

OTTO STERN

The method of molecular rays

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In the following lecture I shall try to analyze the method of molecular rays. My aim is to bring out its distinctive features, the points where it is different from other methods used in physics, for what kind of problems it is especially suited and why. Let me state from the beginning that I consider the directness and simplicity as the distinguishing properties of the molecular ray method. For this reason it is particularly well suited for shedding light on fundamental problems. I hope to make this clear by discussing the actual experiments.

Let us first consider the group of experiments which prove directly the fundamental assumptions of the kinetic theory. The existence of molecular rays in itself, the possibility of producing molecular rays, is a direct proof of one fundamental assumption of that theory. This assumption is that in gases the molecules move in straight lines until they collide with other molecules or the walls of the containing vessel. The usual arrangement for producing molecular rays is as follows (Fig. 1): We have a vessel filled with gas or vapor, the oven. This vessel is closed except for a narrow slit, the oven slit. Through this slit the molecules escape into the surrounding larger vessel which is continually evacuated so that the escaping molecules do not suffer any collisions. Now we have another narrow slit, the collimating slit, opposite and parallel to the oven slit. If the molecules really move in straight lines then the collimating slit should cut out a narrow beam whose cross section by simple geometry can be calculated from the dimensions of the slits and their distance. That it is actually the case was proven first by Dunoyer in 1911. He used sodium vapor and condensed the beam molecules hitting the wall by cooling it with liquid air. The sodium deposit formed on the wall had exactly the shape calculated under the assumption that the molecules move in straight lines like rays of light. Therefore we call such a beam a «molecular ray» or «molecular beam».

The next step was the direct measurement of the velocity of the molecules. The kinetic theory gives quite definite numerical values for this velocity, depending on the temperature and the molecular weight. For example, for silver atoms of $1,000^\circ$ the average velocity is about 600 m/sec (silver mole-

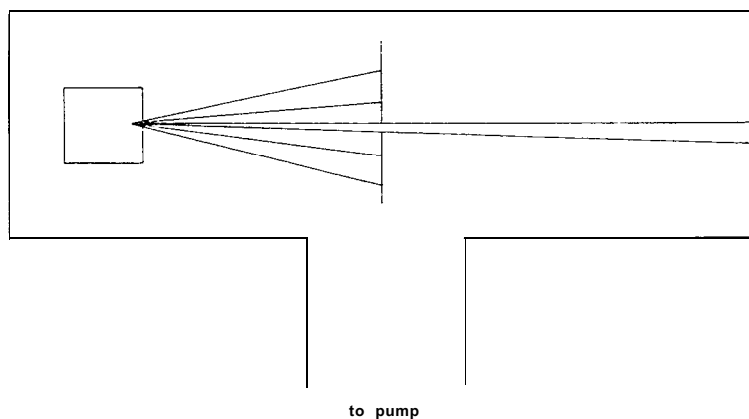


Fig. 1. Arrangement for producing molecular rays.

cules are monoatomic). We measured the velocity in different ways. One way - historically not the first one - was sending the molecular ray through a system of rotating tooth wheels, the method used by Fizeau to measure the velocity of light. We had two tooth wheels sitting on the same axis at a distance of several cm. When the wheels were at rest the molecular beam went through two corresponding gaps of the first and the second wheel. When the wheels rotated a molecule going through a gap in the first wheel could not go through the corresponding gap in the second wheel. The gap had moved during the time in which the molecule travelled from the first wheel to the second. However, under a certain condition the molecule could go through the next gap of the second wheel, the condition being that the travelling time for the molecule is just the time for the wheel to turn the distance between two neighboring gaps. By determining this time, that means the number of rotations per second for which the beam goes through both tooth wheels, we measure the velocity of the molecules. We found agreement with the theory with regard to the numerical values and to the velocity distribution according to Maxwell's law.

This method has the advantage of producing a beam of molecules with nearly uniform velocity. However, it is not very accurate.

As the last one in this group of experiments I want to report on experiments carried out in Pittsburgh by Drs. Estermann, Simpson, and myself before the War, which are now being published. In these experiments we used the free fall of molecules to measure their velocities.

In vacuo all bodies, large and small, fall equal distances in equal times, $s =$

$\frac{1}{2}gt^2$ (t = time, s = distance of fall, g = acceleration of gravity). We used a beam of cesium atoms about 2 m long. Since the average velocity of the atoms is about 200 m/sec the travel time is about 1/100 sec. During this time a body falls not quite a mm. So our cesium atoms did not travel exactly on the straight horizontal line through oven and collimating slit but arrived a little lower depending on their velocity. The fast ones fell less, the slow ones more. So by measuring the intensity (the number of cesium atoms arriving per second) at the end of the beam perpendicular to it as a function of the distance from the straight line, we get directly the distribution of velocities (Fig. 2). As you see the agreement with Maxwell's law is very good. I might mention that we measured the intensity not by condensation but by the so-called Taylor-Langmuir method worked out by Taylor in our Hamburg

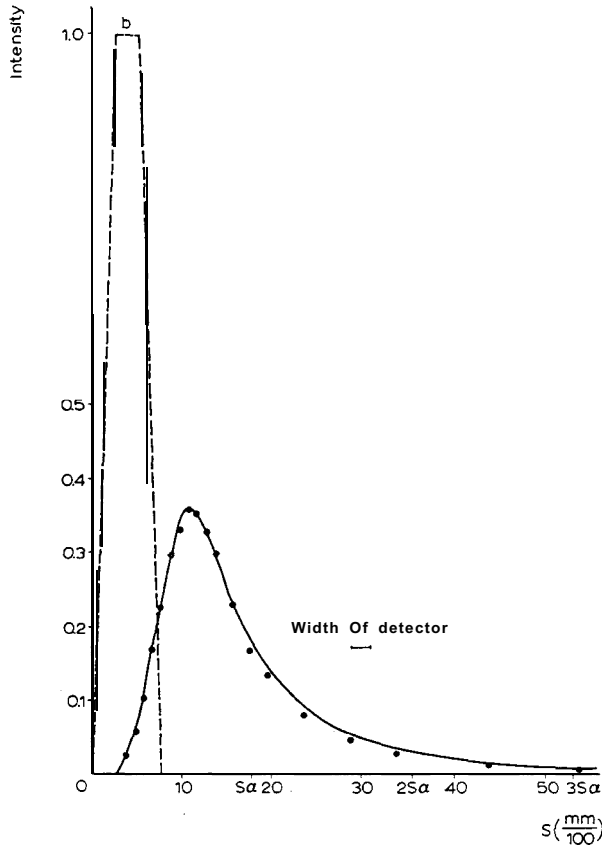


Fig. 2. Gravity deflection of a cesium beam. (Full line): calculated from Maxwell's law; (points): measurements; (pecked line b): undeflected beam.

laboratory in 1928. It is based on Langmuir's discovery that every alkali atom striking the surface of a hot tungsten wire (eventually oxygen-coated) goes away as an ion. By measuring the ion current outgoing from the wire we measured directly the number of atoms striking the wire.

What can we conclude about the method of molecular rays from the group of experiments we have considered so far? It gives us certainly a great satisfaction to demonstrate in such a simple direct manner the fundamentals of the kinetic theory. Furthermore, even if so many conclusions of the theory were checked by experiments that practically no reasonable doubt about the correctness of this part of the theory was possible, these experiments reinforced and strengthened the fundamentals beyond any doubt.

I said this part of the theory.

The classical theory is a grandiose conception. The same fundamental laws govern the movements of the stars, the fall of this piece of chalk, and the fall of molecules. But it turned out that the extrapolation to the molecules did not hold in some respects. The theory had to be changed in order to describe the laws governing the movements of the molecules and even more of the electrons. And it was at this point that the molecular ray method proved its value. Here the experiment did not just check the results of the theory on which there was practically no doubt anyway, but gave a decisive answer in cases where the theory was uncertain and even gave contradictory answers.

The best example is the experiment which Gerlach and I performed in 1922. It was known from spectroscopic experiments (Zeeman effect) that the atoms of hydrogen, the alkali metals, silver, and so on, were small magnets. Let us consider the case of the hydrogen atom as the simplest one even if our experiments were performed with silver atoms. There is no essential difference, and the results were checked with hydrogen atoms a few years later by one of my students in our Hamburg laboratory.

The essential point is that the classical theory and the quantum theory predict quite differently the behavior of the atomic magnets in a magnetic field. The classical theory predicts that the atomic magnets assume all possible directions with respect to the direction of the magnetic field. On the other hand, the quantum theory predicts that we shall find only two directions parallel and antiparallel to the field (the new theory, the old one gave also the direction perpendicular to the field).

The contradiction I spoke of is this. At this time according to Bohr's theory one assumed that the magnetic moment of the hydrogen atom is produced by the movement of the electron around the nucleus in the same way

as a circular current in a wire is equivalent to a magnet. Then the statement of the quantum theory means that the electrons of all hydrogen atoms move in planes perpendicular to the direction of the magnetic field. In this case one should find optically a strong double refraction which was certainly not true. So there was a serious dilemma.

Our molecular ray experiment gave a definite answer. We sent a beam of silver atoms through a very inhomogeneous magnetic field. In such a field the magnets are deflected because the field strength on the place of one pole of the magnet is a little different from the field strength acting on the other pole. So in the balance a force is acting on the atom and it is deflected. A simple calculation shows that from the classical theory follows that we should find a broadening of the beam with the maximum intensity on the place of the beam without field. However, from the quantum theory follows that we should find there no intensity at all, and deflected molecules on both sides. The beam should split up in two beams corresponding to the two orientations of the magnet. The experiment decided in favor of the quantum theory (Fig. 3).



Fig. 3. Discrete beams of deflected molecules.

The contradiction with respect to the double refraction was solved about four years later through the new quantum mechanics in connection with the Uhlenbeck-Goudsmit hypothesis that the electron itself is a small magnet like a rotating charged sphere. But even before this explanation was given, the experiment verified directly the splitting in discrete beams as predicted by the quantum theory.

So again the directness stands out as characteristic for the molecular ray method. However, we can recognize another feature as essential in this experiment, namely that our measuring tool is a macroscopic one. I want to make this point clearer.

The first experiment which gave a direct proof of the fundamental hypoth-

esis of the quantum theory was the celebrated experiment of Franck and Hertz. These workers proved that the energy of one atom can be changed only by finite amounts. By bombarding mercury atoms with electrons they found that the electrons did lose energy only if their energy was higher than 4.7 eV. So they demonstrated directly that the energy of a mercury atom cannot be changed continuously but only by finite amounts, quanta of energy. As a tool for measuring the energy changes of the atom they used electrons, that means an atomic tool. In our experiment we used an electromagnet and slits, that means the same kind of tools we could use to measure the magnetic moment of an ordinary macroscopic magnet. Our experiment demonstrated in a special case a fact, which became fundamental for the new quantum mechanics, that the result of our measurements depends in a characteristic manner on the dimensions of the measured object and that quantum effects become perceptible when we make the object smaller and smaller.

We can see this better when we first consider a group of experiments which demonstrate the wave properties of rays of matter. In his famous theory which became the basis of the modern quantum theory, De Broglie stated that moving particles should also show properties of waves. The wavelength of these waves is given by the equation $\lambda = h/mv$ (h = Planck's constant; m = mass; v = velocity of the particle). The experimental proof was first given in 1927 by Davisson and Germer, and by Thomson for electrons. Some years later we succeeded in performing similar experiments with molecular rays of helium atoms and hydrogen molecules using the cleavage surface of a lithium fluoride crystal as diffraction grating. We could check the diffraction in every detail. The most convincing experiment is perhaps the one where we sent a beam of helium gas through the two rotating tooth wheels which I mentioned at the beginning, thus determining the velocity v in a primitive, purely mechanical, manner. The helium beam then impinged on the lithium fluoride crystal and by measuring the angle between the diffracted and the direct beam we determined the wavelength since we know the lattice constant of the lithium fluoride. We found agreement with De Broglie's formula within the accuracy of our experiments (about 2%). There is no doubt that these experiments could be carried out also by using a ruled grating instead of the crystal. In fact we found hints of a diffracted beam with a ruled grating already in 1928 and with the improved technique of today the experiment would not be too difficult.

With respect to the differences between the experiments with electrons and molecular rays, one can say that the molecular ray experiments go far-

ther. Also the mass of the moving particle is varied (He, H₂). But the main point is again that we work in such a direct primitive manner with neutral particles.

These experiments demonstrate clearly and directly the fundamental fact of the dual nature of rays of matter. It is no accident that in the development of the theory the molecular ray experiments played an important role. Not only the actual experiments were used, but also molecular ray experiments carried out only in thought. Bohr, Heisenberg, and Pauli used them in making clear their points on this direct simple example of an experiment. I want to mention only one consideration concerning the magnetic deflection experiment because it shows the fundamental limits of the experimental method.

First, it is clear that we cannot use too narrow slits, otherwise the diffraction on the slit will spread out the beam. This spreading out can roughly be described as the deflection of the molecules by an angle which is the larger the narrower the slit and the larger the De Broglie wavelength is. Therefore it causes a deflection of the molecules proportional to the distance which the molecule has traversed or to the length of the beam or to the time t since the molecule started from the collimating slit. The deflection by the magnetic force must be appreciably larger if we want to measure the magnetic moment. Fortunately this deflection is proportional to the square of the length of the beam or the time t , essentially as in the case of the gravity ($s = \frac{1}{2}gt^2$). Consequently it is always possible, by making the beam long enough, that means the time t large enough, to make the magnetic deflection larger than the deflection by diffraction. On the other hand it follows that a minimum time is necessary to measure the magnetic moment and this minimum time gets larger when the magnetic deflection, that means the magnetic moment, gets smaller. That is a special case of a general law of the new quantum mechanics. This law - applied to the measurement of moments - says that for *every* method using the same field strength the minimum time is the same. This circumstance was decisive in the group of experiments measuring the magnetic moment of the proton.

The theory predicted that the magnetic moments of electron and proton should be inversely proportional to the masses of those particles. Since the proton has about a two thousand times larger mass than the electron, its magnetic moment should be about two thousand times smaller. Such a small moment could not be measured by the spectroscopic method (Zeeman effect) but we (Frisch, Estermann, and myself) succeeded in measuring it by

using a beam of neutral hydrogen molecules. I do not have time to go into the details. The main point is that in measuring with molecular rays we use a longer time t . In the spectroscopic method this time is the lifetime of the excited atom which emits light by jumping into the normal state. Now this lifetime is generally of the order of magnitude of 10^{-8} sec. Working with molecular rays we use atoms (or molecules) in the normal state whose lifetime is infinite. The duration of our experiment is determined by the time t which the atom (or molecule) spends in the magnetic field. This time was of the order of magnitude of 10^{-4} sec (the length of the field about 10 cm and the velocity of the molecules about 1 km/sec). So our time is about 10,000 times larger and we can measure 10,000 times smaller moments with molecular rays than spectroscopically.

The result of our measurement was very interesting. The magnetic moment of the proton turned out to be about $2\frac{1}{2}$ times larger than the theory predicted. Since the proton is a fundamental particle - all nuclei are built up from protons and neutrons - this result is of great importance. Up to now the theory is not able to explain the result quantitatively.

It might seem now that the great sensitivity as shown in the last experiment is also a distinctive and characteristic property of the molecular ray method. However, that is not the case. The reason for the sensitivity as we have seen is that we make our measurements on atoms in the normal state. But of course many of the other experimental methods do that also.

We can see the situation clearly by considering the last achievement of the molecular ray method, the application of the resonance method by Rabi.

With the deflection method it is difficult to measure the moment to better than several per cent, mainly because of the difficulty of measuring the inhomogeneity in such small dimensions. With the resonance method, Rabi's accuracy is better than 1%, practically the theoretical limit given by the duration of about 10^{-4} sec of the measurement. Theoretically it would be possible to increase the accuracy simply by making this time longer. But that would mean making the beam longer and for practical reasons we cannot go much farther in this direction. In this connection it is significant that perhaps the best new measurements of the magnetic moments of the proton, neutron, and deuteron were made with the resonance method, however not using molecular rays but just liquid water with practically no limit for the duration of the measurement. So the sensitivity cannot be considered as a distinguishing property of the molecular ray method. However, that we have

such clear-cut simple conditions was the reason for applying the ultrasensitive resonance method first to molecular rays.

In conclusion I would like to summarize as follows: The most distinctive characteristic property of the molecular ray method is its simplicity and directness. It enables us to make measurements on isolated neutral atoms or molecules with macroscopic tools. For this reason it is especially valuable for testing and demonstrating directly fundamental assumptions of the theory.