted for their fluid properties very well. But for solids the position was different. To quote from the *Encyclopædia Britannica*: The distances traversed by the atoms of a solid are very small in extent, as is shown by innumerable facts of everyday observation. For instance, the surface of a finely carved metal (such as a plate used for steel engraving) will retain its exact shape for centuries, and again, when a metal body is coated with gold-leaf, the atoms of the gold remain on its surface indefinitely; if they moved through any but the smallest distances, they would soon become mixed with the atoms of the base metal and diffused through its interior. Thus the atoms of a solid can make only small excursions about their mean positions.

Thus the kinetic theory of heat was reconciled with the stability of solid matter by using the idea of allowed regions where $W > V$, and forbidden regions with a sharp boundary between them, as in fig. 1. It is supposed that for each atom of a solid there is a little allowed region in which the atom moves, the whole of the rest of space being the forbidden region. In whatever direction the atom moves, its potential energy rapidly increases, its kinetic energy meanwhile decreasing, as in fig. 1, until the atom is brought to rest and turned back again at the surface where $W = V$. The potential energy along any straight line will be of the form of fig. 2, so that the atom is confined in a kind of potential bowl or box. In this respect the atom resembles the bob of a pendulum, whose potential energy plotted against the displacement will always be like fig. 2, the kinetic energy being greatest in the middle. The width of the allowed region for the atom depends upon the total energy which it has, just as the amplitude of oscillation of a pendulum or of a tuning-fork depends upon its energy. Thus any line PQ lying above AB represents a higher total energy and possesses a wider allowed region. The V-curve may be symmetrical as in fig. 2, or else, when the retardation is much more rapid in one direction than in the other, it may be very unsymmetrical, as in fig. 49 on p. 88.

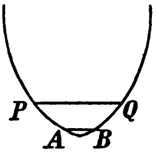

Fig. 2

It is not only in a solid that atoms must be pictured as confined to a small region as in fig. 2, but the same is true for any atom which forms part of a diatomic or polyatomic molecule. Each atom remains attached to the others, because it is in a potential box, surrounded on all sides by a forbidden region. Or, rather, it remains attached so long as its total energy W is less than V on all sides. If at any time the atom acquires so much energy that $(W - V)$ is greater than the depth of the potential bowl, fig. 49, the atom can escape, i.e. the molecule can dissociate.

The next step will be to discuss the motion of an electrically charged particle in an electrostatic field. Let A and B in fig. 3a be two parallel metal plates charged respectively positive and negative. And suppose we throw a ray of ultra-violet light on to the middle of A, so that a photoelectron is ejected from the metal. We will suppose that it is ejected at right angles to the surface, as indicated by the arrow. When the electron has escaped from the metal it moves against a uniform retarding field, in which its potential energy must be represented by a straight line, such as DF in fig. 3b. Now the particle may, or may not, have sufficient energy to get across to the opposite plate. If the total energy of the particle is such as to be represented by the line MN it will arrive; in fact, it will reach the plate with the small kinetic energy NF. If, on the other hand, the total energy is only such as to be represented by the line GC, then the electron will come to rest at Q, and according to classical mechanics will return to the plate from which it came.

In the above we have not considered the initial escape of the electron from the interior of the metal. This will be very similar to the familiar escape of a molecule from the surface of a liquid, a case which we shall treat first. Suppose a straight line AB be drawn perpendicular to the surface of a homogeneous liquid, as in fig. 4a; and consider what will be the potential energy of a molecule along this line. In fig. 4b let the abscissae be the height h along the line AB, and let S represent the point where AB cuts the surface of the liquid, the liquid being to the left of S and the vapour to the right. A molecule at rest in the vapour possesses more energy than a molecule at rest within the liquid; let this difference in potential energy be represented by CE, so that FG represents the potential energy outside the surface, and CD that within. Then the potential energy of a molecule along the line AB will be given by a curve like $CDFG$.

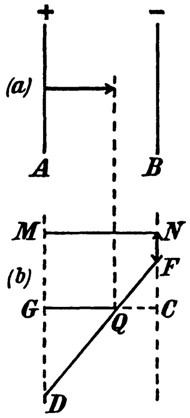

Fig. 3

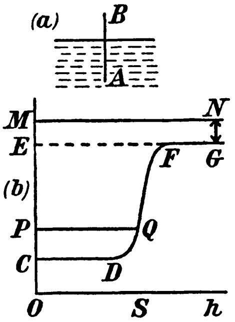

Fig. 4

We know that when a molecule approaches a liquid surface from within with an energy greater than a certain critical energy, it can escape from the liquid. This case will be represented by a molecule moving along the line AB with kinetic energy equal to CM. It will be heavily retarded as it approaches the surface, but will escape with the small residual kinetic energy NG. It is of course only very exceptional molecules which approach with kinetic energies as great as CM. The average kinetic energy will be much smaller; let it be equal to CP. For this molecule the region beyond Q is in classical mechanics a forbidden region, so that the molecule is turned back from the boundary at Q. If P and M have been chosen so that CP and GN are the *average* values of the kinetic energy in the liquid and vapour respectively, then the quantity represented by the vertical distance PM is just the latent heat of vaporisation of the liquid at the temperature considered.

We may now return to the problem of the extraction of an electron from a metal. At room temperature the spontaneous escape of an electron from a metal surface is a comparatively rare occurrence, since the latent heat of evaporation of metallic electrons is many times larger than for molecules of liquids, such as water. But the energy diagram of fig. 4 may be used if we suppose the scale of ordinates to have been changed. Let AB in fig. 4a be a line drawn perpendicular to a metal surface, and let S in fig. 4b now represent the point where AB cuts the surface of the metal, a vacuum being to the right of S, and metal to the left. By considering an electron at rest inside the metal and an electron at rest in the vacuum, we obtain the potential energy curve $CDFG$. An electron having a kinetic energy such as CP is turned back at the surface. If, however, light is incident on the surface, and the electron absorbs from the light a quantum of energy equal to PM in fig. 4b, then the electron may escape from the metal with a residual kinetic energy equal to GN; this is the photoelectric effect.

If, instead of considering only one surface of a metal, we consider the potential energy along a line drawn right through a piece of metal, we shall have the complete curve of fig. 5, showing how an electron is turned back at either surface. And this diagram would apply equally to a molecule in a drop of liquid. In either case any horizontal line which cuts the V-curve (such as W in fig. 5) represents the energy of a particle which is confined to the "potential box", while any W lying wholly above the V-curve will be the energy of a free escaping or entering particle.

In figs. 4 and 5 we have been dealing with large-scale systems; the allowed region was the whole volume of the drop of liquid or piece of metal. But if we alter the scale of abscissae of fig. 5, we arrive at the situation already described in fig. 2, where the width of the allowed region was only one atomic diameter. Fig. 6, which is a simplified version of fig. 2 formed from two straight lines, will be discussed in Chapter III. Here it is only necessary to add that in the same type of diagram is embraced the union of electrons and a positive nucleus to form a neutral atom. Although the electrons within an atom are in rapid motion, with kinetic energy equal to $W-V$, each is of course confined in a very small allowed region. If, for example, we plot the mutual potential energy, $V=-\epsilon^2/r$, of the electron and proton in a hydrogen atom, we have fig. 7. Any value of W lying wholly above this curve represents a free electron; for a bound electron the V- and W-curves must cut, as in fig. 7. It was an essential feature of Bohr's atomic model to suppose that for bound electrons only certain discrete values of W occurred in nature.

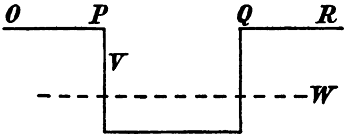

Fig. 5

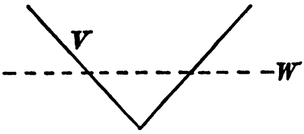

Fig. 6

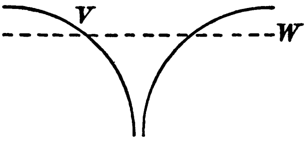

Fig. 7

§ 2. In the following chapters it will often be necessary to consider the actual magnitude of atomic and molecular energies. And this seems the most convenient point to look into the orders of magnitude involved. The spacing of the allowed energy levels in atoms and molecules determines the frequencies ν of the radiation that the system can emit and absorb, according to the relation

$$h\nu = W_m - W_n,$$

where $h = 6{\cdot}5 \times 10^{-27}$ erg secs., and W_m and W_n are any two of the energies expressed in ergs. The frequency of violet light is about 10^{15} sec.$^{-1}$; hence a quantum of violet light contains about 6×10^{-12} ergs. The most convenient unit for measuring atomic energies is the electron-volt, that is, the energy acquired by an electron or proton in falling through a potential difference of one volt; it is equal to $1{\cdot}6 \times 10^{-12}$ ergs. Hence quanta of visible light contain from 2 to 4 electron-volts of energy. (The volt is defined as 10^8 e.m.u.; dividing this by the velocity of light, namely $c = 3 \times 10^{10}$, we find that the volt is 1/300 e.s.u. The electronic charge ϵ is $4{\cdot}77 \times 10^{-10}$ e.s.u., and the value of the electron-volt in ergs, often written "ϵ-volt", is 1/300 of this.) It is useful to remember that the infra-red wave-length 12,345 Ångström units, or $1{\cdot}2345\mu$, corresponds to exactly one ϵ-volt (as may easily be verified from the relation $h\nu = hc/\lambda$). The vibrational energies of molecules are usually a little less than this, while the rotational energies give rise to spectra in the far infra-red, with wave-lengths approaching a millimetre.

It will be useful to compare these values with those of thermal energies at room temperature. The molar gas constant is $8{\cdot}3 \times 10^7$ ergs; dividing this by Avogadro's number, $6{\cdot}06 \times 10^{23}$, we obtain the atomic gas constant, $k = 1{\cdot}37 \times 10^{-16}$ ergs. According to the Boltzmann relation, in an assembly at temperature T the number of atoms or molecules having internal energy equal to E is proportional to $e^{-E/kT}$. It is useful to remember that at room temperature the value of kT is about 1/40 of an electron-volt. If then we ask how many molecules possess energy as great as one ϵ-volt, the answer is that a fraction e^{-40}, or 10^{-17}, will do so. It is only at high temperatures that an appreciable number of atoms or molecules are excited to levels as high as this. On the other hand, the spacing between the rotational levels of molecules, mentioned above, is often of the order of $0{\cdot}01$ ϵ-volt. Consequently, even at room temperature the molecules are distributed among a number of different rotational states.

CHAPTER II

It is a commonplace of scientific observation, that when a particular quantity is measured repeatedly with the highest possible precision, not a single value is obtained, but a series of values lying about a certain mean value. Values differing from the mean by a large amount are obtained less often than nearer values. If against each value obtained we plot the number of times it has been obtained, we shall have some form of the familiar "error curve", fig. 8*a*, p. 11.

When a physicist predicts the result of an atomic experiment, his prediction is often embodied in a distribution curve. His recording instruments are not usually sensitive to individual atoms, and in any case the conditions of experiment cannot be made sufficiently precise to enable him to predict a single definite value for the quantity being measured. Often the best he can do then is to express the expected result by means of a curve showing the number of particles for which the measured value will lie, say, between q and $q+dq$. To such a curve it will be convenient to give a name; we will call it the pattern of the predicted results, characteristic of the particular conditions and apparatus used.

An important innovation of quantum mechanics is that it has entirely altered our attitude to such "patterns". The former method of predicting them was as follows: (*a*) calculate what would happen under various ideally precise conditions, predicting for each ideal experiment, not a pattern, but one definite value; and (*b*) having done this, take into account the finite width of the slits in the apparatus, etc., and putting together the various predicted values in their proper proportions, obtain the required curve. The whole method was thus based on the assumption that any ideally precise measurement would lead to one unambiguous result, and that by compounding these results the required pattern was to be obtained. Quantum mechanics, however, is based on the revolutionary idea that the initial assumption is often wrong. If we imagine ourselves to be using ideal apparatus to make observations on a molecular system, we have to admit that there is often no such thing as a single *correct* value for each measured quantity; even by a series of ideally precise measurements the values obtained will have a certain residual "spread". Quantum mechanics has thus introduced the idea of purely theoretical patterns whose shape depends only on the nature of the universe and not at all on any particular apparatus or conditions of experiment.

The reasons for this innovation may be approached in the following way. To determine the position of a moving object we may direct a beam of light on to it, and look to see where it is at a given moment. The ray of light will, we know, exert a pressure on the object, but this is usually too small to disturb its motion. Unless the object has a very small mass, it will not be appreciably accelerated by the incident light. But when we come to very small particles we are faced with a dilemma. For if, on the one hand, the light is not scattered to our eye or sensitive instrument, it does not tell us where the particle was. And if, on the other hand, the radiation is scattered by the particle, there is a transfer of momentum and the particle suffers a recoil, which changes its velocity. Now it might be thought that we could make an exact allowance for this recoil, and so determine precisely both the position and velocity of the particle at a given moment. But this turns out not to be possible, even by an ideal experiment. And we know of no more delicate way of making the observation than by this method of incident radiation; all other methods are in fact clumsier. A serious oversight had thus been made in atomic theory; the fundamental fact had been overlooked, that we cannot observe an atomic system without disturbing it.

In science it is valueless to make an experiment upon a system about whose condition we have scanty information; for no useful conclusion could be drawn from it. It is essential to get the system as well as possible under control by means of preliminary observations. In the older physics it was assumed that in an ideal experiment this initial information would be obtained as a set of definite values, one for each quantity necessary to describe the state of the system at a given moment. But it is now recognised that the preliminary observations are themselves of the nature of a physical experiment, and can give only a blurred substitute for the information which a physicist used to demand; for some quantities at least, they give patterns instead of definite values. The patterns belonging to any system are not independent. As will be explained in Chapter IV, a moderately accurate knowledge of one quantity involves a proportionately greater "spread" in the pattern for some other quantity.

It was formerly assumed that small particles, such as electrons and protons, would obey the same laws of mechanics as macroscopic particles had been found to obey. But we must now admit that, for the reasons given above, atomic particles will never be found to obey the usual laws of mechanics. Since this involves abandoning to some extent the use of definite values, we have to invent a new language in which to talk about molecular systems. It might be thought that, if definite values are renounced, it would now be impossible to specify a definite state of a system. But this is not so; all we have to do is to use the patterns in place of the corresponding definite values. We have at least a definite pattern for each observable quantity. And the reader will see at once that a complete group of patterns will specify one particular state of the system. Any other state will be specified by a group containing different patterns. These patterns are the new language of physics, and it requires only a slight mental readjustment before we can use them as readily as the older language. It is the business of the theoretical physicist to find the shape of these patterns for various atomic problems, and to study how the shape of the patterns will change when he makes some alteration in the system, e.g. when he applies a magnetic field, a beam of incident radiation, or an impinging particle. When this study has been completed he knows all that he needs to know.