WILLIS E. LAMB, JR.

Fine structure of the hydrogen atom

Nobel Lecture, December 12, 1955

When the Nobel Prizes were first awarded in 1901, physicists knew something of just two objects which are now called « elementary particles »: the electron and the proton. A deluge of other « elementary » particles appeared after 1930; neutron, neutrino, μ meson, π meson, heavier mesons, and various hyperons. I have heard it said that « the finder of a new elementary particle used to be rewarded by a Nobel Prize, but such a discovery now ought to be punished by a $10,000 fine ».

In order to determine the properties of elementary particles experimentally it is necessary to subject them to external forces or to allow them to interact with each other. The hydrogen atom which is the union of the first known elementary particles: electron and proton, has been studied for many years and its spectrum has taught us much about the electron.

In 1885, Balmer found that the wavelengths of fourteen lines of the hydrogen spectrum were given by a simple equation. In 1887, Michelson and Morley discovered a fine structure of some of these lines. The quantum theory was founded by Planck in 1900, and in 1913 Bohr gave rules of quantization which permitted a derivation of Balmer's formula. Sommerfeld showed in 1916 that the fine structure of Bohr's energy levels was caused by relativistic corrections. In 1924, De Broglie attributed wave properties to the electron and soon a quantum mechanics of the hydrogen atom emerged from the hands of Heisenberg, Born, and Schroedinger. Spin and magnetic moment of the electron were suggested by Uhlenbeck and Goudsmit in 1925, and their dynamical equations were worked out by Thomas a year later. In 1928, Dirac discovered an equation which described an electron with wave properties, charge, spin, magnetic moment and a mass depending on velocity as required by relativity theory. The energy levels of hydrogen were given by Dirac's theory with high precision.

Of special interest to us are his predictions, as shown in Fig. 1, of the $n = 2$ group of energy levels which are 10.2 electron volts above the $n = 1$ ground state. The fine structure splitting $2^2P_{3/2} - 2^2P_{1/2}$, which according to Dirac's theory arises from spin-orbit interaction, agrees exactly with the sep-

$2^2P_{3/2}$ ———————— a, b, c, d ———————— ΔE

$2^2S_{1/2}$ ———————— α, β ———————— S
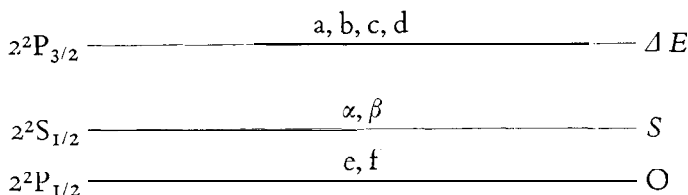
$2^2P_{1/2}$ ———————— e, f ———————— O

Fig. 1. Fine structure of $n = 2$ levels of hydrogen. According to the Dirac theory the $2^2S_{1/2}$ and $2^2P_{1/2}$ levels coincide exactly. The letters a, b, c, d, e, f, α and β denote the magnetic sub-levels which are split in a magnetic field.

aration of the two levels of Sommerfeld's 1916 theory. The exact coincidence in energy of the $2^2S_{1/2}$ and $2^2P_{1/2}$ states is a consequence of the assumed Coulomb law of attraction between electron and proton. Any departure from this law would cause a separation of these levels.

Many spectroscopic studies of the hydrogen fine structure were made to test the Dirac theory, but by 1940 had failed to establish clearly a decision, although there was evidence strongly supporting the theory. (We now know that the work of Houston[1] and Williams[2] indicated a discrepancy which should have been taken seriously.)

For the subsequent developments, some chapters from my own peculiar history may be of interest. After undergraduate training as a chemist, I studied theoretical physics under Professor J. R. Oppenheimer at the University of California from 1934 to 1938. My thesis[3] dealt with field theories of nucleons which predicted a very small discrepancy from Coulomb's law about a proton. At Columbia University after 1938, I came into close relation with Professor I. I. Rabi and members of the molecular beam laboratory. My attention was drawn briefly to metastable atoms[4] in connection with a proposed atomic beam experiment. During the war, at the Columbia Radiation Laboratory, I received some first-hand acquaintance with microwave radar and vacuum-tube construction techniques. One of the wartime projects in the Laboratory was the determinations of the absorption coefficient of centimeter waves in atmospheric water vapor, and my interest was started in what was to become the very active postwar field of microwave spectroscopy.

In teaching a summer session class in atomic physics in 1945 using a textbook[6] by Herzberg, I found references to some attempts[7] made in 1932-1935 to detect absorption of short-wavelength radio waves in a gas discharge of atomic hydrogen. At first it seemed to me that these experiments had failed because of inadequate microwave techniques. I thought of repeating them

with the greatly improved facilities developed during the war. On further study, however, I realized that atoms in a gas discharge are strongly perturbed and that all the $n=2$ states would have nearly equal populations. Under these conditions there would be no appreciable absorption of radio waves caused by transitions between the three states of interest.

It took almost a full year before a workable scheme was clear in my mind. I considered making use of the possible metastability of the $2^2S_{1/2}$ state of hydrogen. In simplest terms this state should be long-lived against radiative transition to the ground state because a spherically symmetrical charge and current distribution cannot radiate according to classical electromagnetic theory. Nevertheless, quite a few papers between 1924 and 1933 were devoted to discussion and experiment to determine whether or not the $2^2S_{1/2}$ state was actually metastable. In 1933, Bethe[8] showed it to be metastable only for the atom in a region sufficiently free of electric fields. However, it was by no means clear that the excitation of the $2^2S_{1/2}$ state could be carried out without destroying the metastability of the state. It was still necessary to detect any interaction of microwaves with the excited atoms, and as already mentioned, a direct absorption method applied to a discharge seemed out of the question. I decided to try to form a beam of metastable hydrogen atoms. If a radio-induced transition to $2^2P_{1/2}$ or $2^2P_{3/2}$ did take place, the atom would lose its metastability and go in about 10^9 sec to the ground state with emission of radiation. The beam of metastable atoms would thereby be diminished.

It had been showed in 1924 by Webb[9] at Columbia University that metastable mercury atoms could liberate electrons from metals, but no one had either produced or detected the strange metastable form of hydrogen, and it was not certain that a beam of it could be detected through its ejection of electrons.

On the basis of these rather doubtful prospects, I persuaded Retherford[10] to attempt the experiment represented schematically in Fig. 2. After several failures, a successful apparatus was made as shown in Fig. 3. Molecular hy-
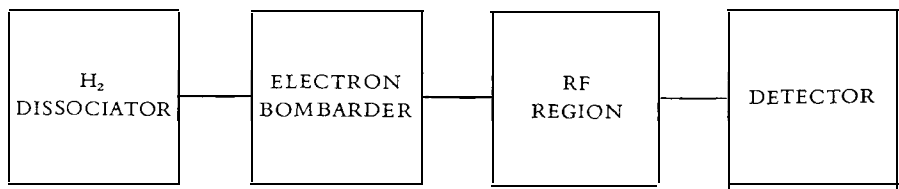

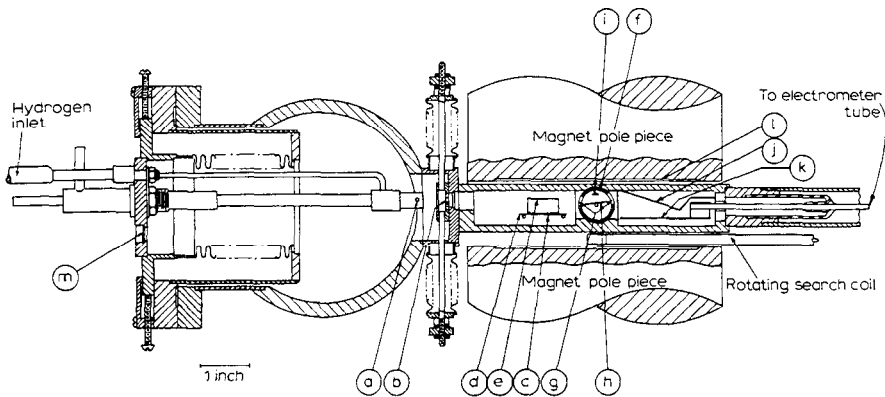Fig. 2. Modified schematic block diagram of apparatus.

Fig. 3. Cross section of second apparatus: *(a)* tungsten oven of hydrogen dissociator, *(b)* movable slits, *(c)* electron bombarder cathode, *(d)* grid, *(e)* anode, *(f)* transmission line, *(g)* slots for passage of metastable atoms through interaction space, *(h)* plate attached to center conductor of r-f transmission line, *(i)* d.c. quenching electrode, *(j)* target for metastable atoms, *(k)* collector for electrons ejected from target, *(l)* pole face of magnet, *(m)* window for observation of tungsten oven temperature.

drogen is dissociated in a tungsten oven, and a stream of hydrogen atoms emerges from a slit to be bombarded by electrons which bring about one atom in a hundred million atoms to the metastable state. After a small recoil deflection, the excited atoms move on to a metal surface from which they can eject electrons and so be detected. Between bombarder and detector, the atoms are exposed to radio waves.

For several good reasons the whole process is carried out in a magnetic field. The fine structure energy levels are subject to Zeeman splitting as shown in Fig. 4, and the frequencies of the possible transitions depend on magnetic field as shown in Fig. 5. As the magnetic field is varied with radio-frequency and amplitude held fixed 2S → 2P → 1S transitions occur and a certain fraction of metastable atoms in the beam are quenched and lose their excitation energy. Since atoms in the ground state are unable to eject electrons from the detector, the electrometer current decreases. A typical resonance curve for deuterium is shown in Fig. 6 and for hydrogen in Fig. 7. The widths of the resonance peaks are partly due to natural radiative decay of the 2P state, and partly to hyperfine structure which is just resolved for one of the hydrogen resonances.

By careful experimental study and theoretical analysis of such resonance curves, it is possible to determine the energy separations $2^2S_{1/2}$ - $2^2P_{1/2}$ and $2\,^2P_{3/2}$ - $2^2P_{1/2}$ in zero magnetic field. The accurate measurements[11] by Day-
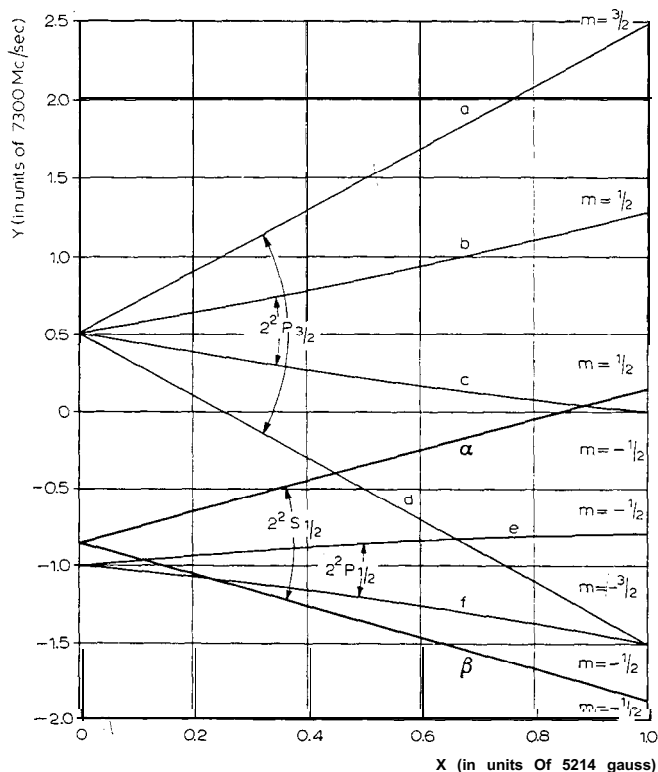
Fig. 4. Zeeman energy levels with the $2^2S_{1/2}$ pattern raised by 1000 Mc/sec.

hoff, Triebwasser, and Lamb gave 1059.0 and 9912.6 Mc/sec for these sep-
arations in deuterium with an accuracy of about 0.1 Mc/sec.

Studies of other fine structure states have been made by microwave meth-
ods. For the $n = 2$ state of singly ionized helium, the separations are 13 to 16
times larger than for hydrogen. In the work of Lamb and Skinner[12], no
beam of metastable ions was formed, but rather the ultraviolet radiation
emitted in the decay of 2P -1S was used to detect the transitions 2P - 2S
induced by microwaves. A similar method was used in the later experiments
of Deutsch[13] on positronium in which a transition from the triplet to singlet
state changes the rate of emission of annihilation radiation. Recently the fine
structure of the $n = 3$ state of hydrogen was studied by Lamb and Sanders[14]
using analogous microwave methods, and the fine structure of the 3^3P state
of helium has been determined[15] by Lamb, Maiman, and Wieder.

Let me now tell briefly about the explanation which has been given of the
departures from the expected fine structure pattern for hydrogen. To come

at once to the heart of the matter: the electron does not behave like a point charge as implied in Dirac's equation. If time permitted, I would trace the long history of attempts to make a theory of the internal structure of electrons. This was begun by J. J. Thomson with his calculation of electromagnetic mass, and developed by Lorentz using classical electromagnetic theory.

According to relativity theory, energy and mass are proportional to one another. In order to obtain a finite mass of the electron on a purely electromagnetic basis, it was necessary to assign an extended structure to the electron. Attempts to form a satisfactory relativistic theory of an extended charged particle failed.

After quantum mechanics had been applied to matter it was used by Dirac and by Heisenberg and Pauli to attack the problem of the electromagnetic field and its interaction with charged particles. This theory had many successes. A good account was given of the phenomena of emission, absorption
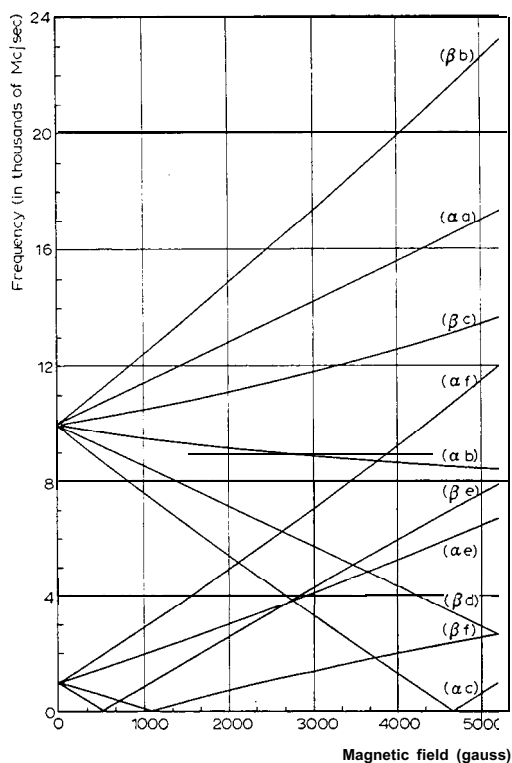

Fig. 5. Expected resonance frequencies as functions of magnetic field with the $2^2S_{1/2}$ state raised by 1000 Mc/sec.
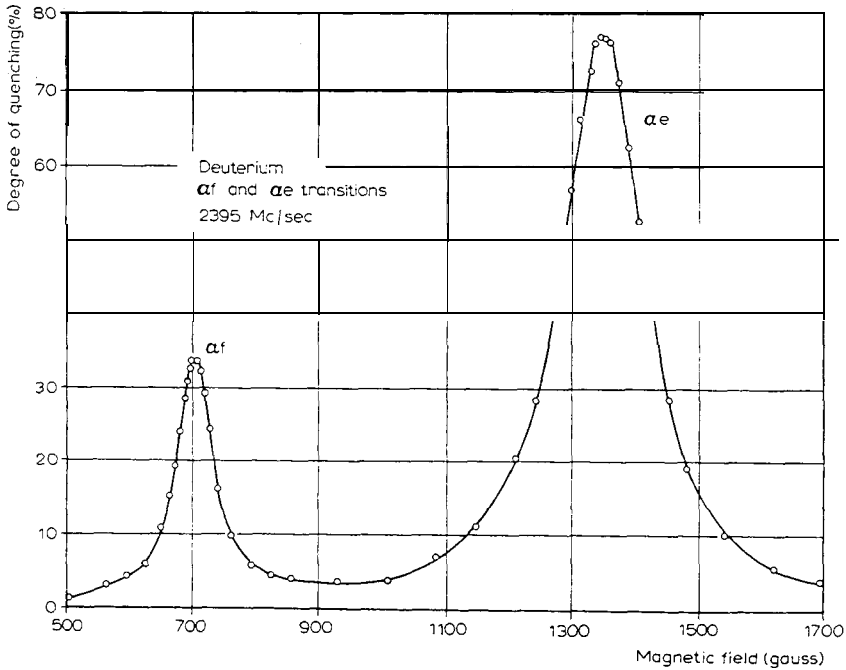
Fig. 6. Observed resonance curves for deuterium.

and scattering of radiation by matter, including the spontaneous radiation postulated by Einstein in 1917. From the quantum electrodynamical point of view, spontaneous emission could be regarded as emission stimulated by the quantum zero-point fluctuations in the electromagnetic fields in the vacuum or lowest energy state.

When, however, the energy of interaction of an electron with the quantized electromagnetic field was calculated by Oppenheimer[16] in 1930, a meaningless result was obtained. According to this theory, not only was the energy infinite but the frequencies of all spectral lines were displaced by an infinite amount from the values predicted without consideration of radiative interactions. It was pointed out by Weisskopf[17] in 1934 that this ultraviolet catastrophe could be ascribed to the above-mentioned zero-point fluctuations in the vacuum electromagnetic field. These fluctuations were needed for the correct spontaneous emission to occur and yet led to violent disagreement with observations in other respects. The theory of electromagnetic energy remained in this highly unsatisfactory state until May 1947 when the fine structure deviations were definitely established experimentally.
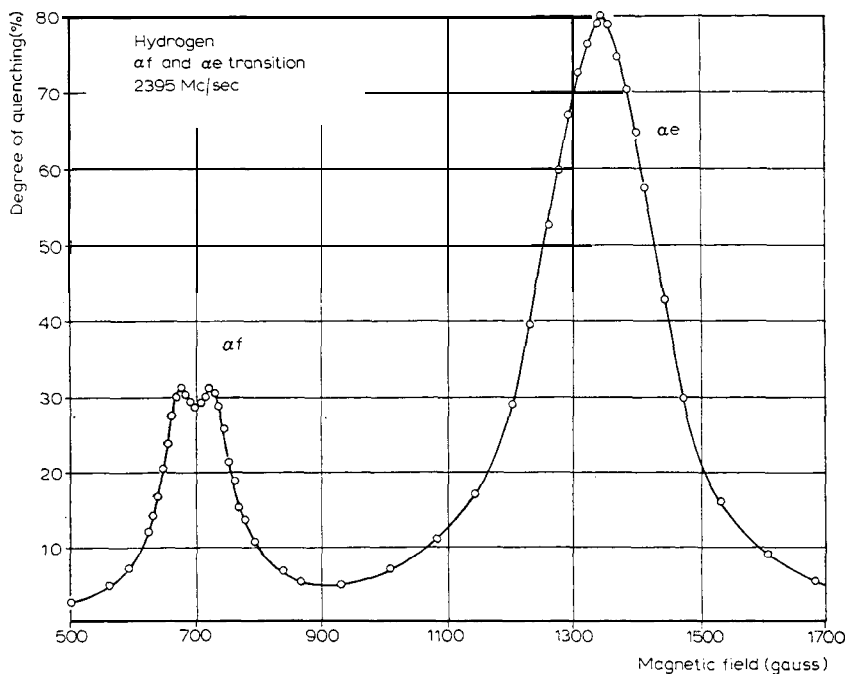
Fig. 7. Observed resonance curves for hydrogen.

A month later, Bethe[18] found that quantum electrodynamics had really hidden behind its divergencies a physical content which was in very close agreement with the microwave observations. The crucial step due to Bethe was a successful application of the very old idea of renormalization of mass. The quantum theory of radiation predicted that a free electron should have an infinite mass. Some explanation must therefore be found for the observed fact that the mass was finite. Bethe recognized that this was outside the scope of the theory at that time and simply ignored the electromagnetic mass difficulty. For an electron bound in a hydrogen atom, an infinite energy also occurs, but this was merely a manifestation of the infinite electromagnetic mass which should be eliminated in some future theory. With the mass terms properly subtracted a finite remainder is obtained which would be zero for a free electron. In the case of a bound electron, the force field modifies the effect of the electromagnetic field and a finite displacement of energy levels results which is in quite good accord with observation.

A qualitative picture of the level shift was given by Welton[19] in 1948. The fluctuating zero-point electric field of the quantized vacuum acts on an elec-

tron bound in a hydrogen atom. As a result, the electron is caused to move about its unperturbed position in a rapid and highly erratic manner. The point electron effectively becomes a sphere of a radius almost 10^{-12} cm. Such an electron in a hydrogen atom is not so strongly attracted to the nucleus at short distances as would be a point electron. States of zero orbital angular momentum like $2^2S_{1/2}$ are therefore raised in energy relative to other states like 2^2P in which the electron has a smaller probability of being found near the nucleus.

In 1949, a relativistic generalization of Bethe's calculation was given by Kroll and Lamb[20], which made his results definite. They confirmed additional small contributions of 27 Mc/sec arising from polarization of the vacuum as calculated in 1935 by Uehling[21] on the basis of Dirac's theory of the positron, and of 68 Mc/sec from the anomalous magnetic moment of the electron as suggested by Breit[22] in 1947. Other small corrections have been calculated by various authors, of which the largest was about 7 Mc/sec made by Baranger[23] who took the binding of the electron more exactly into account. At the present time, there is an unexplained residual discrepancy of 0.5 Mc/sec.

It is very important that this problem should receive further experimental and theoretical attention. When an accuracy of comparison of 0.1 Mc/sec has been reached, it will mean that the energy separations of the 2S and 2P states of hydrogen agree with theory to a precision of a few parts in 10^9 of their binding energy or that the exponent in Coulomb's law of force is two with a comparable accuracy. Another way of putting it is to say that the anomalous magnetic moment of the electron would be determined with an accuracy of one part in 680, which would provide a useful check on Kusch's more directly measured result[24]. Finally, I might mention that the fine structure doublet separation now provides the most accurate and direct determination of the famous dimensionless number called the fine structure constant, whose numerical value of about 1/137 it will be the task of some future theory to explain.

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