FELIX BLOCH AND MAGNETIC RESONANCE

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Among the versatile and fundamental contributions of Felix Bloch to physics, the science of magnetic resonance in condensed matter, also introduced independently by the Purcell Harvard group, was essentially the crowning achievement of his career. The background for the early investigations of the Stanford group in what was then called "nuclear induction" must be viewed in the context of Bloch's early scientific career. In his early youth it was unheard of to think of making an assured living as a theoretical physicist, so a proper career to choose was engineering, and he became a student of engineering in the Institute of Technology in Zurich. He quickly became bored of these studies, and against the advice of his professors switched to physics. He was aware that only fanatics do theoretical physics and was told that he would probably starve at it if he was mediocre. As a young physicist, eager to capitalize on all the new physics which could be solved by the new quantum mechanics, Bloch made a grand tour of studies at prominent centers of European physics before World War II. He interacted with veritable Who's Who of 20th century physicists - Bohr, Schrödinger, Pauli, Debye, Heisenberg, Kramers, Fokker, Ehrenfest and Fermi. Very soon afterward in the early 1930's, Bloch acquired an eminent stature of his own in the physics of solids. Beginning in 1928 to the time of his death in 1983, his papers ranged through a remarkable range of subjects. Leaving out his magnetic resonance publications, they included radiation damping in quantum mechanics, the periodicity of electrons in crystals and metals, susceptibility and conductivity in metals, ferromagnetism, charged particle stopping power, quantum electro-dynamics, x-ray spectra, x-ray and Compton scattering, Auger effect, beta decay and superconductivity. What was most important in Bloch's future development was his decision to leave Europe in 1934 and to begin his career at Stanford where he eventually began to do experimental physics. The seed of his magnetic resonance or "nuclear induction" idea stemmed from his interest in the neutron. I quote from Bloch's words in his magnetic resonance Nobel Lecture, as follows: "The idea that a neutral elementary particle should possess an intrinsic magnetic moment had a particular fascination for me --- It seemed important to furnish a direct experimental proof for the existence of the magnetic moment of the free neutron." In 1936 Bloch published a paper on the magnetic scattering of neutrons in which he suggested that a beam of slow neutrons in passing through iron would experience a highly localized interaction with the iron atoms. He predicted that neutron spins would become polarized as well as scattered, leading to the present day methods of neutron magnetic scattering. His thinking about magnetic resonance began by his conception of a resonance depolarization experiment in which a polarized neutron beam was passed through space with spins parallel to a strong constant magnetic field H.

As acknowledged in 1938 by Rabi and collaborators, Bloch apparently, along with Gorter, had the magnetic resonance principle in mind, with Bloch interested in carrying out neutron spin resonance. Of course Rabi first accomplished the experiment in 1938 with a molecular

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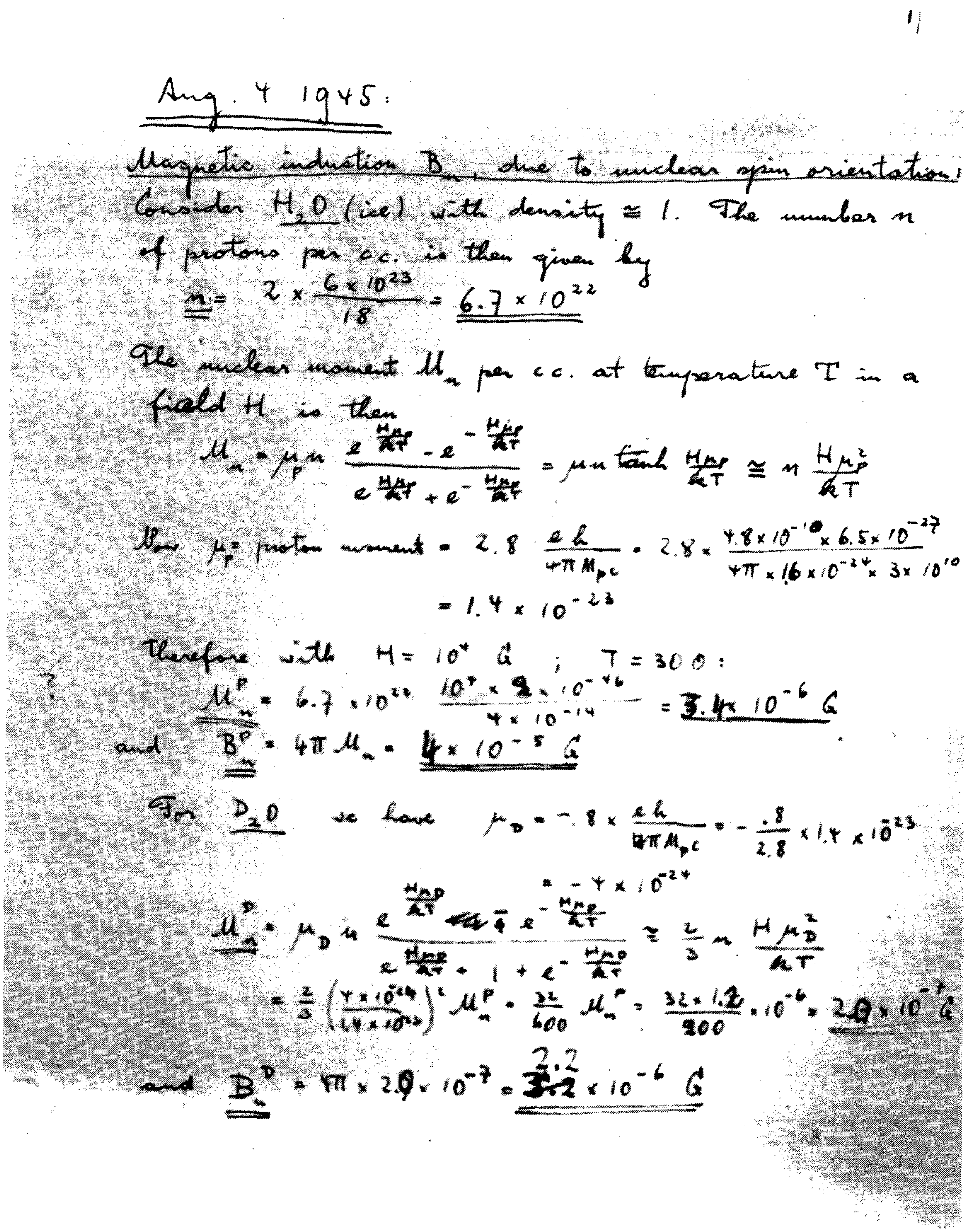
*The author is grateful to Carson Jeffries and Martin Packard for access to source material concerning F. Bloch.



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Aug. 4 1945:

Magnetic induction B_n, due to nuclear spin orientation:
Consider H_2O (ice) with density $\cong 1$. The number n of protons per c.c. is then given by

$$n = 2 \times \frac{6 \times 10^{23}}{18} = 6.7 \times 10^{22}$$

The nuclear moment $\mathcal{M}_n$ per c.c. at temperature T in a field H is then

$$\mathcal{M}_n = \mu_p n \frac{e^{\frac{H\mu_p}{kT}} - e^{-\frac{H\mu_p}{kT}}}{e^{\frac{H\mu_p}{kT}} + e^{-\frac{H\mu_p}{kT}}} = \mu n \tanh \frac{H\mu_p}{kT} \cong n \frac{H\mu_p^2}{kT}$$

Now μ_p = proton moment $= 2.8 \frac{eh}{4\pi M_p c} = 2.8 \times \frac{4.8 \times 10^{-10} \times 6.5 \times 10^{-27}}{4\pi \times 1.6 \times 10^{-24} \times 3 \times 10^{10}}$

$$= 1.4 \times 10^{-23}$$

Therefore with $H = 10^4$ G ; $T = 300$:

? $$\mathcal{M}_n^p = 6.7 \times 10^{22} \frac{10^4 \times 2 \times 10^{-46}}{4 \times 10^{-14}} = 3.4 \times 10^{-6} \text{ G}$$

and $$B_n^p = 4\pi \mathcal{M}_n = 4 \times 10^{-5} \text{ G}$$

For D_2O we have $\mu_D = -.8 \times \frac{eh}{4\pi M_p c} = -\frac{.8}{2.8} \times 1.4 \times 10^{-23}$

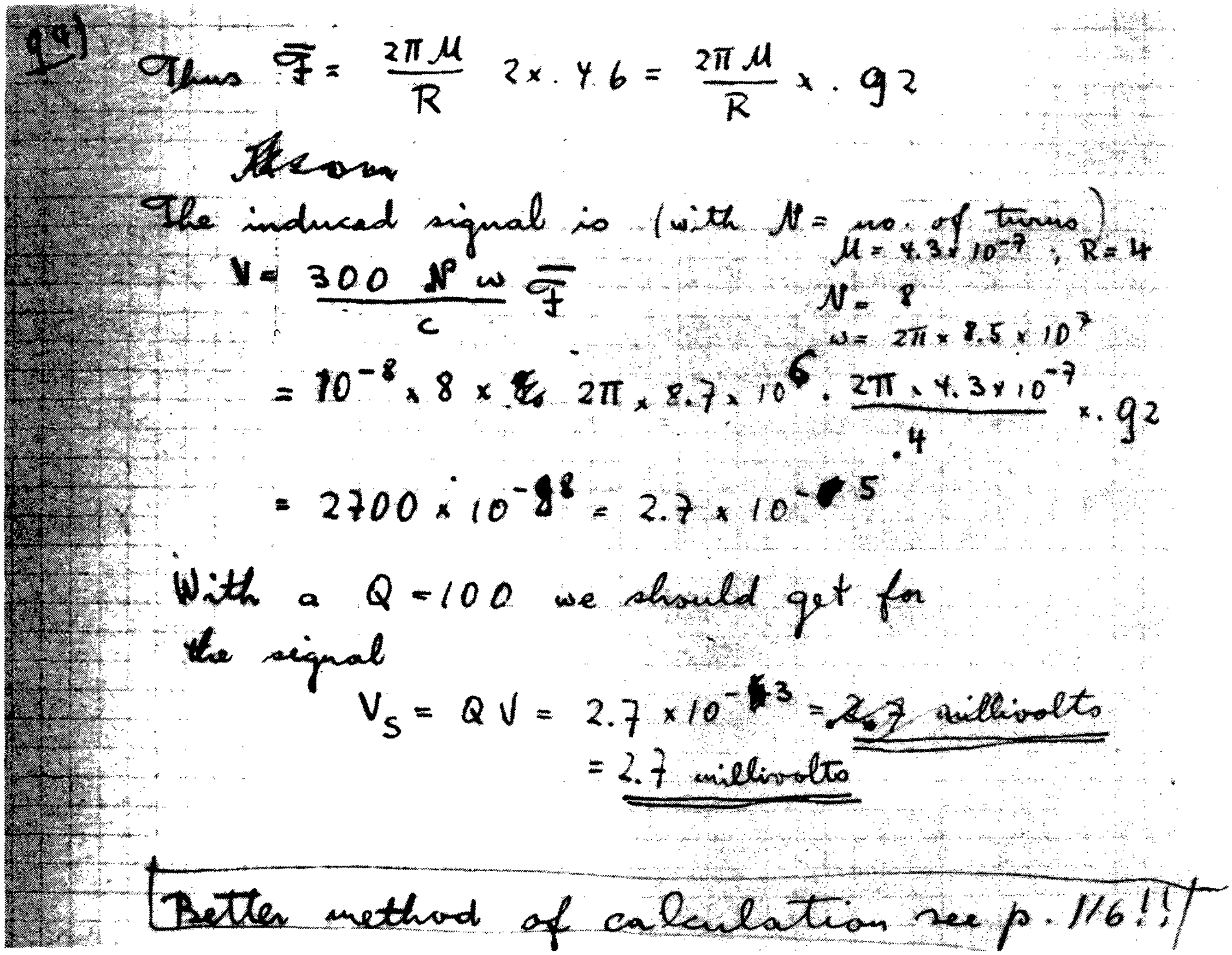
$$= -4 \times 10^{-24}$$

$$\mathcal{M}_n^D = \mu_D n \frac{e^{\frac{H\mu_D}{kT}} - e^{-\frac{H\mu_D}{kT}}}{e^{\frac{H\mu_D}{kT}} + 1 + e^{-\frac{H\mu_D}{kT}}} \cong \frac{2}{3} n \frac{H\mu_D^2}{kT}$$

$$= \frac{2}{3}\left(\frac{4 \times 10^{-24}}{1.4 \times 10^{-23}}\right)^2 \mathcal{M}_n^p = \frac{32}{600} \mathcal{M}_n^p = \frac{32 \times 1.2}{900} \times 10^{-6} = 2.0 \times 10^{-7} \text{ G}$$

and $$B_n^D = 4\pi \times 2.0 \times 10^{-7} = \overset{2.2}{\cancel{3.2}} \times 10^{-6} \text{ G}$$

Figure 1. Calculations of nuclear Boltzmann factors from original notes of F. Bloch.



99)

Thus $\overline{\mathcal{F}} = \frac{2\pi\mu}{R}\, 2\times .46 = \frac{2\pi\mu}{R} \times .92$

[illegible]

The induced signal is (with N = no. of turns)

$\mu = 4.3 \times 10^{-7}$, $R = 4$

$N = 8$

$\omega = 2\pi \times 8.5 \times 10^{7}$

$$V = \frac{300\, N\, \omega}{c}\, \overline{\mathcal{F}}$$

$$= 10^{-8} \times 8 \times 2\pi \times 8.7 \times 10^{6} \cdot \frac{2\pi \times 4.3 \times 10^{-7}}{.4} \times .92$$

$$= 2700 \times 10^{-8} = 2.7 \times 10^{-5}$$

With a $Q = 100$ we should get for the signal

$$V_S = Q\,V = 2.7 \times 10^{-3} = \underline{\underline{2.7 \text{ millivolts}}}$$

$$= \underline{\underline{2.7 \text{ millivolts}}}$$

Better method of calculation see p. 116!!

Figure 2. First estimates of the nuclear induction signal from original notes of F. Bloch.

Figure 3. F. Bloch. H. Staub, and W. Hansen viewing a homemade oscilloscope in the early 50's.

beam. Bloch thereafter acknowledged Rabi's magnetic resonance principle to flip the neutron spin, and in 1940 in collaboration with Luis Alvarez at Berkeley, the neutron moment was measured to an accuracy of 1%. This accuracy was determined by flip coil measurements, which could not be better than 0.4%. Bloch's first notion, which he quickly abandoned as too awkward, was to improve the accuracy of this measurement by calibrating the magnetic field by a molecular beam technique. Bloch began to wonder whether it might be possible to measure the magnetic resonance of nuclei in ordinary condensed matter? He was unaware that Gorter had failed in 1936 and in 1942 to carry out such an experiment in a crystal. This is not surprising since Bloch was not a conscientious surveyor of the literature. He preferred to rediscover and work things out ior himself -- a marked characteristic of his independent personality. Nor was he aware of the experiments contemplated or initially carried out on nuclear adsorption at Harvard.

Bloch began from first simple principles to calculate the voltage that would be induced in an inductance by the precessing macroscopic magnetization due to protons in 1 mL of water at room temperature, subjected to a strong field H and a perpendicular r.f. field H_1. (See Figures 1 and 2). He stated to me personally and to others, on querying him about his train of thought then, that he was amazed how such a simple calculation, taking into account a small Boltzmann factor (of the order 10^{-6}), could give such large voltage signals of the order a millivolt from nuclear induction, well above amplifier noise. He recalled, having confirmed ample nuclear signal size, that the worry of long thermal equilibrium relaxation times might cause failure to see any signal whatsoever. As I proceed further on, this concern about relaxation will be brought out.

The first attempt to measure nuclear induction took place in the fall of 1945, after Bloch returned to Stanford from wartime service at the Radio Research Laboratory in Cambridge, Massachusetts, where he worked on radar scattering and theory of the magnetron. With his student Martin Packard and colleague W. W. Hansen, an apparatus was assembled, with Bloch working on the magnet and Packard and Hansen assembling the radio transmitter and receiver. In those days the physics apparatus at Stanford was in a sorrowfully primitive state with none of the elegant equipment Bloch and Hansen were accustomed to during their research sojourns elsewhere during the war. The Stanford physics basement was cluttered with antique x-ray apparatus -- and that was about *it*. For the nuclear induction experiment they used a rather primitive lecture demonstration magnet (Figure 5) with current supplied by the small Stanford cyclotron.

Figure 4. M. Packard, R. Sands and F. Bloch.

They first failed repeatedly in their search for resonance signals at the field supposedly adjusted to the correct value of 1826 gauss for proton resonance at 7.76 MC. In fact, returning to the worry about thermal equilibrium, the sample of water was allowed to sit in the magnetic field all day to make certain that enough macroscopic magnetization would build up to provide a signal before making a search. Little did they know that they had to wait only about 3 seconds for protons to relax in water. Finally something happened after they switched off the magnet one day (sometime after Christmas, 1945) to see what was wrong. A signal blip appeared on the scope unexpectedly. They saw their first adiabatic fast passage signal by dropping the magnetic field through the resonance condition $\omega = \gamma H$. It was quickly confirmed that the signal could be improved by using a paramagnetic iron nitrate solution to shorten the relaxation time. Now nuclear induction was established as a reality. After this success Bloch gave a colloquium lecture while Martin Packard valiantly tried to reproduce the experiment on the lecture table in front of the audience, but he

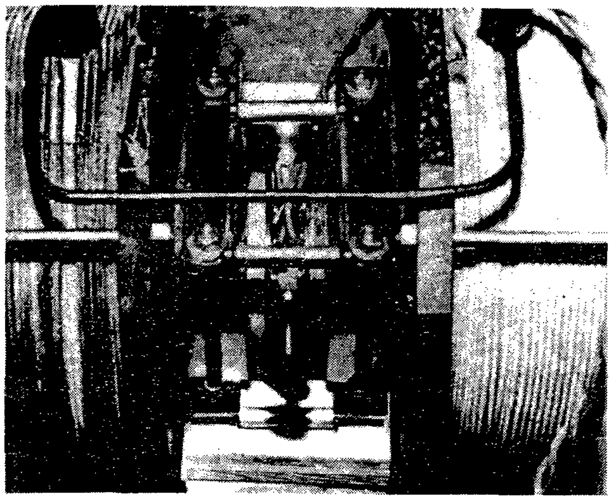


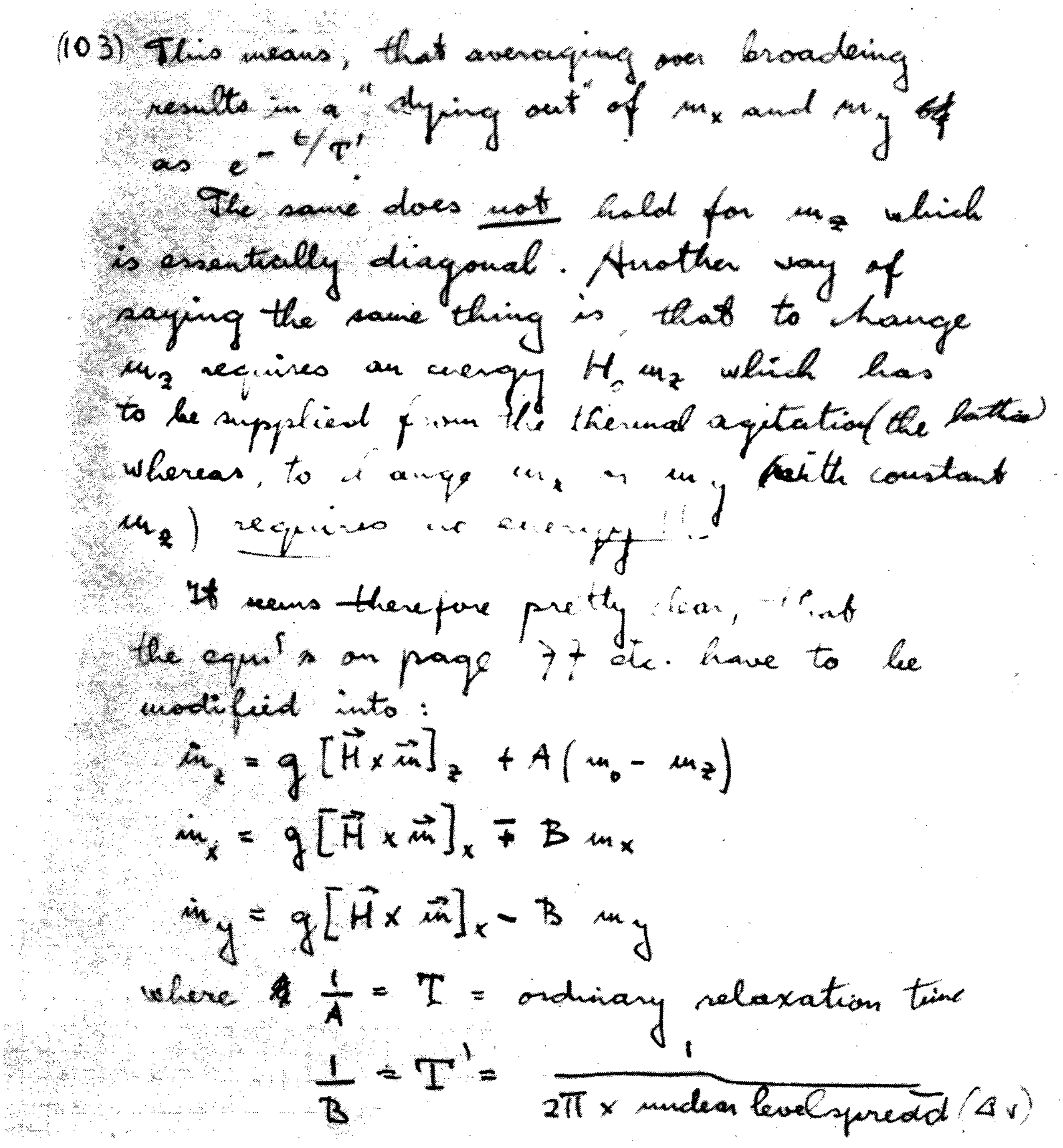
Figure 5. Lecture demonstration magnet used to obtain the first nuclear induction signal.

couldn't find the signal -- the spins were still shy about exposing themselves to the public, having been left alone in their incoherent privacy for an eternity.

These preliminary results, reported in 1946, were followed by Bloch's famous paper on Nuclear Induction in which the phenomenological theory of macroscopic spin dynamics was given. It is of historical interest again to reproduce a certain page (Figure 6) of Bloch's original notebook. This shows clearly his reasoning in arriving at what are now the standard dynamical equations of nuclear magnetic resonance, and the famous transverse T_2 and longitudinal T_1 relaxation times.

A few weeks after the first successful experiments at Stanford, Bloch received the news that a closely related discovery had been made simultaneously at Harvard. Their discoveries were announced in the same issue of Physical Review, January 1946. For a brief period of time it was thought that possibly these two investigations were dealing with different things. Finally it was realized the two experiments were observing the same phenomena from different points of view. Bloch's approach was in terms of dynamic macroscopic voltage signals induced by precession and the Faraday effect, whereas the Purcell group description was in optical terms of quantum mechanical susceptibility and absorption.

Many new findings developed in the years to follow. The concept of motional narrowing in liquids developed explicitly from the Harvard group. Their style focused on microscopic effects of local fields, line widths and shapes, and effects of fluctuations of local fields upon the magnetic resonance signal and its relaxation. When nuclear induction signals in liquids were first investigated at Stanford, their observed line widths, which were predominantly caused by magnetic field inhomogeneity, were interpreted in the beginning to be due to dipolar broadening by neighboring spins in the sample. The germ of motional narrowing was of course finally evident to the Stanford group, since the effect of long relaxation times was included in the Bloch equations. The Stanford group interest, however, was more in the measurement of spins and moments. The Bloch method of crossed-coils was adapted quite efficiently to the search for new resonances which W. W. Hansen had in mind as a master project, interrupted, however, by his untimely death. With Nicodemus and Staub, Bloch returned to his old interest in the neutron, and made a precision measurement of its magnetic moment by observing in the same field two precession frequencies, that of a beam of neutrons in vacuum, and that of protons in water. Later tritium (^3H) was measured by Levinthal, and Packard worked on the precise moment of ^2H. Warren Proctor developed a search NMR spectrometer, and he began to measure the spins and moments of a large number of nuclei. In the course of these searches it was inevitable for Proctor and Yu that they should discover the chemical shift -- the same nucleus in different compounds has a different resonance frequency because contributions of the bonded electrons to the effective field at the nucleus. This shift was also discovered independently by Dickenson at MIT in the laboratory of Francis Bitter. Proctor and Yu observed the NMR shift of nitrogen-14 in NH_4NO_3 dissolved in water: one nitrogen resonance came from the NH_4 group, shifted from a second nitrogen resonance in the NO_3 group. This effect excited Bloch very much at first, thinking that perhaps there existed stable nuclear isomers that had slightly different properties. The other possibility of course was that it could be just a nasty diamagnetic chemical shift which would not and did not excite him. After it was confirmed as chemical in origin the shift did not command Bloch's interest as fundamental in his list of priority problems in physics. To confirm whether or not the two nitrogen resonances



(103) This means, that averaging over broadening results in a "dying out" of m_x and m_y ~~of~~ as $e^{-t/T'}$.

The same does not hold for m_z which is essentially diagonal. Another way of saying the same thing is, that to change m_z requires an energy $H_0 m_z$ which has to be supplied from the thermal agitation (the latter) whereas, to change m_x or m_y (with constant m_z) requires no energy!!

It seems therefore pretty clear, that the equ's on page 77 etc. have to be modified into:

$$\dot{m}_z = g[\vec{H} \times \vec{m}]_z + A(m_0 - m_z)$$

$$\dot{m}_x = g[\vec{H} \times \vec{m}]_x \mp B m_x$$

$$\dot{m}_y = g[\vec{H} \times \vec{m}]_x - B m_y$$

where ~~A~~ $\frac{1}{A} = T =$ ordinary relaxation time

$$\frac{1}{B} = T' = \frac{1}{2\pi \times \text{nuclear level spread } (\Delta\nu)}$$

Figure 6. Formulation of Bloch equations from original notes of F. Bloch.

were not isomers, Bloch telephoned Segre at Berkeley and asked to borrow a little ^{15}N. If the two resonances were not present in ammonium nitrate made up with ^{15}N, then the explanation would be nuclear instead of chemical. Finally the sample arrived and proved again to give two resonances. Thus the matter of chemical shift was a new complicating correction factor which had to be taken into account in measuring magnetic moments.

The above episode was an example of how Bloch was really not enthusiastic about analyzing the numerous side effects brought in by the many body effects of local fields in condensed matter that could not be comprehended without an involved series of empirical measurements. I remember distinctly the time when Dick Norberg and I were in Felix's office, pouring out our resonance research results to him, Norberg on metals, and I with chemical echo modulation effects. Bloch said: "Norberg, you should be a metallurgist, and Hahn, you should be a chemist!"

Figure 7. M. Packard and R. Varian.

Figure 8. F. Bloch in a debating mood, with E. Ginzton.

In 1950 Bloch and Jeffries measured precisely the proton magnetic moment in units of the nuclear magnetic by observing in the same field the NMR and cyclotron resonance of protons using a small anti or inverted cyclotron technique. The body of data obtained by all these measurements was ultimately applied to the nuclear shell model of Mayer and Jensen.

Arnold, Dharmati and Packard observed in a very uniform magnetic field, resolution of hyperfine proton resonances in C_2H_5OH, an effect observed by Gutowsky and Slichter in the steady state, and independently by myself in terms of modulation beats of spin echoes. The existence of these fine structure effects together with the chemical shift serve as the basis of high resolution NMR as it exists today. The enterprise of high resolution NMR instrumentation was pioneered by the Varian Company, and now has spread as an analytic technique throughout the world. Very good scientists, a number of whom came from Bloch's NMR group, worked for Varian in those early days which gave the company the research thrust that enabled it to produce the first efficient instrumentation for analytic NMR chemistry.

At this point I would like to interject some particular remarks about the Bloch equations. The Bloch equations have had wide application to a number of physical effects which do not necessarily involve gyromagnetic spins. They apply directly to any two quantum level or equally spaced quantum level system, and are particularly useful in predicting effects involving electric dipole laser resonance phenomena.

Numerous effects in quantum optics are analogs of spin resonance phenomena discovered in former days and are often predicted by Bloch equations. Although considerations of propagation and fluorescence are not present in NMR cavity resonance experiments, there remain a host of similar effects in the time and frequency domain that also appear in quantum optics.

Although the original phenomenological Bloch equations work very well for fluids, in many cases they are not rigorous for all systems, particularly in solids. Nevertheless, the Bloch formulation has stimulated new statistical investigations with the density matrix that are more rigorous for the particular system under investigation. Exceedingly useful is the property that the Bloch equations enable predictions of nonlinear quantum macroscopic phenomena that no amount of fastidious quantum mechanical perturbation theory could predict as handily.

Personally it was my good fortune and privilege to study under Felix Bloch as a postdoctoral student during the two years 1950 to 1952. It was in his nature to have a profound influence on his students. His love for physics took a high priority in his life, which induced him continually to avoid the impediments of formal rules of bureaucratic restraints that prevented him from doing things for himself. He always invited others to share in his search for answers, and did not distance himself from anyone who would join him in the search, regardless of his or her status. What many of his students gained from him intellectually was often merged with his advice and counsel. Felix was a devoted family man, and not incidentally, he was also an accomplished pianist. With his good wife Lore and the family, the invitations to participate in activities of family life, with musicals, hikes and parties, were all occasions indeed memorable, giving positive incentive and enjoyment in learning physics from Felix.

The legacy of contributions to science by Felix Bloch was already a monument to him while he was alive. Among his versatile contributions to physics I have emphasized his work on magnetic resonance. The application and impact in particular of the science of NMR now involves the activities of thousands of research people in solid state physics, analytical chemistry, and most recently of clinicians in the medical world who apply the technique for imaging the human body for medical diagnosis. Not long before his death Felix indicated to me as well as to others that the extension of magnetic resonance to humanitarian practical use was of great satisfaction to him,

Felix Bloch is among the Greats in the history of science, affecting many who never met him, a living influence for them and a personal one for those of us who were fortunate to have known him, and who shall remember him with affection and gratitude.