EARLY MAGNETIC RESONANCE EXPERIMENTS: ROOTS AND OFFSHOOTS

Branches of this fruitful tree led to masers, radiofrequency spectroscopy, the frequency standard and nuclear magnetic resonance imaging.

Norman F. Ramsey

In 1937 I. I. Rabi described the fundamental theory for magnetic resonance experiments in his great paper "Space Quantization in a Gyrating Magnetic Field."[1] This theory stimulated many subsequent developments, including molecular-beam magnetic resonance, radiofrequency spectroscopy, nuclear magnetic resonance, masers and atomic clocks. Its imprint now stamps a tremendous range of experimental techniques and technological applications.

Although many scientists think that Rabi published this work following his invention of the molecular-beam magnetic resonance method, in fact he devised the method only some months after he published the theory. In his paper Rabi indeed included the correct formula for a magnetic resonance transition, but he developed the expression in a fashion that obscured its sharp resonance character. Furthermore, Rabi's purpose at the time was not to gain greater accuracy but simply to determine the signs of nuclear magnetic moments.

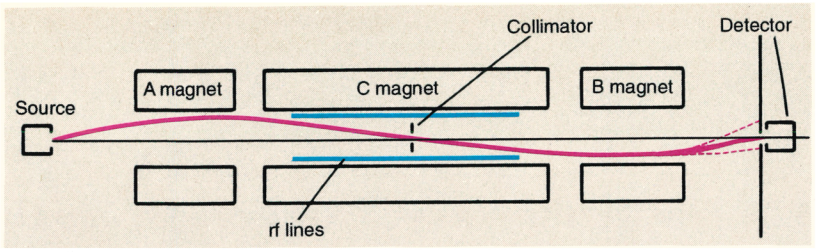
The original motivation

Rabi's laboratory in 1937 had been measuring the magnitudes of many nuclear magnetic moments by passing an atomic beam through an inhomogeneous magnetic field and observing either the deflection or the strength of the field for which there was no deflection. (This latter technique was called the zero-deflection method).

But Rabi also wanted to measure the signs of the magnetic moments. He realized he could do so by measuring the signs of the *atomic* moments in states for which the nuclear and atomic spins were antiparallel; he also realized that atoms with antiparallel spins could be identified by observing the transitions induced by passing the atoms through a magnetic field whose direction changed as a function of position. As the atoms passed through this region, the field vector appeared to rotate in time at a frequency that depended on the velocity of the individual atom. To understand these transitions better, Rabi calculated the solution to a simple related problem, that of the transitions induced by a magnetic field that "gyrated" at a fixed frequency. The resulting paper[1] contains the resonance equation that became the basis of all subsequent magnetic and electric resonance experiments. However, the form of the equation and the subsequent averaging over atomic velocity distributions obscured the resonant nature of the result, and Rabi failed to see it immediately.

Some time later Rabi and his collaborator Jerrold Zacharias casually discussed the possibility of using an

Norman Ramsey is Higgins Professor of Physics at Harvard University, in Cambridge, Massachusetts.



Molecular-beam magnetic resonance experiments featured two regions, A and B, with inhomogeneous magnetic fields, which deflected the beam in opposite directions. If the molecule did not change its spin state as it went through region C, it had no net deflection. An oscillating field was introduced into region C. When the frequency of the oscillator was the same as the Larmor precession frequency, it would flip the spin of the molecule and the beam intensity at the detector would drop sharply.

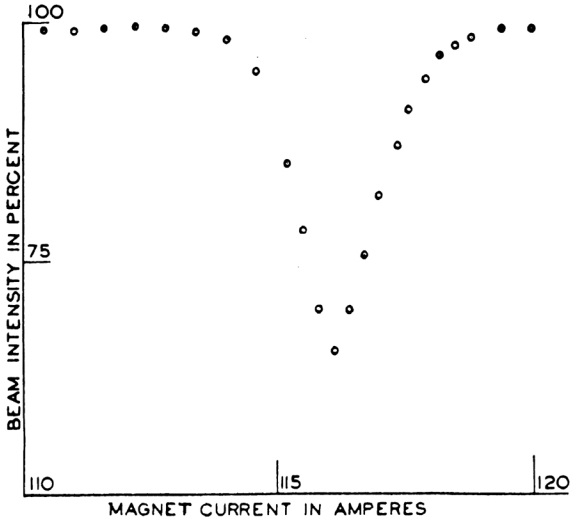
oscillator to produce a magnetic field that truly rotated with time instead of simulating one with the motion of particles. But they were so fully occupied with their highly successful research programs that they gave this idea no further thought. In September 1937 C. J. Gorter, then at the University of Groningen in the Netherlands, visited Rabi and described his published[2] but unsuccessful attempts to observe nuclear magnetic resonance effects in solids.[3] (Gorter discussed his experiments and his visit to Rabi in an article in PHYSICS TODAY, January 1967, page 76. It remains a puzzle why the experiments failed. At one time it was thought that he had made an unfortunate choice of sample, but Nicolaas Bloembergen many years later obtained satisfactory nmr results with the identical sample.) In the course of his discussions with Gorter, Rabi came to appreciate fully how much sharper his resonances would be if the frequencies were generated by an oscillator, because each atom or molecule would see the same frequency. He proposed measuring nuclear magnetic moments by the molecular-beam magnetic resonance method illustrated in the figure above, and he immediately redirected the laboratory research program.

Proving the method

Two groups in Rabi's lab began to modify their separate apparatus to incorporate radiofrequency oscillators based on the Hartley oscillator, which was well described in the *Radio Amateur's Handbook*. One group—Rabi, Zacharias, Sidney Millman and Polykarp Kusch—worked with easily detected alkali molecules and found the sharp magnetic resonance[4,5] shown in the figure below.

Soon thereafter a second lab group—Rabi, Jerome M. B. Kellogg, Zacharias and I—observed resonances with molecular hydrogen (H_2), but at first we were deeply disappointed to find a broadly spread-out and ill-defined transition region rather than a simple resonance like that of the figure below. With the hydrogen–deuterium molecule, HD, however, we found two sharp resonances that enabled us to determine accurately the magnetic moments of the proton and deuteron, despite some puzzling background. For my PhD thesis I began investigating the strange shape of the H_2 resonance and the puzzling backgrounds that appeared in both the D_2 and HD resonances. When I successively lowered the amplitudes of the oscillatory fields, it became clear that the radiofrequency spectrum of H_2 had six lines, presumably due to interactions within the molecule and not just the expected interaction of the nuclear magnetic moment with the external magnetic field. Likewise the puzzling backgrounds in D_2 and HD appeared to be weaker spectral lines, with the D_2 lines being spread over a surprisingly broad background.

We realized then that these features, originally deemed of minor importance and suitable for a thesis



The nuclear magnetic resonance first observed by I. I. Rabi, Jerrold Zacharias, Sidney Millman and Polykarp Kusch. The curve measures the intensity of a lithium chloride beam as a function of the current producing the magnetic field in region C. From the data one can deduce the nuclear moment of lithium. One ampere corresponds to about 18.4 gauss. The frequency of the oscillating field was held constant at 3.518×10^6 hertz. (From ref. 4.)

project, were really of great interest and deserved to be studied by all those who had built the apparatus. Consequently Rabi, Kellogg, Zacharias and I worked together to explore further the radiofrequency spectra of H_2, D_2 and HD in the nuclear resonance region. (My thesis topic shifted to studies of a new spectrum I had discovered, one associated with the molecular rotational magnetic moment.) For H_2 we obtained[6,7] the radiofrequency spectrum shown in the figure below. We were eventually able to account accurately for the spectrum, including its asymmetries, in terms of spin–rotation and spin–spin interactions. With these studies we established the validity of radiofrequency spectroscopy, which differed from previous spectroscopies by using coherent rather than incoherent electromagnetic radiation. In addition we determined that the deuteron has a quadrupole moment, which in turn implied the existence of a new nuclear force, the tensor force.

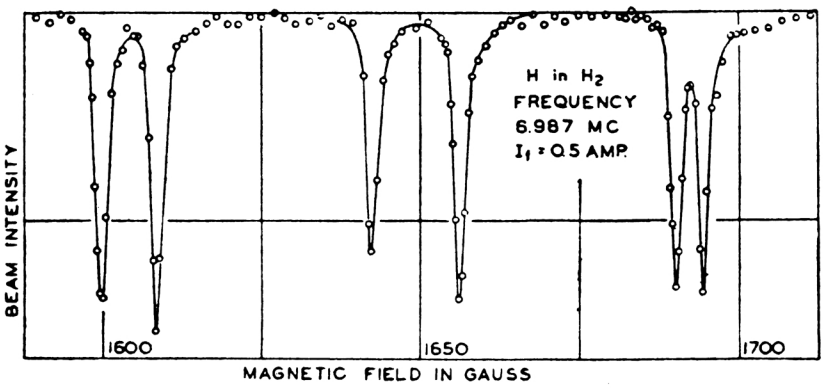
In 1940 Luis W. Alvarez and Felix Bloch[8] applied a similar magnetic resonance method to a beam of neutrons to measure the neutron's magnetic moment. Because their paper appeared three years after the first magnetic resonance papers from Rabi's laboratory, their technique is usually presumed to be an adaptation of Rabi's method. I later learned from Alvarez, however, that Bloch thought of his method before he had seen Rabi's papers. Bloch and Alvarez must have been greatly disappointed to discover that their resonance idea had been published earlier. But instead of allowing disappointment to blight their careers, they went on to other research, each man independently earning a Nobel Prize.

Offshoots

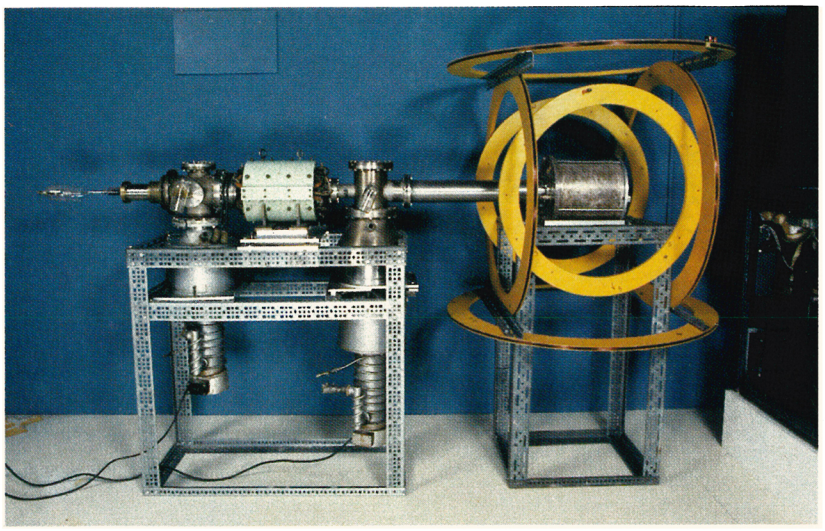
Rarely has an initial group of experiments led to so many important scientific and technological offshoots. In 1940 Kusch, Millman and Rabi successfully applied the magnetic resonance method to beams of paramagnetic atoms, and those experiments were followed by many microwave studies of atomic hyperfine structures. In 1947 John E. Nafe, Edward B. Nelson and Rabi, applying the magnetic resonance method to a beam of atomic hydrogen, discovered the anomalous value of the atomic hyperfine interaction.[9] The same year Willis Lamb and Robert C. Retherford, using quite a different form of atomic-beam magnetic resonance apparatus, observed that the $^2S_{1/2}$ and the $^2P_{1/2}$ levels of atomic hydrogen were not degenerate, unlike what Dirac's theory predicted. Then Kusch and Henry Foley used the atomic-beam resonance method to show that the electron has an anomalous magnetic moment. Although the discovery of the hyperfine anomaly preceded that of the Lamb shift by a few months, the fine-structure effect was larger and more easily calculated, so it stimulated the work on nonrelativistic quantum field theory by Hans Bethe, Julian Schwinger, Victor Weisskopf and Robert Oppenheimer. The hyperfine interaction, however, required a relativistic treatment, and it spurred the development of relativistic quantum electrodynamics by Schwinger, Richard Feynman, Sin-itiro Tomonaga and others.

Harold K. Hughes, working in Rabi's laboratory, extended the nuclear magnetic resonance method in a different direction: to oscillatory electric fields. After further improvements by John W. Trischka, Vernon W. Hughes, myself and others, the electric resonance method continues to be applied to the study of a wide variety of polar molecules.

Stimulated in part by the successes of the beam magnetic resonance experiments, the groups of Edward M. Purcell, Henry C. Torrey and Robert V. Pound and of Bloch, William W. Hansen and Martin Packard in 1945 independently invented and developed methods of nuclear magnetic resonance that detect the resonance transitions by their effects on the radiofrequency system. These methods are what is now usually called nmr. Unlike the beam methods, nmr can detect transitions of nuclei in condensed liquid, solid and gaseous samples, as discussed in the article by George Pake on page 46. Because it can measure the shifts in resonant



Magnetic resonance spectrum of H_2 observed by Jerome Kellogg, Rabi, Ramsey and Zacharias. The experimenters expected one peak due to the proton resonance but instead found six peaks in that vicinity. The spectrum results from internal interactions. (From ref. 6.)



LAURIE MINOR-PENLAND AND RICHARD STRAUSS

The first hydrogen maser, developed by Mark Goldenberg, Daniel Kleppner and Ramsey. With subsequent improvements the atomic hydrogen maser has become an atomic clock with particularly great stability over periods of a few days. (Courtesy of the National Museum of American History, Smithsonian Institution.)

frequency caused by the local environment, nmr has become a powerful tool for chemical analysis. It has been enhanced by techniques such as Fourier-transform spectroscopy, and more recently it has been adapted to magnetic resonance imaging, a powerful tool for medical diagnosis.

Optical pumping can be seen as a partial offshoot of magnetic resonance experiments, if one looks at the events leading to its invention by Alfred J. Kastler and Jean Brossel. In 1949, stimulated by magnetic resonance experiments, Francis Bitter published a paper proposing a method of atomic pumping. When Rabi and I saw Bitter's paper, we immediately telephoned him to point out that it contained a fundamental error that invalidated the proposal. Bitter agreed and felt terrible about his mistake. But Bitter's good friend Kastler reacted differently to the mistake. Figuring that Bitter was too good a physicist to make such an error, Kastler decided he must have had something else in mind. While trying to discover this something else, Kastler realized that with certain modifications, it would be possible to use the method for optical pumping. Because his idea originated from Bitter's paper, Kastler invited Bitter to coauthor the first optical pumping paper with him, but Bitter, out of modesty and embarrassment, declined, perhaps depriving himself thereby of a Nobel Prize.

Clocks and masers

In 1949 I invented the resonance method of separated oscillatory fields, which often provides much narrower resonances and is applicable to higher frequencies. In 1955 Zacharias, J. L. V. Parry, Louis Essen and others adapted the technique to atomic clocks and frequency standards. Since then many improvements have been made to the technique by researchers in government laboratories, universities and industrial labs throughout the world. In 1967 the international time standard for the second was defined in terms of the hyperfine frequency of the cesium atom. Cesium-beam clocks now achieve accuracies better than one part in 10^{14}. Steven Chu recently applied separated oscillatory fields to a "fountain" of very slow atoms to do high-precision spectroscopy: The atoms pass through the oscillatory field once on their way up and again on their way down, and the long travel time gives the enhanced precision.

With my associates, I have been using the separated oscillatory field method to study neutrons. In one set of experiments we accurately measured the neutron magnetic moment, and in a different series of experiments we have searched for its electric dipole moment. We first undertook the electric dipole experiments in 1951 as a test of parity conservation, because that symmetry was almost universally believed to exist at the time, but we planned later experiments as tests of time-reversal symmetry. We are continuing the experiments to this day, with increasing sensitivity, as sensitive tests of the different theories of *CP*-nonconserving forces.

In 1955 James P. Gordon, Herbert J. Zeiger and Charles H. Townes used molecular-beam electric resonance methods to construct the first molecular maser, as discussed in the article by Bloembergen on page 28. Mark Goldenberg, Daniel Kleppner and I made the first atomic hydrogen maser in 1961 (see the photo above) and, with later collaborators, used it to make accurate spectroscopic measurements on atomic hydrogen. With improvements by Robert F. C. Vessot and others, the atomic hydrogen maser has become an atomic clock with particularly great stability over intervals of a few days. Vessot has used it for the best test to date of the gravitational redshift. And subcompact masers have been developed for satellite applications. Masers in turn have stimulated the development of lasers, which are now nearly ubiquitous in research, medicine and industry.

This list of the primary offshoots from early magnetic resonance experiments is already surprisingly long. A further enumeration of all succeeding offshoots would be a formidable undertaking.

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