

Part I

**Precision Spectroscopy of Hydrogen:
Fundamental Physics and Universal Constants**

The Hydrogen Atom

(An Historical Account of Studies of Its Spectrum)

G.W. Series

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1. Introduction

I was honoured and pleased by the invitation from Professor Bassani to give this introductory talk. But I must confess that as I pondered upon the task I had undertaken, my heart began to sink. I have lived through the last forty years of the story, but the active history of the subject takes us back another hundred and forty years, so I went to that great source-book, KAYSER's *Handbuch der Spectroscopie* [1] and that is where most of my early references come from.

Kayser's *Handbuch* lists over 700 publications on the spectrum up to 1927 – sixty years ago, just the time when quantum mechanics had gripped the imagination of the rising generation of mathematically-minded physicists. And since most of you will be more or less familiar with the happenings of those famous days, I shall mention, but shall not dwell on them. I shall suppose, moreover, that you are very well informed about the Lamb shift and QED, so my story will end, not abruptly, but roughly, where Willis Lamb came in. Even so, my task is to summarise, shall we say, 1500 – 2000 papers in forty minutes, so you must excuse me if I do less than justice to the work of some of our predecessors.

2. That the Spectrum exists and betokens Hydrogen

1672. To each colour belongs a definite refrangibility. That had first to be proved, and it was NEWTON who proved it [2]. Until FRAUNHOFER, a hundred and fifty years later [3], made a diffraction grating, what spectroscopy there was rested upon the dispersion of light by glass prisms.

Newton's spectrum of the sun showed the colours spread out in a continuous band. 1802 WOLLASTON [4] introduced a slit about 1 mm broad and viewed the slit through a prism. He saw the solar spectrum crossed by a number (a small number) of dark bands. It is difficult to be certain what bands these were, but it seems likely that one of them – in the yellow – might be attributed today to sodium. This, then, would have been the first time that the sodium D lines had claimed the attention of an observer.

1815. Over ten years later Joseph von Fraunhofer, still under 30, introduced a lens from a theodolite to follow a prism and saw, for the first time, those dark lines

crossing the solar spectrum which, in perpetuity, will bear his name. Fraunhofer had been studying *emission* spectra from a variety of light sources and lamps. He found a bright yellow line coming from everything he tried – what spectroscopist doesn't? His resolution, of course, was far better than Wollaston's had been. And then 1817 he turned his attention to sunlight, wondering whether this also would produce bright lines. He was taken completely by surprise to find here *dark* lines embedded in colour. He counted over 700 of them [5]. Their relative positions remained unchanged as he turned the prism or opened the slit. The line C (which we now call Balmer- α) was of considerable strength, he noted. F (that is, Balmer- β) was fairly strong. The D lines consisted of two dark lines separated by one bright line. He studied the light from heavenly bodies: Venus, in whose spectra the D and F lines were recognised, and Sirius, which displayed three bright lines, having no similarity to sunlight.

These observations of the C and F lines are surely the true beginning of our story. But to label spectral lines, and even to recognise them when you see them again falls far short of associating them with some particular atom or molecule; and we must not forget that a dark line on a bright background was not, at that time, necessarily to be associated with a bright line on a dark background seen in the same place in the spectrum. Key points in what follows are to see how our predecessors were led to the emission/absorption relationship, and to bring hydrogen into the story.

1821. In this year FRAUNHOFER invented the diffraction grating [6]. He was a superb engraver and was able to divide a circle with the utmost delicacy and accuracy. That is why, when he wound wire on fine screw threads and produced spectra whose angular deviations were typically of the order of one degree of arc, he was able to obtain values of wavelength consistent with one another to a few parts in a thousand. For example, he quotes the wavelengths of the C and F lines as 2.422×10^{-5} and 1.794×10^{-5} 'Pariser Zoll', respectively. The ratio is 1.350. The ratios of 6.563×10^{-5} , 4.861×10^{-5} cm, accepted these days as the wavelengths of Balmer- α and Balmer- β , is 1.350. (My conversion of Zoll to centimetres yields the factor 2.7070; a 'Zoll' was rather larger than an inch.)

And so we begin the era of measurement in spectroscopy. Ångström, a few years later, worked in units of 10^{-7} mm. In referring to Fraunhofer's measurements he used the term 'pouce' where Fraunhofer used 'Zoll'. I mention these points to recall to your attention the great importance of having an agreed system of units of measurement. The history of measurement of characteristic features of the hydrogen spectrum has been, and still is, intimately connected with the establishment and maintenance of a system of base units, as many of you well know.

So, then, Fraunhofer observed and labelled characteristic and recognisable dark lines in the solar spectrum and gave us the wavelengths of many of them. But what were these lines and why were they there?

J.F.W. HERSCHEL, in 1831, published a book Vom Licht [7] in which he describes studies of the absorption spectra of dyes and the emission spectra of flames and found

that many substances give a characteristic spectrum, but he did not go so far as to say that a particular spectrum was characteristic of a particular substance.

D. BREWSTER [8] in 1836 gave the true explanation of the Fraunhofer lines, the absorption of light by gases in the outer layers of the sun, superimposed on a continuous spectrum emitted by the material in inner regions.

In 1840 the first photograph of the solar spectrum was published by HERSCHEL [9] - and in 1842 E. BECQUEREL [10] published also a Daguerreplate of the solar spectrum showing beautifully the Fraunhofer lines, but it was the eighteen seventies before the gelatin-silver bromide dry plates became available.

Again, in this period, it was controversial whether the Fraunhofer lines were a property of solar light or whether they were produced by the apparatus; and further, if not by the apparatus, then by absorption in the sun or in the earth's atmosphere? Indeed, some of the lines are so produced, and were identified as such.

1851 is a big date in our time-chart, for it is the date of a publication by A. MASSON [11] when a red line, observed by him in emission from a spark in air using electrodes of different metals, was observed to be present for most of the electrodes he used. And when the air was replaced by hydrogen gas, there was the same red line, 'très prononcée'. He even labelled it α . *So, for the first time, that line which surely is the best-known and most studied line in the spectra of the elements, was associated with hydrogen.* By 1855, MASSON had attributed three more lines to the presence of hydrogen [12].

A.J. ÅNGSTRÖM in 1855 reports a study of the spark spectra of many elements, including hydrogen [13]. 'Remarkable, in the case of hydrogen', he says, 'are the strongly luminous and wide lines at the red end of the spectrum . . .'. And earlier he has written, *'When the solar spectrum is compared with the electric one it is found that some of the lines, such as C, D, E, G (C is Balmer- α) have thin corresponding lines in the solar spectrum'*. In the same paper he clarifies the relationship between *absorption* and *scattering*. He makes the connection between the oscillation of particles in molecules and the oscillations of the aether for absorption lines, and he invokes a principle of Euler to declare that 'the rays which a body absorbs are precisely those it can emit when luminous'. This comes very near to the mathematical connection between 'powers of emission' and 'powers of absorption' which KIRCHHOFF [14] was to formulate some years later, 1859/60, and which, says Kirchhoff, provides us with an 'unexpected' explanation of the origin of the Fraunhofer lines.

ÅNGSTRÖM finally drives home the nail in 1862 [15]. He recapitulates the results of his earlier works, in particular, that they had demonstrated that the spectra of mixtures or compounds presented the same lines as the constituent substances. He then makes a correspondence between lines in the emission spectra of a number of elements taken one at a time with particular groups of Fraunhofer lines identified by their distinguishing letters, remarking that the Fraunhofer lines are the 'inversion' of the bright lines seen in electrical spectra, and eventually he turns to hydrogen:

'assume', he says, 'that the C-line belongs to hydrogen . . . '

and he continues, speaking of the relationship between absorption and emission and adducing evidence concerning the occurrence of two other lines in the electrical spectrum of hydrogen, to the conclusion that *the solar C and F lines do indeed belong to hydrogen*.

So now we are home and dry. Hydrogen manifests a line spectrum. The wavelengths of the first four lines have been measured to a few parts in 10^3 . Lines attributable to hydrogen have been identified in absorption in the solar spectrum.

A few years later ÅNGSTRÖM published an atlas of the solar spectrum [16] and gave accurate values of the wavelengths of the lines: these stood for many years as standards for the determination of wavelengths. ROWLAND's famous atlas [17] followed in 1882.

We now, 1876, 1880, turn briefly to the investigations of HUGGINS [18] [19]. In the first paper he published a photographic spectrum of the star Vega (α -Lyrae) exhibiting a beautiful set of Balmer lines, with a solar spectrum for comparison, showing coincidences. In the second paper is a list of the wavelengths of 14 lines, of which 12 are recorded as 'very strong'. 'There is a high probability that these lines present the spectrum of hydrogen'. But only the first three of these lines can be identified confidently with lines in the solar spectrum.

While this study is important in its own right in the context of astrophysics, nevertheless its greater importance for us is that these were the measurements upon which Balmer, a few years later, was able to try out a formula he had deduced on the basis of the wavelengths of the first four lines only. In passing we notice also a paper by H.W. VOGEL [20] whose determinations of wavelengths of the 5th, 6th, 7th and 8th members of the series agree closely with those of Huggins. And furthermore, at a later stage in his work, Huggins 'was astonished to find' that, in the spectrum of Sirius, the hydrogen lines were all jerked a little to the side of the place they occupied in the spectra of his laboratory sources . . . !

3. The Centenary

I thought you might be amused to hear what was happening a hundred years ago. A paper was written in 1888, published in 1889 [21], by J. TROWBRIDGE and W.C. SABINE, reporting their work from the Jefferson Physical Laboratory, Cambridge, U.S.A. 'On the use of steam in spectrum analysis'. Light from an arc between carbon poles, they point out, gives spectra full of impurities from the carbons. The spark from a Ruhmkorff coil gives clean spectra, but the light is very feeble and needs long photographic exposure times. They had the idea of directing a jet of steam upon the spark, and were rewarded by a spectacular improvement in the brilliance of the spectra. The moral for us is clear: if your laser needs tweaking, try steam. But take a hint from Trowbridge and Sabine. Shoot the steam into the spot the light is coming from, not into the power supplies.

4. Playing with Numbers

It is more than a hundred years since JOHANN JAKOB BALMER, a schoolteacher and privatdocent in Basle, a man coming up to 60 years old, gave us, in 1885, the first clue to the understanding of the hydrogen spectrum [22].

But that wasn't the first published report of the mathematical relationships between numerical values of the wavelengths. Reported in some text books is STONEY's result [23] that the first, second and fourth lines of hydrogen can be represented as the 20th, 27th and 32nd harmonics of a fundamental vibration having a wavelength of 131,274.14 Å. A further attempt by Stoney is reported in a footnote to Huggins' paper [19]. This search for harmonics is evidence of the belief that was held that the properties of the light were direct reflections of anharmonic motions of particles in the emitting bodies. Ten years later Stoney's result was shown to be no more than coincidental by SCHUSTER [24]. A lesser known formula is that of D'ARREST: $\lambda_\gamma^3 = \lambda_\beta \cdot \lambda_\delta^2$ [25], which we now understand to derive from the numerical result $27(21)^3 \approx (500)^2$.

How, then, did Balmer arrive at the formula we know so well? He first observes that the wavelengths of the first four lines bear the relations 9/5; 4/3; 25/21; 9/8 to one another, and that the common factor $h = 3645.6 \text{ mm}/10^7$ converts these numbers to the wavelengths. Multiplying then the second and fourth fractions by 4, one arrives at 9/5, 16/12, 25/21, 36/32, of which the numerators are $3^2, 4^2, 5^2, 6^2$. Representing these numbers by m^2 , the fractions are given by $m^2/(m^2 - n^2)$, where n , for this set, is 2.

Balmer's derivation of his formula is made on the basis of these four lines only. Professor Hagenbach, who has encouraged him in the project, now introduces him to Huggins' determinations of wavelengths from white stars. With ten more lines which fit his formula, the matter is clinched. (True, there are more or less progressive differences between observed and calculated wavelengths as one proceeds along the series, but these can throw no serious doubt on the underlying validity of the formula.) Of Stoney's attempt to interpret the numbers as harmonics of a fundamental, Balmer concludes politely, 'interesting as this attempt is, I am doubtful whether it really demonstrates an inner connection between the phenomena'.

Let experimentalists and empiricists gain strength from this work: harmonic oscillations and their overtones were surely at the heart of theoretical physics in the nineteenth century. We should not lose sight of the courage, and of the confidence in the accuracy of measurement, which were required of an elderly schoolmaster at that time, to fly in the face of received wisdom.

5. Fine Structure Observed

How well known is it, I wonder, that only two years after Balmer's publication, and twenty six years before Bohr's interpretation of it, MICHELSON and MORLEY, in 1887, showed that Balmer- α consisted of two lines [26]. In this research the prime objective was to investigate the possibility of making the wavelength of sodium light the

actual standard of length. They first used an etalon of the Fabry-Perot type, then the interferometer. After the sodium yellow lines they studied the red hydrogen line. 'The fringes disappeared at about 15,000 wavelengths and again at about 45,000 wavelengths, so that the red hydrogen line must be a double line with the components about 1/60th as distant as the sodium lines.' The recognition of Balmer- α , then, as twinned, was one of the first fruits of Fourier transform spectroscopy!

In 1904 J. BARNES at Johns Hopkins finds three components in Balmer- α [27]. But the centre line was much stronger than the outer lines! No, this was not the fine structure we know today. Experienced spectroscopists will already have guessed the interpretation that was to come later: self-reversal in the light source. So now we begin to realise the need for restrained excitation. From now on, self-absorption, self-reversal and Stark broadening emerge as diagnostics for physical conditions in light sources. To study hydrogen itself we shall use Geissler tubes at low pressures, and we shall begin the struggle against the Doppler enemy.

6. Systematics and Spectral Series

Time is getting on and there is much more to tell, but there are one or two landmarks I must mention before theory begins to assert itself. So far, you will notice, the story has been of experiment guided by curiosity and accident. A great achievement which cannot be ignored is RYDBERG's great work of 1889 [28] a monumental assessment of series spectra, the recognition that reciprocals of wavelengths, wavenumbers, make more sense than wavelengths; that wavenumbers of lines may best be represented by differences of terms; the building of the ordinal number of a line in a sequence into a formula for the term values; the existence of a universal constant; and finally, the recognition that Balmer's formula was a very special case of his own. And then, closely related to Rydberg's work, came RITZ's Combination Principle in 1908 [29].

On the experimental side came the discovery of other spectral series in hydrogen which beautifully fit Balmer's formula. 1908 - Paschen's series ($m = 3$) in the infrared, followed by Brackett's ($m = 4$) in 1922, Pfund's ($m = 5$) in 1924 - these are mentioned in all the text-books, but you may supplement them by Humphrey's series ($m = 6$) in 1953. Further into the infrared, in more recent times GRIEM *et al.* in 1973 [30] observed 11α , 12α , 13α at about 100 μ , and in the microwave region the line 109α at 5 GHz has made its appearance as a maser in the sky [31]. The series in the ultraviolet discovered by LYMAN in 1916 ($m = 1$) [32] has a longer history in astrophysics and is no less important in the laboratory. Many of you have already devoted years of your lives to enhancing the spectral purity of Lyman- α . And other series of lines were found, before the end of the last century, lines which appeared in astrophysical but not in laboratory sources. PICKERING, in 1896, discovered these first in stellar spectra [33]. Later, FOWLER found a related line at 4686 Å in the sun's chromosphere [34]. The common feature of all these lines was that they fitted Balmer's formula if *half-integral* quantum numbers were permitted. They were at first attributed

to hydrogen, but that was wrong. BOHR, in 1913, [35] gave the correct interpretation, that they belonged to an element having $Z = 2$. Glancing ahead to Bohr's formula $E = -R_H Z^2/n^2$, we write this as $-R_H/(n/Z)^2$ and identify the $\frac{1}{2}$ as $1/Z$. This interpretation was at first doubted, but two further observations settled the matter. One was the refinement of his theory by Bohr in admitting finite nuclear mass M : the replacement of electron mass m_0 by reduced mass $m_0 M/(m_0 + M)$ accounted precisely for small differences in wavelength - which had been noted experimentally - between the hydrogen lines and the Pickering lines; the other was the observation [36] of the line 4686 Å in a discharge which showed no trace of the hydrogen lines.

7. At last, theory: the Old Quantum Theory

Not always emphasised in discussions of Bohr's theory (1913) is its success in accounting for the *stability* of atoms. We should be in trouble, should we not, if there were no stationary states. Right at the beginning of his famous paper [37] BOHR discusses this question of stability: Thomson's model (which is to be discarded) is actually superior to Rutherford's (until Bohr quantizes it) because it allows certain configurations and motions of electrons for which the system is in stable equilibrium.

And observe that Bohr introduces h , not by going to angular momentum, but by way of Planck's quanta of energy and the relation between the harmonic vibrations of an atom and the frequency of the light it emits. The binding energy of the electron is emitted as n quanta of radiation of frequency ν (this is a preliminary postulate, later he talks of single quanta at the harmonic frequency), which frequency is set equal to the average of the orbital frequencies of the electron at infinity, zero, and when bound in a stationary state, ω . So $W = nh\nu = \frac{1}{2}nh\omega$. Now use classical dynamics to relate ω to W and you arrive at the famous equation $W = -\text{const}/n^2$, with angular momentum $= h/2\pi$ as an incidental (though profoundly significant) result. The constant is that combination of e , h , m_0 , c which we now call the Rydberg constant.

8. Fine Structure Explained

But no fine structure - yet - until in 1915 Bohr considered the effect of relativistic variation of mass with velocity in elliptical orbits under the inverse square law of binding, and pointed out that the consequential precessional motion of the ellipses would introduce new periodicities into the motion of the electron, whose consequences would be satellite lines in the spectra. The details of the dynamics were worked out independently by SOMMERFELD [38] and WILSON [39] in 1915/16 based on a generalisation of Bohr's quantization, namely, the quantization of action: the values of the phase integrals $J_i = \oint p_i dq_i$ of classical mechanics should be constrained to assume only integral multiples of h .

To each degree of freedom we now have an independent quantum number, of which one, the space quantum number, has no effect on the energies of the system in free space. The relativistic energy is now

$$E_{\text{rel}} = m_0 c^2 \left\{ 1 + \frac{\alpha^2 Z^2}{\left[n' + \sqrt{k^2 - \alpha^2 Z^2} \right]^2} \right\}^{-\frac{1}{2}}$$

with $n' = 0, 1, \dots, k = 1, 2, \dots$

The energy levels generated by this formula are those you are all entirely familiar with. They are the Dirac energy levels. I need hardly say that α is the fine structure constant, now written as $e^2/\hbar c [\mu_0 c^2/4\pi]$, that you will recognise k as $(j+\frac{1}{2})$ and discover that $(k+n')$ has the same values as our present integer n , which is Bohr's n .

We all know that Sommerfeld's action integrals are no longer taken as the basis of quantization, and we may recall evidence against them from specific heats and from molecular spectra, but, you may say, if they lead to Dirac's energy levels they have a good claim on our attention, haven't they? Did we *have* to give them up?

Yes, we did. They didn't offer a satisfactory basis for predicting the relative *intensities* of spectral lines, and insofar as intensities could be predicted, the predictions were not supported by experiment.

But experiments to resolve the fine structure of the Balmer lines were difficult: as you all know, resolution was impeded by the Doppler broadening of components. So ionized helium comes into the picture, because, as Sommerfeld's formula predicted, fine structure intervals are a function of $(\alpha Z)^2$, so in helium they are of order four times as wide as in hydrogen and one has more chance of resolving the Doppler-broadened lines. So PASCHEN [40], in 1916, undertook an extensive study of the He^+ lines and in particular, 4686 Å ($n = 4 \rightarrow 3$). Fine structure, indeed, was found and matched against Sommerfeld's formula. The measurements were used to determine a value of α . But the structure did not really match the theory in that the quantum numbers bore no imprint of electron spin, so even the orbital properties – which dominated the intensity rules based on a correspondence with classical radiation theory – were wrongly associated with components, and the value of α derived from this first study was later abandoned.

It may surprise you to know that, right up into the nineteen fifties, experimental determinations of the fine structure constant were based upon measurements of spin doublet intervals in X-ray spectra, that is to say, effectively the $2P_{1/2} - 2P_{3/2}$ interval belonging to the hole in the L-shell. But the interpretation at this time rested upon the new form of quantum mechanics, and perhaps more important than the new mathematics, a piece of physics which had first to be discovered: *the spin and magnetic properties of the electron*.

9. The New Quantum Theory

The story is too well known to call for much elaboration here. We simply recall some names and important results.

1925/6 Schrödinger, Heisenberg. Non-relativistic quantum mechanics. Wave equation yields Bohr energy levels.

1928 Goudsmit and Uhlenbeck: electron spin. Thomas: spin-orbit energy. Heisenberg and Jordan: relativistic correction to energy. Net result: recovery of Sommerfeld energy levels, different quantum numbers.

1928. Dirac theory applied to hydrogen. Closed form of solution for energy levels first obtained by TEMPLE [41], 1930.

It is now appropriate to look at an actual term diagram: we choose Balmer- α , figure 1.

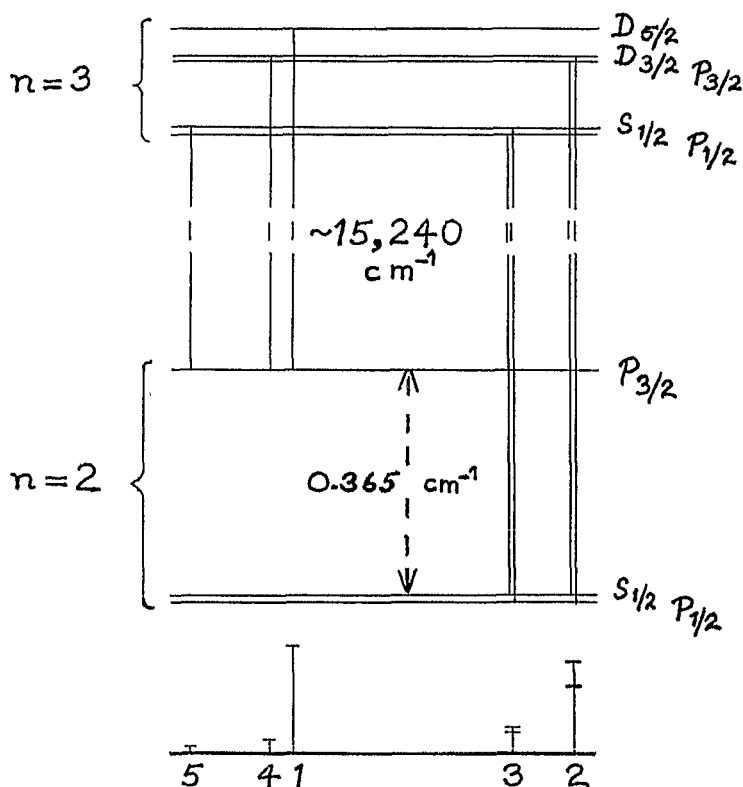


Figure 1 Fine structure of Balmer- α according to the Dirac theory.

We notice the following points:

- (i) the interval 0.365 cm^{-1} in $n = 2$ is the spin-orbit interval $P_{1/2} - P_{3/2}$. This is essentially the doublet interval first observed and measured by Michelson, and is characteristic of all the Balmer lines.
- (ii) levels of the same j but different l (e.g. $S_{1/2}$, $P_{1/2}$) are degenerate. This is certainly the prediction of theory in that the energy eigenvalues are functions of

(n,j) , not of l . But the implications of this and the evidence from experiment was the occasion of profound and protracted controversy in the nineteen thirties: a controversy decidedly settled by the famous experiment of Lamb and Retherford published in 1947.

- (iii) the fine structure is predicted to consist of seven components of which two pairs are degenerate.

10. Experimental Studies of Fine Structure

With improvements in spectroscopic techniques and particularly with the recognition that Doppler broadening was the obstacle to resolution of the fine structure, efforts were concentrated on improving light sources: spectroscopic resolving power was no problem. Resolution was improved by running discharges at low current, by cooling the discharge tubes, and above all by the use of deuterium instead of hydrogen: a factor 1.4 in the reduction of Doppler broadening was thereby gained painlessly. Results of wavelength determinations were used (i) to determine the Rydberg constant (with reliance on the validity of Dirac's energy levels), (ii) to check Dirac's theory (by concentrating on the fine structure), and (iii) to obtain a value for e/m_0 by combining the Faraday constant with values of m_0/M_p derived from measurements of the mass-dependent isotopic shift between the lines of hydrogen and deuterium (about 2 Å for Balmer- α).

Experimental recordings of Balmer- α showed three components: Michelson's doublet - (5,4,1) of fig. 1 appeared as one strong line, 2 as a somewhat weaker line, and 3, weak and barely resolved even in the best work, as the third. Attention focussed on the position of 3. In 1938 the most distinguished schools of spectroscopists were divided as to whether it was, or was not, in the position predicted by Dirac's theory. R.C. WILLIAMS [42] asserted that it was not so, and PASTERNAK [43] pointed out that Williams's observations could be explained on the assumption of an upward shift of the $2S_{1/2}$ level by 0.03 cm^{-1} . And that is how it is.

11. Interaction with Radiation

It is remarkable how enormously successful were the theories of Bohr, Sommerfeld, Schrödinger and Dirac, of an atom in an empty universe. Agreement with experiment is secured before the admission of QED at a level better than 1 part in 10^6 of the total energy. This is an accuracy surpassing all ordinary needs of measurement and statistics. What millionaire knows his fortune to within one dollar, what psephologist can interpret a swing in votes, even of 1%? But physicists know that danger and divergences are hidden in the seemingly-innocuous empty universe, and the vacuum asserted itself powerfully in DIRAC's theory of radiation [44]. The interaction energy between a charged particle and even the zero-point radiation field, which is zero in first order of a perturbation expansion, diverges in second and higher orders. This is not the occasion to introduce QED; I wish merely to emphasise that theorists had been worried

about divergences for twenty years before BETHE, in 1947, produced the first quantitative resolution of the problem [45]. An excellent account of that period has been given by WEISSKOPF [46].

I take it that the experimental work of those days is known to you: the epoch-making determination by LAMB and RETHERFORD, in 1947, of the finite, non-zero value of the $2S_{1/2} - 2P_{1/2}$ interval in hydrogen [47] and the subsequent determination of this interval, of order 1000 MHz, in hydrogen and in deuterium, to an accuracy of 0.1 MHz. Notice how this experiment marks a complete break with classical, optical spectroscopy. Atomic beams rather than gas discharges; stimulated resonances as against the spontaneous decay of excited atoms; the determination of fine structure intervals by direct measurement rather than as the difference between two gross structure lines of enormously greater frequency. Notice also, since Doppler broadening is proportional to frequency, that the microwave spectra are effectively free of it – even when, as some studies have contrived, the microwave resonances are elicited from hydrogen atoms moving randomly in a gas discharge.

Before I turn from fine to hyperfine structure, you will not deny me, I trust, the pleasure of describing my own contribution to the story. In 1947 my thesis supervisor, Heini Kuhn, invited me to 'have another go' at Balmer- α by classical, interferometric spectroscopy, hoping to gain improved resolution and firm confirmation of the Lamb shift by the use of liquid hydrogen as coolant for a gas discharge. The experiment was successful – though the accuracy of our measurement fell short of Lamb's by two orders of magnitude. However, I can claim, in addition to having secured good resolution of component 3, the first observation of component 5, from which it was possible to measure for the first time the displacement of $3S_{1/2}$ from the Dirac position. I went on from this to study the 4686 Å line of He^+ , and here I was able to resolve a pair of components ($3S_{1/2}, P_{1/2} - 4P_{1/2}, S_{1/2}$) which showed the Lamb shift, not as the *displacement* of a component, but as a *splitting* into two distinguishable components of a pair which, on the basis of Dirac's theory, would have been strictly superimposed, one on top of the other.

This work, in its turn, was superseded in the late nineteen fifties and sixties before tunable lasers changed the whole complexion of optical spectroscopy. An account of this period is given in the recently published text: The Spectrum of Atomic Hydrogen: Advances [48].

12. Hyperfine Structure and the g -Factor of the Electron

Barely had spectroscopists absorbed news of the Lamb shift when another bombshell burst: the g -factor of the electron was not exactly 2. You, who (for the most part) have grown up knowing this will find it difficult to realise how shattering it was to see that beautiful symmetry destroyed. The news came also from Columbia in 1947: NAFE, NELSON and RABI [49] discovered that the hfs of the ground state of hydrogen was 1 part in 10^3 larger than its value evaluated from the Fermi formula using $g_e = 2$. There followed a succession of experiments (also described in [48]) whereby the

numerical value of this important interval was progressively sharpened by new techniques in microwave spectroscopy until we arrived at the hydrogen maser – a story in its own right.

To the *theoretical* interpretation of the 1420 MHz value belong also puzzles and controversies centering round the value of α , the fine structure constant. The value obtained from hyperfine structure differed quite significantly from the value obtained from fine structure. That particular controversy is now dead: it was settled in favour of the hyperfine value by determinations of $2e/h$ based on the Josephson effect, and of the gradual building up of confidence in those values. Butressing these values nowadays are determinations of e^2/h from the quantized Hall effect, and most especially, values of α itself obtained by comparing highly accurate determinations of $g-2$ for the free electron with exceedingly far-reaching evaluations of QED formulae.

That brings us to the nineteen eighties, our feet now firmly in the laboratory. But we began with the sky, and let us finish there. In 1945 VAN DE HULST [50] predicted that hydrogen in celestial bodies would make itself felt through radiation at a wavelength of 21 cm, 1420 MHz, corresponding to the ground state hyperfine interval. It was observed in 1957 by EWAN and PURCELL [51] and independently by MULLER and OORT [52]. You will be well aware of the importance of the 21 cm line, the signature of atomic hydrogen, in mapping the sky.

Which of Balmer- α , the 21 cm line, or – nowadays, when we can get above the atmosphere if we have money enough – Lyman- α is the more important line for astrophysicists and cosmologists it would be unprofitable to speculate. But certain it is that our study, the spectrum of atomic hydrogen, takes us deeply into theory and far into the universe, and gives us an inexhaustible mine for employment of the sharpest tools which experimental physics can provide.

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