

## RECENT WORK IN MOLECULAR BEAMS

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The production and detection of molecular beams is described briefly. Then follows a discussion of a number of recent problems which have been solved wholly or partially by the application of molecular-beam technique. Special emphasis is placed on the determination of the magnetic properties of atomic nuclei, and a rather complete table of nuclear moments is given.

### I. INTRODUCTION

It is hoped that the following résumé of some of the more important recent work in molecular beams will be of interest, not only to those who have specialized in this field, but also to others. It is our conviction that to some of these latter the molecular-beam method will appear especially appropriate for the solution of new problems. The method has been very fruitful in the past, and there is every reason to expect that as more and more people become proficient in its use, a greater and greater variety of problems will be successfully solved.

The basis of the molecular-beam method lies in the kinetic theory of gases. This is a very beautiful and satisfying theory. Developing gradually, it had acquired such distinction by the first decade of this century that very few people doubted its main features. In brief, these are that all gases are composed of particles moving constantly in straight lines and continually colliding with each other and with the walls of the confining vessel. The speeds of these particles will in general change with each collision; therefore there will be a wide range of velocities in every gas sample. However, at a constant temperature there will be an average velocity which does not change with the time and which can be easily calculated. Furthermore, it is a very simple matter to obtain an expression for the average distance each molecule travels between collisions; this mean free path turns out to be inversely proportional to the pressure.

From these simple assumptions was developed an elegant theory, which, although not directly tested, gave predictions sufficiently close to experimental results to satisfy almost everyone. Deviations from the theory were explained qualitatively as due to the neglect of the finite sizes of the particles and the forces of interaction between them.

Nevertheless, it is always a very satisfying procedure to make a direct test

of fundamentals. As long ago as 1895 (4), manufacturers of incandescent light bulbs found evidences of the rectilinear propagation of gaseous particles. Sharp shadows in the evaporated coatings on the insides of old bulbs could be explained only by assuming such a straight-line motion. However, they performed no experiments for the purpose of testing this point alone. This was first done in 1911 by Dunoyer (37), who heated some sodium in the bottom of an evacuated tube with several collinear constrictions in it. He found that the condensate at the other end was very sharply defined and had exactly the shape expected under the assumption of rectilinear motion, just as in the corresponding optical case. To test the matter further, he placed peculiarly shaped obstacles in the beam path and found shadows, sharp and clear, of the same shape and size. He suggested that this method might be used to test other fundamental ideas of the kinetic theory, but did not seriously attack the problem himself.

Stern (235), in 1920, adapted Dunoyer's "one-dimensional gas" to the simple and direct measurement of the average velocity of the atoms of silver in the vapor state. This was the first of a long and brilliant series of experiments with what he preferred to call atomic or molecular rays. Although this first measurement was rather crude, yet it was sufficiently precise to give the kinetic theory value for the average velocity, to within experimental error. Soon thereafter, Born (14, 19), using a well-defined beam of metallic atoms, obtained estimates of their mean free path in a gas at low pressure. His results showed that the product of the pressure and the mean free path was a constant, as expected.

Many more experiments have been performed with molecular rays since these three which established in such a beautiful and direct manner the fundamental concepts of the kinetic theory. The apparatus is still built like Dunoyer's, with improvements, of course. The basic idea is still the same: to produce a beam of particles of small cross-sectional area, all the members of which are moving in essentially the same direction in a space where the pressure is sufficiently low so that these individuals do not collide with each other or with other atoms. If one does something to the beam (as, for example, passing it through a force field), the results will simply be the statistical sum of performing that same act upon each particle in the beam, independently of all the rest. Although a single atomic process is not in general observable, if the beam is sufficiently intense the accumulative effect will be measurable. Thus the molecular-ray method provides the possibility of observing atomic behavior directly, and has consequently been applied to the solution of many problems.

The distribution of velocities in a beam has been analyzed and found to be in agreement with the theoretical prediction. Beams have been scattered in various gases, and the mean free paths and collision cross sections determined. Various interactions between atoms and surfaces have been investigated.

It was pointed out by Stern (238) that, if the ideas of de Broglie on the wave nature of matter were correct, then under the proper conditions a beam of particles should be diffracted similarly to a beam of light. The wave length  $\lambda$  associated with a molecule of mass  $m$  and velocity  $v$  is determined from the relation  $\lambda = (h)/(mv)$ , where  $h$  is Planck's constant. The molecular-beam

method has been used many times to test this theory and offers the only direct confirmation of it in the case of uncharged particles.

In 1921, Stern (236) suggested that the molecular-beam method could be used as a crucial test to decide between the classical theory and the quantum theory predictions for the magnetic properties of atoms and molecules. If a beam of atoms, each with a magnetic moment, is passed through an inhomogeneous magnetic field, the direction of the inhomogeneity being essentially parallel to the field, the angular momentum vector of each atom will precess about this direction, and the atom will be deflected by the magnetic force. The magnitude of the deflection will be proportional to the projection of the moment upon the field direction. According to the classical theory, the magnetic moment may be oriented in any direction whatsoever, so that its projection might be anything between zero and the absolute value of the moment itself. Then there would be deflections of all magnitudes, and the beam would merely be broadened. According to the quantum theory, on the other hand, there are only a few possible orientations of the moment with respect to the field, and consequently there will be a splitting of the beam into discrete components. The case of silver is a good example. If it behaves classically, a beam of silver atoms will be broadened, but with the position of maximum intensity still located at the position of the undeflected beam. If, on the contrary, the quantum theory applies,—since according to this theory there are only two possible orientations of the moment axis,—the beam will be split into two parts with a minimum of intensity at the undeflected position. An experiment of this type was performed by Gerlach and Stern (80). They passed a beam of silver atoms through a strong field produced by a powerful electromagnet with pole pieces shaped like a slot and a wedge. The results confirmed completely the predictions of the quantum theory. This brilliant and spectacular experiment was the forerunner of a large number of precise measurements of the magnetic properties of atoms and molecules.

There have been many other applications of molecular rays, some of which will be discussed more in detail in the following. This brief description has perhaps served to indicate the power and scope of the method. Aside from its simplicity and directness, it has the obvious advantage that any external applied forces can be made to act on molecules the positions and directions of motion of which are known. Furthermore, there are no mutual interactions in the beam to produce spurious effects. In addition, the molecular-beam method is particularly useful in the measurement of exceedingly small nuclear quantities (see footnote, page 255).

## II. THE PRODUCTION AND DETECTION OF MOLECULAR BEAMS

A gas at low pressure is allowed to escape through an orifice or slit into a highly evacuated space. The emerging particles will move out radially from this slit, travelling in straight lines until they strike an obstruction. If a diaphragm containing another small opening is placed in front of the first slit, those particles which pass through will all be moving in essentially the same direction; that is,

a beam of unidirectional particles has been selected out of the randomly moving ones. The apparatus thus consists of a source chamber or oven, a series of collinear slits to define the beam, and a detector. To prevent scattering of the beam particles, the apparatus must be highly evacuated and the oven slit must not be too large.

Beams are made of permanent gases or the vapors of condensed substances. The condensed matter is enclosed in a small oven or furnace in which there is an oven slit. The oven is heated until the vapor pressure of the contents reaches a value great enough to produce a beam of the desired intensity. In order to prevent scattering within the apparatus, large cooled surfaces are supplied to freeze out any molecules not in the main beam itself. The technique is a little more complicated when the permanent gases are used. In this case there must be a constant supply of the gas at a predetermined low pressure. Because these gases can not be condensed when they are scattered out of the beam but will be reflected diffusely at the walls of the apparatus and thus increase the residual pressure, it is necessary to use very high speed pumps.

In order to produce a true molecular beam one must have a sufficient number of slits to define it. This means that at least two must be used. Sometimes it is found more advantageous to use three; this is especially helpful in the case where the beam is made of a non-condensable gas. These slits are made of metal or glass and are aligned approximately by optical or mechanical means. In experiments where questions of intensity arise or where precise quantitative measurements are desired, the final adjustment of the slits is often made by observation of the effect of moving them upon the intensity and shape of the beam itself.

The first beams were made with metals of relatively low melting point. These were easily purified and vaporized, and their detection offered no difficulties. All that was necessary was to interpose a cooled plate in the path of the beam. Many investigations<sup>1</sup> have been made concerning the effect of beam pressure and temperature upon the nature of the trace produced. It was even found possible by either physical or chemical methods to develop a trace which was too faint to be seen. Since many deposits are destroyed upon contact with the air, devices have been used to photograph them in the vacuum.

It was soon found that certain beams could be detected by their chemical activity. For example, atomic hydrogen beams will reduce the yellow oxide of molybdenum to the blue one, or will blacken the Schumann plate (128). These are the so-called accumulative methods and are very sensitive; if one waits long enough the result is almost certain to be visible. However, there are serious disadvantages. There are many substances which can be neither condensed nor detected chemically. Furthermore, because the molecules in a thin film have a tendency to move sideways along the supporting surface, the reproducibility is poor, and there is no possibility of obtaining quantitative results.

<sup>1</sup> For a complete discussion see R. G. J. Fraser: *Molecular Rays*, University Press, Cambridge (1931).

Various investigators have weighed the deposits or analyzed them with a micro-photometer, but without much success.

Since several other methods have been developed which will give quantitative results, these early ones have been largely superseded. However, very recently Simons and Glasser (231) have perfected a sensitive chemical detector in the form of a tellurium oxide; it will react with atomic hydrogen, oxygen, chlorine, and bromine, and perhaps with some of the organic free radicals.

The first reliable quantitative detector was the ionization gauge, used by Johnson (108) in 1926. He found that it did not behave well, but several other investigators have since used it for relatively heavy molecules with complete success. Stern and Knauer (132) constructed a very sensitive Pirani gauge or hot-wire manometer. It is very useful for the light permanent gases, but its sensitivity decreases with increasing molecular weight. These two gauges measure simply the pressure built up in the manometer by the beam. Radiometer vanes (30, 32, 161), bolometers (254), and thermopiles (unpublished work by various investigators) have been used, but have never proven entirely satisfactory.

In 1929, Taylor (243) developed a quantitative detector for atoms with low ionization potentials, based upon Langmuir's investigations of surface ionization. It is useful for the alkali metals, either as atoms or molecules, and for a few other substances such as indium and gallium; it will also detect beams of alkali salts (209) and other compounds containing the alkali-metal atoms. As customarily used, this gauge consists of a hot tungsten filament, sometimes with an oxide coating, and a negative plate. A definite fraction (usually practically 100 per cent) of all the atoms which strike the wire are ionized and repelled to the negative collector. The positive-ion current is thus a measure of the intensity of the beam. Rabi and Cohen (196) have developed a modification of this regular procedure for cases in which the intensity is extremely low. They allow the atoms to strike and to accumulate upon a cold wire which is flashed at regular intervals. The total charge received by the collector is proportional to the total number of atoms arriving at the detector during the whole time. Tests show that this accumulative method is very reliable, even for periods of collection of as much as 10 min. Koderá (135) has recently used a modification of this gauge to measure the total intensity of very broad beams.

Langmuir and Villars (147) have suggested that it might be possible to use a tungsten wire to detect beams of oxygen. Electron emission from such a wire, activated by small amounts of cesium vapor, is very sensitive to changes in the oxide coating. As far as the authors know, no one has attempted to make use of this idea.

All of the above quantitative instruments, although very good for a few molecular species, have the disadvantage of being relatively insensitive for the majority of beam materials. In 1933 Estermann and Stern (59) constructed a universal gauge of extremely great sensitivity. It is based on the investigations of Kingdon and Langmuir on the elimination of space charge by positive ions, and consists simply of a hot filament surrounded by a positive cylinder. If the

filament temperature and anode potential are adjusted properly, and if there is a good vacuum between the electrodes, the current will be limited by the space charge. If now a gas is admitted to the gauge, some of the gas molecules will be ionized by the electrons. These ions will spiral round and round the filament, thus effectively decreasing the space charge; this will produce a large change in the plate current, the amount of change depending of course upon the number of ions present. Kingdon used a device of this type (the Kingdon cage) to measure small pressures. It is extremely sensitive because the electron current can be amplified by appropriate means.

Using this device, Stern and Estermann made some rough experiments with a mercury beam, and were able to measure the beam intensity when the mercury oven was kept at  $-30^{\circ}\text{C}$ . They used as a filament a thorium-free tungsten wire. The positive plate was a cylinder of nickel sheet capped at both ends; the beam passed in through a hole in one of the caps. A second gauge exactly like the first was used to balance out fluctuations in residual pressure, pumping speed, and the like. A sensitive galvanometer measured the difference between the two plate currents. It was found that there was an optimum value of the anode potential for which the sensitivity was a maximum. This was, of course, greater than the ionization potential of mercury. It was also discovered that for extremely low pressures the galvanometer throw was not exactly proportional to the beam pressure as determined from the temperature of the oven. This means either that the gauge must be placed in a room with a small residual pressure so that it will give linear readings, or else that the gauge must be calibrated carefully over its whole range if it is to be used in a good vacuum.

This is a universal method, since all substances which can be made into beams can be ionized by swift electrons. It has been pointed out by Fraser (68) that it would be useful for investigating the organic free radicals. It is extremely sensitive; however, the sensitivity is greater for the heavier molecules, since they have a smaller velocity and will therefore remain in the space charge region for a longer time. In spite of these very obvious advantages, this method has been used very infrequently.

### III. VELOCITY DISTRIBUTION IN MOLECULAR BEAMS

One of the consequences of the kinetic theory is that the molecules in a molecular beam do not all have the same velocity. This complicates considerably the interpretation of a molecular-beam experiment. For example, if a beam is passed through a force field, there will be a different deflection for every velocity. Thus, it is usually desirable and frequently necessary to know the distribution of velocities in a beam.

Three methods have been used in velocity measurements: mechanical selection, deflection in a force field, and selective reflection. Costa, Smyth, and Compton (32), Eldridge (39), and Lammert (146) have used the toothed-wheel method of measuring the velocities of beam particles. Similar to the old Fizeau method of measuring the velocity of light, it consists in passing a beam through two or more coaxial rotating notched disks. From a knowledge of the number of teeth,

the speed of rotation, and the distance between the wheels, one may easily calculate the velocity of the particles which are able to pass through. Zartman (263) and later Ko (134) used a refinement of the Stern method (235) of measuring average velocities. Their experiments were performed with a claimed precision sufficient to indicate more slow particles in a beam of bismuth than were predicted by the theory. This result they explained by assuming that not only were there bismuth atoms in the beam, but also some diatomic molecules, and perhaps even some molecules of  $\text{Bi}_2$ . The experiment also gave a heat of dissociation of  $\text{Bi}_2$  molecules of 77,100 calories per mole. This is to be compared with the value of 56,000 calories obtained by Leu (151) in a careful magnetic deflection experiment.

Rabi and Cohen (194) and Ellett and Cohen (29, 41) have made use of the deflection of beams in a magnetic field to determine the velocity distribution. Stern and his colleagues (56) have studied the free fall of atoms in a beam. Here, too, the particles of different velocities undergo different deflections. This gives a very easy method of sorting velocities; however, the beam must be very long because the force of gravity is quite small, so that the intensity becomes very low.

Since the angle of diffraction of an atom at a crystal surface depends upon the de Broglie wave length, and therefore upon the velocity, the diffracted beam in any particular direction will be essentially monochromatic. As will be described later, this method of velocity selection was used by Estermann, Frisch, and Stern (52) in their study of the diffraction of helium at cleavage surfaces of lithium fluoride.

In every case, the results agreed fairly well with the predictions made from kinetic theory considerations. There were always some deviations which could be ascribed to scattering, finite wall thicknesses, and the like.

#### IV. SCATTERING OF MOLECULAR BEAMS

The molecular-beam method seems to be the only possible method for the study of the scattering of neutral particles by neutral particles. As was mentioned earlier, the first experiments of this type was performed by Born (14, 19), who showed roughly that the product of the mean free path and the pressure was a constant. The main features of the more recent investigations are the following: A narrow beam of a substance for which there is a quantitative detector is passed through a chamber containing a gas at controllable pressure. The shape and intensity of the scattered beam is compared with the shape and intensity of the parent beam for various scattering pressures. From these data the mean free paths and scattering cross sections may be determined.

The problem has been treated quantum-mechanically by Mizushima (180) and by Massey and Mohr (159). According to them the collision cross section for slowly moving hard spheres is two times the classical value if the particles are different, but four times the classical value if the particles are similar. If there are attractive forces between atoms, the newer theory gives a finite cross section, while the classical theory gives an infinite value. All of the investigators

in this field—Knauer (130), Zabel (258), Eldridge (40), Fraser and Broadway (24, 69), Mais (154), and Rosin and Rabi (213)—have found cross sections much larger than those expected from the classical hard-sphere theory. Also Knauer (130), in his investigations of the scattering of helium by mercury, found that beams at high temperature are scattered more than beams at low temperature. These results are in disagreement with the older theory, but are to be expected on quantum-mechanical considerations. Mais (154) used an apparatus of sufficient resolution that particles deflected through 4.5 min. of arc were counted as scattered. He found that the scattering of potassium atoms by helium and by hydrogen agreed quite well with the quantum-mechanical predictions of Mizushima, Massey, and Mohr for hard spheres. However, for the cases of the scattering of potassium by neon, nitrogen, argon, and carbon dioxide, the collision radii were much larger than given by the theory, indicating considerable interatomic attraction. Rosin and Rabi (213), using a very refined apparatus with resolution of 1 min. of arc, studied the scattering of all the alkali atoms from the gases hydrogen, deuterium, helium, neon, and argon. The cross sections for potassium were in good agreement with those obtained by Mais, being in every case only a little higher. This indicates that the cross sections are really finite. Furthermore, the scattered beam had the same shape as the parent beam. These results all lead to the conclusion that the classical theory is entirely inadequate for the treatment of this particular problem of the scattering of a molecular beam.

Rabi (189) has stated that this leads to a new kinetic theory. The authors wish to point out, however, that for the majority of problems, such as the transport phenomena in gas (diffusion, heat conduction, and viscosity), the classical theory does give the correct result. There are a few exceptions at low temperatures. For these a quantum-mechanical kinetic theory must be used.

It is even possible, with some assumptions, to obtain the van der Waals forces from scattering experiments. This was done by Fraser, Massey, and Mohr (72) for the scattering of potassium and sodium by mercury, using data obtained by Broadway (24). Torrey and Spremulli (247), who have just begun work on the problem, hope to do the same for the scattering of alkali atoms by alkali atoms.

Rosenberg (212) has compared the scattering of atoms and molecules of lithium and potassium by various inert gases. He separated the atoms from the molecules by deflecting them in a strong inhomogeneous magnetic field.<sup>2</sup> Although he has not published complete results, he has shown that the cross sections are very nearly the same for the two types of particles. For example, in the case of potassium, the ratio  $\sigma_{\text{mol.}}/\sigma_{\text{atom}}$  varies from 1.20 to 1.36.

## V. SURFACE PHENOMENA

As has been mentioned, many investigations have been made on the character and behavior of the deposit produced by the condensation of a molecular beam.

<sup>2</sup> Compare Lewis, page 60.



Following Langmuir, it was assumed that, at least in the majority of cases, an atom striking a surface was adsorbed for a time and then reëvaporated at random. Holst and Clausing (98) devised a molecular-beam method of measuring the time of adsorption, but were able to show only that it was very small. Veszi (251), with an improved apparatus, reflected a beam of heavy atoms from an olive oil surface moving rapidly at right angles to the beam. The last slit was in a large thin metal sheet kept cool with liquid air, and was just 2 mm. from the oil surface. Particles leaving this surface, either by reflection or reëmission after adsorption, were condensed on the cold plate. After taking into account the sidewise impulse given to the particles by the moving surface, Veszi found it possible to calculate the time of adsorption on the oil from the shape of the deposit.<sup>3</sup> For zinc and bismuth he found times of the order  $10^{-5}$  to  $10^{-4}$  sec.

Beeck (11) has determined the relative accommodation coefficients with respect to argon of various hydrocarbons at a nickel surface. He measured the sensitivity of a Pirani gauge used to detect the hydrocarbon beams as a function of the oven pressure, and extrapolated to zero oven pressure. By applying the Knudsen formula for the heat conducted by a gas at low pressure, both for the hydrocarbon with unknown specific heat and for argon, he was able to calculate the relative accommodation coefficients. By assuming that their actual value tends to unity for the more massive molecules, he was able to obtain absolute values for his whole series. This assumption also led to some information about the variations of specific heat with mass. As a check, it was found that the results for hydrogen were in good agreement with previous measurements.

The molecular-beam method is excellent for producing uniform thin films of an easily condensed material on a cool surface. It has therefore been used several times in the studies of such films. One can calculate the thickness of a layer laid down in a given time from a knowledge of the intensity of the beam if he assumes that the molecules are spaced as they are in the bulk. Mayer (162), following the previous work of Brady (20), investigated the photoelectric properties of thin films as a function of their thickness. He deposited a film of potassium on a platinum foil. In order to test the constancy of the beam over a period of time, he used the receiver as the filament of a Taylor surface-ionization gauge and measured the ionization current. Saturation current was reached when the foil was hot enough. Mayer was thus able to calculate the intensity of his beam by assuming that the efficiency of ionization was 100 per cent. He found that if he outgassed the potassium and the platinum carefully, the photoelectric emission stimulated by a quartz mercury lamp increased strictly linearly with the time

<sup>3</sup> In this work it was found that cadmium and thallium were immediately reflected without being adsorbed. The deposits of these metals showed a remarkable structure. Around the central, approximately oval, spot were from six to eight rings showing a doublet structure, and entirely separated from each other. Veszi (252) has explained these as due to diffraction by the individual randomly oriented oil particles. He exhibited a photograph of a similar pattern produced by scattering light, with wave length  $10^5$  times the de Broglie wave length of the atoms, from lycopodium powder  $10^5$  times the size of the oil particles. This could not possibly be a Debye-Scherrer pattern, because the slit was long and narrow, so that the structure would be smeared out.

until a little less than a monatomic layer had been deposited. After this, it increased less rapidly, but gave no evidence of a maximum. However, if the potassium was not carefully outgassed, the emission showed a maximum at the same thickness where the other curve broke. The secondary electron emission stimulation by electron bombardment was studied by Mayer in a similar manner. Johnson and Starkey (107) made measurements of the same type on the electrical conductivity of thin films of mercury. Starkey (234) has also studied the reflectivity of thin films of cadmium for visible light.

Copley and Phipps (31) have used the molecular-beam method to measure the surface ionization of potassium on tungsten as a function of temperature. For each temperature, they compared the ion current with that from an oxide-coated tungsten filament, for, according to Langmuir, the ionization is complete at that surface. They found a discrepancy with the theory which they explained by assuming that the work function varies with the temperature (205). Hendricks, Phipps, and Copley (96) have applied the same method to the study of the surface ionization of the potassium halides at an oxygen-free tungsten surface. For high temperatures (1800–2400°K.) the molecules were dissociated, the halogens leaving the wire as atoms, and part of the potassium being ionized. For lower temperatures, halogen layers appeared on the tungsten. Guthrie (87) has done similar experiments with barium. It has an ionization potential (5.16 volts) larger than that of tungsten (4.5 volts), and therefore should not be detected by a surface-ionization gauge. In disagreement with the theory, however, barium is ionized by clean tungsten. Guthrie estimated that the ionization efficiency was about 100 per cent if the temperature of the wire was 2000°K. or higher. It has been pointed out by Hay (95) that Becker, in some unpublished work, found efficiencies only about one-third to one-half as great. This is evidently a problem not as yet completely solved.

#### VI. DIFFRACTION AND REFLECTION OF MOLECULAR BEAMS

In the discussion of surface phenomena (page 247) it was shown that the time of adsorption for some atoms is extremely small or even zero. If the de Broglie postulate of the wave nature of matter is correct, atoms which are not adsorbed will be reflected *specularly*, provided the projections of the unevennesses of the reflecting surface upon the beam direction are less than the wave length. Any surface will give specular reflection if the glancing angle is small enough. The existence of this type of reflection is inferential proof of the wave nature of the beam particles.

In 1927, Knauer and Stern (133) obtained specular reflection of beams of molecular hydrogen and helium from highly polished metal surfaces at grazing angles of a few minutes of arc. However, they could find no evidence of diffraction at a grating ruled on speculum metal. These results were to be expected if the molecules had the de Broglie wave length. They soon announced the specular reflection of helium and hydrogen at large glancing angles of incidence from cleavage surfaces of sodium chloride crystals. Johnson (109) and Kerschbaum (129) showed the same for beams of atomic hydrogen.

Since hydrogen and helium have de Broglie wave lengths of the order of an Ångström unit, and since that is also the approximate lattice spacing of the alkali halide crystals, these latter should act as diffraction gratings for molecular beams. Certainly they will be *surface* gratings, not space gratings, for there can be no penetration of the particles into the crystal. Since the crystals are of the cubic type, they will act as two-dimensional, or crossed, gratings with the principal axes at right angles to each other. If the incident beam makes angles  $\alpha_0$  and  $\beta_0$  with these axes, and the diffracted beam angles  $\alpha$  and  $\beta$  with the same two directions, then

$$\begin{aligned}\cos \alpha - \cos \alpha_0 &= h_1(\lambda/d) \\ \cos \beta - \cos \beta_0 &= h_2(\lambda/d)\end{aligned}$$

where  $d$  is the grating constant and  $h_1$  and  $h_2$  are integers, the orders of diffraction. These equations are, of course, just the ordinary grating law applied twice. They are the equations of cones the axes of which are the rulings on the grating at the point of incidence of the beam. There will be diffraction maxima where two cones intersect. If one put a sensitive plate in a position to receive the reflected beam of atomic hydrogen, he might expect to find a spot representing the specularly reflected beam, and symmetrically placed around it other spots corresponding to the various orders of diffraction. Unfortunately, this will not really occur, for, as was mentioned previously, the particles in the beam have a wide range of velocities and therefore of wave lengths. Since each wave length is diffracted through a different angle, each spot will be spread out into a broad band.

Stern and Knauer (133) looked for evidences of the diffraction of hydrogen molecules and helium atoms at cleavage surfaces of sodium chloride. They used as a detector a hot-wire manometer so arranged as to receive successively all the diffracted atoms of order  $(0, \pm 1)$ . Faint evidences of maxima were found in the expected place (239). When lithium fluoride was substituted for the rock salt, in a later experiment of Estermann and Stern (57), absolute proof of the existence of the diffraction of atoms was obtained. The maxima were found exactly where one would expect them if the velocity distribution is taken into consideration. This was true for both hydrogen and helium. Further, the maxima were shifted in the proper directions and by the proper amount when the temperature of the incident particles was changed. The grating rulings are the rows of like ions, and the grating space which must be used in the calculations is the distance between these rows. Thus this constitutes a direct experimental proof of the validity of the de Broglie relation for heavy particles. Similar results were found for atomic hydrogen by Johnson (110, 111).

Not satisfied with this, Estermann, Frisch, and Stern (52) studied the reflection and diffraction of monochromatic beams. These were produced either by a mechanical velocity sorter or by the use of a double-crystal spectrometer. Using a rather crude mechanical velocity sorter, Stern and his coworkers in Hamburg proved the correctness of the wave picture of matter and verified the de Broglie relation between wave length and velocity. This simple experiment is thought to be one of the most beautiful and direct demonstrations in modern physics.

With the double-crystal spectrometer, the atoms diffracted in a particular direction from the first crystal have only a small range of wave lengths and therefore of velocities. If these are reflected again, the resulting pattern will be much more highly resolved than with only a single crystal. Again de Broglie's expression for the wave length was valid to within the experimental error of about 1 per cent. Incidentally, these experiments also gave a very good proof of the Maxwell law for the distribution of velocities.

In their further investigations, both Stern and his collaborators and Johnson found some unexpected results. The latter (111, 112), who worked with atomic hydrogen and detected it with a molybdenum oxide plate, found faint traces of diffracted beams very close to the specularly reflected beam. He assumed that they were due to a secondary lattice of the type postulated by Zwicky. This lattice spacing was estimated to be 100 Å. or more. However, even with high resolution and almost grazing incidence, he could not separate these secondary maxima from the specularly reflected beam. This led him to make the suggestion (113) that the spacing in the secondary lattice is not constant.

Frisch and Stern (76) found that with high resolution the diffraction patterns were not smooth curves, as expected, but had reproducible minima. Similar effects were found in the curves of reflectivity as a function of the orientation of the crystal. Frisch (73) summarized these results as follows: An atom will not be specularly reflected whenever a certain very simple (but empirical) relationship exists between the two components of its incident momentum perpendicular to the surface and parallel to one of the lattice directions. Furthermore, an atom will not be diffracted in such a direction that the same relation would obtain between the components of its momentum as it leaves the crystal surface.

These results were given a theoretical explanation by Lennard-Jones and Devonshire (33, 149). They showed that under certain conditions it is possible for an atom to be adsorbed by the crystal without change of kinetic energy, instead of being diffracted. The conditions necessary for this selective adsorption had the same form as those found empirically by Frisch. From a comparison of theory and experiment, Lennard-Jones and Devonshire were able to calculate the energies of adsorption of helium at a lithium fluoride surface. These investigators and Lenz (150) and Brandt (21) have calculated the intensities of various orders of diffraction maxima; however, no one has as yet performed a sufficiently precise experiment on the higher orders which would suffice to substantiate or contradict their results.

Stern and Frisch (76) also found that the reflectivity of lithium fluoride for helium differed slightly when they used differently shaped slits. They suggested that this also might be due to other beams very close to the specularly reflected beam, such as could be produced by diffraction from a secondary lattice. To test this latter hypothesis, Bessey (13) investigated the specularly reflected beam very carefully, but could find no evidence of a secondary diffraction maximum. He found, however, that the specularly reflected beam had a fine structure which varied from crystal to crystal and from place to place on the same crystal. This could not be a diffraction phenomenon, since the reflection patterns were identical

for beams of helium and molecular hydrogen, although the wave lengths were different. The simplest explanation is that the crystals, although supposedly single, are actually made up of many tiny crystallites tipped at small angles (a degree or less) with respect to each other. Such a crystal structure might be responsible for the effect found by Johnson. This explanation would seem to confirm the work of Renninger (64, 206), who was led to essentially the same hypothesis during his study of the reflectivity of rock salt for very narrow beams of x-rays.

Diffraction curves have been definitely found only for helium and for both atomic and molecular hydrogen. Best results are obtained with lithium fluoride. Zabel (257) showed that with extremely great precautions good results can be obtained with rock salt; however, since it is so hygroscopic, the crystal surface is soon spoiled. In fact, when the crystal is exposed to water vapor, the diffraction pattern changes and various anomalous results are obtained. Zabel tried experiments with neon and argon also, but the results were inconclusive.

It is not to be expected that diffraction patterns would be found for metal beams, for the wave lengths are much smaller than those of hydrogen and helium, and are therefore small compared to the lattice spacing. More important is the fact that all metal atoms have a tendency to be adsorbed. The results which are found agree in certain cases with the cosine law of reflection (255). For example, Taylor (244) reflected beams of potassium, lithium, and cesium from sodium chloride and lithium fluoride over a wide range of angles of incidence. Although he could have detected specular reflection present to one part in 10,000, he found no trace of it; the angular distribution of the reflected beam followed the cosine law exactly. Ellett and Cohen (42) found the cosine law to hold for potassium atoms reflected from magnesium oxide. They made a velocity analysis of the reflected beam and found the distribution to be the expected one, that corresponding to the temperature of the crystal and not of the incident beam. In this case, at least, the mechanism is indeed the one postulated by Langmuir,—adsorption and consequent reëvaporation.

However, in some investigations, intense reflection was found in approximately the direction of the specularly reflected beam (44, 45, 46, 47, 90, 114, 119, 261, 262). Although there is not complete agreement between the various results, it seems that when the crystal surface is carefully prepared and when the diffuse background (cosine-law scattering) is subtracted from the total reflection, there remains a beam the direction of which does not deviate very much from that to be expected for specular reflection. However, this beam is very much wider than would be expected from considerations of the geometry involved.

## VII. MAGNETIC DEFLECTION

### A. Theory

According to theory, every system which has a single angular momentum vector  $j$  (measured in units of  $h/2\pi$ ) has also a magnetic moment  $\mu = gj$ , where  $\mu$  is measured in units of the Bohr magneton  $\mu_0 = eh/4\pi Mc$ , and  $g$  is the gyromagnetic ratio in units of  $e/2Mc$ . Here  $M$  is the mass of the electron. Often a

unit called the nuclear magneton is used; it is defined in the same way, except that  $M$  is in that case the mass of the proton. The quantum number  $j$  may have integral or half-integral values. If this system is placed in a magnetic field, its behavior can be explained by assuming that its angular momentum vector precesses about the field direction with frequency  $\nu = gH(e/2Mc)$ . This is the well-known Larmor precession. The projection of the angular momentum  $j$  upon the field direction will have only the  $2j + 1$  values  $\pm j, \pm(j-1), \pm(j-2)$ , and so on, each designated by quantum number  $m_j$ . The energy of the system will be changed by an amount  $\Delta E = m_j h\nu$ . A beam of atoms will thus be split in a magnetic field into  $2j + 1$  parts, each of which is in a separate energy state. We say such a beam has been space-quantized.

If a system has more than one angular momentum vector (such as electron orbital momentum, electron spins, nuclear spins, and molecular rotation), the magnetic moment associated with each one will interact with all the rest. This interaction is called coupling. When such a system is placed in a magnetic field, the resulting motion of the momentum vector is very complex. However, if the energy changes produced by the field are large compared to those due to the coupling, that is, if the field is strong enough, the individual angular momentum vectors will precess independently about the field direction. In fields which are not strong, one may use the perturbation method to calculate the energy changes. In any case the force in a certain direction on a system in a magnetic field is equal to the directional derivative of the energy change produced by the field.

In the following, we shall use the usual notation: in units of  $h/2\pi$ ,  $j$  is the total extranuclear angular momentum,  $i$  is the nuclear spin, and  $f$  is the resultant of the two. The projections of each of these on the field direction are denoted  $m_j$ ,  $m_i$ , and  $m$ .

### B. Electronic moments

After the power of the molecular-beam method for the measurement of the magnetic properties of atoms and molecules had been demonstrated by Stern and Gerlach (80), many investigations of magnetic moments were made. Although in recent years the emphasis has been on nuclear measurements, there have been several important studies of electronic moments.

In 1933, Meissner and Scheffers (165), at the Reichsanstalt in Berlin, made a determination of the atomic moments of lithium and potassium. With the wedge-slot field such as was used by Stern (151) in Hamburg, the results for both materials were identical, i.e.,  $(0.916 \pm 0.005) \times 10^{-20}$  c.g.s. units for the Bohr magneton. The limit of error seems to be a bit optimistic, in view of the large amount of scattering of the beam which would distort the Maxwell velocity distribution.

In 1938, Ramsey and Kellogg (127) passed beams of helium, argon, and neon through magnetic fields with extremely high inhomogeneities. As was to be expected, these atoms exhibited no magnetic property beyond that attributable to their diamagnetism.

Certain molecules have an electronic magnetic moment; examples are oxygen

and nitric oxide. Van Vleck (249) has worked out the theory of space quantization for these molecules. The problem was attacked experimentally by Simpson (232) and Schnurmann (224) independently. They found that the beam behaved qualitatively as expected, but that there was a strong interaction between the rotation and the electronic angular momentum. Their results were similar, indicating that the prediction of Van Vleck would not be valid until much higher fields were obtained.

Recently, Stern (56, 240) and his colleagues in the Molecular Physics Research Laboratory began working on a new precision method of measuring the Bohr magneton. In principle, it is very simple; it consists merely in balancing the gravitational force on a very long beam by an upwards magnetic force (produced by the inhomogeneous field surrounding a conductor of electric current). Thus

$$N\mu \frac{\partial H}{\partial X} = Nmg$$

where  $N$  is Avogadro's number,  $m$  is the mass of the atom, and  $g$  is the acceleration of gravity. Since  $g$ ,  $Nm$ , and  $\partial H/\partial X$  are well known, it should be possible to obtain a very precise value of the molar magneton  $N\mu = Neh/4\pi mc$ .  $F = Ne$  and  $c$  are known very accurately; therefore we have here a method of obtaining  $h/m$  precisely. This general method of the molecular balance should be very powerful. For instance, Stern (241) has suggested that one could get complete separation of isotopes by balancing a magnetic force against a centrifugal force.

### C. Requantization

It is of interest to inquire as to the effect on a space-quantized beam of passing it through a magnetic field. Will requantization take place, or will the atoms remain in the same states? The first experiments on this problem were performed by Stern and his collaborators (75, 186) in Hamburg. They selected one component of a beam which had been split in a Stern-Gerlach apparatus, passed it through a field which changed direction along the path of the beam, and analyzed it in a second inhomogeneous field. When more than one maximum was found, it was obvious that requantization had occurred.

Special cases of this problem have been treated theoretically by Güttinger (88), Majorana (155), and others (181, 192, 211, 228). They showed that if the transition is adiabatic, the atom which was precessing in the first field will precess in the same way in the second field. However, in the case of non-adiabatic transitions, that is, in case the time during which the field changes direction is of the same order of magnitude or less than the time for the Larmor precession, there will be a reorientation of some of the atoms. In the simple case of the alkalis, where only two states are possible, these reoriented atoms may be said to have "turned over"<sup>4</sup> from the original state to the other one. The results of the experiments in general agreed with the theory.

<sup>4</sup> Because these "turning over" experiments were first performed by Phipps, they are known familiarly as the Phipps flops.

At present Winslow, in Stern's laboratory, is continuing experiments to examine the effect, if any, of the presence of paramagnetic scattering gases on the amount of reorientation. Rabi and his colleagues have used non-adiabatic transitions very effectively in their recent measurements of nuclear magnetic moments.

#### *D. Nuclear moments*

Stern (238) had already predicted in 1926 that the molecular-beam method could be applied to the measurement of nuclear magnetic moments. Since these have magnitudes about 1/2000 those of the electronic moments, the problem is, of course, very difficult. If substances with the latter are used, the deflections due to the nuclear moment will be only of the order of 0.1 per cent of the total deflection and will not be easily observable. One method of avoiding this is to measure the very small deflections of molecules with zero electronic moment. This method was applied to hydrogen by Estermann, Frisch, and Stern (53, 58, 60, 61, 62, 77). The total nuclear moment of a hydrogen molecule will be either zero or twice that of the proton, depending on whether it is of the para or ortho variety. The experiments were performed with hydrogen at the temperature of liquid nitrogen in order to reduce the complications due to the presence of rotational magnetic moments. These are of the same order of magnitude as the nuclear moments and are obtained to a sufficient degree of approximation from the deflection of pure para-hydrogen in the higher rotational states and a knowledge of the population of these states. The results of the first measurements were very surprising; the moment of the proton was two and one-half times as great as expected.

These experiments were continued and refined in this country. In the final work, besides beams of ortho-hydrogen, beams of HD were used (54), because the populations of the higher rotational states are small. The proton moment could be calculated from the ratio of the beam intensities at the undeflected position when the field was on and when it was off. This calculation depends upon a knowledge of the geometry of the slit system, the validity of the Maxwellian velocity distribution, the value of the inhomogeneity of the field, and the approximate values of the deuteron and rotational magnetic moments. To eliminate any deviations from the assumed velocity distribution, measurements were taken for various residual scattering pressures and extrapolated to zero pressure. The inhomogeneity was measured by three methods: the variation of the resistance of a bismuth wire with field strength, the force on a piece of bismuth suspended in the field by a quartz fiber, and by the use of a flip-coil. The values of the deuteron and rotational moments come in only as small corrections and therefore do not need to be known very precisely. As their final result, Estermann, Simpson, and Stern (54, 55) obtained for the proton moment the value  $2.46 \pm 3$  per cent nuclear magnetons; the deuteron and rotational moments are roughly one-third as great.

In 1931, Breit and Rabi (23) published a molecular-beam method of determining both the nuclear spin and the hyperfine structure separation. From a



knowledge of these two quantities, one may calculate the nuclear magnetic moment by using equations of Goudsmit (83) and Fermi and Segré (65). However, these calculations depend upon the evaluation of wave functions at the nucleus, and are therefore only approximate except in the case of the hydrogen atom, the wave function of which is exactly known. The method is based on a deflection in a field sufficiently weak that the electronic and nuclear spins are still coupled to some extent; that is, the electronic angular momentum and the nuclear angular momentum are not quantized separately, and therefore do not precess about the field direction independently of one another.

Rabi (197, 198, 202) first applied this method to the hydrogen isotopes. In these measurements he used beams of atoms, deflecting them in a weak magnetic field and detecting them with a molybdenum oxide plate. He obtained in this way a value of the proton moment of  $3.25 \pm 10$  per cent nuclear magnetons, thus confirming the extremely high value of Stern. This experiment can not be considered as anything more than preliminary work. However, it has one notable feature: the weak magnetic field was produced without iron, by passing very large electric currents through two long water-cooled copper tubes placed parallel to the beam path. The field was thus absolutely calculable.

Rabi (28) soon introduced a refinement into his experimental method which simplified the calculations considerably and which made the results independent of the velocity distribution in the beam. Consider atoms with electronic angular momentum  $1/2$  and nuclear spin  $i$ . Then there will be two possible states with total angular momentum  $f = i + 1/2$  and  $f = i - 1/2$ . These states will be separated by an energy  $\Delta W = hc\Delta\nu$ , where  $\Delta\nu$  is the hyperfine structure separation which can be obtained spectroscopically in certain cases.<sup>5</sup> If now the atoms are placed in a magnetic field, their energies will be changed and each of the two states will be split into  $2f + 1$  separate levels of equal probability and designated by total magnetic quantum number  $m$ . The atoms in each of these states will have effective moments  $\mu_m$  (in units of the Bohr magneton  $\mu_0$ ) which depend upon the amount of coupling between the nuclear and electronic spins, that is to say, upon the field strength  $H$ . The effective moment is given by the formula

$$\mu_m = \pm \frac{2m/(2i + 1) + x}{[1 + 4mx/(2i + 1) + x^2]^{1/2}} \mu_0$$

Here  $x$  is equal to  $(2\mu_0 H)/(hc\Delta\nu)$ . In this formula the nuclear moment has been neglected with respect to the electronic moment. The different signs refer to the two original degenerate  $f$  states. If the nuclear magnetic moment is in the same direction as the nuclear spin (positive moment), then the positive sign

<sup>5</sup> Here we see the superiority of the molecular-beam method. If  $\Delta\nu$  is very small, it is impossible to resolve the lines of the spectrum. However, as Stern has pointed out, it is always possible, by making a molecular beam long enough, to resolve two components which suffer different deflections. We can see this by applying the uncertainty principle in the form  $\Delta W \Delta t \cong h$ . If the particles have an average velocity  $v$ , then the time of flight through the distance  $L$  is  $L/v$ ; therefore the length  $L$  necessary for separation will be of the order  $(hv)/W$ .

refers to the state  $f = i - 1/2$ . Figures 1 and 2 show plots of  $\mu_m/\mu_0$  against  $x$  for the cases  $i = 6/2$  and  $i = 7/2$  under the assumption that the nuclear moment is positive. The dotted lines refer to the  $2f + 1$  states for  $f = i - 1/2$ . If the nuclear moment is negative, the figure will be exactly the same, except that the effective moment corresponding to each state will be reversed in sign.

As can readily be seen, for certain values of  $x$ , that is, for certain values of  $H$ , some of the states will have effective moments equal to zero. This is true when

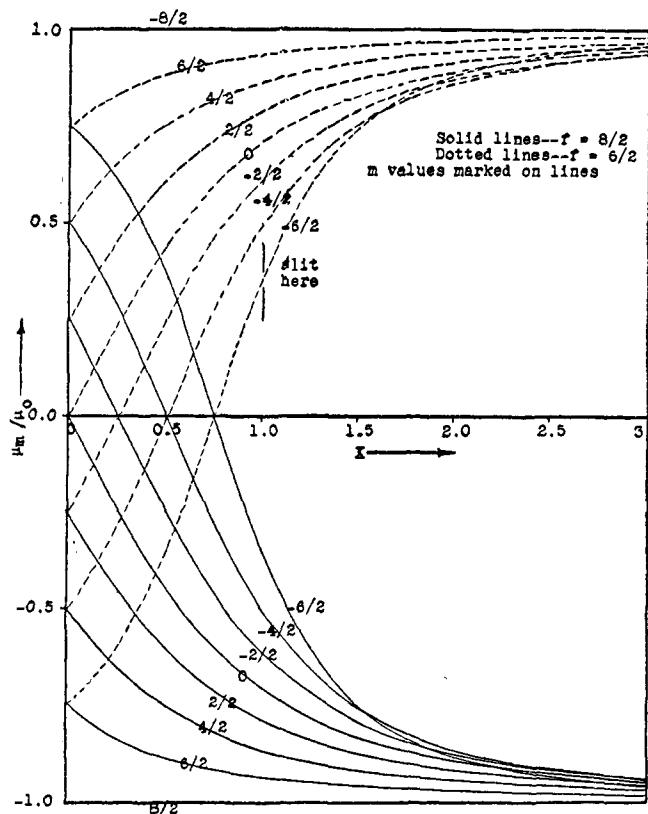


FIG. 1. Effective magnetic moment *versus* field strength. Nuclear moment assumed positive. Case 1:  $i = 7/2$ .

$x = (-2m)/(2i + 1)$ . If the magnetic field is inhomogeneous, all the atoms except those with zero moment will be deflected. The number of different values of  $x$  for which this can occur depends upon the value of  $i$ . For the cases shown in the figures there are three such zero moments; for the cases  $i = 4/2$  and  $i = 5/2$  there are two, and so on. From the determination of the relative  $x$  values (relative  $H$  values) and the number of zero moments it is possible to specify the spin exactly. It is then a simple matter to determine the absolute value of  $x$  for one of the states, and therefore the hyperfine structure separation.

Experiments of this type were performed by Rabi and his colleagues (67, 166).

The resolving power of the apparatus was very high; the atoms with non-zero moments were deflected enough so that they missed the detector completely. Values of the nuclear magnetic moments were obtained by means of the Goudsmit-Fermi-Segré formulas (65, 83). All the alkali metals, atomic hydrogen and deuterium, indium, and gallium were studied in this way. For the cases in which the nuclear spin was  $3/2$  or less, the actual procedure was a little more complicated than indicated above, but the principle was essentially the same.

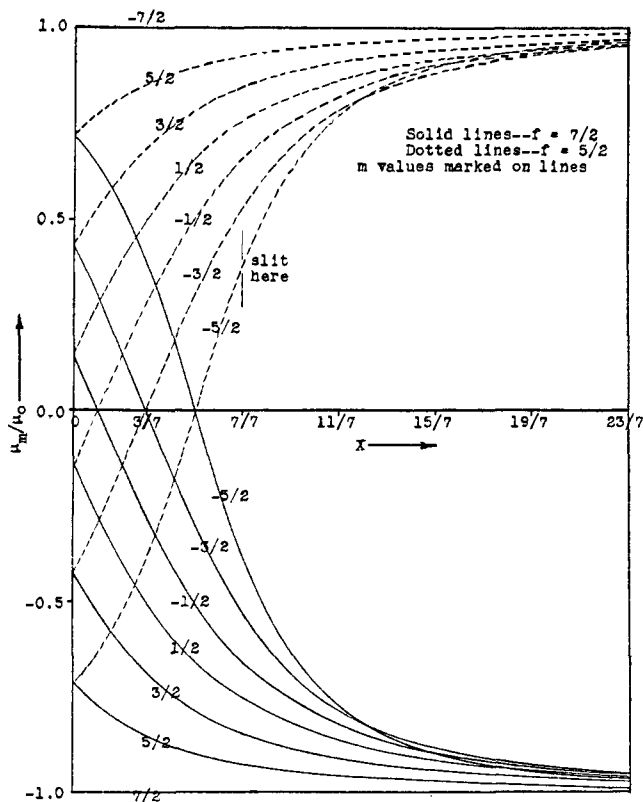


FIG. 2. Effective magnetic moment *versus* field strength. Nuclear moment assumed positive. Case 2:  $i = 6/2$ .

The results in general agreed with the spectroscopic values, where these were known. The case of hydrogen is of especial interest; the proton moment was found to be 2.85 nuclear magnetons, a value considerably higher than that found by Estermann, Simpson, and Stern. This method is applicable to mixtures as well as to pure substances and has, therefore, been used to measure the moments of isotopes without separating them (190).

Two important extensions of this method were made. The first (178, 191) permits a determination of the sign of the nuclear magnetic moment. As was pointed out previously, if a beam of atoms is passed through an inhomogeneous

magnetic field, it is split into a number of overlapping beams, the Zeeman components of the two original states. It can easily be seen from the figures that, if the field is very strong, the deflection pattern will have two components, corresponding to the two possible orientations of the electronic moment. However, if the field is rather weak, the different components will all have different deflections. For simplicity, let us consider a field of such a magnitude that the parameter  $x$  has a value about equal to unity. In this case, all the atoms in the state  $f = i - 1/2$  have effective moments of the same sign, and will therefore be deflected in the same direction. All the atoms in the state  $f = i + 1/2$  except those for which  $m = -f$  are deflected in the opposite direction. We do not, of course, know which group of atoms has the positive effective moment. Let us choose one of the components for which  $m = -(f - 1)$  by means of a selector slit and pass it through a weak field varying non-adiabatically. Transitions will occur, subject to the selection rule  $\Delta f = 0$  (181). Now pass the beam through such a strong field that there is complete uncoupling and the effective moment is only  $\pm \mu_0$ . If we had picked a component of the state with the smaller value of  $f$ , corresponding to a dotted line in the figure, we would now find only one maximum in the deflection pattern. This is because all the components of this state had originally a deflection in the same direction, and transitions can not occur which give deflections in the opposite direction. However, if we had picked a component of the state with  $f = i + 1/2$ , corresponding to a solid line in the figure, we would find two maxima in the deflection pattern, because some of the transitions would have been to the state with  $m = -f$ , which had an effective moment and consequently a deflection of the opposite sign. From a knowledge of the quantum number  $f$  and the sign of the atomic moment, one can tell the sign of the nuclear moment. Rabi and his collaborators showed that all the nuclear moments studied by this method were positive.

The second important extension (192) of the zero moment method was to increase the resolution to such a point that the nuclear magnetic moment was no longer negligible with respect to the electronic moment. In this case the nuclear moment can be determined directly. Millman, Rabi, and Zacharias (176) studied beams of indium in this way; detection was with a Taylor surface-ionization gauge using an oxide-coated filament. They found it necessary to use iron fields again; the fields produced by the long wires parallel to the beam did not give large enough deflections. However, instead of using the bulky magnet with the wedge-slot pole pieces of Stern and Gerlach, they used one which was small enough to go into the vacuum system, was easily constructed, and for which it was not difficult to calculate the inhomogeneities. This consisted of a long piece of Armco iron tubing with a slot cut in it lengthwise; in the slot were fitted pole pieces of simple design. The iron was magnetized by passing large currents through four turns of water-cooled copper tubing.

Zero moment peaks were found, not only for the normal  $2p_{1/2}$  state, but also for the metastable  $2p_{3/2}$  state. It was suggested that careful examination and location of these peaks would give information on the interval rule and the magnitude of the nuclear quadrupole moment. This latter was actually measured in

this way by Hamilton (89); later Renzetti (207) did the same thing for gallium. It is interesting to note that Stern had predicted such measurements twelve years before (238).

In 1937 Rabi (193) published the theory for a more elegant method of determining both the sign and the magnitude of the nuclear magnetic moment in cases where the nuclear spin is known (16, 26, 242, 246). This method is absolutely independent of the velocity distribution in the beam, and necessitates only measurements of frequencies in the radiofrequency range and magnetic field strengths. It is relatively insensitive to nuclear transitions in systems with electronic angular momentum, and therefore has usually been used to study beams of molecules with zero electronic moment. However, extensions have been made to atomic beams; from a study of these it is possible to learn something about their spectra in the radiofrequency range.

Suppose a molecule with zero electronic moment is placed in a magnetic field  $H_0$  which is strong enough to uncouple all moments of nuclear magnitude but which is too weak to uncouple the electronic spins. The original energy state represented by the nuclear quantum number  $i$  will be split in the field into  $(2i + 1)$  states, each designated by a quantum number  $m$ . This means that the angle of precession between  $i$  and  $H_0$  will be different for the atoms in different states, and therefore the effective moments will be different. If now we apply, perpendicular to the original field, an additional small magnetic field  $H_1$  which rotates with the frequency  $f$ , the probability can be calculated for transitions between states  $m_1$  and  $m_2$ . This probability is very small, except when the direction of rotation is the same as the direction of precession and the frequency is very close to the Larmor frequency  $\nu$ ; the maximum occurs when  $f = \nu$ . The frequencies necessary are of the order of a few kilocycles.

Rabi's method is very simple indeed. A beam is sent through a strong field  $H_0$  with a superimposed weak rotating field  $H_1$  and a combination of field strength  $H_0$  and frequency is found which produces the largest number of transitions. Then this frequency is the Larmor frequency corresponding to the magnetic moment being studied. From a knowledge of the field, the frequency, and the angular momentum, the moment can easily be calculated. The direction of rotation of the weak field gives immediately the direction of the precession and therefore the sign of the magnetic moment.

In order to put this method into practice, Rabi gave up the rotating field and used an oscillating one instead. The frequency of oscillation plays the same rôle as the frequency of rotation in the theory outlined above. The experimental details are as follows (201): The molecular beam passes through a strong inhomogeneous magnetic field and is therefore deflected. The individual beam particles have different effective moments and different velocities; therefore the deflections will all be different. The beam now passes through a strong homogeneous field and into a second inhomogeneous field exactly like the first, except that its inhomogeneity is in the opposite direction. Thus all the particles will be given a deflection equal and opposite to the first, so that the beam intensity at the receiver is the same as when the fields are off entirely. Now a small oscillating

field of variable frequency is applied perpendicular to the middle homogeneous field; obviously, if transitions occur, those molecules undergoing such transitions will have different effective moments than before, and therefore will not be refocused at the detector by the second field. Thus there will be a decrease in the intensity recorded by the detector. The frequency is changed until this decrease is a maximum; that is, until the beam intensity is a minimum. When this occurs, the frequency is equal to that of the Larmor precession. It is essential for the success of the experiment that the three fields be connected together with iron. Otherwise, there is a danger that the change from field to field would be so sudden as to induce non-adiabatic transitions, which would invalidate the results of the experiment.

Rabi thought at first that by using the oscillating field he was giving up the ability to determine the sign of the nuclear moments, because the oscillating field is perfectly symmetric. This field was produced by passing an alternating current through a hairpin-shaped piece of wire. Millman (167) pointed out, however, that as a molecule enters and leaves this field, the end effects are exactly the same as if the field were rotating. These end effects lead to an asymmetry in the intensity-frequency curve which depends upon the sign of the moment. (Actually, the prediction is for a second minimum, but the resolution is insufficient to obtain it.) From this asymmetry the sign can easily be determined.

The first application of this method was to the alkali metals (200, 203), since the Taylor gauge is such a sensitive detector for these materials. The first moments measured were those of  $\text{Li}^6$ ,  $\text{Li}^7$ , and  $\text{F}^{19}$ ; these were used in the molecules lithium chloride, lithium fluoride,  $\text{Li}_2$ , and sodium fluoride. In every case the values of  $f/H_0$  for the observed minima were constant over wide ranges of the magnetic field. This indicates that they are due to nuclear and not molecular transitions; the latter would not possess a frequency proportional to the field. Two of the minima observed for the three molecules containing lithium were the same for all three molecules; these must certainly correspond to the nuclear moments of the two lithium isotopes. The deeper one was ascribed to the more abundant variety. There was also a common resonance minimum for the two molecules containing fluorine; this must of course be due to  $\text{F}^{19}$ .

Resonance minima are never ascribed to nuclei unless they are found in at least two different molecules. Then, if the spins are known, the nuclear moments are easily calculated. Since the time of the first publication of this magnetic resonance method, Rabi and his colleagues have applied it to a great many nuclei, usually in molecules containing an alkali atom, because of the ease of detection.

The one big exception is in the study of hydrogen. In this case gaseous hydrogen was used, and detection was by means of the Pirani gauge. Furthermore, because of the fundamental nature of the problem and because of the discrepancy between the previously obtained results, Rabi made a much more detailed investigation of the hydrogen molecules than of any others (125, 126).

The calibration of the apparatus was checked by using dichlorodifluoromethane; the value obtained for the nuclear moment of  $\text{F}^{19}$ , 2.623 nuclear mag-

netons, agreed well with the value 2.622 obtained with the previously used apparatus and a surface-ionization gauge.

The hydrogen experiments were made with  $H_2$ , HD, and  $D_2$ , all at the temperature of liquid nitrogen. At this low temperature the majority of the molecules are in rotational states with quantum number  $j$  equal to 0 or 1; the higher states are so thinly populated that they can be neglected.  $H_2$  will be made up of molecules of para-hydrogen with nuclear spin  $i = 0$  and rotational angular momentum  $j = 0$ , and ortho-hydrogen with  $i = 1$  and  $j = 1$ .  $D_2$  will consist of three types of molecules with the following  $(i, j)$  values: ortho-deuterium,  $(0, 0)$  and  $(2, 0)$ , and para-deuterium  $(1, 1)$ . HD molecules can have any combination of spin and rotational angular momentum. The molecules with zero spin and zero rotational momentum are not deflected in the magnetic field, and consequently behave as inert gases. Thus no results can be obtained from para-hydrogen, or from the ortho-deuterium for which  $i = 0$ . The ortho-deuterium molecules for which  $i = 2$  will behave similarly to alkali molecules. Transitions can occur in either direction between the various  $m$  states; the frequencies and field strengths corresponding to these transitions give the deuteron moment. Similar measurements can be made with HD in the zero rotational state; from these may be obtained values of both the proton and the deuteron moments. The results are as follows:  $\mu_H = 2.785 \pm 0.02$  nuclear magnetons,  $\mu_D = 0.855 \pm 0.006$  magnetons. The former value agrees with the previous results of Rabi but disagrees with that of Stern.

To complement these results, Rabi made further measurements of the magnetic resonance spectra of molecules not in the lowest rotational state. In this case there is an interaction between the spins and the rotation so that the simple theory no longer holds; transitions will not occur when the applied frequency is exactly the Larmor frequency, but at small deviations from it.

Rabi solved the wave equation for the rotating hydrogen molecule in the magnetic field, including in the Hamiltonian the interaction of the nuclear spins with the applied field, of the rotational moment with the applied field, of each nuclear spin with the field produced by the rotation of the molecule, and the mutual interaction of the two nuclear moments. For the case of ortho-hydrogen in the first rotational state, the energy levels can be expressed in terms of two parameters,  $H'$ , the field at a proton due to the rotation, and  $H'' = \mu_H/r^3$ , the field at one proton due to the magnetic moment of the other. Here  $r$  is the internuclear distance. In case the energy term due to the interaction with the external field is large compared to all the other terms, as was true for the experimental arrangement, there are nine levels. These correspond to the three orientations of the nuclear spin for each of which three orientations of the rotational moment are possible.

In performing the experiment the frequency  $f$  was kept constant and the magnetic field varied. Whenever the field had such a value that the Bohr relation  $hf = E_n - E_m$  was satisfied, transitions would occur, accompanied by the absorption or emission of radiofrequency radiation. There are rigorous selection rules:  $\Delta m_i = \pm 1$  or  $\Delta m_j = \pm 1$ , where  $m_i$  and  $m_j$  are the projections

of  $i$  and  $j$  in the field direction. These give rise to two groups of six lines each, one located at approximately the field such that the applied frequency is equal to the Larmor frequency of the proton moment, the other at approximately the field such that the applied frequency is the Larmor frequency of the rotational moment. For the time being, we shall consider only the former group.

All six lines (minima in the resonance spectrum) were found experimentally. From the changes in the asymmetry of the pattern with frequency, it was possible to assign the appropriate quantum numbers to each line. Then from the theory and the position of the lines it was a simple matter to calculate the constants  $H'$  and  $H''$ . Completely consistent results were obtained, thus indicating that the theory must be essentially correct. To make a real check, the value of  $H'' = \mu_{\text{H}}/\gamma^3$  was multiplied by the average cube of the separation of the nuclei, obtained by Nordsieck from band spectra, to give a value of  $\mu_{\text{H}}$  identical with that obtained directly from the Larmor frequency.

The theory which worked so beautifully for the gas ortho-hydrogen should also apply to para-deuterium, for everything is the same,—spin, rotational angular momentum, and internuclear distance. It is easy to calculate the effect of the change of mass on the spacing of the lines. However, the prediction does not agree with experiment; there are six lines as expected, but they are six times as far apart as they should be.

Rabi explained this discrepancy by assuming that the deuteron has an electric quadrupole moment, the reaction of which with the gradient of the molecular electric field tends to increase the separation. This interaction can be represented by a parameter  $H'''$  (in gauss)  $= -(5e^2qQ)/(4\mu_{\text{D}})$ , where  $Q$  is the quadrupole moment,  $q$  is defined by  $qe = \frac{\partial^2 V}{\partial z^2}$ ,  $e$  is the electronic charge, and  $V$  is the electrostatic potential at the nucleus. It turns out that the quadrupole interaction is of the same spin-spin type as that between the two deuteron moments. Therefore, the theory applied to  $\text{H}_2$  will apply here if the quantity  $H''_{\text{H}}$  is replaced by  $(H'' + H''')_{\text{D}}$ . As indicated above, one can calculate from the proton value what  $H''$  should be, and subtract it from the measured value to obtain  $H'''$ .

It is possible to obtain  $H'''$  directly from similar experiments on HD in the first rotational state. Here there are two groups of lines, one of nine components near the position of the Larmor frequency of the proton, the other of twelve components near that of the deuteron. The analysis is quite similar to that discussed above.

From the experimental value of the quadrupole interaction constant and the theoretical value of the field gradient as calculated by Nordsieck (183), Rabi computed the quadrupole moment and found that it was  $2.73 \times 10^{-27}$  cm.<sup>2</sup>, good to about 2 per cent. In every case the values of the proton and deuteron magnetic moments agreed with the previous results.

Ramsey (204) performed similar experiments with the hydrogens, studying the groups of lines near the Larmor frequencies of the rotational moments. He outlined a theory showing that the rotational moment is proportional to the reduced mass of the molecule. This means that the moments of  $\text{H}_2$ , HD, and



$D_2$  should vary as 4:3:2. The experimental values for the moments in the first rotational state are  $0.8787 \pm 0.0070$ ,  $0.6601 \pm 0.0050$ , and  $0.4406 \pm 0.0030$  nuclear magnetons, respectively. The value for  $H_2$  agrees with the experimental value of Estermann and Stern (53, 58) and with the theoretical values of Wick (253) and Brooks (25). A further experiment with para-hydrogen in the state  $j = 2$  gave the moment  $1.757 \pm 0.014 = 2 \times 0.8787$  nuclear magnetons, as expected. It will be noticed that there is a slight discrepancy in the 4:3:2 ratio. It was persistent, and always in the direction of smaller moments for the lighter molecules. This might indicate an effect of the zero state vibrational motion upon the mean separation of the nuclei.

Ramsey's analysis of the fine structure of the spectra confirmed completely all of Rabi's previous work on the interaction constants of H and D. He carried the interpretation still further, and deduced the high-frequency contribution to the diamagnetic susceptibility of  $H_2$ , and the dependence of this susceptibility upon the orientation.

Recently Rabi and his colleagues (144, 145, 172) extended the magnetic resonance method to the study of the radiofrequency spectra of *atoms*, in order to determine the hyperfine structure separations. Most of the experimentally observed hyperfine structures of atomic ground states lie in the radiofrequency range. The life-times of these energy states are very long, and consequently the intensity of spontaneous emission is low. Therefore, direct optical observation of the radiation is difficult. However, if an atom is irradiated with electromagnetic radiation of the proper frequency and intensity, it will either absorb or emit a quantum of this frequency. This change of state will cause a reorientation of the atom in a magnetic field, and can therefore be detected by the magnetic-resonance method. This gives extremely high resolution; thus it is superior to optical methods and to the method of zero moments.

In performing experiments of this type two cases must be considered: In the first, the central homogeneous field is very weak; therefore the energy states of atoms with angular momentum  $f$  are split into  $2f + 1$  levels. Transitions will occur subject to the selection rules  $\Delta f = 0, \pm 1$ ;  $\Delta m = 0, \pm 1$ . For weak enough fields, the center of gravity of the spectral pattern is the hyperfine structure separation  $\Delta\nu$ . In the second case the middle field is very strong. Here transitions give rise to lines the frequencies of which are independent of the field strength, and approach the limit  $\Delta\nu/(2i + 1)$ . This enables measurements to be made at a more convenient range of frequencies. Both cases lead to the same results.

For example, in the case of  $K^{39}$  the Zeeman pattern was well resolved at a magnetic field of 0.05 gauss. The hyperfine structure separation determined in weak fields is  $(461.75 \pm 0.02) \times 10^6 \text{ sec.}^{-1}$ , or  $0.015403 \text{ cm.}^{-1}$ ; that measured in strong fields (3950 gauss) is  $(461.75 \pm 0.02) \times 10^6 \text{ sec.}^{-1}$ . This precise agreement shows that the quantum-mechanical expressions for the variation of the magnetic levels in external magnetic fields must be accurate to at least one part in ten thousand. Thus one can use the Zeeman effect to calibrate a magnetic field for other purposes, such as the more exact measurement of nuclear moments.

One of the most important results from these studies is the value of the ratio

of the hyperfine structure separations of the lithium isotopes (145). From this value can be calculated the ratio of the nuclear magnetic moments on the assumption that only electromagnetic interactions between the electrons and the nucleus have an effect on the atomic energy levels. The value obtained in this way is  $\mu_7/\mu_6 = 3.9610 \pm 0.0004$ . The directly determined value, from molecular-beam experiments, is  $3.9601 \pm 0.0015$ . This indicates that the assumption is valid. In the case of rubidium, the agreement is not quite so good:  $2.0261 \pm 0.0003$  for the atomic-beam value (172),—Millman and Fox (168) obtained 2.026 by the method of zero moments,—and  $2.238 \pm 0.010$  for the molecular-beam value. Millman and Kusch point out that because of the great experimental difficulties of the latter experiment, the discrepancy does not give conclusive evidence of a non-electromagnetic interaction between the electron and the nucleus.

During the past year, Millman and Kusch (173) have combined the atomic- and molecular-beam magnetic-resonance experiments to obtain more precise values of the nuclear magnetic moments. The accuracy of all the previous moment measurements was limited by the uncertainty of the strength of the homogeneous magnetic field in which the transitions took place. It was possible to obtain moment ratios much more accurately than the moments themselves, for these depend on a frequency ratio in a constant magnetic field. However, the studies of the radiofrequency spectra show that it is possible to make very precise measurements of the hyperfine structure separations from lines the positions of which are practically independent of the field. The frequencies of lines arising from certain other transitions show a very marked dependence upon the field strength and the hyperfine structure separation, a dependence the mathematical form of which is known. Thus it is possible to calculate the field strength from the frequency of the spectral line (see reference 185 for a justification of this calculation).

Millman and Kusch calibrated the field and measured the nuclear moments in the same experiment. They used an oven with two compartments connected only at the slit. In one was placed the substance ( $\text{Na}^{23}$ ,  $\text{Rb}^{85}$ , or  $\text{Cs}^{133}$ ) used for measuring the field; in the other, the compound containing the nucleus the moment of which was desired. This compound contained also, in every case, an alkali atom, so that the Taylor gauge could be used as the detector.

For the important case of hydrogen, the beam consisted of sodium hydroxide or potassium hydroxide. The magnetic field was kept at a constant value, and the frequency changed so as to get the minimum corresponding to the Larmor frequency of the proton moment. Before and after every experiment, the field was calibrated by running through the radiofrequency spectrum of one of the reference materials. The value obtained in this way for the proton moment was  $2.7896 \pm 0.0008$  nuclear magnetons. This value was multiplied by the previously obtained ratio of the deuteron and proton moments to give the former a magnitude of  $0.8565 \pm 0.0004$ . The difference between these two is  $-1.933 \pm 0.001$  nuclear magnetons, a result to be compared with the neutron moment of  $-1.935 \pm 0.02$  obtained by Alvarez and Bloch (1).

TABLE 1  
Nuclear moment values obtained by molecular-beam methods

NUCLEUS	$i$	$\Delta\nu$	$\mu$	SIGN OF $\mu$	METHOD*	DATE	REFERENCE
H <sup>1</sup>	1/2	0.0482	2.5 ± 10%	+	D	1933	(53, 58, 77)
			3.25 ± 10%		D	1934	(197)
			2.85 ± 0.15		Z	1936	(121, 122, 199)
			2.46 ± 3%		D	1937	(55)
			2.785 ± 0.02		M	1939	(124, 125)
			2.7896 ± 0.0008		MA	1941	(173)
H <sup>2</sup>	2/2 2/2	0.0108	0.7	+	D	1933	(60, 61, 62)
					S	1933	(152)
					S	1934	(182)
			0.75 ± 0.2		D	1934	(198)
			0.85 ± 0.03		Z	1936	(120, 122)
			0.855 ± 0.006		M	1939	(124, 125)
0.8565 ± 0.0004	MA	1941	(173)				
Li <sup>6</sup>	≥2/2	0.0077	0.5-0.8	+	Z	1935	(67)
	2/2		0.6±0.2		S	1936	(226)
			0.85		Z	1936	(157, 158)
					Z	1938	(82)
			0.820 ± 0.005		M	1938	(200, 201)
			0.007613		M	1939	(167)
		A	1940	(145)			
		0.8213 ± 0.0005	MA	1941	(173)		
Li <sup>7</sup>	3/2	0.0267	3.29	+	S	1932	(84)
	3/2				S	1933	(86)
	3/2		3.20		Z	1935	(67)
			3.33		T	1936	(7)
			3.250 ± 0.0016		Z	1937	(178)
					M	1938	(200, 201)
			0.026805		M	1939	(167)
					A	1940	(145)
		3.2532 ± 0.0015	MA	1941	(173)		
Be <sup>9</sup>	3/2?		1.176 ± 0.005	-	M, MA	1939	(142, 173)
B <sup>10</sup>	2/2?		0.598 ± 0.003	+	M, MA	1939	(173, 175)
B <sup>11</sup>	3/2?		2.686 ± 0.008	+	M, MA	1939	(173, 175)
C <sup>13</sup>	1/2			+	T	1940	(99)
			0.701 ± 0.002		M	1940	(93, 95)
N <sup>14</sup>	1		≤0.2	+	S	1933	(5)
			0.402 ± 0.002		M	1938	(143, 174)
			0.403 ± 0.002		MA	1941	(173)
N <sup>15</sup>	1/2		0.280 ± 0.003	??	M, MA	1940	(173, 260)

TABLE 1—Continued

NUCLEUS	$i$	$\Delta p$	$\mu$	SIGN OF $\mu$	METHOD*	DATE	REFERENCE
F <sup>19</sup>	1/2		2.622 (with Taylor gauge)	+	S	1929	(79)
			2.623 (with Pirani gauge)		M	1938	(200, 201)
			2.625 ± 0.003		M	1939	(124, 125)
					M	1939	(167)
					MA	1941	(173)
Na <sup>23</sup>	3/2	0.0596	~2.6	+	D	1933	(195, 196)
	3/2				S	1933	(106)
	3/2				S	1933	(248)
	3/2				S	1934	(43, 148)
	3/2				Z	1935	(67)
	0.059103				Z	1937	(245)
					M	1938	(143, 170)
					A	1940	(172)
					MA	1941	(173)
Al <sup>27</sup>	9/2		3.6–4.1	+	S	1938	(104)
	5/2		3.7		S	1938	(97)
	5/2		3.630 ± 0.010		M, MA	1939	(171, 173)
Cl <sup>35</sup>	5/2		1.368 ± 0.005	+	S	1930	(48)
					M, MA	1939	(140, 141, 173)
Cl <sup>37</sup>	5/2		1.136 ± 0.005	+	S	1940	(229)
					M, MA	1939	(140, 141, 173, 230)
K <sup>39</sup>	3/2	0.0152	0.38	-	Z	1934	(166, 169)
	≥3/2	0.0154	0.10		T	1935	(81)
			0.43–0.47		S	1935	(102, 103)
			0.397		Z	1935	(67)
			0.0156		Z	1937	(245)
					S	1937	(164)
0.015403	M	1938	(143, 170)				
		A	1940	(145)			
K <sup>40</sup>	4		1.290	-	M	1941	(259)
K <sup>41</sup>	>1/2	0.00853	0.22	+	Z	1935	(166)
	≤5/2				Z	1935	(67)
	3/2				Z	1936	(156)
					Z	1938	(82)
					A	1940	(145)
					MA	1941	(173)
		0.215 ± 0.002					
Ga <sup>69</sup>	3/2		2.11		S	1932	(27, 100, 225)
	3/2				Z	1940	(207)

TABLE 1—Continued

NUCLEUS	<i>i</i>	$\Delta\nu$	$\mu$	SIGN OF $\mu$	METHOD*	DATE	REFERENCE	
Ga <sup>71</sup>	3/2				S	1932	(27, 100, 225)	
	3/2		2.69		Z	1940	(207)	
Rb <sup>85</sup>	3/2		1.4		S	1933	(101)	
	5/2		1.44 ± 1%		S	1933	(137)	
	5/2	0.1018	1.8 ± 30%	+	Z	1936	(168)	
					Z	1937	(178)	
	5/2	0.10127	1.340 ± 0.005	+	Modified Z	1937	(176)	
					M, MA	1939	(140, 141, 173)	
A	1940	(172)						
Rb <sup>87</sup>	5/2		2.8		S	1933	(101)	
	3/2	0.229	2.92 ± 1%	+	S	1933	(137)	
					Z	1936	(168)	
	3/2	0.22797	2.733 ± 0.009	+	Z	1937	(178)	
					M, MA	1939	(140, 141, 173)	
	A	1940	(172)					
In <sup>113</sup>	9/2	No trace found	0.998 × $\mu_{115}$	+	Modified Z	1938	(177)	
					A	1941	(92)	
In <sup>115</sup>	9/2	0.381	5.3 ± 0.5 6.40 ± 0.20 5.43 ± 0.03	+	S	1937	(227)	
					Modified Z	1938	(177)	
					A	1941	(91)	
Cs <sup>133</sup>	7/2	0.295			Z	1934	(28)	
	7/2	0.3067	2.38–3.01		S	1935	(85)	
					S	1936	(138)	
	7/2	0.307	2.72 ± 1%			Z	1936	(168)
	7/2	0.30661	2.558 ± 0.007	+	Z	1937	(178)	
					S	1937	(66)	
					M, MA	1939	(139, 143, 173)	
A	1940	(172)						
Ba <sup>135</sup>	3/2		0.837 ± 0.003	+	M	1940	(94, 95)	
Ba <sup>137</sup>	3/2		0.936 ± 0.003	+	M	1940	(94, 95)	
(H <sup>1</sup> ) <sub>2</sub>		$\mu_R = 0.36-0.93$ $\mu_R = 0.8-0.9$ $\mu_R = 0.8787 \pm 0.0070$ ( <i>j</i> = 1) $\mu_R = 1.757 \pm 0.014$ ( <i>j</i> = 2) $\mu_R = 0.885$			T	1933	(253)	
					D	1933	(53, 58)	
					M	1939	(204)	
					T	1941	(25)	
(H <sup>1</sup> H <sup>2</sup> )		$\mu_R = 0.6601 \pm 0.0050$			M	1939	(204)	
(H <sup>2</sup> ) <sub>2</sub>		$\mu_R = 0.4406 \pm 0.0030$			M	1939	(204)	
H <sup>2</sup>		$Q = (2.73 \times 10^{-27}) \pm 2\%$ cm. <sup>2</sup>			M	1939	(123, 126)	

TABLE 1—*Concluded*

NUCLEUS		METHOD*	DATE	REFERENCE
Ga <sup>69</sup>	$Q = 1 \times 10^{-24}$ $0.20 \times 10^{-24}$	S	1936	(225)
		Z	1940	(207)
Ga <sup>71</sup>	$Q = 0.5 \times 10^{-24}$ $0.13 \times 10^{-24}$	S	1936	(225)
		Z	1940	(207)
In <sup>115</sup>	$Q = 1.0 \times 10^{-24}$ $(0.8 \pm 0.2) \times 10^{-24}$ $0.84 \times 10^{-24}$	S	1936	(6)
		S	1937	(227)
		Z	1939	(89)

\* A = atomic magnetic resonance.

D = deflection.

M = molecular magnetic resonance.

MA = molecular and atomic magnetic resonance combined.

S = spectroscopy.

T = theory.

Z = zero moments.

The proton moment has now been measured more precisely than any other; therefore all other moments have been referred to it. Li<sup>7</sup> is used as a secondary standard because of the ease of making a beam of these atoms and of detecting it. This beautiful and epoch-making work of Rabi and his collaborators has brought the accuracy of the value of the proton moment up to that of many of the other physical constants. The discrepancy between this value and the lower one obtained by Stern and his colleagues may have physical significance, although at present it cannot be explained in a completely satisfactory manner (233a, 264).

In table 1 is given a list of all the nuclear moment values obtained by molecular-beam methods. These have not been corrected for the diamagnetism of the atoms. The spectroscopically obtained values for the same nuclei are given for comparison.

#### VIII. ELECTRIC DEFLECTION

In 1921, Kallmann and Reich (117) suggested that the electrical properties of molecules could be studied by a molecular-beam method. Stern (237) also pointed out that the same method was applicable to both the electric and magnetic cases. The two experiments are similar in principle, but in actual practice the former is far more complicated and therefore less amenable to interpretation.

In the first place, atoms are so symmetrical electrically that they have no electric moment (see later, however). Thus the investigations are almost entirely limited to beams of molecules. These molecules will rotate with the axis of rotation in any direction whatsoever. We must distinguish, therefore, two cases; that in which the electric moment of the molecule is perpendicular to the axis of rotation (dumbbell molecules; example, hydrogen chloride) and

that in which the moment is not perpendicular to the axis of rotation. In the first case, in the absence of a field, the moment will average to zero because of the rotation. However, in an electric field the rotation will no longer be uniform, and therefore there will be a time-averaged moment proportional to the electric field strength. Its value will be from 1/1000 to 1/100 of the permanent moment. Since the energy of the molecule in the field, and also its deflection in an inhomogeneous electric field, are proportional both to the field strength and to the average moment, the deflection and energy will be proportional to the square of the field strength. This is the quadratic Stark effect.

In order to predict the shape of the deflection pattern, one must average the individual deflections over all possible velocities of the molecules, all possible rotational states, and all possible directions of the axis of rotation. A slight consideration will show that the molecular beam will not be split, but will simply be broadened. This broadening is not quite symmetric; furthermore, with an infinitely narrow beam and detector, it would be found that the position of maximum intensity had been shifted by a very small amount. However, as ordinarily used, the molecular-ray apparatus has insufficient resolution to detect this shift. Nevertheless, from the weakening of the beam as it passes through the electric field, it is possible to calculate the electric moment (see 218, 220, and Fraser's book).

In the above considerations there has been omitted one thing which must be taken into account. The electron cloud surrounding the nuclei in the molecule will be distorted somewhat by the electric field; therefore there will be an induced moment proportional to the field strength. The effect of this will be to displace the whole deflection pattern toward the direction of higher inhomogeneity.

Experiments have been performed on hydrogen chloride (51, 163, 208), the alkali halides (70, 210, 217, 256), and various organic molecules (49, 50, 63, 254) for the purpose of measuring their electric moments. The apparatus was in every case essentially a Stern-Gerlach apparatus. The fields were produced either by parallel-plate condensers (188) or by cylindrical condensers with the beam passing very close to and parallel to the inner electrode. Quantitative measurements were attempted in only a few cases. While the results of various investigators do not agree very well, still the disagreement is less than the experimental error. The values agree roughly with those obtained by other methods.

If the molecular moment has a component parallel to the axis of rotation, the moment will not average to zero. Thus there will be a permanent moment, and the energy and deflection will be proportional to the first power of the field. This linear effect, being of the first order, is, of course, much greater than the quadratic effect. The theory has been quite completely worked out by Scheffers (220). In practice it can be applied only to symmetric molecules, because the shape of the deflection pattern must be known beforehand. That is, the direction of the moment with respect to the axis of rotation must be known; otherwise the interpretation of the deflection pattern is practically impossible.

The only quantitative molecular-beam experiment on a molecule exhibiting

the linear Stark effect was performed by Scheffers (221) on ammonia. He found, as he had predicted, that the deflection was linear with the field. However, the value of the moment of the ammonia molecule was only one-third that obtained by other methods. Scheffers insists that this discrepancy is definitely not due to experimental error.

As has been mentioned, atoms have no permanent moments. However, with atoms, just as with molecules, there is the possibility of induced moments. Scheffers and Stark (219, 222, 223) deflected beams of lithium, potassium, cesium, hydrogen, and oxygen atoms in an inhomogeneous electric field. In every case the beam was shifted bodily in the direction of the gradient. Thus, from the simple measurement of the displacement, it is possible to calculate the polarizability  $\alpha = \mu/E$ . The values so obtained were of the same order of magnitude as the theoretical values, but the agreement was not particularly good.

#### IX. MISCELLANEOUS MOLECULAR-BEAM EXPERIMENTS

##### *A. Life-time of excited states*

Dunoyer's (38) main application of his method was to the study of spectroscopy. He found that if a beam of sodium atoms was illuminated with sodium light, it luminesced because of the resonance radiation. The lateral boundaries of the irradiated portion of the beam were very sharp, and those in the direction of motion were equally distinct. This gave direct proof that the time of excitation was very small, a result in agreement with the Drude theory.

Koenig and Ellett (136) have actually measured this time for cadmium resonance radiation; usually it is of the order of  $10^{-8}$  sec., but in this case spectroscopic results led to the belief that it was much longer. They irradiated a part of a beam of cadmium perpendicularly with a very narrow ray of the line  $\lambda$  3261. This portion was screened from a camera, yet film blackening was found for a distance of 4 mm. beyond the illuminated part. The temperature, and therefore the average velocity of the beam, were known. From this it was determined that the life-time was of the order of  $10^{-6}$  sec.

##### *B. Spectral lines*

The molecular-beam method has a very great advantage in the field of spectroscopy. Because there are practically no collisions in the beam and very little mutual interaction, and because the velocities of the beam particles are essentially parallel, there will be practically no pressure broadening of the spectral lines emitted by an excited molecular beam. If the light is viewed at right angles to the direction of motion, there will also be almost no Doppler broadening; this alone is equivalent to having a spectral source at a temperature of only a few degrees Absolute. Thus such a light source is adapted for studies of the hyperfine structure of spectral lines.

Several methods of exciting the radiation have been used. Bogros (17), Dobrezov and Terenin (35), and Jackson and Kuhn (102, 104) have used optical excitation, and have studied either the resonance radiation itself (emission spectrum) or the absorption due to the passage of the original light through the



beam. The intensity of the spectrum produced in this way is not very great. Bogros and Esclançon (18) increased the intensity very much by stimulating emission with a high-frequency discharge. For this purpose it was necessary that the beam pass through a low pressure ( $2 \times 10^{-3}$  mm. of mercury) of argon or nitrogen which conducts the discharge. They found the lines to be just as sharp as the absorption lines produced in a beam in a good vacuum. Minkowski and Bruck (179) have obtained very high resolution by bombarding a sharp beam of cadmium with electrons. Meissner (164) has made some very careful spectral measurements on beams of potassium, using optical excitation. A value of the nuclear magnetic moment of  $K^{39}$  was obtained from the hyperfine structure which agreed very well with that obtained by magnetic deflection.

### *C. Ionization*

Closely allied to the spectroscopic problem is that of the ionization of a beam of neutral particles. It is often of importance to obtain a large positive-ion current in a good vacuum. This may be done easily with the use of a molecular beam. Planiol (187) and Sasaki and Nishibori (216) have developed the method in considerable detail. Planiol obtained currents as high as 40 milliamperes from the collision of mutually perpendicular rays of cadmium atoms and electrons. Bleakney, Blewett, Sherr, and Smoluchowski (15) and Ditchburn and Arnot (34) have applied this same technique to obtain ions for a mass spectrograph, following the earlier example of Smyth (233).

Jewitt (105) and Fraser and Jewitt (71) have used a molecular-beam method to measure the ionization potential of formaldehyde, the halogen-substituted methanes, and the free radicals methyl and ethyl. The beams were passed either into a Kingdon gauge or an ionization gauge. Curves were plotted of beam intensity against anode voltage and extrapolated to zero to get the ionization potential. The results for the free radicals were in agreement with estimates made from other methods.

### *D. Degree of dissociation*

As has already been described, Zartman and Ko made an analysis of the velocity distribution in a beam of bismuth. They found that in order to explain their results, they must assume the presence of diatomic bismuth molecules, and perhaps even  $Bi_3$ .

Lewis (153) has perfected a much more sensitive method of determining the degree of dissociation of non-magnetic molecules composed of atoms with a magnetic moment. The experiment is very simple. A beam is passed through a Stern-Gerlach field and its intensity measured at the undeflected position. Then the field is decreased to zero and the intensity determined again. The latter measurement is proportional to the total number of particles in the beam; the former only to the number of molecules, since all the atoms were deflected in the field. If the same process is repeated for a whole range of temperatures, it is possible to obtain the degree of dissociation as a function of temperature, and from this to calculate the equilibrium constant and the heat of dissociation.

Lewis studied the equilibrium of  $\text{Li}_2$ ,  $\text{Na}_2$ , and  $\text{K}_2$  in this way. In a similar manner Leu (151) determined the heat of dissociation of  $\text{Bi}_2$ .

#### *E. Chemical studies*

Molecular beams have been used by Sasaki (216) and his coworkers in a series of chemical studies upon the mechanism of reactions and the direct determination of radii of spheres of action between combining atoms. These unique experiments are mentioned because they indicate the power of the method and will perhaps suggest other applications. For instance, it might be possible to study the rates of some first-order chemical reactions by measuring the decrease in the number of particles in the beam as a function of the distance from the source. The difficulty due to chain reactions experienced in the ordinary method would not appear in the beam method.

#### *F. Einstein recoil*

Frisch (74) illuminated a very narrow ribbon-shaped beam of sodium sidewise with sodium light, and found that the beam was displaced by about the correct amount and in the correct direction; when the beam was illuminated edgewise, it was broadened a little. This is presumptive evidence of the existence of the Einstein recoil. This experiment, although difficult to perform, is very simple in principle, and provides another example of the power of the molecular-ray method to give results of a fundamental nature.

#### *G. High-energy beams*

With all the experiments described above, the beams were produced by the temperature motions of the gaseous materials, and therefore had velocities appropriate to the temperature of the oven. Recently an entirely new method of production of molecular beams has been developed which gives particles of very high energy (10, 115, 116, 118, 214, 215). Positive ions are to a large extent neutralized when passing through low pressures of the un-ionized gas. It is found that very many of them change neither the direction nor the magnitude of their velocities during this discharging process. Thus, if a focused beam of positive ions is neutralized and then collimated again, and if all the remaining ions are deflected to the side, there will remain a beam of neutral particles of essentially homogeneous but controllable velocity. The beams produced in this way have energies of the order of a few hundred electron volts; in contrast to this, particles at room temperature have energies  $1/40$  of an electron volt.

The detection of these beams is not a difficult matter; two methods have been used quite successfully. Beeck (12) and others (2, 36, 160, 215) have used a thermopile which theoretically could give the absolute intensity. The other method, which at present is limited to qualitative results, is simply the measurement of the number of secondary electrons emitted from a negative plate by the impact of the molecules (22, 115, 184, 214).

Amdur and Pearlman (3) have measured the collision cross sections of such beams of helium in helium and of hydrogen atoms in molecular hydrogen. The

beam energies varied from 200 to 1000 electron volts. With such energies, a study of the scattering reveals information about the repulsive forces between atoms. They found a marked lowering of the cross sections with increasing energies. This is not in agreement with the hard-sphere theory or the theory of Lennard-Jones. For the case of helium, they calculated a potential for the repulsive force which leads to the observed results.

Studies have been made by Beeck (8, 9, 12) and Varney (250) on the ionization produced in various gases by fast beams. The latter found that the energies of the beams must be about three times the ionization potential before ions are produced.

These fast beams can also be used to produce optical excitation. Maurer (160) has stimulated emission of thirteen lines of the helium spectrum by passing beams of helium atoms through helium. The light intensity was strictly proportional to the beam intensity, and, except for the singlet principal series, proportional to the pressure. The excitation in the range from a few hundred to 6000 volts was very similar to that produced by electrons in the range 0-40 volts. Gailer (78) studied the excitation of magnesium by helium and hydrogen atoms. He found arc and spark lines of magnesium, but no lines of helium or hydrogen. This is in agreement with the Döpel impact model.

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