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Molecular Beam Research in Hamburg 1922–1933

I. ESTERMANN
Office of Naval Research, Washington, D.C.

Although the first molecular beam experiments were carried out by Dunoyer in 1911,[1] molecular beam research as a planned scientific endeavor began in 1919, when Stern started a series of experiments on the direct determination of the thermal velocity of molecules. The two papers on this subject,[2] which appeared in 1920, were followed in 1921 and 1922 by four papers dealing with the problems of space quantization and atomic magnetic moments.[3] These experiments came at a time when the then new quantum theory, under the leadership of Bohr and Sommerfeld, developed concepts which were in direct contrast with those of classical physics. It was characteristic of Stern's approach to analyze controversial theories and to suggest and perform simple—in principle, if not always in practice—experiments to decide a question in one way or the other. The work described in the papers mentioned above became a classic and is known as the Stern-Gerlach experiment, W. Gerlach having been Stern's collaborator in the last three of these papers. In addition to establishing the reality of Sommerfeld's space quantization, these experiments led to the first direct measurement of an atomic magnetic moment: the moment of the silver atom which was found to be equal to the Bohr magneton, a value predicted theoretically by Bohr for the moment of a hydrogen atom.

In 1922, Stern became professor of physical chemistry at the University of Hamburg, where he began to organize a laboratory devoted mainly to molecular beam research, though occasionally other investigations were carried out there also. Most of the scientific proceedings of this epoch are recorded in a series of thirty papers with the subtitle: "Untersuchungen zur Molekularstrahlmethode" (U.z.M.) which appeared in the *Zeitschrift für Physik* between 1926 and 1933. These papers contain the basic ingredients of the method, and with few exceptions the later and current work can be traced directly or indirectly to their content. In the following paragraphs, I shall try to establish this connection, but before doing so, I would like to make a few observations.

The Hamburg Institute was never very large, and the number of doctoral students associated with it during this period was quite small, about six. Most of the important work was performed by Stern and a number of post-doctoral associates of whom a good fraction were research fellows from foreign countries. It was there where I. I. Rabi was introduced to molecular beam research, which he brought to full bloom after his return to Columbia, and in whose laboratory there most of the present workers received their introduction to the field. Among other guests were Ronald Fraser, who wrote the first monograph[4] on the subject; John B. Taylor, who developed the surface ionization detector, which is still one of the most valuable tools; T. E. Phipps and Emilio Segrè, who together with Stern and Frisch observed the "flops" of atoms in magnetic fields which play such an important part in the current molecular beam technology as applied to atomic, molecular, and nuclear moments and spins.

The highlights of this period were the confirmation of the wave properties of material particles and the quantitative verification of the de Broglie equation $\lambda = h/mv$, and the first measurements of the magnetic moments of the proton and deuteron. But these experiments would not have been possible without the previous painstaking work in which the principles and many experimental details were worked out and checked out, especially in view of the fact that the general level of the relevant technology (vacuum, electronic, etc.) was in its very early stages and that in most cases experimental techniques had to be stretched to the limit.

In the first paper of the U.z.M. series, U.z.M. No. 1, Stern discussed the general principles of the method and also developed a "Program" for its application. The problems listed in this paper as particularly suitable for molecular beam investigations mentioned are

1. Measurements of magnetic moments of atoms or molecules of the order of one Bohr magneton
2. Nuclear and other moments of order of 1/2000 Bohr magneton
3. Moments of higher order
4. "Natural" electric dipole moments of molecules
5. Higher order electric moments
6. Intermolecular forces
7. The radiation reaction according to Einstein
8. The existence of de Broglie waves.

These problems had been attacked with some degree of success during the Hamburg period, though in many cases much more complete and precise work was performed later elsewhere, particularly in Rabi's laboratory at Columbia University and the various laboratories started by Rabi's students, as evidenced by the papers in the present volume. In addition, several problems not listed in the "Program" were started in Hamburg, and some of them are still of contemporary interest. On the other hand, new techniques and problems were originated after the Hamburg period which make the earlier work appear primitive and unsophisticated, but basically most of the various branches of the current research can be traced to roots planted during this period.

The second paper, U.z.M. No. 2, deals with the technical problem of producing very narrow molecular beams of high intensity, a problem which had been stated in U.z.M. No. 1 as paramount for the various applications. The principles laid down in this paper are still basic for design of molecular beam equipment. Other papers dealing essentially with techniques are U.z.M. No. 5, where the equations for the intensity distribution of magnetically deflected beams are developed; U.z.M. No. 10, which describes the handling of beams of permanent gases and the Pirani gauge detector system; and U.z.M. No. 12, which deals with Rabi's first effort in the molecular beam area and discusses a new arrangement for magnetic deflection of molecular beams and its application to the measurement of the magnetic moment of the K atom. In U.z.M. No. 14 the now famous surface ionization detector and its application to the measurement of the moments of the K and Li atoms are described for the first time. This detector, though only applicable to atoms and molecules of low ionization potential, is still used extensively and has opened many new avenues to investigation by molecular beam techniques. Another potentially very powerful detection method based on the destruction of electronic space charge by ions is described in U.z.M. No. 28, but in spite of its universal applicability, it has yet to be utilized for specific investigations. Experiments dealing with the condensation of molecular beams, the first method used for their detection, were carried out during this period, and reported in several papers not included in the U.z.M. series; they are listed in reference 5. After remaining dormant for many years, this method is currently used again for experiments with radioactive atoms, and other problems, as mentioned in papers Nos. 2 and 9 of this volume.

The other papers will be reviewed in the order of Stern's "program". A group dealing with measurements of magnetic moments of the order of the Bohr magneton by means of the Stern-Gerlach arrangement are

U.z.M. No. 4 (K, Na, Tl), No. 6 (H), No. 8 (Bi), No. 9 (Li), No. 14 (K) and No. 26 (O_2). The application of the "Rabi field" to the measurement of the K atomic moment in U.z.M. No. 12 has already been mentioned. The first attempt to measure "small" moments of the order of 1/1000 Bohr magneton, which may result from the rotation of heavy particles (protons) or from intrinsic nuclear moments, was reported in U.z.M. No. 3, but the observations on beams of H_2O molecules deflected in a modified Stern-Gerlach field of an inhomogeneity of the order of 10^6 gauss/cm were only of a qualitative nature and did no more than demonstrate the feasibility of using the molecular beam method for the detection of magnetic moments of this order of magnitude.

The subject remained dormant until 1932, when improvements in technique permitted a more promising attack on this problem. The U.z.M. Nos. 24, 27, and 29 give account of a series of measurements with a (for that period) remarkable accuracy of 10% of the magnetic moment of the proton,* the rotational magnetic moment of the H_2 molecule and an estimate of the magnetic moment of the deuteron. All three values turned out to be quite different from the theoretical predictions, a probably well-known fact, but worth mentioning as an illustration for the need to obtain experimental verification for even apparently "sure" theories. This is also an appropriate place to refer to the subsequent brilliant work on nuclear moments by Rabi and his students of which examples are given in this volume.

Regarding the third item on the "Program", I am not aware of any successful work during the Hamburg period, but in later research at Columbia and elsewhere, the molecular beam method has been successfully applied to the measurement of quadrupole and octopole moments.

The next problem, electric dipole moments, was attacked at a rather early stage. U.z.M. No. 7 describes experiments leading to an order-of-magnitude determination of the electric dipole moments of binary salts, e.g. KCl, and U.z.M. No. 19 to the measurement of the moment of *p*-nitraniline. Other measurements of moments of organic molecules were reported outside of the U.z.M. series,[6] but really accurate measurements were only performed later at Columbia with the resonance method. The same applies to item 5 of the "Program".

Regarding point 6, the Hamburg period can account only for a beginning in U.z.M. No. 20. The problem has been more extensively investigated at various places later.

Point 7 has been investigated and verified in U.z.M. No. 30, but I am not aware of any later experiments concerning this subject.

In contrast, point 8 has received a great deal of attention. Probably

* This work was specifically referred to in Stern's Nobel Prize Citation.

the most accurate measurements of the Hamburg period were made in this area, and I am not aware of any subsequent work improving on these measurements, although the subject cannot by any standards be considered to have been exhausted by these experiments. In U.z.M. No. 15 the basic diffraction experiments with He and H_2 beams on crystal surfaces (LiF) and the theory of diffraction from crossed gratings are presented with great detail. The dependence of the de Broglie wavelength on the mass and velocity (temperature) of the beam molecules was tested over a wide range and the effective grating constant of the lattice was found to be the distance between ions of the same sign, not the crystallographic lattice constant. In U.z.M. No. 18, the diffraction experiments with He beams from LiF surfaces were refined by the use of monoenergetic beams in order to obtain sharper diffraction patterns. Monochromization was obtained in two ways, either by a "spectroscopic" method, i.e. by diffraction from a crystal and selection of atoms within a narrow range of diffraction angle, or by a procedure analogous to the Fizeau arrangement for the measurement of the velocity of light, consisting of two toothed wheels rotating with a fixed phase difference at various angular velocities so as to permit only atoms of certain velocity ranges to pass.* In both cases, the monoenergetic beams were analyzed with respect to their de Broglie wavelength (velocity) by a LiF crystal surface. The second method allowed a verification of the de Broglie relation $\lambda = h/mv$, where v was measured by purely mechanical means and λ computed from the diffraction angle and the lattice constant, with an accuracy of about 1%.

The foregoing paragraphs contain the extent of the realization of the 1926 "Program" during the Hamburg period. It is not surprising that a few other subjects were taken up which were not anticipated in 1926. Among them are the investigations of the reflection of molecular beams from surfaces, which are, of course, strongly related to the diffraction experiments. In U.z.M. No. 10, specular reflection of He and H_2 beams on glass and metal surfaces at small glancing angles of incidence was first observed; in U.z.M. No. 21 the reflection of Hg atoms from NaCl and LiF surfaces was investigated, and U.z.M. Nos. 23 and 25 deal with the finer details of the reflection and diffraction of molecular beams; (these papers could just as well be listed under point 8 of the "Program"). Another paper, U.z.M. No. 16, deals with the utilization of the different magnetic properties of monoatomic and diatomic molecules of alkali metals for the determination of the dissociation constant

* This procedure, in a less refined form, has been used in U.z.M. No. 13 for a verification of the Maxwellian distribution law of velocities. A later, much more elaborate version of this method is described in paper No. 3 of this volume.

and the heat of dissociation of these molecules by deflection of beams consisting of monomers and dimers as a function of the source temperature.

Finally, a subject marking the beginning of a new and powerful technique is contained in U.z.M. Nos. 17 and 22. This is the reorientation of space quantized atoms passing abruptly from a magnetic field of a certain direction to one of a different direction, colloquially known as "flopping" in the later literature. It is this effect which was so brilliantly exploited by Rabi for the development of the molecular beam resonance method which made possible measurements of an accuracy rivalling the most accurate physical measurements.

In the summer of 1933, the molecular beam work in Hamburg came to an abrupt end. Stern and the author went to Carnegie Institute of Technology and began to rebuild a laboratory. Starting on a small scale, they concentrated first on refining the measurements of the nuclear magnetic moments of the proton and deuteron. Later other subjects were taken up, but the momentum of the Hamburg laboratory was never regained. With the outbreak of the war, research shifted to other problems. Stern retired in 1945, and the author left in 1950. A small program is still in operation, devoted at present to the detailed study of the interaction of molecules with solid surfaces. (See paper No. 3 of this volume.)

In the meantime, the laboratory at Columbia University, started by Rabi after his return from Hamburg in 1929, had become the focal point of molecular beam research. An example of the current work there is paper No. 5 of this volume, but the authors of papers Nos. 2, 4, 6, and 7 also received their introduction to molecular beams at Columbia. The influence of Stern's work can be recognized throughout.

A few words will be said about the last paper. This is reprinted from the *Physical Review*, with the permission of the editor, for the following reasons: First, it contains a direct application of the procedure used in U.z.M. No. 27. Secondly, the desirability of performing such an experiment was discussed by Stern as soon as neutron beams became available, but it could not be carried out except at a National Laboratory possessing a pile with a sufficiently large thermal neutron flux. Dealing no longer with molecular beams in the conventional sense, it has been included as an example for the broad influence of Stern's thinking beyond the scope of his original program.

The last year has finally given proof to the theorem that even the purest research leads ultimately to practical applications. I am sure that Stern never expected to see a molecular beam device in a commercial catalog. But now a cesium beam clock, guaranteed to be accurate to one part in 10^{10}, and thus exceeding the accuracy of all other time measuring devices, can be purchased ready for use. It is suggested as an interesting speculation to contemplate the effects of a molecular beam industry on the future of molecular beam research.

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