Quantum states and precession: The two discoveries of NMR

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Nuclear magnetic resonance in bulk matter was discovered independently by Purcell, Torrey, and Pound at Harvard and by Bloch, Hansen, and Packard at Stanford towards the end of 1945. Their experiments were so different that members of neither group were quick to recognize their own experiment in the other. The magnetic resonance phenomenon was conceptualized differently by the two groups, and the design of their experiments differed accordingly. The Purcell group thought of magnetic resonance in terms of transitions between quantum states while the Bloch group visualized magnetic moments being reoriented with respect to a magnetic field. The conceptual approach adopted by each group can be seen as a natural consequence of earlier influences.

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I. INTRODUCTION

Nuclear magnetic resonance (NMR) was discovered independently by two groups of physicists. During the final weeks of 1945, Purcell, Torrey, and Pound observed a signal they could attribute to the behavior of protons in a bulk sample of paraffin. At about the same time, Bloch, Hansen, and Packard observed a signal they could attribute to the behavior of protons in a bulk sample of water. These signals, coming from the nuclei of hydrogen atoms, were the beginnings of NMR.

The Cambridge and Stanford research groups were not only separated geographically, they were also separated conceptually. Both Purcell and Bloch were fully aware of the magnetic resonance method discovered by Rabi and his students in 1937. However, Rabi's magnetic resonance experiment can be conceptualized in two different ways: on the one hand, particles in the molecular beam can be thought of as absorbing energy from an oscillating field and undergoing a transition from one quantum state to another. Such is the spectroscopic view. On the other hand, the same beam particles can be viewed as precessing about the direction defined by an external magnetic field and having their spatial orientation changed by an oscillating field. Such is the dynamical view. Purcell, Torrey, and Pound thought of magnetic resonance in terms of quantum transitions, while Bloch, Hansen, and Packard visualized magnetic moments as being reoriented with respect to an external magnetic field. The spectroscopic and dynamic schemes for portraying the NMR phenomenon are very different. The former is couched in quantum mechanics and involves the exchange of energy quanta between a system and its environment. The latter is, in its essence, conveyed by the classical ideas of precession, torques, and electromagnetic induction. How did these two approaches to NMR originate? To what extent were Purcell's and Bloch's approaches to NMR foreordained by their individual experiences prior to 1945? How did their individual modes of conceptualization reveal themselves in their experimental designs? How do their experiments differ? The answers to questions such as these bring understanding to these historic experiments and, in the process, they provide insight into the conduct of physical research more generally.

II. THE MAGNETIC RESONANCE METHOD

The magnetic resonance method was discovered in the laboratory of Rabi late in 1937 (Rabi, Zacharias, Millman, and Kusch, 1938). This discovery was made in the context of molecular-beam experiments in which individual, isolated atoms or molecules were the object of investigation (Rigden, 1985). Throughout the 1930s a series of molecular-beam experiments was carried out at Columbia University, experiments that enabled the magnetic moments of atomic nuclei to be determined with ever increasing accuracy. During the latter half of the decade, new experimental methods were created so that the signs of nuclear magnetic moments could be determined as well.

From 1934 to 1940, experiments on the hydrogens—hydrogen and deuterium—occupied a center-stage position in the molecular-beam experiments of the Rabi group (Rigden, 1983). The magnetic moment of the proton was anomalously large and, as a result, the sign of this particular magnetic moment was in itself an open question. Equally important, the sign of the deuteron's magnetic moment was needed so that the magnetic moment of the neutron could be inferred. If it was assumed that the deuteron was a compound nucleus made up of the proton and the neutron, and if, within the confines of the deute-

ron, the magnetic moments of the proton and deuteron were assumed to be additive, then the magnetic moment of the neutron could be deduced from a knowledge of the magnitudes and the signs of the proton's and deuteron's magnetic moments.

In 1936 Rabi showed how the signs could be determined (Rabi, 1936). In this method the beam of particles passed through a static magnetic field whose configuration was such that a traversing particle experienced one-half cycle of a rotating field. The effective frequency of this "rotating" field was proportional to the speed of the traversing beam particle. For some speeds, particles left the static-field region with a different space-quantized orientation than they had upon entering, and, as a consequence, they responded very differently to the deflecting field that followed. From this difference in response, the sign of the magnetic moment could be inferred.[1]

The static-field method was inherently qualitative: since the speed of a particular beam particle was unknown, the frequency of the "rotating" field was unknown as well. This method, however, not only did the job for which it was created, it also provided a conceptual framework whose further refinement resulted in the magnetic resonance method.

In the fall of 1937, the source of the static magnetic field was removed from the molecular-beam apparatus and into its place went (1) the pole pieces of a magnet and (2) a hairpin-shaped wire. The former was designed to produce a uniform magnetic field; the latter would carry an oscillating current and thereby produce an oscillating magnetic field. The uniform field H_0, whose magnitude could be measured precisely, brought a quantitative sharpness to the Larmor precession frequency.[2] The oscillating field $\mathbf{H}_1$ was oriented at right angles to the uniform field ($\mathbf{H}_1 \ll \mathbf{H}_0$) and its frequency was controlled precisely by a radio-frequency oscillator. A beam particle passing between the pole pieces experienced both a strong magnetic field and many cycles of a weak, rotating magnetic field.[3] The resonance condition was achieved by bringing the Larmor precession frequency ν_L into coincidence with the frequency of the oscillating field ν. In other words, the frequency ν was held constant while the magnetic field H_0 was slowly varied (thereby varying ν_L) until the resonance condition $\nu_L = \nu$ was achieved. The first nuclear magnetic resonance curve ever published, the magnetic resonance of ^{7}Li, was sent to *Physical Review* on January 15, 1938.

The magnetic resonance method was a great advance over previous molecular-beam methods for measuring magnetic moments. Consider, for example, the classic Stern-Gerlach method. The principal objective of this method was to measure the extent to which beam particles were deflected by an inhomogeneous field. The size of this deflection was in proportion to (1) the magnitude of the field inhomogeneity, (2) the magnitude of the magnetic moment of the beam particle, and (3) the time interval spent within the deflecting field. The deflections were distributed about an average deflection because of the distribution of beam-particle speeds. From an analysis of the deflection pattern, magnetic moments could be determined; however, the inhomogeneous magnetic field had to be calibrated, and assumptions had to be made about the speed distribution of the beam particles. In spite of many improvements in this basic method, the accuracy of results obtained by it was no better than 5% (Fraser, 1931, 1937). By contrast, no assumptions are required with the resonance method. Furthermore, only two parameters are needed to determine a magnetic moment: the frequency of the oscillating magnetic field and the field strength of the uniform magnetic field. Both parameters can be determined with high precision: the former to within 0.01% and the latter to within 0.5%. With the resonance method, the accuracy of the result was better than 1%.

The magnetic resonance method can be conceptualized in spectroscopic terms or in quasiclassical, dynamical terms. Let us consider a nuclear magnetic moment $\boldsymbol{\mu}_I$ in a homogeneous magnetic field $\mathbf{H}_0$. From the spectroscopic perspective, the Hamiltonian for this system is very simple:

$$H = -\boldsymbol{\mu}_I \cdot \mathbf{H}_0 = -\gamma \hbar \mathbf{I} \cdot \mathbf{H}_0 \, ,$$

where γ is a constant called the gyromagnetic ratio (Slichter, 1963). (For this Hamiltonian it is assumed that the magnetic field at the nucleus originates exclusively with the external field.) The eigenvalues of this Hamiltonian are given by

$$E = -\gamma \hbar H_0 m_I \, .$$

We shall consider only spin-$\frac{1}{2}$ systems (i.e., $I = \frac{1}{2}$) for which m_I has the values $\pm\frac{1}{2}$. Thus there are two allowed energy states:

$$E_- = \tfrac{1}{2}\gamma \hbar H_0, \quad E_+ = -\tfrac{1}{2}\gamma \hbar H_0 \, .$$

Transitions between these two states are allowed,[4] and the transition frequency is given by the Bohr relation,

$$E_- - E_+ = \hbar\omega_0 = \gamma \hbar H_0 \, ,$$

[1]For details, see Rigden, 1983.

[2]A magnetic moment in a magnetic field precesses around the field direction with a particular frequency called the Larmor precession frequency.

[3]The oscillating magnetic field produced by the hairpin-shaped wire is equivalent to two equal-magnitude components rotating in opposite senses. One of these components rotates in the same sense as the precessing magnetic moment.

[4]The perturbation that couples these two energy states is a small oscillating magnetic field $H_1 \cos\omega t$, applied perpendicular to H_0. The Hamiltonian for such a perturbation is $H_{\text{pert}} = -\gamma \hbar H_1 I_x \cos\omega t$. The matrix elements $\langle m' | I_x | m \rangle$ are zero unless $m' = m \pm 1$. Thus transitions are allowed between the states $m_I = \frac{1}{2}$ and $m_I = -\frac{1}{2}$.

where the resonance frequency ω_0 is seen to be given by

$$\omega_0=\gamma H_0 \ . \tag{1}$$

The fact that Planck's constant has disappeared from the resonance frequency expression suggests a close relationship between the quantum-mechanical and classical descriptions.

Classically, the behavior of a magnetic moment in a magnetic field is deduced from the equation of motion. The magnetic field $\mathbf{H}_0$ exerts a torque on the magnetic moment $\boldsymbol{\mu}_I$. This torque is related to the rate of change of the angular momentum, that is,

$$\hbar\frac{d\mathbf{I}}{dt}=\boldsymbol{\mu}_I\times\mathbf{H}_0$$

or, since $\boldsymbol{\mu}_I=\gamma\hbar\mathbf{I}$,

$$\frac{d\boldsymbol{\mu}_I}{dt}=\boldsymbol{\mu}_I\times\gamma\mathbf{H}_0 \ . \tag{2}$$

From this equation of motion it is clear that the change in $\boldsymbol{\mu}_I$ is always perpendicular to the plane defined by $\boldsymbol{\mu}_I$ and $\mathbf{H}_0$. In other words, the *magnitude* of $\boldsymbol{\mu}_I$ is constant, only its direction changes [see Fig. 1(a)]. The change in $\boldsymbol{\mu}_I$ is thus a precession around the field $\mathbf{H}_0$.

The angular velocity associated with this precession is collinear with $\mathbf{H}_0$. From Fig. 1(b) it is clear that both the magnitude and the direction of $d\boldsymbol{\mu}_I$ are given by

$$\frac{d\boldsymbol{\mu}_I}{dt}=\boldsymbol{\mu}_I\times\boldsymbol{\omega} \ .$$

Consistency with the equation of motion [Eq. (2)] requires that $\omega=\gamma H_0$; that is, the magnetic moment $\boldsymbol{\mu}_I$ precesses with a frequency given by $\omega=\gamma H_0$. This frequency is called the Larmor precession frequency ω_L.

The quantum-mechanical transition frequency ω_0 and the Larmor precession frequency ω_L are equal: $\omega_0=\omega_L=\gamma H_0$. Let us now introduce a second magnetic field $\mathbf{H}_1$ that rotates with a frequency ω in a plane perpendicular to $\mathbf{H}_0$, as shown in Fig. 2. We shall assume that $H_1 \ll H_0$.

In quantum-mechanical terms, the effect of H_1 on our spin-$\frac{1}{2}$ system can be treated in terms of perturbation theory. The resultant field $\mathbf{H}=\mathbf{H}_0+\mathbf{H}_1$ gyrates around the direction of $\mathbf{H}_0$ with a frequency ω. Rabi has shown that in such a gyrating field the probability for a transition $m_I=\frac{1}{2}\rightarrow m_I=-\frac{1}{2}$ is at a maximum when $\omega=\omega_0=\gamma H_0$ (Rabi, 1937). In other words, when $\mathbf{H}_1$ rotates with a frequency ω_0, transitions are stimulated between two quantum energy states. These transitions are observable.

In classical terms, the rotating field $\mathbf{H}_1$ exerts a new torque on the precessing magnetic moment. This new torque tends to increase (or decrease) the angle between $\mathbf{H}_0$ and $\boldsymbol{\mu}_I$; however, for this change to be cumulative, the frequency of the rotating field ω must have the same sense as and be equal to the Larmor precession frequency; that is, the condition $\omega=\omega_L=\gamma H_0$ must hold. Hence, if $\omega=\omega_L$, a precessing magnetic moment can be pulled from one space-quantized orientation into another. These reorientations are observable.

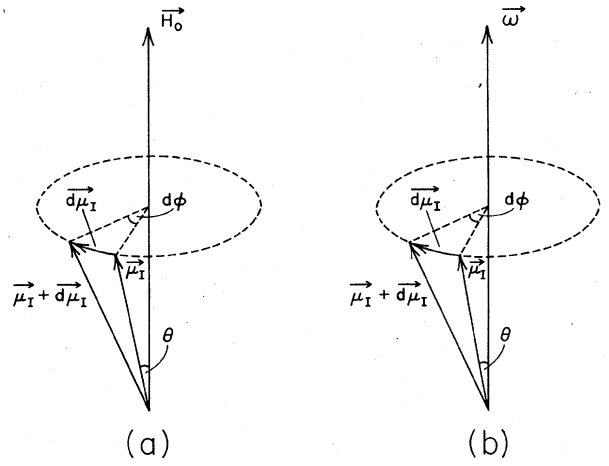

FIG. 1. A magnetic moment $\boldsymbol{\mu}_I$ in a magnetic field $\mathbf{H}_0$. Because of the angular momentum associated with this moment, it does not align itself with the field; rather, it precesses about the field direction. The magnitude of the precessional frequency is ω, where $d\varphi=\omega\,dt$. From (b) it is clear that $d\mu_I=\mu_I\sin\theta\omega\,dt$. The classical equation of motion [Eq. (2)] gives $d\mu_I=\mu_I\gamma H_0\sin\theta\,dt$. Comparison of these two equations gives the precession frequency as $\omega=\gamma H_0$.

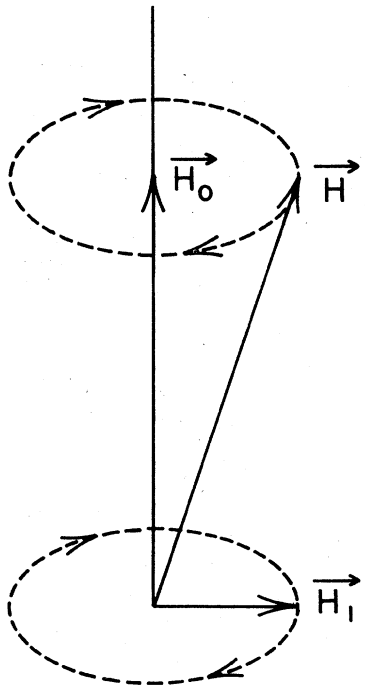

FIG. 2. The net magnetic field, the vector sum of the constant field $\mathbf{H}_0$ and the oscillating field $\mathbf{H}_1$, gyrates around the direction of $\mathbf{H}_0$. The effect of this field on a magnetic moment can be explained in either quantum-mechanical terms or classical terms.

The close correspondence between the quantum-mechanical and classical treatments of a magnetic moment in an external field can be demonstrated in a more formal fashion. The expectation value of an observable such as the x component of the magnetic moment is given in quantum mechanics by

$$\langle \mu_x(t) \rangle = \int \psi^*(t) \mu_x \psi(t) d\tau ,$$

where $\psi(t)$ is the most general time-dependent wave function. The result of such a calculation gives an expectation value $\langle \mu_x(t) \rangle$ that oscillates in time at the classical precession frequency. Moreover, with

$$\langle \boldsymbol{\mu} \rangle = \langle \mu_x \rangle \mathbf{i} + \langle \mu_y \rangle \mathbf{j} + \langle \mu_z \rangle \mathbf{k} ,$$

we find that the quantum-mechanical expectation value $\langle \boldsymbol{\mu} \rangle$ obeys the classical equation of motion; that is,[5]

$$\frac{d\langle \boldsymbol{\mu} \rangle}{dt} = \langle \boldsymbol{\mu} \rangle \times \gamma \mathbf{H} .$$

This agreement between quantum and classical equations is formally expressed by Ehrenfest's theorem (Ehrenfest, 1959; Schiff, 1968).

With the close affinity between the quantum and classical descriptions of the magnetic resonance phenomenon, it should not be surprising that both descriptions have figured prominently in the history of the method. The classical description is vivid in its imagery and has appeal to one's physical intuition. By contrast, the quantum description is formal and more abstract. In the experiments that preceded the discovery of the magnetic resonance method, the image of precessing moments "flopping" from one orientation to another was prominent in the minds of Rabi's group. The classical view remained the prominent conceptual framework of Rabi's laboratory through the early molecular-beam magnetic resonance experiments. It was the molecule H_2, with its spin-spin and spin-orbit interactions, that was instrumental in bringing the spectroscopic description to the foreground. In the 1939 paper on the hydrogens—H_2, HD, and D_2—*both* the dynamical and the spectroscopic descriptions were employed (Kellogg *et al.*, 1939b); however, after 1939, papers were written from the perspective of spectroscopy, which is couched explicitly in the formalism of quantum mechanics (Kusch *et al.*, 1940). Over the period of 1937—1940, a transformation took place in Rabi's laboratory, a transformation from one mode of conceptualization to another.[6]

III. THE CONCEPTUAL BACKGROUND TO THE TWO DISCOVERIES

The *magnetic induction* approach of NMR taken by Bloch was in preparation for at least a decade. Its conceptual basis is so logically consistent with that of his earlier work that it is difficult to imagine Bloch approaching NMR any differently. This is much less the case with Purcell. Somewhat junior to Bloch, Purcell had not had time to produce a body of research before World War II interrupted his work.

Both men were active in the war effort. Purcell was at the MIT Radiation Laboratory, engaged in the development of microwave radar. Bloch was at the Harvard Radio Research Laboratory, where he worked on the development of counter-radar measures. "What I did there . . . was very important for me," acknowledged Bloch, "because I learned about noise and all those things [radio techniques], which are terribly important" (Bloch, 1982). Both men learned and benefited from their wartime activities; however, for the younger Purcell, the MIT Rad Lab experiences were particularly important. The conceptual groundwork for Purcell's *resonance absorption* approach to NMR was largely laid by his experience at the Radiation Laboratory.

A. Bloch and the neutron

The neutron was one focus of physical research during the 1930s; it was also a focus of Bloch's interest from 1936 until the war interrupted his research at Stanford University. Interest in the proton and deuteron, important in their own right, was further enhanced because these particles provided a means to learn the physical properties of the neutron. When the magnetic moments of the proton (Rabi *et al.*, 1934a) and deuteron (Rabi *et al.*, 1934b) were measured, the magnetic moment of the neutron could be deduced as either ± 4.0 or ± 2.5 nuclear magnetons, depending on (1) whether the signs of these measured moments were positive or negative and (2) whether the proton and neutron were aligned parallel or antiparallel within the deuteron. When the *signs* of the proton's and deuteron's moments were determined (Rabi, Kellogg, and Zacharias, 1936; Kellogg, Rabi, and Zacharias, 1936a), the moment of the neutron was inferred to have the anomalous value of -2.0 nuclear magnetons (Kellogg, Rabi, and Zacharias, 1936b). To infer a quantity is one thing, to measure it directly is quite another. In 1936 Bloch was thinking about a method that would provide direct information about the magnetic properties of the neutron.

"The idea that a neutral particle should possess an intrinsic magnetic moment had a particular fascination to me," said Bloch in his Nobel lecture, "since it was in such striking contrast to the only existing theory of an intrinsic moment which had been given by Dirac for the electron. Combining relativistic and quantum effects, he had shown that the magnetic moment of the electron was a direct consequence of its charge, and it was clear that the magnetic moment of the neutron would have to have an entirely different origin. It seemed important to furnish a direct experimental proof for the existence of a magnetic moment of a free neutron . . ." (Bloch, 1964).

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[5]For a fuller treatment, see Slichter, 1963 or Abragam, 1961.

[6]This conceptual transformation is treated in more detail by myself in a forthcoming paper, "From Precession to Quantum States: The Birth of Radiofrequency Spectroscopy."

Throughout the 1930s the principal means for determining the magnetic moments of nuclei was the Stern-Gerlach method coupled with Breit-Rabi theory (Breit and Rabi, 1931). However, the application of the Stern-Gerlach method to a beam of neutrons held the prospect of considerable experimental difficulties. First, very large magnetic fields would be required for deflection purposes; second, the magnetic fields would have to be calibrated accurately. Bloch was aware of these difficulties; consequently, he proposed to measure the neutron's magnetic moment by a scattering experiment (Bloch, 1936). ". . . [W]e want to propose a different way of obtaining information about the magnetic moment of the neutron which seems considerably simpler and promising in several other respects" (Bloch, 1936, p. 259). Bloch pointed out that the scattering of a neutron by an atom was a consequence of two interactions: first, the interaction of the neutron with the atomic nucleus, and, second, the interaction of the neutron's magnetic moment with the field arising from the magnetic moment of the atom. The first is a strong interaction, but it is short ranged. The second interaction is weaker, but it is long ranged; consequently, this magnetic interaction acts over "distances so much larger that the scattering effect [due to both causes] on slow neutrons becomes of the same order of magnitude" (Bloch, 1936, p. 259). On the basis of his analysis, Bloch proposed the measurement of "the magnetic moment of the neutron by measuring the scattering cross section for very slow neutrons" (Bloch, 1936, p. 260).

In Bloch's theoretical treatment, he assumed a classical interaction between two magnetic dipoles. Schwinger (still a teenager) maintained that Bloch's calculation of a scattering cross section from such an assumption would be in error (Schwinger, 1937). He did a theoretical analysis of the scattering process based on "the use of the correct Dirac value of the current density and the corresponding magnetic field" (Schwinger, 1937, p. 545). Bloch responded. He claimed that Schwinger's treatment was not based on his use of the Dirac operator, but upon his implicit assumption that the neutron could be regarded as a little amperian current. Given the uncertainties about the neutron, there was, Bloch suggested, no basis for concluding (at that early date) the exact nature of the interaction between nuclear magnetic moments and atomic electrons (Bloch, 1937).

Bloch was also able to show how a polarized beam of neutrons could be produced. If a beam of neutrons is incident on an iron plate that is magnetized by an external magnetic field, those neutrons with moments parallel to the magnetization are scattered more, with the result that the emerging beam of neutrons is partially polarized. A second magnetized iron plate can be used as an analyzer. After the beam has passed through two plates of iron, its intensity "should be different, whether both are magnetized parallel to the beam or one is magnetized parallel and the other antiparallel" (Bloch, 1936, p. 260).

Bloch's proposed ideas were quickly implemented by physicists who attempted to observe directly the magnetic moment of the neutron. The experimental arrangement

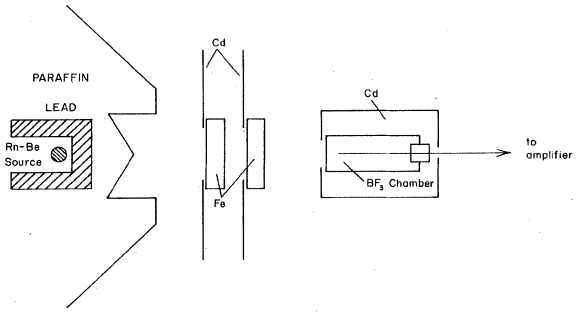

FIG. 3. The experimental arrangement used by Hoffman, Livingston, and Bethe in the first attempt to verify directly the existence of the neutron's magnetic moment (Hoffman, Livingston, and Bethe, 1937).

(Fig. 3) used by Hoffman, Livingston, and Bethe (1937) illustrates the essentials of the method used by this and other groups (Dunning *et al.*, 1937; Powers, Beyer, and Dunning, 1937). A beam of neutrons was sent through two pieces of magnetized iron, and the beam intensity was measured for parallel and antiparallel alignments of the polarizer and analyzer. These early experiments provided direct proof of the neutron's magnetic moment; further, the intensity data were consistent with the earlier value of -2.0 nuclear magnetons inferred indirectly by Rabi.

Early in the experiments on the magnetic scattering of neutrons, it was recognized that stray magnetic fields could complicate the experimental results (Hoffman *et al.*, 1937; Powers, Carroll, and Dunning, 1937). Stray magnetic fields in between the polarizer and analyzer alter the state of polarization of the neutrons in the beam, in that the precession axis of the neutron follows the direction of a fringe field and enters the analyzer with a different orientation than it had as it emerged from the polarizer. Thus the intensity predicted for the neutron beam emerging from the analyzer is at variance with the experimental results.

The reorienting effects of stray magnetic fields could be a nuisance, as they altered experimental results in an unpredictable way. On the other hand, a systematic analysis of these reorienting effects could bring detailed information about atomic and nuclear magnetic moments. Stern had initiated such studies when he investigated the effect of a changing magnetic field on a magnetic moment (Phipps and Stern, 1931; Frisch and Segrè, 1933). A little later, Rabi extended Stern's work and showed how a changing magnetic field could be used to determine the signs of magnetic moments (Rabi, 1936,1937). In their method, Rabi and his associates created a static magnetic field by passing an electric current through a configuration of wires. As beam particles passed through his rapidly changing static field, nonadiabatic transitions were induced, and the signs of magnetic moments were determined.[7]

[7]For more details, see Rigden, 1983 and Rigden, 1985.

The group of nuclear physicists at Columbia University who were engaged in neutron research employed Rabi's method to determine the sign of the neutron's magnetic moment (Powers, Carroll, Beyer, and Dunning, 1937). Two current-carrying wires were placed in between the polarizer and the analyzer. Neutrons emerged from the polarizer with many neutrons having a particular orientation. The static magnetic field produced by the current-carrying wires exerted a torque on these magnetic moments and "flipped" them from one spatial orientation to another. This reorientation changed the neutron intensity coming from the analyzer. From these experiments, it was determined "that [the sign of] the neutron moment must be negative" (Powers, Carrol, Beyer, and Dunning, 1937, p. 38).

The neutron research motivated by Bloch's 1936 paper was infused with the visualizable image of the precessing and reorienting magnetic moment. This image, implicit in the work of some, was made explicit in the papers of Frisch, von Halban, and Koch (1937a,1937b,1938a, 1938b). Their apparatus (Frisch *et al.*, 1938b, p. 720) is shown in Fig. 4. Neutrons emerged from a source housed in paraffin, passed successively through (1) a magnetized iron ring acting as a polarizer, (2) a magnetic field produced by a long solenoid, and (3) a magnetized iron ring serving as the analyzer. From the analyzer, the neutrons entered an ion-chamber detector. This experiment was the first attempt to determine the *magnitude* of the neutron moment by a change of the polarization produced by a magnetic field between the polarizer and analyzer. The results were qualitative. However, they determined the sense of the neutron's precession and thus they verified the sign of the neutron's moment. The principle of Frisch, von Halban, and Koch's precession experiments is illustrated in Figs. 5 and 6 (Frisch *et al.*, 1938b, pp. 721 and 723), in which neutron moments are explicitly shown being reoriented by the homogeneous magnetic field of the solenoid.

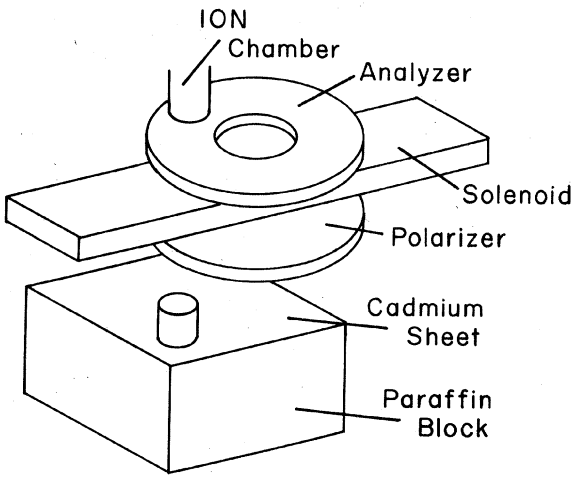

FIG. 4. The experimental apparatus used by Frisch *et al.* in their attempt to measure the magnitude of the neutron's magnetic moment (Frisch *et al.*, 1938b).

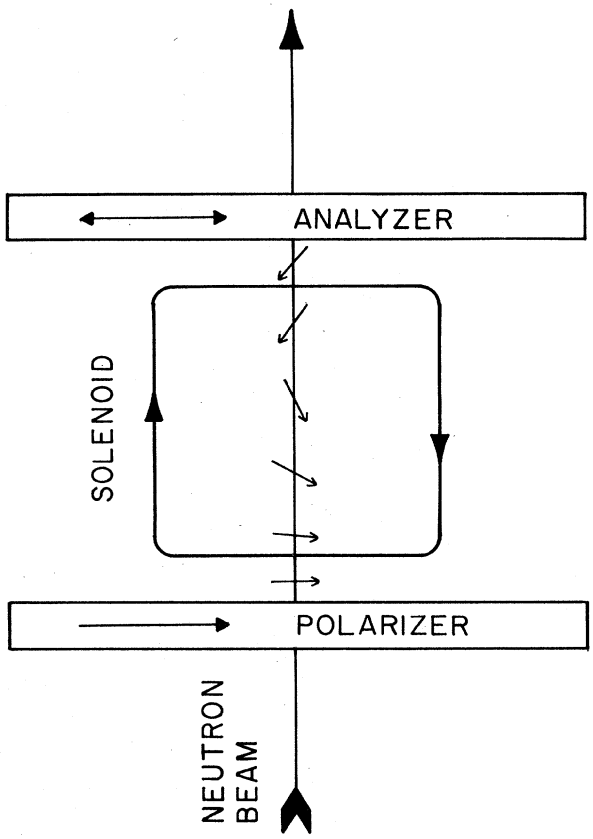

FIG. 5. The experimental method used by Frisch *et al.* to demonstrate the existence of neutron precession and to measure its rate "in a rough way" (Frisch *et al.*, 1938b).

The doctoral dissertation of Columbia University student Philip N. Powers, published in 1938, summarized the experiments and the results of neutron research prompted by Bloch's 1936 paper (Powers, 1938). These experiments verified directly the existence of the neutron's moment as well as its sign. As for the magnitude of the moment, however, they were less successful. ". . . [T]he experiment cannot be expected to yield a highly accurate value for the magnitude of the neutron moment," wrote Powers, "because of the lack of uniformity in magnetic field conditions over the large beam area necessary for intensity, and because of the velocity distribution of the neutrons . . . the results are consistent with the value of -2 nuclear magnetons" (Powers, 1938, p. 838).[8]

The value of -2.0 nuclear magnetons inferred from molecular-beam experiments was not good enough. "The most desirable goal . . . was that of accurately measuring

[8]The effect of the static field produced by the current-carrying wires set up between the polarizer and analyzer was dependent on the speed of the neutrons passing through it. The neutrons had a distribution of speeds; therefore, the speed of any neutron was unknown. This made the method inherently qualitative.

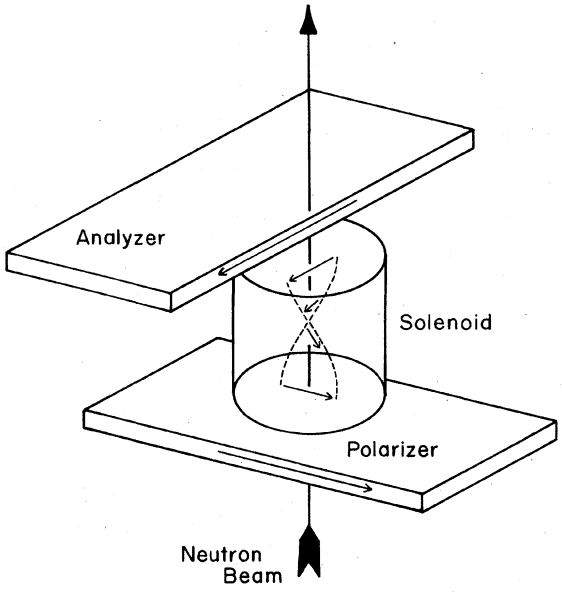

FIG. 6. Schematic diagram of the experiment of Frisch *et al.* using precession as a means to determine the sign of the neutron's magnetic moment (Frisch *et al.*, 1938b).

the magnetic moment of the neutron," said Bloch as he looked back on the neutron scattering experiments during his Nobel lecture (Bloch, 1964, p. 208). How was this accurate measurement to be done? Bloch's answer to this question can be understood when one recognizes the conceptual similarity between the neutron scattering experiments during the years 1937 and 1938 and the molecular-beam experiments during the earlier years 1935—1937. A comparison will be instructive. The 1936 version of the molecular-beam experiment and the 1938 version of the neutron scattering experiment are compared in Fig. 7. As can be seen, the neutron experiments substitute a polarizer and analyzer for the Stern-Gerlach A- and B-deflecting fields. Both experiments employ current-carrying wires to create a flopping field. The B field in the molecular-beam experiment plays a very similar role to that of the analyzer in the neutron scattering experiment; namely, both allow a select subset of beam particles to enter the detector.

The next step in the evolution of Rabi's beam experiments was to transform the qualitative flopping-field method into the quantitative magnetic resonance method. This was done in 1937. The current-carrying wires were

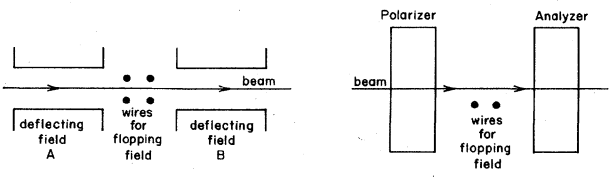

FIG. 7. The 1937 molecular-beam flopping experiment (left) and the 1938 version of neutron scattering experiments (right).

removed from the apparatus and in their place went the means to produce a homogeneous magnetic field (the C field) and an oscillating magnetic field. The same transformation became the next step in the evolution of the neutron scattering experiments.

The step was taken by Bloch. "I felt that one should make an exact measurement of the neutron moment. And that idea occurred to me . . . in '37 . . . a much more complicated arrangement that had to do with polarizing and analyzing a neutron beam with a constant magnetic field and a radio frequency field in between" (Bloch, 1968). The idea came in 1937; why did it take so long to do the experiment? ". . . [O]ur [neutron] source was not sufficient. We tried first with our artificial source, then we tried with a radium source, which was also still too weak. That brings me to the cyclotron . . . in the fall of '38 . . . I spoke to [E.O.] Lawrence . . . . [He] also felt this would be an important experiment . . . . Alvarez said he would like to do it with me . . ." (Bloch, 1968).

They started in the fall in 1938. Once again we can ask, why did it take so long to do the experiment? "Once in a while," said Bloch, "it [the 37-inch cyclotron at Berkeley] worked. There were frequent interruptions. In fact once we had our apparatus built, I remember for weeks and weeks what we did mostly was sit around waiting until the cyclotron beam was on . . ." (Bloch, 1968). The cyclotron was their indirect source of neutrons. Deuterons were accelerated by the cyclotron and were directed to a beryllium target that initiated the reaction-producing neutrons: $^{9}\mathrm{Be} + {}^{2}\mathrm{D} \rightarrow {}^{10}\mathrm{B} + n^{1}$. When the cyclotron ran, they had a sufficient flux of neutrons to do their experiment. Their result was first announced at a meeting of The American Physical Society held in Columbus, Ohio during December 28—30, 1939 (Alvarez and Bloch, 1940a). Their basic paper appeared two weeks later (Alvarez and Bloch, 1940b).

The Bloch-Alvarez experiment was conceptually very similar to that of Frisch *et al.* (see Fig. 5). The difference was that Bloch and Alvarez used the resonance method. This method "consists in the variation of a magnetic field H_0 to the point where the Larmor precession of the neutrons is in resonance with the frequency of an oscillating magnetic field. The ratio of the resonance value of H_0 to the known frequency of the oscillating field gives immediately the value of the magnetic moment" (Alvarez, and Bloch, 1940b, p. 113).

The beam of neutrons emerged from the polarizer with an abundance of neutrons oriented antiparallel to the magnetizing field of the polarizer. These neutrons then entered an oscillating field. The oscillating field, at the resonance frequency $\nu = \nu_L$, flipped the moments from one orientation to another and reduced the degree of polarization of the beam. Off resonance, that is $\nu \neq \nu_L$, the degree of polarization remained intact. Since the intensity of the neutron beam emerging from the analyzer depends on the polarization, the intensity is a function of the oscillating field frequency. This enabled Bloch and Alvarez to determine the magnetic moment of the neutron, which they reported to be -1.935 ± 0.02 nuclear magnetons (Al-

varez and Bloch, 1940b, p. 121).

The result of the Bloch-Alvarez experiment was consistent with the magnetic moment of the deuteron (Kellogg, Rabi, and Zacharias, 1936b) if one assumed that it was the additive result of the proton and neutron moments, that is, $\mu_d = \mu_p + \mu_n$. However, Rabi had discovered that the deuteron has a quadrupole moment (Kellogg, Rabi, Ramsey, and Zacharias, 1939a,1940), and Rarita and Schwinger (1941) had shown that, as a consequence of this quadrupole moment, there should be small departures from additivity within the deuteron. If these slight deviations from the additivity of the proton and neutron were to be tested experimentally, the accuracy of the neutron result would have to be improved still further.

The 1% uncertainty in the Bloch-Alvarez result was primarily a consequence of the inherent uncertainties associated with measuring the strength of the magnetic field. Bloch wanted to reduce the uncertainty of the neutron moment result to one part in a thousand. To do this he would have to find a way to measure the magnetic field strength more accurately. The war years provided the opportunity for Bloch to think about this problem.

B. Purcell and the two-level system

As mentioned earlier, Purcell did not complete a large body of research prior to the war. Specifically, he authored three papers and one abstract. One of these papers was based on his doctoral dissertation; another was based on a term paper he wrote with M. H. Hebb for a course taught by Van Vleck. These papers did not share a common theme; however, the Hebb-Purcell paper is important for our considerations.

The Hebb-Purcell paper (Hebb and Purcell, 1937) was the first major paper on adiabatic demagnetization cooling. It is a phenomenological paper in which they applied theory developed by Van Vleck (1937) to various paramagnetic salts and compared these theoretical results with the experimental data of other scientists. In the process of cooling by adiabatic demagnetization, low spin temperatures are established by successively applying, then removing, a magnetic field. The bulk sample is then cooled as quanta are exchanged between the crystalline lattice and the spin system. (This same process would be important in Purcell's magnetic resonance experiment.) One of the salts considered by Hebb and Purcell (caesium titanium alum) was a simple spin-$\frac{1}{2}$ paramagnet—a two-level system. This encounter with the two-level system was in the dispassionate context of academic research. A few years later, the two-level system became a focus of Purcell's attention, and the context was neither academic nor dispassionate.

In November 1940, a small group of nuclear physicists came together under a shroud of secrecy on the campus of the Massachusetts Institute of Technology. Their purpose was to organize a laboratory to develop microwave radar systems that would exploit the cavity magnetron, a revolutionary source of 10-cm electromagnetic waves that had just been invented by the British physicists J. T. Randall and H. A. H. Boot in the Birmingham laboratory of N. L. Oliphant. The new laboratory was called the Radiation Laboratory so that it would be suggestive of Ernest Lawrence's Radiation Laboratory at Berkeley—a center for nuclear physics research. In 1940, a nuclear physics laboratory at MIT would be construed as an innocent academic endeavor.

When Purcell arrived at the Rad Lab, the small staff of physicists required little organization. As the magnitude of the effort grew (by the end of the war over 4000 people were employed), however, a formal divisional structure was adopted. Rabi was the head of the Research Division, Division 4, and Purcell eventually became the head of Group 41, the Fundamental Development Group, within Rabi's division.

From the beginning, the atmosphere at the Rad Lab was intense. Radar systems based on 10-cm microwaves involved technical problems never before encountered. Waveguide methods had to be developed in order to transmit and to detect microwave power. On the one hand, a new technology had to be developed; on the other hand, the Rad Lab physicists were keenly aware of the deteriorating situation in Europe. Ambitious goals were adopted. As the physicists groped with the problems associated with 10-cm waves, they also began to push the technology down to the 3-cm region.

The technical challenges of microwave radar, carried out as they were against the backdrop of the Nazi threat, made the Rad Lab a consuming experience for the participants. Purcell, for example, lived off Massachusetts Avenue near Harvard Square, and each day on his way to the Rad Lab he walked a route that took him within a few yards of the Harvard physics building; yet he was so absorbed in his radar work that, throughout the five years of the war, it rarely occurred to him to stop off at his Harvard office. His mind was on microwave radiation, its production, its transmission, and its detection.

A radar system produces electromagnetic radiation that propagates through the Earth's atmosphere until it encounters a reflecting surface. A small part of the reflected energy propagates back towards the source and is detected. Ideally, the Earth's atmosphere should be transparent to the electromagnetic radiation produced: appreciable absorption would so attenuate the outgoing and reflected waves that, over long path lengths, there would be little or nothing left to detect. The absorption of electromagnetic energy by matter is a quantum phenomenon; in fact, nowhere are quantum effects more vividly displayed than when radiation interacts with matter. In the push to shorter wavelengths, this display was dramatically exhibited.

After the 10-cm radar system was in production, after an experimental 3-cm system was operating, the push to even shorter wavelengths continued. "Going down to 1-cm was the next step," recalled Lee DuBridge, the Director of the Rad Lab, "but this we knew would be harder and take longer . . . . A curious piece of bad luck intervened here. It turned out to be convenient to choose

1.25-cm as the working wavelength" (DuBridge, 1977).

The range of detection with the 1.25-cm system was disappointing, but in a somewhat fickle fashion. The range varied—sometimes better, sometimes worse. It was Van Vleck who pointed out that the choice of 1.25 cm had, unfortunately, put them right in the middle of a water vapor absorption band. Hence the useful range of the new system depended on the water content of the air.[9] The absorptivity of air due to water vapor came to be known as the "water problem."

Military personnel had become accustomed to the uninhibited propagation of radar through the atmosphere, and they were alarmed by the water problem. Perhaps their alarm influenced others. In any event, everyone took the water problem very seriously; "more seriously," said Purcell, "than in retrospect it deserved to be."[10]

The water problem came to be regarded in terms of a two-level quantum-mechanical system.[11] The two troublesome states for the Rad Lab physicists were the $5_{2,3}$ and $6_{1,6}$ rotational states of the water molecule (Van Vleck, 1947). Selection rules allowed a transition between these two states, and the frequency of this transition was such that a broad absorption occurred that was centered on a wavelength of approximately 1.3 cm.

Microwave spectroscopy, a very productive area of postwar research, had its root in the water vapor problem. For the Rad Lab physicists, however, the absorption of 1.25-cm microwaves introduced the question of atmospheric absorption in a more general sense. Both water and atmospheric oxygen attracted attention. As Purcell wrote, ". . . because of the urgent need for quantitative information on the water-vapor and oxygen effects, direct measurements of microwave absorption have been undertaken by a number of methods . . ." (Purcell, 1951, p. 665). Purcell's concern with the absorption of microwave energy by matter during the latter stages of the war had a direct influence on his resonance absorption approach to NMR.

When Allied victories in Europe and the Pacific made it apparent that the war would soon end, both Purcell and Bloch began to think about the physics they might do when they were back at Harvard and Stanford. "Came the end of the war and we were all thinking about what we shall do when we go back and start doing physics," said Purcell. "In the course of knocking around with these people [Rabi's people at the Rad Lab], I had learned enough about what they had done in molecular beams to begin thinking about what can we do in the way of resonance . . . . Another very important association there was with Bob Dicke . . . . He invented the Dicke radiometer . . . applied it to measure molecular absorption . . . of water vapor in the atmosphere" (Purcell, 1977).

Across Cambridge at Harvard, Bloch was thinking similarly. "In early '45, the end of the war was very much in sight. At that time I began to think about what one could do after the war. And Bill Hansen came quite often to Cambridge. He was a great expert . . . on microwaves. I also talked with Rabi quite a lot at that time. I told him I would like to go back to the neutron work. That was my obsession. I said to Rabi, 'Now, look, there's this trouble with the magnetic field—we don't know that accurately.' We had all sorts of ideas that perhaps we could ship a permanent magnet to Columbia for calibration with molecular beams and then he would ship it back to us. Then I realized that one doesn't really need molecular beams to study the nuclear magnetic resonances . . . that one should be able to do it in condensed matter, not a vacuum, in liquids in fact. So I had this idea then of what I called nuclear magnetic induction . . . . I did my work mostly in the evening, my calculations, convincing myself that this should at least be possible; that the size of the signals was big enough" (Bloch, 1968, 1982).

Purcell and Bloch came to their discoveries of NMR from different background experiences; however, they had one thing in common—they shared an association with I. I. Rabi. Throughout the war, Purcell worked at the Rad Lab with Rabi, and Bloch lived on Bates Street, two blocks from Rabi's Cambridge home on Avon Hill Street. Interestingly enough, Purcell and Bloch met only once during the war, and the occasion was festive: they met at the party celebrating Rabi's winning the Nobel Prize.

IV. MAGNETIC RESONANCE IN BULK MATTER

As stated earlier, the magnetic resonance method was discovered in the context of molecular-beam research. In a highly evacuated environment, individual beam particles, isolated one from another, pass through a homogeneous magnetic field $\mathbf{H}_0$. A much weaker magnetic field $\mathbf{H}_1$ oscillates in a plane at right angles to $\mathbf{H}_0$. For a spin-$\frac{1}{2}$ particle under the influence of this oscillating field, one can say either

(1) that the magnetic moments periodically spiral upward or downward between two space-quantized orientations and, in the process, the orientation of the magnetic moments with respect to the field H_0 is changed, or

(2) that a transition occurs between two quantized energy states with either an absorption or emission of energy.

The two descriptions are conceptually quite different, but are equivalent.

With the molecular-beam magnetic resonance method, every reorientation, or transition, is effectively measured. It does not matter whether the reorientation is a flip *up* or a flip *down,* whether the quantum transition is due to absorption or to stimulated emission. Furthermore, because

[9]In Vol. 13 of the Radiation Laboratory Series, Van Vleck wrote, "Naturally, the amount of absorption depends on the humidity—at saturation at 20°C . . . to about 0.4 db/km—enough to have some bearing on radar performance over long path lengths" (Van Vleck, 1951, p. 647).

[10]E. M. Purcell, private communication.

[11]In actual fact, the two energy levels involved were two of many rotational energy states of the water molecule.

each beam particle is isolated, there are no interactions between the resonating particle and its neighbors.

The situation changes when nuclear magnetic moments are imbedded in bulk matter such as a block of paraffin or a sample of water. The magnetic moments in such a microscopic sample are oriented randomly. When the sample is placed in a magnetic field, these moments immediately begin to precess with the Larmor frequency, regardless of their spatial orientation; however, an ordered system of orientations, parallel and antiparallel, begins to appear. Concurrent with the ordering, energy is transferred from the system of moments to the bulk medium. The time required for the magnetic moments to take on the ordered configuration consistent with the sample's temperature is called the relaxation time.

When thermal equilibrium is established, the magnetic moments of protons may be divided between two orientations—parallel and antiparallel. The energies associated with these two orientations are slightly different; consequently the distribution of moments between these orientations is determined by the temperature of the sample through the Boltzmann factor. At thermal equilibrium, there is a small excess of moments having the parallel configuration. Under typical experimental conditions, there are 999 993 moments with the antiparallel orientation for every 1 000 000 moments with the parallel orientation (Purcell, 1954a). Since the probability of a flop up or flop down is the same, an *equal* distribution of moments between the two orientations would give rise to no *net* change. It is the small excess with the parallel configuration that leads, at resonance, to a measurable effect. The information potential of that small excess, however, is great, offering not only the information about nuclear magnetic moments *per se,* but also information about the environment of the moments—all this with equipment that is quite simple compared to a molecular-beam apparatus.

The earliest attempts to observe nuclear magnetic effects in bulk matter were unsuccessful simply because there were *no* excess moments in the parallel configuration. These attempts were made by Gorter in 1936 (Gorter, 1936a,1936b) and in 1942 (Gorter and Broer, 1942). In the earlier effort, Gorter tried to detect nuclear magnetic resonance by absorption through the heating effects in the crystalline medium. In the 1942 experiment, detection was by dispersion rather than by absorption: Gorter and Broer looked for a frequency change that resulted from inductive effects.

The negative results in both experiments were discussed by Gorter in terms of the long time required to establish equality between the nuclear spin temperature and the temperature of the crystal lattice. The idea of a long relaxation time was supported not only by Gorter's experimental results, but also by a theoretical estimate made by Heitler and Teller (1936). Years later Van Vleck looked back on Gorter's experiments: "His apparatus was primitive but the real difficulty arose from the fact that he used too much power and too pure materials, things that are advantages in most physical experiments. He tried to detect the resonance in LiF, where the nuclear resonance times are inordinately long, sometimes minutes or so, although this was not known at the time. In consequence, the line saturates exceedingly easily. In other words, the populations of the upper and lower states become substantially equal" (Van Vleck, 1970, p. 4).

Later, Gorter himself recalled his near miss: "I tried to observe a sudden rise in the temperature of the sample upon very slowly varying the transverse magnetic field .... I searched in the radio-frequency region where nuclear magnetic resonance of lithium-seven and hydrogen could be expected. In the short paper in which I announced the negative result, I stated that in the case of resonance the occupation of the higher levels had been obviously increased, the corresponding increase of spin temperature by a factor of at least one hundred having cancelled the expected effect" (Gorter, 1967). Casimir has referred to Gorter as the man "who almost discovered nuclear spin resonance, who almost was the first to orient nuclear spins .... Certainly, he has been close to results that would probably have earned him a Nobel Prize ..." (Casimir, 1983).

V. RESONANCE ABSORPTION AND NUCLEAR INDUCTION: THE TWO DISCOVERIES

Purcell was finishing his work at the Rad Lab when he, Pound, and Torrey began meeting in the evenings at Harvard to design their resonance experiment and to assemble the necessary equipment. In the meantime, Bloch had returned to Stanford for the 1945 fall semester, and he, together with Hansen and Packard, began the preliminaries that would end in the induction experiment. Neither group enjoyed the affluence of the research money that would come to physicists a few years later.

For their experiment, the Cambridge group brought together idle and cast-off equipment. They borrowed a large electromagnet that had been constructed and used earlier by Harvard physicist J. C. Street. The yoke of this magnet had been fashioned out of an old generator discarded earlier by the Boston Street Railways. In the 12-inch gap between the poles of this magnet, Street and Assistant Professor E. C. Stevenson had placed a cloud chamber and had photographed the track of a new particle (Street and Stevenson, 1937). The curvature of this track indicated a mass some 130 times larger than the mass of the electron. This photograph was, for many physicists, the most impressive evidence for the muon (Galison, 1982–1983). The Harvard magnet had a distinguished history.

Bloch's magnet also had an important history: it was a lecture-demonstration magnet used to educate Stanford students. Except for an oscilloscope, everything for the Stanford induction experiment was homemade; consequently, the entire cost of the experiment—all $450—was financed out of the departmental budget. "It's amazing how much one could do with little money if one needed to," said Bloch (Bloch, 1968).

At both Harvard and Stanford it was a team effort.

Purcell made new pole pieces for the Street magnet in order to reduce the gap width from 12 inches to approximately 4 inches, so that the cavity they were designing would fit snugly between the poles. Pound, soon to be Junior Fellow at Harvard University, had become a world expert on questions of signal-to-noise ratios associated with electronic circuitry. He designed the electronic circuit to detect the anticipated signal. Torrey, a student of Rabi's, did some theoretical calculations to estimate the relaxation time for the nuclear case.

Bloch returned to Stanford from the Harvard Radio Research Laboratory with the basic ideas for the experiment well thought out. Bloch took charge of the magnet system. He modified the 3-inch poles of the magnet with extensions made from $\frac{1}{2}$-inch-wide transformer laminations that were clamped together and placed next to the solid pole pieces. Since the magnetic field was modulated at 60 Hz, this design reduced the eddy currents in the pole pieces. Hansen, codeveloper of the klystron and a powerful intellect in the microwave field, built the audio preamp box, the rf matching circuits, and the cross-coil assembly. Packard, who had worked during the war on transmit-receive boxes and on microwave cavities for frequency control at Westinghouse Research in Pittsburgh, designed and constructed the radio-frequency oscillator, the sweep circuits, the amplifiers, and the display system. Packard also assembled the entire system.[12]

As the two groups prepared their individual experiments, each was fully aware of the uncertainty associated with observing nuclear magnetic resonances in bulk matter. The uncertainty resided in the unknown relaxation time—the time for a system of nuclear spins to come to equilibrium in a magnetic field. This uncertainty was well founded. Atomic and molecular relaxation times are very short, as thermal equilibrium is estimated within a few collisions. The nucleus, however, is isolated from the effects that so quickly smooth out energy inequities among atoms. Furthermore, the situation changes within bulk matter: the obvious mechanisms for exchanging energy between a spin system and the lattice all implied very long relaxation times. Waller, for example, had investigated the theory of electronic paramagnetic relaxation by examining the interaction between electronic spins and lattice vibrations (Waller, 1932). At room temperature, the predicted values of the spin-lattice relaxation times for electronic spins were at least 10^4 s. Against this background of uncertainty, the experiment of Purcell, Torrey, and Pound and that of Bloch, Hansen, and Packard took form.

For the Cambridge group, the essence of magnetic resonance was a transition between two quantum energy states. One way or another, the energy absorbed when hydrogen nuclei were excited to the higher Zeeman level had to be detected. Torrey, in his calculations, applied Waller's theory of electronic paramagnetic relaxation to a system of nuclear spins and established an upper limit for the relaxation time. This limit was on the order of ten hours. The Cambridge group designed their experiment accordingly. (Perhaps it was fortunate that they did not learn of Gorter's failures until their own experiment was well underway.)

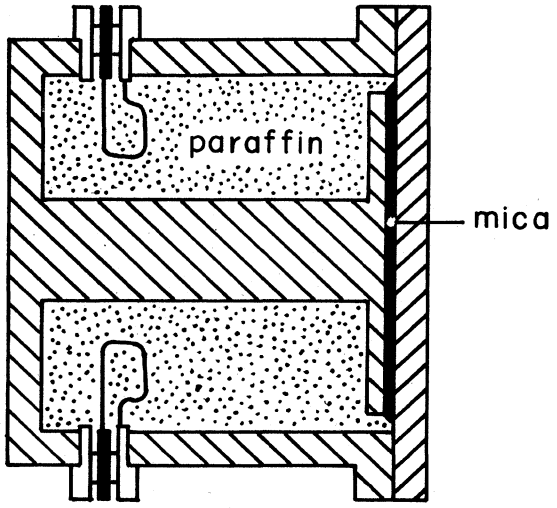

FIG. 8. The resonant cavity used in Purcell's 1945 experiment to detect the resonant absorption of hydrogen nuclei in a sample of paraffin.

The heart of their system was an electromagnetic cavity oscillator (see Fig. 8). They designed this resonant cavity to oscillate at 30 MHz in a mode where a magnetic field circulated about the center post of the cavity. The frequency of 30 mHz was selected because there were intermediate-frequency amplifiers, designed for a narrow bandwidth centered on 30 MHz, readily available at the Rad Lab. More significantly, however, the state-of-the-art noise figure of the Rad Lab amplitudes allowed weak signals to be detected. In anticipation of the long relaxation time, they made the magnitude of the 30-MHz magnetic field very weak, so that absorption would persist for hours regardless of the relaxation time. They filled the volume (850 cm^3) of the cavity with paraffin—approximately 2 pounds of sample.

The cavity was part of a bridge circuit (Fig. 9) that was inductively coupled to a receiver. The cavity itself was

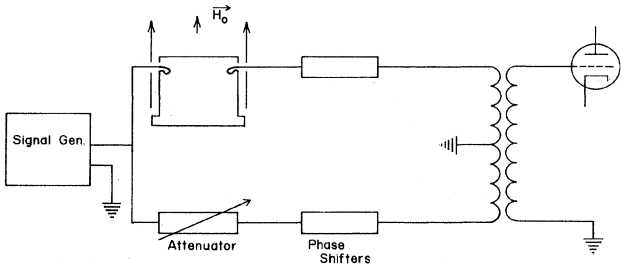

FIG. 9. A schematic diagram of the experimental arrangement used in the 1945 discovery of NMR at Harvard University (Purcell, Torrey, and Pound, 1946). The resonant cavity was placed between the poles of a magnet.

[12]Martin E. Packard, private communication.

placed between the poles of a magnet, which supplied a magnetic field H_0. They drove the bridge circuit with an rf-signal generator at a fixed frequency. The magnetic field H_0 was slowly changed, thereby changing the energy separation between the two Zeeman energy levels. At resonance, the energy-level separation ΔE and the fixed frequency of the weak oscillating magnetic field ν satisfied the Bohr relation $\Delta E = h\nu$, and the protons absorbed energy, changed the Q of the cavity, and unbalanced the bridge circuit. The bridge unbalance was to be detected.

The first attempt failed. Excessively long relaxation times were considered one possible reason for the failure. However, in the face of the failure, they made two responses. First, they improved the magnetic field homogeneity by using the appropriate shims for the magnet pole pieces. Second, they "cooked" the paraffin sample in the magnetic field for 10 hours (3.6×10^4 s) in the hopes that the equilibrium distribution of nuclear spins between the two energy states would be reached. Their experiment was designed so that once the relaxation time was reached, it did not matter how long that time was. Actually, the relaxation time was eventually found to be on the order of 10^{-3} s; thus, the 10-hour "cooking" time was more than 10^7 times longer than necessary. It was the improved field homogeneity that brought success to the resonance absorption experiment. In a letter dated December 24, 1945 they sent their results to the editors of *Physical Review* (Purcell *et al.*, 1946).

For the Stanford group, the essence of magnetic resonance was a flip in the orientation of a nuclear magnetic moment. One way or another, the spatial reorientation of a magnetic moment with respect to the direction fixed by a magnetic field had to be detected. The heart of their system was a set of coils surrounding a spherically shaped container of water (see Fig. 10). The axes of these coils were oriented at right angles to each other. This coil system was placed between the poles of a magnet that produced a fixed magnetic field $\mathbf{H}_0$ in the z direction. The magnetic moments of the protons precessed around this fixed-field direction with the Larmor frequency. One coil, the transmitter coil, carried an alternating current that produced an oscillating magnetic field $\mathbf{H}_1$ in the x direction. The second coil, the receiver coil, was oriented with its symmetry axis along the y axis. A modulated signal was detected and displayed on an oscilloscope (Fig. 11).

Bloch, Hansen, and Packard also anticipated a very long relaxation time. Van Vleck recalls that Bloch asked him "whether there was any relaxation process fast enough to make the experiment work." Van Vleck further recalls "that I didn't have any ideas that helped him . . ." (Van Vleck, 1970, p. 4). Bloch constructed a little set of ancillary pole pieces, which were placed in the fringe field of the main magnet and, in the early experiments, were used for prepolarizing. It is rumored that in one early experiment Bloch went on a skiing trip while the water sample was "equilibrating" in a magnetic field. This rumor has been neither denied nor confirmed (see footnote 12). Here again, however, the relaxation time was much shorter than expected: 2 s for water.

The early Stanford experiments also failed to detect a signal. The transmitter and receiver coils vibrated mechanically and thereby varied the coupling between them. Several experiments were tried with no success. Finally, Hansen devised a "paddle," a semicircular copper plate that was located at one end of the transmitter coil and could be rotated in a plane perpendicular to its axis. With this device, the direction of the magnetic flux from the transmitter coil could be varied and, in the process, both the magnitude and sign of the voltage induced in the receiver coil could be finely adjusted.

The first observation of a signal was made by Packard. It was a fleeting observation. Packard, drawing on his wartime experience looking at radar signals on an A scope, saw it. Since they were not sure about the magnetic field calibration, Bloch had suggested that they go to a higher field, turn the magnet off, and since the magnetic

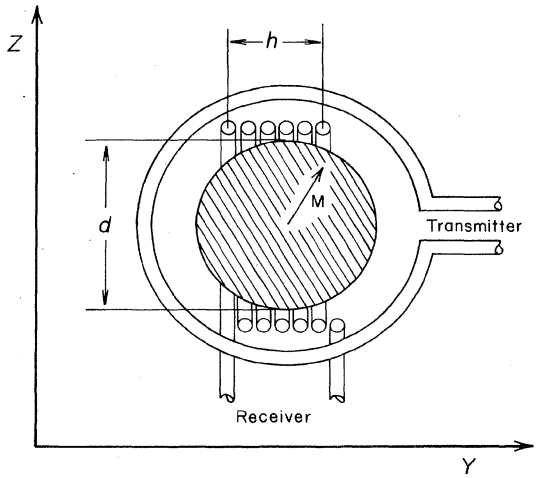

FIG. 10. The orthogonal coil system used by Bloch in 1945 to detect the reorientation of hydrogen nuclei in a sample of water. The coil system was placed between the poles of a magnet (Bloch, Hansen, and Packard, 1946a).

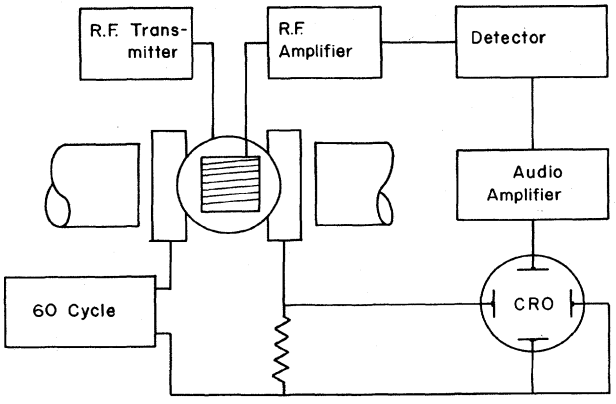

FIG. 11. A schematic diagram of the apparatus used in the 1945 discovery of NMR at Stanford University (Bloch, Hansen, and Packard, 1946a).

field decreased exponentially with an appreciable time constant, they could scan back through the field region where the signal was expected. It was on such a scan that Packard saw a small signal pass across the face of their oscilloscope, entering from the high-field side and disappearing about $\frac{1}{2}$ second later on the low-field side. From this first sighting, it was some time before they were able to reproduce a signal consistently. "I remember a seminar," recalls Packard, "at which Bloch described the experiment and I was bold enough to transport the equipment to the lecture room with the expectations that I could demonstrate the signal, which I couldn't, much to my embarrassment." (See footnote 12.)

Bloch described the experiment as follows: ". . . the radio-frequency field [H_1] is deliberately chosen large enough so as to cause at resonance a considerable change of orientation of the nuclear moments" (Bloch, 1946, p. 460). Off resonance, the resultant nuclear magnetic moment per unit volume of sample is oriented along the z axis. As the frequency of the oscillating field approaches the Larmor precession frequency of the protons in water, the reorientation of individual nuclear magnetic moments causes the resultant magnetic moment to move away from the z axis. The precession of this resultant magnetic moment around the z axis thereby has a component rotating in the xy plane. The magnetic flux associated with this precessing resultant magnetic moment "links the 'receiver coil' . . . and the resultant [induced] voltage which appears at the terminals is led off . . . to be measured" (Bloch, Hansen, and Packard, 1946a, p. 475). On January 29, 1946, the Stanford group sent a letter to *Physical Review* reporting their success in observing magnetic resonance by the induction method (Bloch, Hansen, and Packard, 1946b).

The two discoveries of magnetic resonance in bulk matter were the highlight of The American Physical Society meeting held in Cambridge, Massachusetts during April 22—24, 1946. Both groups presented papers. The abstract of the paper presented by the Harvard physicists begins as follows:

> "If a 'diamagnetic' solid containing nuclei of spin I and magnetic moment μ, is placed in a steady magnetic field H, there will be $2I+1$ Zeeman levels separated in energy by $\Delta W=\mu H/I$. Application of a radio-frequency magnetic field perpendicular to H induces transitions between adjacent levels when the frequency is near the resonant value, $\nu=\Delta W/h$" (Torrey, Purcell, and Pound, 1946).

The Stanford group, on the other hand, begins their abstract with these words:

> "The nuclear magnetic moments of a substance in a strong magnetic field H_z would be expected to give rise to a small magnetic polarization, provided thermal equilibrium be established, or at least approached. A superimposed oscillating field H_x in the x direction will produce a change in orientation of the polarization with a component perpendicular to the strong field" (Bloch, Hansen, and Packard, 1946c).

As these abstracts reveal, the same phenomenon was regarded very differently by the two research groups. In both experiments, the sample is subjected to a weak magnetic field oscillating at right angles to a strong constant magnetic field. However, for Purcell the oscillating field "induces transitions" while for Bloch it produces "a change in orientation." This difference in conceptualization led Purcell to do electrically with one coil what Bloch accomplished geometrically with two coils.

VI. DISCUSSION

The cover study of the November 5, 1984 *Chemical and Engineering News* was "Modern NMR Spectroscopy." In the article that followed, NMR was portrayed as "a powerful and indispensable tool for obtaining new chemical information" (Jelinski, 1984). Two weeks later, on November 19, 1984, the Washington University Medical Center in St. Louis took a full page in the *St. Louis Post-Dispatch* to promote magnetic resonance imaging (MRI). "As no other instrument, MRI can reveal the very chemical composition of the body, detecting multiple sclerosis, strokes and even metabolic loss of brain function."[13]

When the two discoveries of NMR were made in December 1945 and January 1946, neither Purcell nor Bloch foresaw the chemical and medical applications that would follow. Their most immediate concern was to examine the unexpectedly short relaxation times associated with nuclear-spin systems. "The time of establishment of 'relaxation time' can be expected to vary anywhere between fractions of a second and many hours, depending in the most delicate manner upon the nuclear moments, the electronic structure of the atoms in the sample, their distance, and their motion. To study experimentally and theoretically this interesting relationship between nuclear relaxation time and atomic features seems to us, in fact, to be one of the fruitful fields of investigation which have now opened," wrote Bloch (1946, p. 461). In the same vein, the second full-length paper from Purcell's laboratory after the discovery of resonance absorption was on the subject of relaxation effects (Bloembergen *et al.*, 1948).

Both Purcell and Bloch understood clearly the importance of their discoveries for physics: accurate measurements of nuclear magnetic moments, relaxation times in liquids and crystalline media, the potential for frequency measurements[14] to 1 part in 10^8. There was less clarity, however, when they first considered each other's experiments. The initial contact between the two research groups occurred in February 1946. "When Bill Hansen came east," recalls Purcell, "we talked with each other for over $\frac{1}{2}$ hour before either of us understood exactly what

[13] *St. Louis Post-Dispatch*, November 19, 1984, p. 6F.

[14] The uncertainty principle links time and energy (or frequency). Because of the long relaxation times—2 seconds in water—the frequency uncertainty can become very small.

the other was doing" (Purcell, 1980). One month later, Bloch came east for the APS meeting in Cambridge and there he met Purcell for the second time. "We were speaking an entirely different language," and Bloch, "but realized very quickly that it was basically the same thing" (Bloch, 1968).

The meeting during which Bloch and Purcell came to understand each other's experiments was surprising to members of the Stanford group. "It was quite clear to us that it was the same phenomenon," wrote Packard, "but we were simply approaching it from a different experimental viewpoint. The Stanford group had used very strong radio-frequency fields in anticipation of wide linewidths and had used modulation procedures. The signal which was observed was dispersion, simply because that was the phase of the residual leakage. The Harvard experiment was done at low [radio-frequency fields] and the absorption component observed. It is true that prior to Bloch's meeting with Purcell, he could not accept the fact that the results were equivalent." (See footnote 12.)

Kuhn has referred to the wrenching experience of entering into an older mode of thought (Kuhn, 1984). Kuhn is correct. The mode of thought, however, need not necessarily be older for it to present difficulty; it need only be different. Purcell and Bloch were contemporaries; yet, because they conceptualized the nuclei in bulk matter as responding in different ways to the influences of magnetic fields, each found it difficult—at first—to think like the other.

Both physicists knew Rabi well and both were very familiar with his work. However, each conceptualized the resonance method in his own way. For Bloch, "the observation of the resonance point is based upon the fact that in its neighborhood there will be a finite probability P for a *change in orientation* . . ." (emphasis mine) (Alvarez and Bloch, 1940b, p. 113). For Purcell, on the other hand, "In the well-known magnetic resonance method for the determination of nuclear magnetic moments by molecular beams, *transitions are induced between energy levels* . . ." (emphasis mine) (Purcell *et al.*, 1946, p. 37). In these comments, both men were referring to the same phenomenon and they both cited the same paper.[15]

The imaginations of both Bloch and Purcell regarding nuclear magnetism were shaped by their earlier experiences: for Bloch the conceptual background was his "obsession" with the magnetic properties of the neutron, and for Purcell it was his wartime concern with the atmospheric absorption of microwave radiation. From their individual conceptual frameworks, it was difficult for each of them to understand the experiment of the other. Bloch looked at Purcell's cylindrical cavity and saw no geometrical framework that would allow his reorienting magnetic moments to be detected. Purcell looked at Bloch's orthogonal coils and did not imagine Ehrenfest's theorem with an expectation value obeying the classical equations of motion.

The difficulty of entering another mode of conceptualization reinforces the appeal of one's own conceptual mode, contributing to its stability and staying power. After both Purcell and Bloch became familiar with each other's work, they continued to think about NMR in their own terms. In his 1953 Richtmyer Memorial Lecture, Purcell's conceptual commitment to quantum transitions was apparent (Purcell, 1954b). Likewise, when Bloch wrote on the topic of nuclear magnetic resonance for an encyclopedia of physics in 1981, it was the precessing magnetic moment that served as his explanatory vehicle (Bloch, 1981).

The two methods, resonance absorption and nuclear induction, are essentially equivalent.[16] They are equivalent in the scientific sense that there is no scientific reason to choose one and reject the other. As Feynman has pointed out, however, methods that are scientifically equivalent can be psychologically quite different (Feynman, 1965). For example, they can be distinctly unequivalent as starting points for new research or for understanding new effects. The nuclear induction approach has associated with it vivid imagery, and it can be conceptualized in classical terms. For this reason, it is particularly useful when discussing dynamical or transient effects.[17] The visualizability of the precessing moment being reoriented has appeal for many individuals. In a report on tests of Lorentz invariance, the *Science* writer began his description of a magnetic-resonance-type experiment as follows:

> "Although their method can be explained in terms of quantum states, it is easier to consider the motion of the atomic spin angular momentum vector" (Robinson, 1985, p. 747).

The resonance absorption approach, on the other hand, brings with it the formal appeal of quantum mechanics and the powerful methods of spectroscopy. Some practitioners of NMR are spectroscopic in orientation; so much so, in fact, that they assume everyone has *always* thought in spectroscopic terms.[18] In his Richtmyer Memorial Lecture cited above, Purcell recognized the value of both conceptual approaches when he acknowledged that the "idea of resonance transition" and the "vivid picture of the . . . precessing magnetic top" were both inspirational.

"Having made a discovery," wrote Polanyi, "I shall never see the world again as before. My eyes have become different" (Polanyi, 1962, p. 143). In his Nobel Lecture

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[15]Both Bloch and Purcell cited Rabi, Zacharias, Millman, and Kusch, 1938.

[16]There is one practical difference: the nuclear induction method permits the signs of magnetic moments to be determined.

[17]Pulse methods are discussed almost exclusively in the dynamical terms appropriate for nuclear induction. See, for example, Hahn, 1950.

[18]In Jelinski, 1984, Bloch and Purcell are credited with first observing that "transitions could be induced between magnetic spin energy levels . . . ."

given on December 11, 1953 Purcell described how his discovery changed the way he looked at the world. "I remember," said Purcell, "in the winter of our first experiments, just seven years ago, looking on snow with new eyes. There the snow lay around my doorstep—great heaps of protons quietly precessing in the earth's magnetic field. To see the world for a moment as something rich and strange is the private reward of many a discovery" (Purcell, 1964).

The two discoveries of NMR were not the outcome of serendipitous events. The discoveries were the product of experiments that had been carefully designed on the basis of particular conceptual commitments. In the mounds of snow Purcell saw "great heaps of protons quietly precessing in the earth's magnetic field." On this Bloch would agree. However, if within that pile of snow the earth's magnetic field had an oscillating field of variable frequency associated with it, Bloch and Purcell would "see" things quite differently. As the oscillating magnetic field passed through the Larmor frequency, Bloch would have the image of magnetic moments being reoriented, while Purcell would imagine transitions occurring between two quantum states.

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