EARLY HISTORY OF MAGNETIC RESONANCE

Norman F. Ramsey

Lyman Laboratory of Physics
Harvard University
Cambridge, Massachusetts 02138

INTRODUCTION

In the title of this report, emphasis should be given to the word *early*. Some readers may even believe that "Pre-History" would be a better title than early history. The report will cover the period from 1921 to the first nuclear resonance absorption experiments of Purcell, Torrey and Pound and the first nuclear induction experiments of Bloch, Hansen and Packard even though from some points of view the history of magnetic resonance can be said to begin with the experiments that end this report.

My interest in the history of magnetic resonance began with preparations for my Ph.D. final examination in 1939. Since mine was the first Ph.D. thesis based on nuclear magnetic resonance, I feared that my examining committee would ask searching questions as to the origins of the ideas of magnetic resonance and of the molecular beam technique we used to detect the resonance transitions.

EARLIEST SEARCH FOR A DEPENDENCE OF MAGNETIC SUSCEPTIBILITY ON FREQUENCY

The earliest reported search for a dependence of magnetic susceptibility on frequency was carried out by Belz(1) in 1922 for solutions of a variety of paramagnetic salts. No frequency dependence was found. Acting on a suggestion of Lenz and Ehrenfest, G. Breit(2) searched for a frequency dependence of the magnetic susceptibility of various paramagnetic substances but found no dependence on frequency. Perhaps this disappointment contributed to Breit's decision to concentrate in theory, where he later had such a productive career.

SPACE QUANTIZATION WHEN DIRECTION OF MAGNETIC FIELD CHANGES

The origins of the molecular beam magnetic resonance method can be traced back to early theoretical speculations and experiments on the change in the quantum mechanical space quantization when the direction of a magnetic field is changed. The problem was first posed and partially solved in 1927 by C. G. Darwin(2) and his analysis was subsequently improved by P. Gutinger(3), E. Majorana(4), and L. Motz and M. Rose(4).

In the period 1931-33 several experiments in Otto Stern's laboratory in Hamburg successfully measured the changes in the space quantization when the direction of the magnetic field was changed. The experiments of Phipps and Stern(5) and Frisch and Segre(6) partly agreed with the best theory and partially disagreed. I. I. Rabi(7) pointed out that the discrepancy between theory and experiment was due to the neglect of nuclear spins in previous theories. Although the magnetic moment of the electron is about 2000 times larger than the typical nuclear magnetic moment, the angular momenta are comparable in size and at the low fields used in some of the experiments the nuclear spin angular momenta were tightly coupled to the electron spin making large effects on the observations. In all of these experiments the direction of the field was changed in space as the atoms went by. Since the atoms had a thermal velocity distribution the frequency components were different for different velocities, so on averaging over the velocity distribution, no sharp resonances were either anticipated or observed. Rabi(8) and Schwinger(9) in 1937 calculated the transition probability for molecules that passed through a region in which the direction of the field varied rapidly.

FIRST ATTEMPT TO OBSERVED NUCLEAR MAGNETIC RESONANCE IN CONDENSED MATTER

In 1936 with calorimetric techniques, C. J. Gorter(10) successfully observed a frequency dependence of the paramagnetic relaxation of a number of alums. He found that the observed effects depended on the frequency, ν, as ν^x where x was a number, usually between 1 and 2. No resonance effects were observed. Gorter(10)

also utilized the same calorimetric method in an attempt to look at ^{7}Li nuclear magnetic resonance in LiCl and for an ^{1}H resonance in AlK alum but found no such resonance. The following year, Lasarew and Schubnikowt(21) showed at low temperature that the nuclear magnetic moments in solid hydrogen contributed significantly to the observed static magnetic susceptibility of solid hydrogen.

In an experiment reported in 1942 subsequent to the successful molecular beam nuclear magnetic resonance experiments described in the next two sections, Gorter and Broer(10) attempted to observe nuclear magnetic resonance in powders of LiCl and KF, but no resonance was observed. It is still a mystery as to why Gorter did not detect a resonance. In part he suffered from a poor choice of material since R. V. Pound much later showed that pure crystalline LiF has an unusually long nuclear spin-lattice relaxation time. However, that alone does not explain the failure of Gorter's inspired experiments since at a much later date N. Bloembergen found one of Gorter's original crystals and was able to observe an NMR signal with it even though the relaxation time was large. The most likely explanation for the failure of Gorter's experiments was an unfavorable signal-to-noise ratio in his apparatus. It is of interest to note that the first appearance of the phrase "nuclear magnetic resonance" in a publication title is in Gorter's 1942 paper, but he attributes the coining of this phrase to I. I. Rabi.

TRANSITIONS INDUCED BY PASSAGE OF MOLECULES THROUGH DIFFERENTLY ORIENTATED MAGNETIC FIELDS

While Gorter was pursuing his unsuccessful NMR experiments, I. I. Rabi was independently studying transitions induced when atoms or molecules in a molecular beam traversed a region in space of space in which the directions of the magnetic field change successively. In his brilliant 1937 theoretical paper entitled "Space Quantization in a Gyrating Magnetic Field", Rabi(8) assumed for simplicity that the field was oscillatory in time even though the initial application was to a field varying along the beam rather than oscillatory with time. As a consequence, all the formulae in that paper are applicable to the resonance case with oscillatory fields and the paper, without alteration, provides the fundamental theory for present molecular beam magnetic resonance experiments as well as for other experiments with magnetic resonance.

MOLECULAR BEAM MAGNETIC RESONANCE

While writing his paper on the gyrating field, Rabi discussed with some of his colleagues the possibility of using oscillatory rather than space varying magnetic fields, but Rabi's laboratory had a full program of important experiments which did not require oscillatory fields, and no experiments utilizing oscillatory fields were started during the first six months following the submission of Rabi's theoretical paper on the gyrating magnetic field. In September 1937, C. J. Gorter visited Rabi's laboratory(12) and described his brilliantly conceived but experimentally unsuccessful efforts to observe nuclear magnetic resonance in lithium fluoride, as described in Gorter's publications of the previous year(10). The research efforts in Rabi's laboratory at Columbia University were soon directed primarily toward the construction of molecular beam magnetic resonance experiments with oscillator driven magnetic fields. Two successful magnetic resonance devices were soon constructed by Rabi(13,14), Zacharias(13,14), Millman(13), Kusch(13), Kellogg(14), and Ramsey(14, 15), A schematic view(13) of the method is shown in Figure 1. In these experiments the atoms or molecules were deflected by a first inhomogeneous magnetic field and refocused by a second one. When the resonance transition was induced in the region between the two inhomogeneous fields, the occurrence of the transition could easily be recognized by the reduction of intensity associated with the accompanying failure of refocusing. For transitions induced by the radiofrequency oscillatory field, the apparent frequency was almost the same for all molecules independent of molecular velocity. As a result, when the oscillator freguency was equal to the Larmor angular frequency ω_0 of a nucleus, a sharp resonance was obtained where

$$\omega_0 = \gamma_I H_0 \qquad (1)$$

is the angular precession frequency of a classical magnetized top with the same ratio γ_I of magnetic moment to angular momentum when in a magnetic field H_0. Figure 2 shows the first reported nuclear magnetic resonance curve; the curve was obtained with a beam of LiCl molecules(13).

Kellogg, Rabi, Ramsey, and Zacharias(14, 15) soon extended the method to the molecules H_2, D_2 and HD for which the resonance frequencies depended not only on eqn. 1 but also on

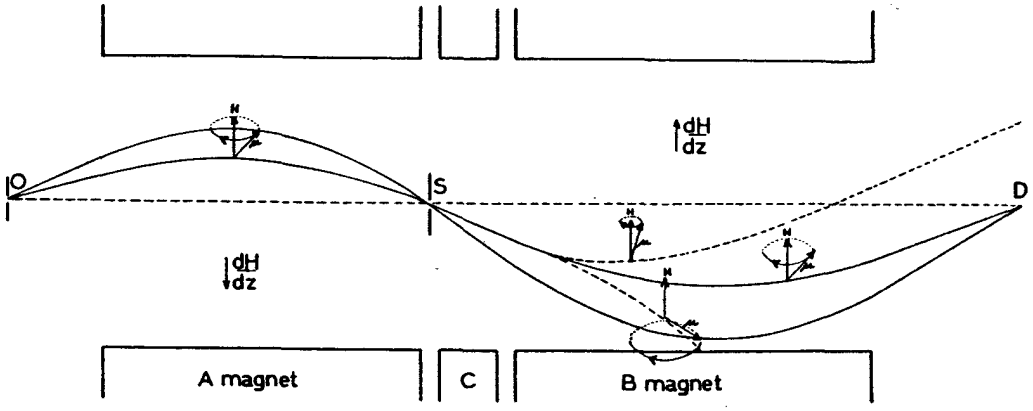

Figure 1. Schematic diagram(13) showing the principle of the first molecular beam magnetic resonance apparatus. The two solid curves indicate two paths of molecules having different orientations that are not changed during passage through the apparatus. The two dashed curves in the region of the B magnet indicate two paths of molecules whose orientation has been changed in the C region so the refocusing is lost due to the change in the component along the direction of the magnetic field.

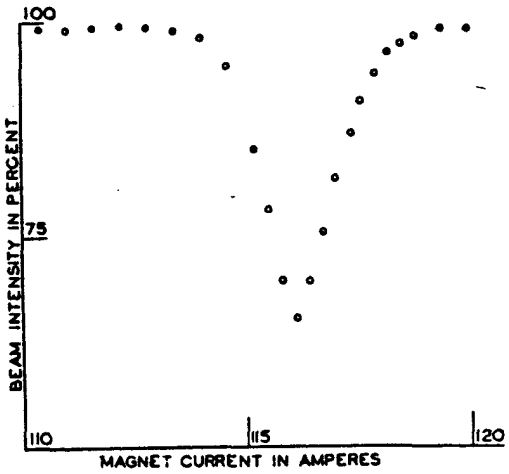

Figure 2. Curve showing refocused beam intensity at various values of the homogeneous field. One ampere corresponds to about 18.4 Gauss. The frequency of the oscillating field was held constant at 3.518×10^6 cycles per second.

internal interactions within the molecule. The transitions in this case occurred whenever the oscillatory field was at a Bohr angular frequency for an allowed transition

$$\hbar\omega = E_i - E_f \qquad (2)$$

For the first time the authors described their results as "radiofrequency spectroscopy". The radiofrequency spectrum for H_2 is shown in Figure 3.

The first molecular beam magnetic resonance experiments were with $^1\Sigma$ molecules for which the primary interactions were those of the nuclear magnetic moments in external magnetic fields, but in 1940 Kusch, Millman and Rabi(16, 17) first extended the method to paramagnetic atoms and in particular to $\Delta F = \pm 1$ transitions of atoms where the relative orientation of the nuclear and electronic magnetic moments were changed, in which case the resonance frequencies were determined dominantly by fixed internal properties of the atom rather than by interactions with an externally applied magnetic field.

In 1949, N. F. Ramsey(18,20) invented the separated oscillatory field method for magnetic resonance experiments. In this new method, the oscillatory field, instead of being distributed throughout the transition region, was

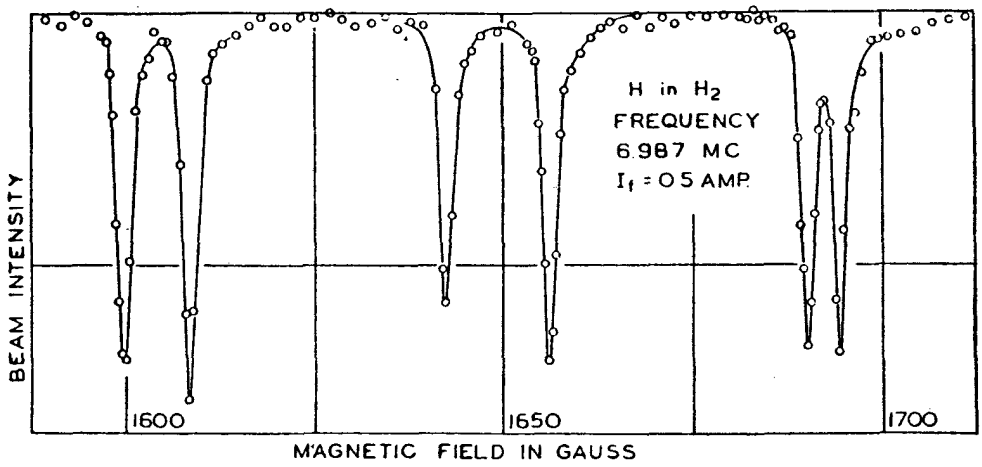

Figure 3. Radiofrequency spectrum of H_2 in the vicinity of the proton resonance frequency(14). The resonance frequencies are primarily determined by the interaction of the proton magnetic moment with the external magnetic but the state of different m_I and m_J are displaced relative to each other by the different values of the nuclear spin-nuclear spin interaction energies and of the spin-rotational interaction.

concentrated in two coherently driven oscillatory fields in short regions at the beginning and end of the resonance region. In an alternative version of the same method, the coherent oscillatory fields are applied in two short pulses -- at the beginning and end of the observation time. The method has the following advantages(20): (1) the resonances are 40% narrower than even the most favorable Rabi resonances with the same length of apparatus; (2) the resonance are not broadened by field inhomogeneities: (3) the length of the transition region can be much longer than the wavelength of the radiation, provided that the two oscillatory field regions are short, whereas there are difficulties with the Rabi method due to phase shifts when the length of the oscillatory region is comparable to the wave length; (4) the first-order Doppler shift can mostly be eliminated when sufficiently short oscillatory field regions are used; (5) the sensitivity of the resonance can be increased by the deliberate use of appropriate relative phase shifts between the two oscillatory fields; and (6) with short lived states the resonance width can be narrowed below that expected from the lifetime of the state and the Heisenberg uncertainty principle if the separation of the oscillatory fields is sufficiently great that only molecules living longer than average in the excited state can reach the second oscillatory field before decaying.

Essentially the same magnetic resonance technique as developed by Rabi for measuring nuclear magnetic moments with a molecular beam was used by Alvarez and Bloch(21) to measure the magnetic moment of the neutron with a neutron beam. Since the first publication on the neutron magnetic resonance studies was published about two years after the first molecular beam magnetic resonance papers appeared, it is often considered that the neutron studies of Alvarez and Bloch were merely adaptations of the resonance methods developed by Rabi and his associates. However, Alvarez recently has told me that Bloch had thought of doing the neutron beam magnetic resonance experiment before either Alvarez or Bloch had heard of the molecular beam magnetic resonance experiments of Rabi and his associates. It must have been a bitter disappointment to Bloch and Alvarez to learn that their clever idea for magnetic resonance had been anticipated by Rabi and his associates. It is to their credit that they did not let this disappointment blight their research careers; instead each went on to win separate Nobel Prizes for subsequent research.

Work on both molecular beam and neutron

beam magnetic resonance experiments were interrupted by World War II. In 1944 Rabi and Ramsey spent one evening together in Cambridge, Massachusetts, planning possible postwar research experiments. Two ideas emerged as leading candidates. One was to use the molecular beam magnetic resonance method to measure the hyperfine separation in atomic hydrogen since a presumably exact theoretical calculation of this separation existed. This experiment was eventually carried out and led to the first indication of an anomalous magnetic moment of the electron. The other idea was to detect the existence of nuclear magnetic resonance transitions by their effect on the oscillator. To our pleasant surprise, the signal-to-noise calculations were favorable and we became quite enthusiastic about the possibility. We then realized that we were merely reinventing Gorter's nuclear magnetic resonance experiments and that those experiments had failed for unknown reasons. We, therefore, decided that efforts in that direction should be given a low priority compared to the various molecular and atomic beam experiments, including the one on the atomic hydrogen hyperfine separation.

ELECTRON PARAMAGNETIC RESONANCE EXPERIMENTS IN CONDENSED MATTER

In addition to his unsuccessful efforts to observe nuclear magnetic resonance, Gorter(10) successfully observed paramagnetic relaxation in condensed matter. However, his attempts to observe an electron paramagnetic resonance failed. The first successful paramagnetic resonance experiments in condensed matter were those of Zavoisky(23). His observed paramagnetic resonance with $CrCl_3$ is shown in Figure 4, was first reported in a 1944 Ph.D. thesis, and several years elapsed before there was widespread recognition of his accomplishment. Shortly after Zavoisky's pioneering work, observations of electron paramagnetic resonances were made by Cummerow and Halliday (24) and others.

NUCLEAR MAGNETIC RESONANCE EXPERIMENTS IN CONDENSED MATTER

Following World War II, two groups in the United States sought to develop nuclear magnetic resonance experiments with condensed matter. One was E. M. Purcell, N. G. Torrey and R.V. Pound(25) at Harvard University and the other was F. Bloch, W. Hansen and M. E. Packard(26) at Stanford University. Each group had different reasons for being willing to procede with its experiments despite the failure of Gorter's earlier experiments.

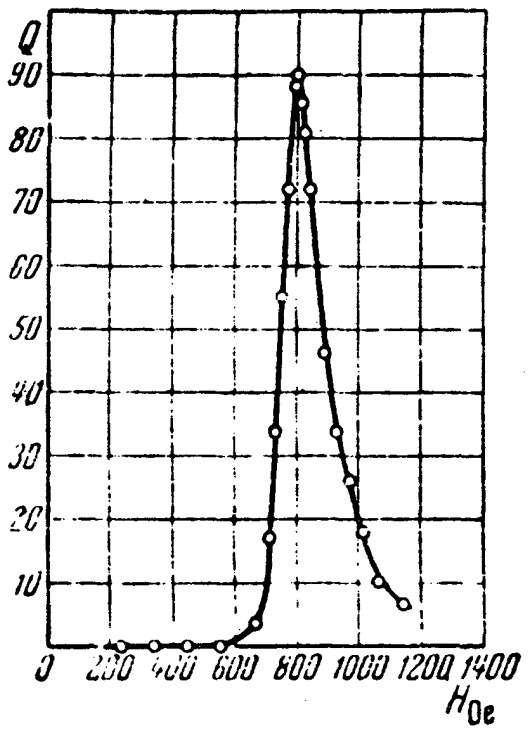

Figure 4. Electron paramagnetic resonance curve obtaine d by Zavoisky(23) with $CrCl_3$. The microwave radiation wavelength was $\lambda = 13.70$ cm and T = 298 K.

In the case of Purcell, Torrey and Pound(25) they were initially unaware of Gorter's work when they first started their experiment. When Rabi learned of their plans and pointed out to Purcell that Gorter's experiment was similar and had failed, Purcell was disappointed by the news but felt that the work on the new experiment had already gone so far that it should be completed, particularly since their extensive theoretical calculations of relaxation and other feasibility requirements appeared favorable. Purcell and his associates observed the absorption in the resonance circuit and devoted considerable attention to problems of signal size and noise. On December 24, 1945 their letter(25) was received

by the Physical Review announcing the successful observation of nuclear magnetic resonance absorption of the protons in a paraffin filled 30 MHz resonant cavity whose output was balanced against a portion of the signal generator output. When the magnetic field passed through resonance, an unbalanced signal 20 times noise was observed.

When Bloch, Hansen and Packard (26) started their experiments, they were fully aware of Gorter's experiments but they were encouraged to proceed because they thought they knew the source of the previous failure and a means for overcoming it. They believed that Gorter's experiment had failed because the thermal relaxation time T_1 was much longer than Gorter had allowed for. To overcome this difficulty they proposed to put their water sample in a strong magnetic field for several days to allow the nuclear spin system to reach thermal equilibrium. They in fact did so: when their apparatus was all ready for a first test they inserted the water in the high field and before attempting a careful search for a resonance Bloch went off on a ski trip to allow the system to come to equilibrium. When he returned he and his associates found the desired resonance after some initial searching, but they also found that the relaxation time was short and not long. Instead of waiting several days to begin their observations, a few seconds would have sufficed. The detection method of Bloch, Hansen and Packard(26) was rather different from that of Purcell, Torrey and Pound(25). Instead of observing the absorption signal with a single coil, they used two orthogonal coils and picked up the signal induced in the second coil by the coherently precessing nuclei driven by the first coil. For this reason they called their experiments nuclear induction. A letter(26) announcing their successful experiment was received by the Physical Review on January 29, 1946.

From the time of these experiments onward, developments in magnetic resonance occurred at a rapid pace. For this reason, I have chosen that time to bring to an end this account of the *early* history of magnetic resonance.

REFERENCES

[1] M. H. Belz, *Phil. Mag.* **44,** 479 (1922) and G. Beit, *Comm. K. Lab.* 168c (1926).

[2] C. G. Darwin, *Proc. Roy. Soc.* **117,** 258 (1927).

[3] G. Gutinger, *Zeits. f. Physik* **73,** 169 (1931).

[4] E. Maiorana, *Nuovo Cimento* **9,** 43 (1932) and L. Motz and M. E. Rose, *Phys. Rev.* **50,** 348 (1936).

[5] T. E. Phipps and O. Stern, *Zeits f. Physik* **73,** 185 (1931).

[6] O. Frisch and E. Segre, *Zeits f. Physik* **80,** 610 (1933).

[7] I. I. Rabi, *Phys. Rev.* **49,** 324 (1936).

[8] I. I. Rabi, *Phys. Rev.* **51,** 652 (1937).

[9] J. Schwinger, *Phys. Rev.* **51,** 645 (1937).

[10] C. J. Gorter, *Physica* **3,** 503, 995 and 1006 (1936) and C. J. Gorter and I. J. F. Broer, *Physica* **9,** 591 (1942).

[11] R. V. Pound, *Phys. Rev.* **81,** 156 (1951).

[12] Rabi(13) refers to the visit of Gorter in a footnote to the first paper experimentally demonstrating a successful molecular beam magnetic resonance and Gorter 29 years later published an article giving his own somewhat different recollections of the same visit [*Physics Today* **20,** 76 (Jan. 1967)].

[13] I. I. Rabi, J. R. Zacharias, S. Millman and P. Kusch, *Phys. Rev.* **53,** 318 (1938) and **55,** 526 (1939).

[14] J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey and J. R. Zacharias, *Phys. Rev.* **55,** 729 (1939); **57,** 728 (1939); and **57,** 677 (1940).

[15] N. F. Ramsey, *Phys. Rev.* **58,** 226 (1940).

[16] ;P. Kusch, S. Millman and I. I. Rabi, *Phys. Rev.* **57,** 765 (1940).

[17] S. Millman and P. Kusch, *Phys. Rev.* **57,** 438 (1940).

[18] N. F. Ramsey, *Phys. Rev.* **76,** 966 (1949).

[19] N. F. Ramsey and H. B. Silsbee, *Phys. Rev.* **84,** 506 (1951).

[20] N. F. Ramsey, *Physics Today* **33,** 25 (July 1980).

[21] L. Alvarez and F. Bloch, *Phys. Rev.* **51,** 11 (1940).

[22] J. E. Nafe. E. B. Nelson and I. I. Rabi, *Phys. Rev.* **71,** 914, (1947) and **73,** 718 (1948).

[23] E. K. Zavoisky, Ph.D. Thesis 1944 and *J. Phys. USSR* **9,** 211 and 245 (1945) and **10,** 197 (1946).

[24] R. L. Cummerow and D. H. Halliday, *Phys. Rev.* **70,** 483 (1946).

[25] E. M. Purcell, H. G. Torrey and R. V. Pound, *Phys. Rev.* **69,** 37 (1946).

[26] F. Bloch, W. Hansen and M. E. Packard, *Phys. Rev.* **69,** 127 (1946).

[27] B. G. Lasarew and L. W. Schubnikow, *Phys. Zeits. Sowjet.* **11,** 445 (1937).