

THE QUADRATIC ZEEMAN EFFECT
IN HYDROGEN

by

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ABSTRACT

The Balmer series lines in hydrogen corresponding to $n = 5$ and $n = 6$ have been photographed in magnetic fields ranging from 40,000 to 60,000 gauss. It was found, in contradiction to theory, that the π and σ components of the Zeeman pattern were shifted towards the red rather than towards the violet. However, certain anomalies in the line shape of the hydrogen spectra and the position of the no-field hydrogen lines place the validity of the red shift in some doubt. Suggestions are made for further work.

INTRODUCTION

The quadratic Zeeman effect is a displacement toward higher energies of the term values of an atom, proportional to the square of the magnetic field, and to the square of the "radius" of the atom. This results in a displacement of the Zeeman components of any spectral line towards shorter wavelength. In both classical and quantum mechanical treatment of the Zeeman effect, this term is usually neglected because it is unobservable in most cases. However, with the fields made available by the Bitter magnet, and with the spectrograph used, the quadratic shift in the Balmer series is detectable from H_γ on up.

The quantum mechanical expression for the quadratic Zeeman effect was first worked out by Guth.⁽¹⁾ The first experimental observation of the shift was made by Segre⁽²⁾ in a study of the last members of the principal series of sodium. However, the shift could only be detected qualitatively, and no comparison with theory could be made from his measurements. In 1938, Jenkins and Segre⁽³⁾ measured the quadratic shift in the absorption spectra of sodium and potassium. They found excellent agreement with the simple theory as far as $n = 20$. Beyond this they found an additional shift which was interpreted by Schiff and Snyder⁽⁴⁾ as a perturbation of the P levels by F states.

- (1) Guth, Zeit. f. Physik 58, (1929)
- (2) E. Segre, Nuovo Cimento 11, 303 (1934)
- (3) F. A. Jenkins and E. Segre, Physics Rev. 55, 53 (1939)
- (4) L. I. Schiff and H. Snyder, Phys. Rev. 55, 59 (1939)

The usefulness of an experiment on Hydrogen is obvious. In this case there is no inner core of electrons to introduce approximations into the theory. Quantum mechanics should be able to predict, exactly, the results of this experiment.

THEORY

The theoretical expression for the quadratic Zeeman shift can be derived from classical considerations once it can be shown that the effect of spin can be neglected. In a large magnetic field where the magnetic splitting is very much larger than the fine structure separation, l and s are quantized separately around the field direction. In hydrogen this effect begins at fields of about 3000 gauss. In this case the energy of a particular sublevel of a given level may be expressed as:

$$W'(n, l, m_l, m_s) = W_0' + (m_l g_l) \left(\frac{e}{2mc} \hbar H \right) + (m_s g_s) \left(\frac{e}{2mc} \hbar H \right) + f(l, s) + g(H^2);$$

where w^1 is the energy of the sublevel in the field; w_0^1 is the energy of the hypothetical center of gravity of the level in the absence of a field; m_l is the orbital magnetic quantum number; g_l is the orbital "g" factor; m_s is the magnetic quantum number and g_s is the "g" factor associated with the spin; f is the small interaction energy between l and s and $g(H^2)$ is the quadratic shift. In a transition to another state (2), the energy change will be:

$$\Delta W = W_0^1 - W_0^2 + \frac{e}{2mc} \hbar H \left[(m_{l1} g_{l1}) - (m_{l2} g_{l2}) + (m_{s1} g_{s1}) - (m_{s2} g_{s2}) \right] + \Delta f(l, s) + \Delta g(H^2)$$

The energy $f(l, s)$ is of the same order of magnitude as the

doublet separation of a hydrogen level in field free space⁽⁵⁾ and may be neglected compared to the other terms in the energy. Then assuming the g factors to be the same for any level, the energy may be expressed as:

$$\Delta W = W_0^1 - W_0^2 + (\Delta m_l g_l + \Delta m_s g_s) \frac{e \hbar}{2mc} H + \Delta g(H^2).$$

The selection rules for the Zeeman effect in a huge field⁽⁶⁾ (Paschen-Back effect) are:

$$\Delta m_l = \begin{cases} \pm 1 \\ 0 \end{cases} \quad \Delta m_s = 0$$

in any transition. The transition energy may now be written as:

$$\Delta W = W_0^1 - W_0^2 + \Delta m_l g_l \frac{e \hbar}{2mc} H + \Delta g(H^2)$$

showing that the spin drops out in the calculation of energies.

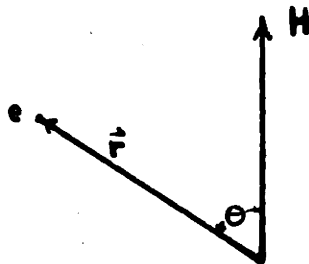


Figure 1.

Consider the situation illustrated in figure 1. A charge e is situated at a distance r from the origin, the

(5) H.E. White; Introduction to Atomic Spectra, first edition, McGraw-Hill Book Co., 1934, p. 164

(6) Ibid., p. 168

radius vector making an angle θ with the field axis. As the field is established, the e.m.f. induced around a circular path whose center is on the field axis is:

$$\epsilon = - \frac{d\phi}{dt} = - \pi r^2 \sin^2 \theta \frac{dH}{dt} .$$

This e.m.f. exerts a torque on the particle of magnitude

$$\tau = r \sin \theta \frac{e\epsilon}{2\pi r \sin \theta} = \frac{e}{2c} r^2 \sin^2 \theta \frac{dH}{dt} = \frac{dG_z}{dt} ;$$

where G_z is the orbital angular momentum of the particle.

$$dG_z = \frac{e}{2c} r^2 \sin^2 \theta dH .$$

This increase in angular momentum increases the magnetic moment (m).

$$dm = - \frac{e}{2mc} dG_z = - \frac{e^2}{4mc^2} r^2 \sin^2 \theta dH .$$

The increase in magnetic moment results in an increase in the energy of the system.

$$dE = - dm \cdot H = \frac{e^2}{4mc^2} r^2 \sin^2 \theta H dH .$$

The total increase in energy in establishing the field is:

$$\Delta E = \frac{e^2}{8mc^2} r^2 \sin^2 \theta H^2$$

To interpret this expression for the hydrogen atom we take the average value of $r^2 \sin^2 \theta$ which is given by: (7)

(7) Guth, Op. cit.

$$\overline{r^2 \sin^2 \theta} = \int \psi r^2 \sin^2 \theta \bar{\psi} d\tau$$

$$\overline{r^2 \sin^2 \theta} = \frac{r_0^2 n^2 [5n^2 - 3l(l+1) + 1] [l^2 + l + m^2 - 1]}{(2l+3)(2l-1)}$$

where r_0 is the radius of the first Bohr orbit, and n is the principal quantum number.

Then, the final expression for the energy increase is:

$$\Delta E = \frac{e^2 r_0^2 H^2 n^2 [5n^2 - 3l(l+1) + 1] [l^2 + l + m^2 - 1]}{8\pi m c^3 (2l+3)(2l-1)}$$

which is exactly the expression given quantum mechanically^(8,9)

(8) Guth, op. cit.

(9) Schiff and Snyder, op. cit.

EXPERIMENTAL

The huge fields required for this experiment were supplied by the large Bitter magnet located in the spectroscopy laboratory at the Massachusetts Institute of Technology. This magnet is essentially an air core solenoid capable of producing fields up to 90,000 gauss over a limited region of the core. The core of the magnet is 2.85 cm. in diameter and 59 cm. long.

The discharge tube was a four meter Wood's tube⁽¹⁰⁾ bent into a U shape with the base of the U running through the magnet. The section of the tube running through the magnet was constructed of 8 mm. quartz tubing with a short section of 2 mm. bore capillary at its center. This part of the tube was water cooled in an effort to reduce the effective temperature of the discharge and the consequent Doppler broadening of the spectral lines.

The discharge was excited with an alternating voltage of approximately 3000 volts. The electrodes were aluminum cylinders 1 inch in diameter and 6 inches long. (It was found that smaller electrodes would not dissipate heat rapidly enough, and would melt.) Small safety electrodes were placed in the vacuum system about two meters behind the main electrodes and grounded in case the discharge should fire back into the system instead of through the tube. "U" tubes filled with glass beads were placed between the main electrodes and the safety electrodes to inhibit this backwards

(10) J. R. Wood, Proc. Royal Society of London 97, (1920)

discharge.

Hydrogen, at a few pounds above atmospheric pressure, was admitted at one end of the system. By forcing the gas to travel through a small, glass capillary leak, and by continuous pumping, the pressure in the system was maintained at approximately 200 microns. The band spectra of molecular hydrogen was kept to a minimum if the gas was used just as it came from the tank, and no attempt made to trap out any impurities.

The light was viewed at an angle of 50 degrees to the field by placing a mirror in the core of the magnet directly over the capillary section of the discharge tube. This particular angle was chosen because at that position the π and σ components of the radiation have roughly equal intensities. The light was then focused on the slit of a 35 foot, concave-grating spectrograph with a resolving power of 90,000, and a dispersion of about 0.8 angstroms per millimeter in the region near 4000 A. Eastman spectroscopic plates, type 103a-o, were used for the exposures. Two spectra of hydrogen at different fields and one at zero field were taken on the same plate along with two iron spectra, one at the top, and one at the bottom of the plate. The separation of the iron lines served to determine the dispersion of the spectrograph, and the corresponding lines in the two spectra were used to define a vertical line on the plate so that the displacement of the Zeeman components of the hydrogen lines from the no field lines could be accurately measured.

Lines in the Balmer series corresponding to $n = 5$ and $n = 6$ were photographed at four different fields, the exposures being 5 minutes for $n = 5$ and 15 minutes for $n = 6$. Exposures of an hour and a half did not bring out the line corresponding to $n = 7$ with sufficient intensity for measurements to be made.

DATA AND CALCULATION

The position of the spectral lines was measured on a comparator which projected an enlarged image of the lines onto a ground glass screen. Measurements were made with respect to fiducial marks on this screen. The spectrum plates were mounted on a carriage which could be moved both horizontally and vertically by means of micrometer screws accurate to a ten-thousandth of an inch. The plate was positioned vertically by adjusting it so that corresponding lines in the two iron spectra would appear at the same place on the screen when only the vertical screw was turned.

In the course of each measurement of the relative positions of the Zeeman components and the no field line, the plate was moved in only one direction to eliminate the effect of backlash in the screw. The separation of the two σ components, the quadratic shift of the center of gravity of the σ components, and the shift of the π component were computed for each traverse of the plate. In all, ten traverses of each plate were made, and the results averaged. The value of the splitting of the σ components is accurate to better than one percent. Since two lines (corresponding to $n = 5$ and $n = 6$) were photographed at each value of the field, the separations were averaged and the field computed from the relation:

$$\Delta \bar{\nu} = 4.67 \times 10^{-5} H$$

where $\Delta \bar{\nu}$ is $1/2$ of the separation of the σ components in

wave numbers (cm.^{-1}) and H is in gauss.

The average value and standard deviation of the measured shifts are presented in table II. The standard deviation is defined as that range of values within which 68% of the measured values would lie if a very large number of measurements were taken. It is computed from the relation:

$$\sigma^2 = \frac{1}{n-1} \sum_{i=1}^n (\bar{x} - x_i)^2$$

where σ is the standard deviation, n is the number measurements made, \bar{x} is the average value of the measurements, and x_i is the value of an individual measurement.

There is a certain difficulty involved in computing the theoretical shifts. Even neglecting the effect of spin, each component of a Zeeman pattern contains five components - one from the $2p - n s$ transition, one from the $2S - nP$ transition, and three from the $2P - nD$ transition. Each of these has a different quadratic shift. How, then does one compute the theoretical shift of the composite line? The problem is partially solved by noting the relative intensities of the various transitions. The Handbuch der Physik lists them as follows. (11)

n	2S-nP	2P - nS	2P - nD
5	1.61	2.20	15.0
6	1.73	2.00	14.4

(11) Handbuch der Physik, Vol. 24, p. 445

Since the 2S - nP and the 2P - nS transitions are relatively weak, they can be neglected, and only the 2P - nD transitions considered. It is now necessary to weight the quadratic shift of each of the three transitions making up a Zeeman component with the intensity of the corresponding transition. This will give an expression which will correspond to the shift of the center of gravity of an observed Zeeman line. The relative intensities are given in table I, and were derived by K. Darwin.⁽¹²⁾

	$(m_1)_D$	$(m_1)_P$	Relative Intensity
$m = +1$	0	+1	15
	-1	0	45
	-2	-1	90
$m = 0$	1	1	90
	0	0	120
	-1	-1	90
$m = -1$	2	1	90
	1	0	45
	0	-1	15

TABLE I

Relative intensities of the various 2P - nD transitions which make up a given component of a Zeeman pattern in a strong magnetic field.

(12) K. Darwin, Proc. Royal Soc. of London 118, 264 (1928)

With the data on relative intensities and the equation for the quadratic shift:

$$\Delta E = \frac{e^2}{8mc^2} \mu_B^2 H^2 n^2 \frac{[5n^2 - 3l(l+1) + 1] [l^2 + l + m^2 - 1]}{(2l+3)(2l-1)}$$

the theoretically expected shift may be computed.

TABLE II

Experimental and theoretical values of the shift of the Zeeman pattern

Magnetic field (gauss)	n = 5			
	π shift (cm. ⁻¹)		σ shift (cm. ⁻¹)	
	exp.	theor.	exp.	theor.
43700	0.089 ± 0.033	0.00777	0.12 ± 0.026	0.0107
52900	0.34 ± 0.029	0.00974	0.37 ± 0.025	0.0135
54400	0.24 ± 0.033	0.0103	0.20 ± 0.030	0.0143
59100	0.20 ± 0.044	0.0122	0.24 ± 0.031	0.0168
n = 6				
Magnetic field (gauss)	n = 6			
	π shift (cm. ⁻¹)		σ shift (cm. ⁻¹)	
	exp.	theor.	exp.	theor.
43700	0.20 ± 0.052	0.0171	0.11 ± 0.019	0.0237
52900	0.45 ± 0.027	0.0215	0.52 ± 0.022	0.0296
54400	0.36 ± 0.069	0.0227	0.36 ± 0.040	0.313
59100	0.51 ± 0.072	0.0269	0.41 ± 0.049	0.371

The data shown in table II is illustrated graphically in figures II and III.

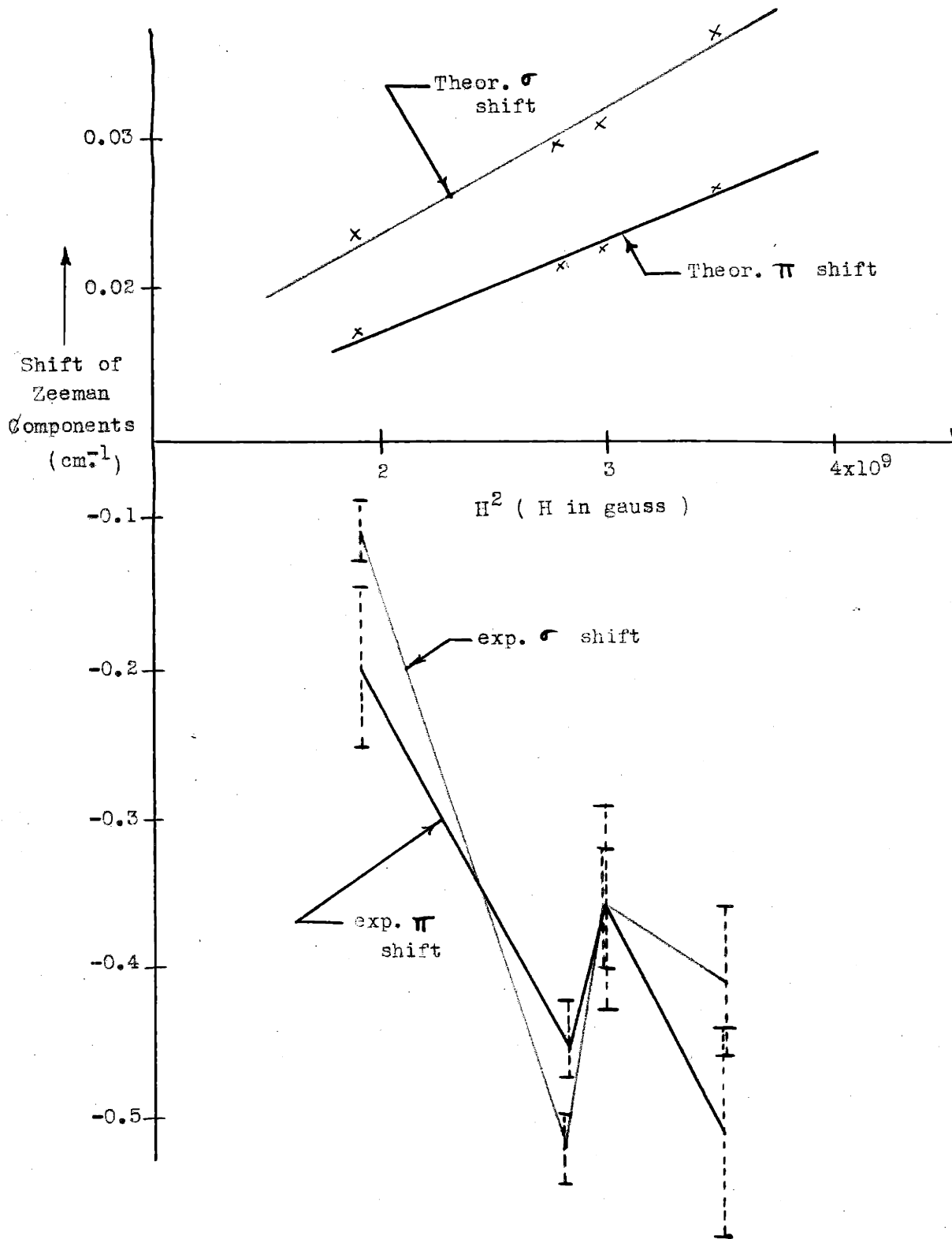


Figure 3

Experimental and theoretical values for the σ and π shifts in the 2P - 6D transition. Note the difference in scale between the positive and negative vertical axis.

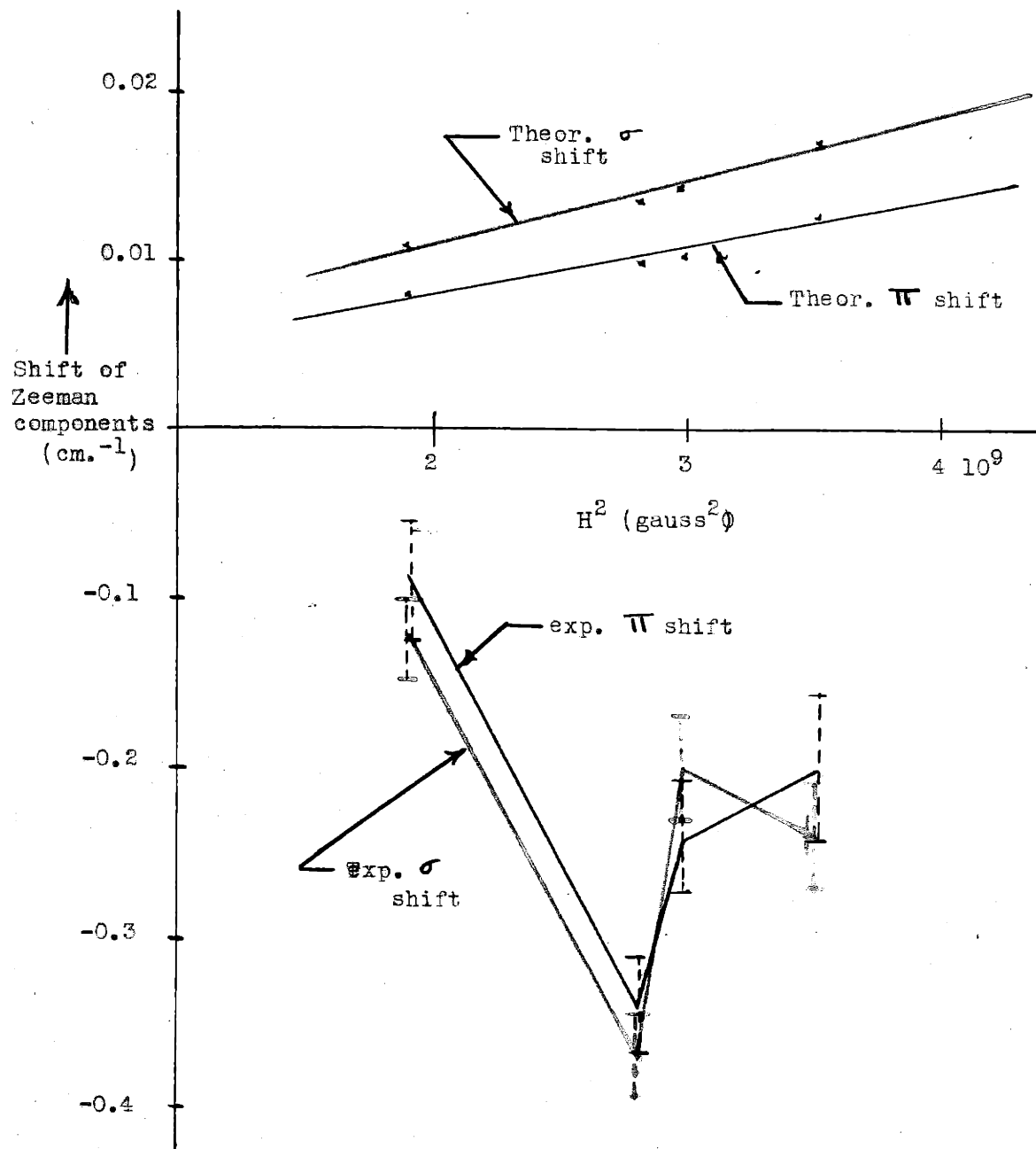


Figure 2

Experimental and theoretical values for the σ and π shifts in the 2P - 5D transition. Note the difference inscale between the positive and negative vertical axis.

In examining the plates, two anomalies were noted. On one plate the no-field hydrogen line was shifted from the position it should occupy, as calculated from the iron spectra. On the other plate, the no-field line fell exactly at the position it should occupy. In any case, the shifts were measured from the actual position of the no field line. No explanation has as yet been evolved for this "false" shift.

Second, is the line shape. All of the hydrogen lines, with and without the magnetic field, show a trapezoidal shape as illustrated in figure IV.



figure IV

Typical shape of a hydrogen line.

It was at first thought that this line shape might be caused by a rotation of the slit of the spectrograph; that is, the slit and the lines on the grating not being parallel. However, this hypothesis was discarded, for the fact that the plate in the spectrograph was masked so as to allow only a small section of it to be used would eliminate this effect in the central region of the plate where the hydrogen spectra were photographed. The trapezoidal line shape must, then, also be considered as unexplained.

DISCUSSION

As can easily be seen from figures II and III and table II, the experimental shifts are ten times larger than the theoretical shifts and in the wrong direction. That is, the lines are shifted toward lower energies instead of higher. While it is true that one could draw almost any shaped curve one desired through the range of measured shift values indicated on the graphs, there can be no doubt that the measured shifts are towards lower energies. Speaking statistically, using the "99%" deviation for the range of measured values still does not allow the range to cross the axis to shifts towards higher energies. (The "99%" deviation is 2.58 times the standard deviation and is that range of values within which 99% of the measured values of its shift would lie if a very large number of measurement were taken.)

It is extremely improbable that changes in the temperature of the grating could have caused this shift. It is true that a change of 3 or 4 degrees in the grating temperature would change the line spacing on the grating enough to shift the pattern by the required distance. However, the temperature change would have to occur as a step function to produce a shift between the hydrogen spectra with field and the hydrogen spectra without field since the second of these exposures was taken immediately following the first. Besides this, the temperature of the room where the grating is located does not fluctuate by more than a degree; and the low conductivity of the grating which is ruled on a one-

inch thick, pyrex disk, eight inches in diameter, would make its temperature fluctuation much less than those of the room. For the same reasons, temperature changes cannot explain the shift of the no-field hydrogen lines relative to the iron spectra since the two iron spectra were taken immediately after the no-field hydrogen spectra.

One might attempt to explain the shift on the basis of the quadratic Stark effect. However, as we shall see, the fields required are inconsistent with the line width. Since any electric fields present in the discharge will be inhomogeneous and randomly oriented, the first order Stark effect would cause a broadening of any spectral line and the second order effect would cause a shift in the position of the line. A rough calculation of the quadratic Stark shift may be made using the graph in White's Introduction to Atomic Spectra.⁽¹³⁾ For the line H_{γ} , corresponding to the 2P-5D transition, the electric field required to shift the line by 0.3 wave number (cm^{-1}) is approximately 50,000 volts-per-cm. The line width is approximately 1.0 wave number. Doppler broadening accounts for 0.1 wave numbers of the broadening, but let us assume that all of it is due to the first order Stark effect. The expression for this effect⁽¹⁴⁾ is:

$$\Delta T = 6.42 \times 10^{-5} n (n_2 - n_1) F$$

(13) H. E. White; op.cit. p. 412

(14) Ibid; p. 402

where $\Delta\Gamma$ is the shift in wave numbers; n is the principal quantum number; n_2 and n_1 are the electric quantum numbers; and F is the electric field strength. The maximum electric field for a given shift will occur when $(n_2 - n_1)$ has its smallest value, which is one. The wave number shift involved here is half the line width. In this case $n = 5$. Then:

$$F = \frac{0.5}{5 \times 6.47} \times 10^5 = 1,600 \text{ volts/cm.}$$

The maximum value of the field compatible with the line width is completely incompatible with the field required to explain the shift, the difference being a factor of 30. Actually, these figures are not as conclusive as they seem to be. No one has, as far as the author has been able to determine, calculated the effect of the Stark effect on the components of the Paschen - Back effect. However, the figures probably give a rough idea of how things would go; and they do make it very doubtful that the Stark effect could have caused the red shifts observed in this experiment.

CONCLUSION

The results of this experiment appear to indicate the need for further work on this subject. Whether or not the red shift of the Zeeman pattern described herein is due to some as yet undiscovered fault in the apparatus, its origin should be settled to clear the way for subsequent investigation of the quadratic Zeeman shift, and other studies in hydrogen.

It appears that the simplest way to further investigate this problem is spectroscopically, in emission, as was done here. Microwave resonances between the Zeeman sublevels are difficult because of the problem of obtaining a sufficient number of atoms in an excited state, and the difficulty of handling the short wavelengths involved (on the order of millimeters). Absorption experiments are also difficult; first because the magnetic field is required to be uniform over the length of the absorbing column which must be fairly long to get reasonable intensities; and second, because the absorption spectra of hydrogen (the Lyman series) lies in a region in which it is extremely difficult to work - the vacuum ultraviolet.

With more time available for work with the discharge tube in the magnet core, a more thorough investigation could be made. A procedure similar to that used here is recommended with two modifications. The diameter of the central portion of the discharge tube should be increased to reduce the effective electric field and the consequent Stark broadening.

Also, the light should be viewed parallel to the field to increase the intensity of illumination entering the spectrograph. This could be accomplished without smearing out the lines by portions of the discharge in different parts of the field by using a tube such as illustrated in figure V. With these modifications,



figure V

Discharge tube to allow viewing light parallel to field.

and with plenty of time, the questions raised in this paper might be conclusively answered.

In conclusion, I would like to thank Prof. F. Bitter for his invaluable aid in this experiment. I would also like to thank Dr. J. E. Archer of the spectroscopy laboratory for his help in spectroscopic matters.