JAMES FRANCK

Transformations of kinetic energy of free electrons into excitation energy of atoms by impacts

Nobel Lecture, December 11, 1926

Ladies and gentlemen!

The exceptional distinction conferred upon our work on electron impacts by the Royal Swedish Academy of Sciences requires that my friend Hertz and I have the honour of reporting to you on current problems within this province.

The division of the material between us left me with the task of presenting, in a historical setting, the development of these projects which have led to an association with Bohr´s atomic theory.

Investigations of collision processes between electrons, atoms and molecules have already got well under way. Practically all investigations into the discharge of electricity through gases can be considered under this heading. An enormous amount of knowledge, decisive for the whole development of modern physics, has been gained, but it is just in this gathering that I feel it is unnecessary for me to make any special comment, since the lists of the men whom the Swedish Academy of Sciences have deemed worthy of the Nobel Prize contain a large number of names of research workers who have made their most significant discoveries in these fields.

Attracted by the complex problems of gas discharges and inspired particularly by the investigations of my distinguished teacher E. Warburg, our interest turned in this direction. A starting-point was provided by the observation that in inert gases (and as found later, also in metal vapour) no negative ions were formed by the attachment of free electrons to an atom. The electrons remained rather as free ones, even if they were moving slowly in a dense gas of this type, which can be inferred from their mobility in an electric field. Even the slightest pollution with normal gases produced, at once, a material attachment of the electrons and thus the appearance of normal negative ions.

As a result, one can perhaps divide gases somewhat more clearly than has been the case up to now from the observations described in the literature, into one class with, and one class without, an electron affinity. It was to be

expected that the motion of electrons in gases of the latter kind would obey laws of a particularly simple kind. These gases have exhibited special behaviour during investigations of other kinds into gas discharges. For instance, according to Ramsay and Collie, they have a specially low dielectric strength, and this was, further, extremely dependent upon the degree of purity of the gas (see, for example, Warburg's experiments). The important theory of the dielectric strength of gases, founded by Townsend, the equations of which even today, when used formally, still form the basic foundation of this field failed in these cases. The reason for this seemed likely to be that Townsend's hypothesis on the kind of collisions between slow electrons and atoms, particularly inert-gas atoms, differed from the reality, and it seemed promising to arrive at a kinetic theory of electrons in gases by a systematic examination of the elementary processes occurring when collisions took place between slow electrons and atoms and molecules. We had the experiences and techniques to support us, which men like J. J. Thomson, Stark, Townsend, and in particular, however, Lenard, had created, and also had their concept of the free path-lengths of electrons and the ionization energy, etc., to make use of.

The free path-lengths in the light inert gases were examined first. By "free path" in this connection is to be understood that path which, on the average, is that which an electron traces between two collisions with atoms along a straight track. The distance is measurable as soon as the number of atoms per unit volume is sufficiently small, this being attained by taking a low gas pressure. The method of measurement itself differed but slightly from that developed by Lenard. It is unnecessary to go into closer detail since the results gave the same order of values for the free path-length as Lenard obtained for slow electrons in other gases. The value is of that order which is obtained by calculation if the formulas of the kinetic gas theory are used for the free path-length, taking for the impact radius of the electron a value which is very small compared with the gas-kinetic atom radii. With this assumption, the electrons behave, to a first approximation, like a gaseous impurity in the inert gas, not reacting chemically with it – an impurity, however, which has the special quality of consisting of electrically charged particles and having a vanishingly small impact radius. As a result of significant experiences, we know, today, from the work of Ramsauer and others on the free path-lengths of electrons in heavy inert gases that the picture we had formed at that time was a very rough one, and that for collisions of slow electrons the laws of quantum theory are of far more significance than the

mechanical diameter, but as a first approximation for the establishment of the kinetics it suffices. Further, it also sufficed, as it turned out, to gain an understanding of the energy conversion on the occurrence of a collision between the slow electrons and the atoms of the inert gases and metal vapours. Since the mass of the electron is 1800 times smaller than that of the lightest atom we know, the hydrogen atom, the transfer of momentum from the light electron to the heavy atom during customary gas-kinetic collisions, i.e. collisions such as between two elastic balls, must be exceptionally small according to the laws of momentum. A slow electron with a given amount of kinetic energy, meeting an atom at rest, ought to be reflected without practically any energy loss, much the same as a rubber ball against a heavy wall. These elastic collisions can now be pursued by measurements.

I will pass over the detection of the single reflection and mention in more detail a simple experimental arrangement which, by means of an accumulation of collisions, enables us to measure the energy loss which is otherwise too small to measure in one elementary process. The mode of action might well be clear from a schematic layout (Fig. 1).

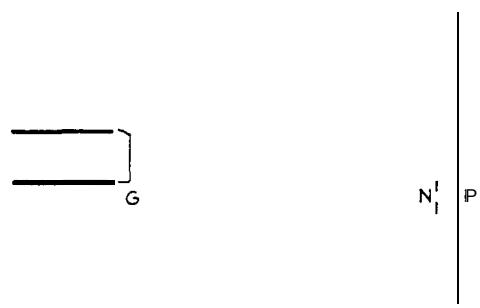

Fig. 1.

G indicates the electron source. It consists of a tungsten wire, heated to a bright-red glow by an electric current. That such a glowing wire is a source of electrons can, I think, be taken as read in this age of radio. A few centimetres away is a wire-screen electrode N. If we now charge the screen positively with respect to the glowing wire, by means of an accumulator, the electrons emitted by the wire towards the screen will be accelerated. The kinetic energy which the electrons must gain through this acceleration can easily be found for the case where no gas exists between G and N, that is, when the electrons fall through the field of force freely without collisions. We have the relationship:

$$\tfrac{1}{2} mv^2 = e \cdot V$$

Here, $\frac{1}{2}mv^2$ is the kinetic energy of each electron, e is its electrical elementary charge, and V the applied potential difference. If the latter is measured in volts, then, for instance, the kinetic energy of an electron which has fallen through 10 volts is approximately 10^{-11} ergs. We have become accustomed to speak of x-volt electrons, and to simply denote the acceleration voltage (x volts) as a measure of energy. Thus in our arrangement the electrons fall upon the screen with an energy of x volts (the potential difference between G and N). Some of the electrons are caught by the screen, some fly through the mesh. The latter, assuming no field between N and P which would throw the electrons back, all reach the electrode P and produce a negative current which flows to earth through a galvanometer. By introducing an electric field between N and P the energy distribution of those electrons passing through the screen can be determined. If, for example, we take only 4-volt beams, which pass perpendicularly through the screen, then the electron current measured at the galvanometer as a function of a decelerating potential difference applied between N and P, must be constant, until P becomes 4 volts more negative than N. At this point the current must become suddenly zero since henceforth all electrons will be so repelled from P that they return to N. If now we introduce an inert gas such as helium or a metal vapour between the three electrodes and choose such a pressure as will ensure that the electrons between G and N will make many impacts upon atoms, whilst passing freely through the space between N and P, we can determine, by plotting the energy distribution of the electrons arriving at P, whether the electrons have lost energy by impacts on the atoms. In discussing the resulting current-voltage curve it should be noted that the electrons no longer pass through the screen mesh perpendicularly, but are scattered in all directions due to reflection from the atoms. As a result of this, there is an easily calculable change in shape of the curve, and this holds, too, for uniform kinetic energy of the electrons. From a consideration of the resulting curves it was found that for not too high pressures, particularly for monatomic gases of high atomic weight, the kinetic energy of slow electrons was the same as for those in vacuum under the same acceleration voltage. The gas complicates the trajectory of the electrons in the same way that a ball's trajectory is affected by rolling down a sloping board bedecked with a large number of nails, but the energy (because of the large mass of the atom compared with that of the electron) is practically the same as for conditions of free fall. Only for high pressures, that is, with the occurrence of many thousands of collisions, can the energy loss corresponding to elastic

collision be demonstrated.* A calculation of the number of collisions was later carried out by Hertz. Taking this as a basis and evaluating the curves measured for higher pressures accordingly, it emerges that, for example, energy is transferred to a helium atom amounting to $1.2-3.0 \times 10^{-4}$ of the energy of the electron prior to the collision, whilst the calculated value for the mass ratio under conditions of pure mechanical elastic impact is 2.9×10^{-4}. We may therefore, with close approximation to reality, speak of elastic collisions.

For polyatomic gases a significantly greater average energy loss was determined. Using the methods available at that time, it was not possible to distinguish whether this latter effect was contingent upon attachment of the electrons to the molecule, that is, the formation of negative ions, or whether a transfer of the kinetic energy of the striking electrons into vibrational and rotational degrees of freedom of the molecules was taking place. An investigation just carried out in my institute by Mr. Harries shows that the latter elementary process, even though at a low level, does occur, and is important in the explanation of the energy losses.

Can the principles of action found for slow electrons in the case of elastic collisions hold good for higher electron velocities? Apparently not, for the elementary knowledge of gas discharges teaches us that with faster electrons, i.e. with cathode rays, the impacted atoms are excited to luminescence or become ionized. Here, energy of the impacting electrons must be transferred into internal energy of the impacted atoms, the electrons must henceforth collide inelastically and give up greater amounts of energy. The determination of the least amount of energy which an electron must possess in order to ionize an atom was therefore of interest. Measured in volts, this energy is called the ionization voltage. Calculations of this value of energy by Townsend were available for some gases and these were based upon the validity of his assumptions about the course of the elementary action on collision. I mentioned already the reasons for doubting the correctness of these indirectly determined values. A direct method had been given by Lenard, but it gave the same ionization voltage for all gases. Other writers had obtained the same results within the range of measurement. We therefore repeated Lenard's investigations, using the improved pumping techniques which had become available in the meantime, and obtained characteristic, marked differences in values for the various gases. The method used by

* It is better to USC here the experimental arrangements indicated later by Compton and Benade, Hertz, and others.

Lenard was as follows. Electrons, from a glowing wire, for example, were accelerated by a suitable electric field and allowed to pass through a screen grid into a space in which they suffered collisions with atoms. By means of a strong screening field these particular electrons were prevented from reaching an electrode to which was connected a measuring instrument. Atoms ionized by the impact resulted in the newly formed positive ions being accelerated through the screening field, which repelled the electrons, towards the negatively charged electrode. A positive current was thus obtained as soon as the energy of the electrons was sufficient for ionization to take place. I will talk later about the fact that a positive charge appears if the impacted atoms are excited to emit ultraviolet light, and that, as shown later, the charges measured at that time are to be attributed to this process and not to ionization, as we formerly supposed.

In any case, as already discussed, inelastic collisions were to be expected between electrons and atoms for the characteristic critical voltages appertaining to each kind of atom. And it proved easy to demonstrate this fact with the same apparatus as was used for the work on elastic collisions. Measurement of the energy distribution of the electrons, on increasing the accelerating voltage above the critical value, showed that electrons endowed with the critical translation energy could give up their entire kinetic energy on collision, and that electrons whose energy exceeded the critical by a fraction, likewise gave up the same significant amount of energy, the rest being retained as kinetic energy. A simple modification of the electric circuit diagram of our apparatus produced a significantly sharper measurement of the critical voltage and a visual proof of the discontinuously occurring release of energy from the electrons on collision. The measurement method consisted of measurements of the number of those electrons (possessing markedly different energies from zero after many collisions) as a function of the accelerating voltage.

The graph (Fig. 2) shows the results of measurements of electron current in mercury vapour. In this case, all electrons whose energy is greater than the energy of ½-volt beams were measured. It can be seen that in Hg vapour this partial electron current increases with increasing acceleration, similar to the characteristic of « glow-electron » current in vacuum, until the critical energy stage is reached when the current falls suddenly to almost zero. Since the electrons cannot lose more or less than the critical amount of energy, the cycle begins anew with further increase of voltage. The number of electrons whose velocity is greater than ½ volt, again climbs up until the critical value is

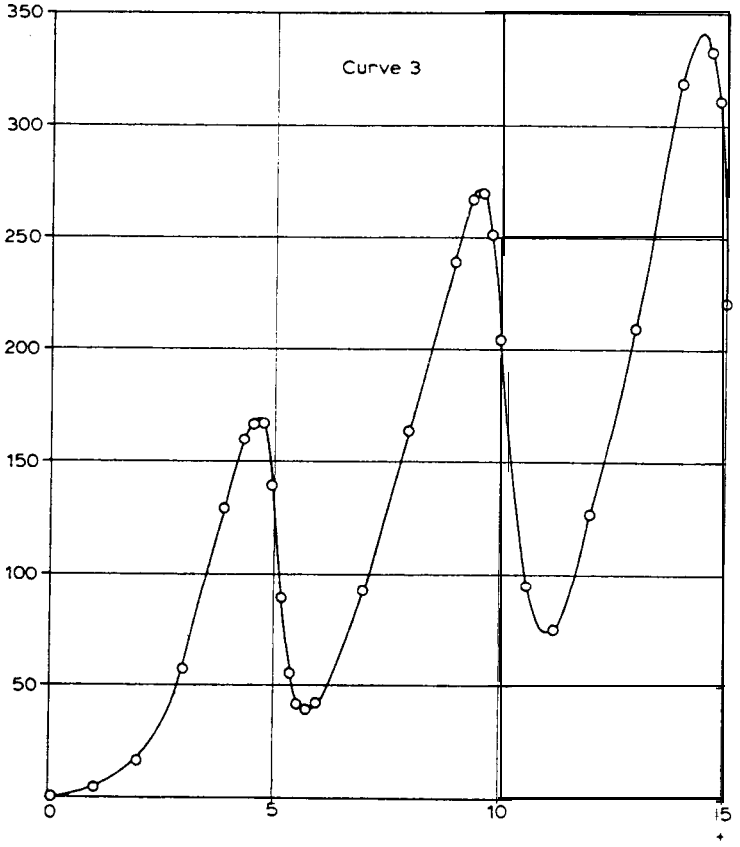

Fig. 2.

reached, the current again falls away. The process repeats itself periodically as soon as the accelerating voltage overreaches a multiple of the critical voltage. The distance between the succeeding maxima gives an exact value of the critical voltage. This is 4.9 V for mercury vapour.

As already mentioned we took this value to be the ionization voltage (the same applied to He which was determined by the same method and was about 20 V). Nevertheless, the quanta-like character of the energy transfer could not help but remind us - who practically from the start could witness from nearby the developments of Planck's quantum theory - to the use of the theory made by Einstein to explain the facts of the photoelectric effect! Since here, light energy is converted into the kinetic energy of electrons, could not perhaps, in our case, kinetic energy from electrons be converted into light energy? If that were the case, it should be easy to prove in the case of mercury; for the equation $\frac{1}{2}mv^2 = h\nu$ referred to a line of 2,537 Å which is

easily accessible in the ultraviolet region. This line is the longest wavelength absorption line of Hg vapour. It is often cited as Hg-resonance line since R.W. Wood has carried out with it his important experiments on resonance fluorescence. If the conjectured conversion of kinetic energy into light on impact should take place, 'then on bombardment with 4.9 eV electrons, the line 2,537 A, and only this line out of the complete line spectrum of mercury should appear.

Fig. 3 shows the result of the experiment. Actually, only the 2,537 Å line appears in the spectrogram next to a continuous spectrum in the long-wave region emitted by the red-glowing filament. (The second spectrogram shows the arc spectrum of mercury for comparison.) The first works of Niels Bohr on his atomic theory appeared half a year before the completion of this work. Let us compare, in a few words, the basic hypothesis of this theory with our results.

According to Bohr an atom can absorb as internal energy only discrete quantities of energy, namely those quantities which transfer the atom from one stationary state to another stationary state. If following on energy supply an excited state results from a transfer to a stationary state of higher energy, then the energy so taken up will be radiated in quanta fashion according to the *hv* relationship. The frequency of the absorption line having the longest wavelength, the resonance line, multiplied by Planck's constant, gives the energy required to reach the first state of excitation. These basic concepts agree in very particular with our results. The elastic collisions at low electron velocities show that for these impacts no energy is taken up as inner energy, and the first critical energy step results in just that amount of energy required for the excitation of the longest wave absorption line of Hg. Subse-

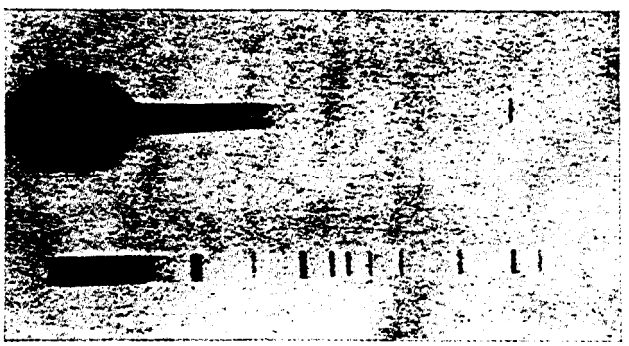

Fig. 3.

quently it appeared to me to be completely incomprehensible that we had failed to recognize the fundamental significance of Bohr's theory, so much so, that we never even mentioned it once in the relevant paper. It was unfortunate that we could not rectify our error (due in part to external circumstances) ourselves by clearing up the still existing uncertainties experimentally. The proof that only monochromatic light was radiated at the first excitation step, as Bohr's theory required, and that the gas is not simultaneously ionized (as we were also obliged to think for reasons other than those mentioned) came about instead during the war period through suggestions from Bohr himself and from van der Bijl. The appearance of positive charge at the first excitation step in Lenard's arrangement was explained by them on the basis of a photoelectric effect at the collector electrode, an hypothesis which was substantiated by Davis and Goucher.

Time does not allow me to describe how our further difficulties were clarified in the sense of Bohr's theory. And in regard to further development, too, I would like to devote only a few words, particularly since my friend Hertz's lecture covers it more closely. The actual ionization voltage of mercury was for the first time determined by Tate as being 10.3 volts, a value which agreed exceptionally well with that resulting, according to Bohr, from the limit of the absorption series. A great number of important, elegantly carried out, determinations of the first excitation level and the ionization voltage of many kinds of atoms was made during the war years and also in the following years, above all by American scientists; research workers such as Foote and Mohler, K. T. Compton and others are to be thanked for extensive clarification in this field.

Without going into details of the experimental arrangements, I should like to mention that it later proved successful, by the choice of suitable experimental conditions, to demonstrate also, from the current-voltage curves, the stepwise excitation of a great number of quantum transitions, lying between the first excitation level and ionization. A curve plotted for mercury vapour might well serve again as an example. It shows the quantum-like appearance of higher excitation levels by kinks in the curve (Fig. 4). It is noteworthy that, in addition, transitions which under the influence of light according to Bohr's correspondence principle do not appear, manifest themselves clearly. When, as is the case with mercury, and still more decidedly so with helium, the first transition is such that it cannot be achieved by light, we have excited atoms in a so-called metastable state. The discovery of a metastable state by means of the electron-impact method was first suc-

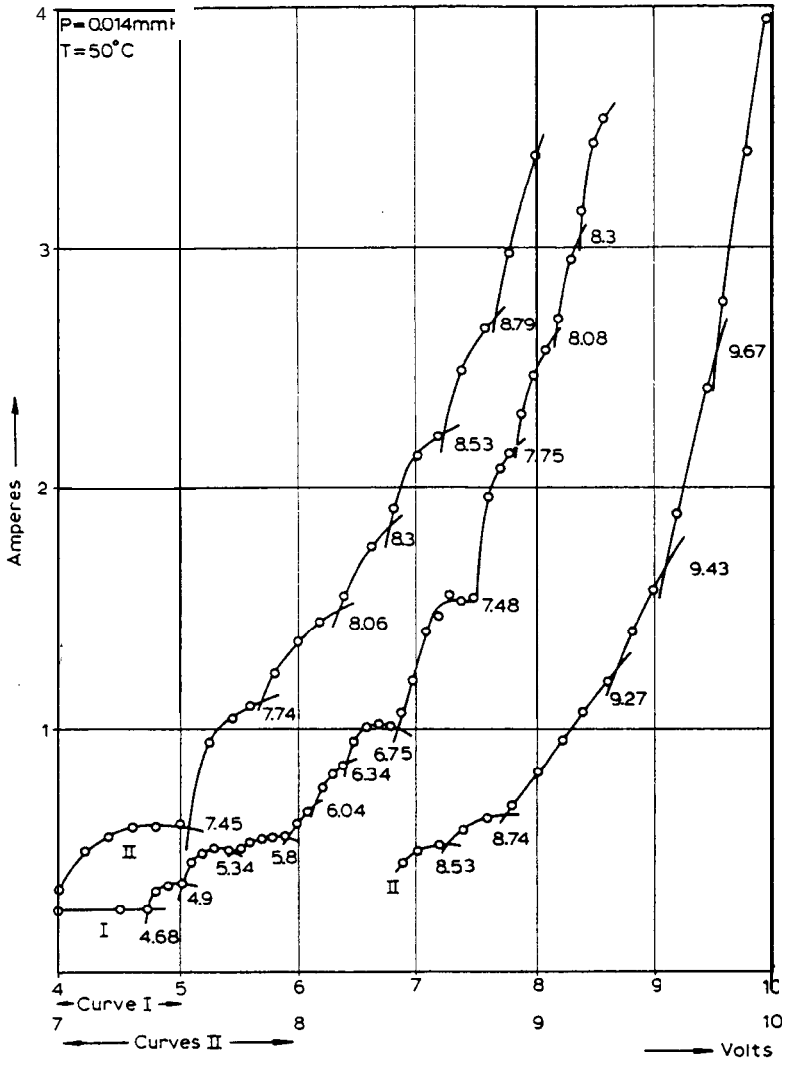

Fig. 4.

cessful with helium. Since helium is a gas in which the absorption series lies in the far ultraviolet-it was later found optically by Lyman - and on the other side, helium, apart from hydrogen, is the most simply constructed atom, the approximate determination of the energy levels of helium and perhaps too, the appearance, in particular, of the metastable level has proved useful for the development of Bohr's theory.

Much more could be said, but I think I have given you the main outline as far as is possible within the framework of a short survey, and must there-

fore draw to a close. The desire to describe, historically, our part in the development of the investigations leading to the establishment of the quantum transfer of energy to the atom by impacting electrons has forced me to take up your time with the description of many a false trail and roundabout path which we took in a field in which the direct path has now been opened by Bohr's theory. Only later, as we came to have confidence in his leadership, did all difficulties disappear. We know only too well that we owe the wide recognition that our work has received to contact with the great concepts and ideas of M. Planck and particularly of N. Bohr.