

The Rydberg Constant and the Atomic Mass of the Electron*

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A re-evaluation of the spectroscopic data pertinent to the Rydberg constant and the atomic mass of the electron yields the values $R_\infty = 109737.326 \pm 0.014 \text{ cm}^{-1}$ and $m = (54.895 \pm 0.008) \times 10^{-6} \text{ amu}$. If the "micro-wave" value of the electron atomic mass, $m = (54.8785 \pm 0.0019) \times 10^{-6}$, is used, the Rydberg constant is $R_\infty = 109737.311 \pm 0.012 \text{ cm}^{-1}$. It is furthermore concluded that Houston's and Chu's data can be brought into agreement with that of Drinkwater, Richardson, and Williams by ascribing the discrepancy to differences in wavelength standards used by these investigators.

INTRODUCTION

IN 1941 Birge¹ published a careful study of the existing experimental data on the $H\alpha$ and $D\alpha$ lines and reached the conclusion that the Rydberg constant had the value $R_\infty = 109737.303 \pm 0.017 \text{ cm}^{-1}$ (international angstrom scale). The existence of the recently discovered fine structure splitting of the spectrum of hydrogen²⁻⁴ and ionized helium⁵⁻¹¹ has indicated that small corrections must be made to the previously accepted Dirac theory. Since these corrections modify the predicted positions of the electronic energy levels, they inversely modify also the value of the Rydberg constant as inferred from the observed positions of those levels. The observed energy difference of $1062 \pm 5 \text{ Mc}$, for example, in the $2S_{1/2} - P_{1/2}$ level of hydrogen implies a shift of 0.035 cm^{-1} in the wave number of the $3P_{3/2} - 2S_{1/2}$ transition; this in turn produces a shift of 0.010 cm^{-1} in the apparent position of the $H\alpha_2$ line, which is a blend of the $3P_{3/2} - 2S_{1/2}$ transition and the $3D_{3/2} - 2P_{1/2}$ transition with relative intensities¹² 2.08 and 5. If this line then is used to determine the hydrogen Rydberg constant, this shift will introduce an error of 0.072 cm^{-1} , which is well outside the accuracy with which the Rydberg can be determined. Furthermore, the shifts in energy levels have bearing on the spectroscopic determination of the atomic mass of the electron, which can be an important source datum in the more general question of the best values of the fundamental atomic constants.

* This investigation was carried out as a preliminary to a general re-evaluation of the values of the atomic constants by J. W. M. DuMond and the author, at the request of the National Research Council Committee on Constants and Conversion Factors, and serves in part as a report to that committee.

¹ R. T. Birge, Phys. Rev. **60**, 766 (1941).

² W. E. Lamb, Jr., and R. C. Retherford, Phys. Rev. **72**, 241 (1947); **75**, 1325 (1949); **79**, 549 (1950).

³ H. Kuhn and G. W. Series, Nature **162**, 373 (1948).

⁴ H. Kuhn and G. W. Series, Proc. Roy. Soc. (London) **202**, 127 (1950).

⁵ W. E. Lamb, Jr., and M. Skinner, Phys. Rev. **78**, 539 (1950).

⁶ J. E. Mack and N. Austern, Phys. Rev. **72**, 972 (1947); **73**, 1233 (1948); **74**, 1262 (1948).

⁷ G. R. Fowles, Phys. Rev. **73**, 639 (1948); **74**, 219 (1948).

⁸ H. Kopfermann and W. Paul, Nature **162**, 33 (1948).

⁹ Murakawa, Suwa, and Kamei, Phys. Rev. **76**, 1721 (1949).

¹⁰ Kopfermann, Krüger, and Öhlmann, Z. Physik **126**, 760 (1949).

¹¹ J. G. Hirshberger and J. E. Mack, Phys. Rev. **77**, 745 (1950).

¹² A. Sommerfeld and A. Unsöld, Z. Physik **38**, 237 (1926).

FINE STRUCTURE OF HYDROGEN AND HELIUM

The theoretical formula for the Lamb shift has been given by several authors¹³⁻¹⁶ and can be written as

$$\Delta E(n, 0, 1/2) = \frac{8Z^4 \alpha^3 R}{n^3 3\pi} \left[\ln \frac{\mu}{k_0} - \ln 2 + \frac{19}{30} \right], \quad l=0$$

$$\Delta E(n, l, j) = \frac{8Z^4 \alpha^3 R}{n^3 3\pi} \left[\ln \frac{\alpha^2 \mu}{2k_l} + \frac{3(j-l)}{2(2j+1)(2l+1)} \right], \quad l \neq 0$$

where $\mu = mc^2$, $\alpha = "1/137" = e^2/\hbar c$, $k_l =$ average excitation energy, and $R =$ Rydberg constant associated with the atom in question.

The most complete calculation of the logarithmic terms seems to be that of Bethe, Brown, and Stehn¹⁶, who give $\ln(2k_0/\alpha^2\mu) = 2.8121$ and $\ln(2k_l/\alpha^2\mu) = -0.0300$ for the $2S$ and $2P$ states of hydrogen. These values lead to a Lamb shift of 1051.4 megacycles. Baranger¹⁷ has calculated the corrections to this shift, which are of order α^6 , involving the effects of vacuum polarization. These much smaller quantities contribute an additional 6.89 megacycles which brings the Lamb shift to 1058.3 megacycles, in reasonably good agreement with the observed value² of 1062 ± 5 .†

For the helium II spectrum the observed⁵ Lamb shift is 14020 ± 100 megacycles for the $2S - 2P$ separation. The computed value is 14040 megacycles, including Baranger's correction term. (The shift as inferred from the calculations of Bethe, Brown, and Stehn is 13820 megacycles, and on the assumption that the proper parameter is αZ , the Baranger correction increases this by 220 megacycles).

Because of the somewhat uncertain theoretical values (there may still be further corrections of the order of a

¹³ H. A. Bethe, Phys. Rev. **72**, 339 (1947).

¹⁴ J. B. French and V. F. Weisskopf, Phys. Rev. **75**, 1240 (1949).

¹⁵ N. M. Kroll and W. E. Lamb, Jr., Phys. Rev. **75**, 388 (1949).

¹⁶ Bethe, Brown, and Stehn, Phys. Rev. **77**, 370 (1950).

¹⁷ M. Baranger, Phys. Rev. **84**, 866 (1951).

† Note added in proof⁹—W. E. Lamb, Jr., and R. C. Retherford, Phys. Rev. **86**, 1014 (1952), give a final result for the experimentally determined shift in hydrogen of $1058.27 \text{ Mc} \pm 1.0 \text{ Mc}$ (limit of error) to be compared with a calculated shift (including further corrections for anomalous magnetic moment of the electron and reduced mass effects) 1057.27 Mc . These corrections have negligible effect on the present analysis since 3 Mc corresponds to only 0.0001 cm^{-1} .

TABLE I. Calculated fine structure of hydrogen^a and helium.^b The line positions are given relative to the "Balmer line,"

$$W = R(n_0^{-2} - n_1^{-2}).$$

	Transition	Intensity	Position cm ⁻¹	Position of peak cm ⁻¹
H	3S _{1/2} -2P _{3/2}	0.2	-0.06092	-0.06092
	3D _{3/2} -2P _{3/2}	1.0	0.03687	0.06937
	3D _{5/2} -2P _{3/2}	9.0	0.07298	
	3P _{1/2} -2S _{1/2}	1.04	0.25900	0.26303
	3S _{1/2} -2P _{1/2}	0.1	0.30492	
	3P _{3/2} -2S _{1/2}	2.08	0.36740	0.39234
	3D _{3/2} -2P _{1/2}	5.0	0.40271	
H	4S _{1/2} -2P _{3/2}	0.2	0.02114	0.02114
	4D _{3/2} -2P _{3/2}	1.0	0.06244	0.07615
	4D _{5/2} -2P _{3/2}	9.0	0.07767	
	4P _{1/2} -2S _{1/2}	1.04	0.34752	0.34752
	4S _{1/2} -2P _{1/2}	0.1	0.38698	0.41755
	4P _{3/2} -2S _{1/2}	2.08	0.39325	
	4D _{3/2} -2P _{1/2}	5.0	0.42828	
He	4F _{7/2} -3D _{5/2}	2.803	0.1968	0.1968
	4D _{5/2} -3P _{3/2}	1.073	0.6514	0.6526
	4F _{5/2} -3D _{3/2}	1.962	0.6532	
	4S _{1/2} -3P _{1/2}	0.156	1.4699	1.4699

^a The hydrogen spectrum values can be adapted to deuterium simply by multiplying by the scale factor $R_D/R_H = 1.00027$.

^b The complete He pattern consists of 13 lines but most of these are low intensity and have never been carefully measured or even observed. Only those components are listed which have been measured.

few megacycles), we have chosen in the present calculation to use the experimentally observed separation rather than the theoretical ones. This choice is actually inconsequential with respect to the numerical results, since the spectroscopic data which we shall analyze do not have sufficient resolution more than merely to indicate the existence of this shift. The use of experimental values rather than theoretically computed ones is, however, to be preferred for logical reasons. We have, specifically, set the logarithmic term equal to zero for $l \neq 0$ and have used the observed separation to determine the value of the logarithmic term for $l = 0$.

We have furthermore assumed k_0 to be independent of the principal quantum number, n ; this is actually very nearly true. Such an assumption probably is not independent of the assumption that k_l is zero for all except s states and is consistent with it. This procedure cannot be completely justified, but it can be excused on the basis that it appears to be an adequate approximation within the accuracy of the experimental data.

The quantity $\Delta E(n, l, j)$ as given above is the value of the shift of the level away from the "Dirac position", and hence the complete formula for the energy levels is

$$E(n, l, j) = -\frac{1}{n^2}R - \frac{\alpha^2}{n^3}R \left[\frac{2}{2j+1} - \frac{3}{4n} \right] + \Delta E(n, l, j).$$

The pertinent experimental data are concerned with the transitions $n_1=3 \rightarrow n_0=2$ and $n_1=4 \rightarrow n_0=2$ for hydrogen and $n_1=4 \rightarrow n_0=3$ for helium. In each case we can define the "Balmer line" by the relation $W = R(n_0^{-2} - n_1^{-2})$ and calculate the expected pattern relative to it. The Balmer line, of course, is a fictitious

line and is the energy level if the fine structure were nonexistent. The theory allows us to determine the energy shift of an observed line from the Balmer line, however, and from this latter, the Rydberg constant is easily computed. In determining the shift of a line only an approximate value of the Rydberg constant is necessary, since the shifts are relatively small. In this way the shifts tabulated in Table I have been computed, and the fine structure pattern for hydrogen is shown in Fig. 1. In general, the individual lines cannot be separated—an observed line is actually a blend of two or more unresolved components and the position of the peak is determined by the superposition of the various component lines. The actual determination of this position depends on the line widths as well as their separations and intensities. A simple first-order approximation has been used that if lines are closer together than their half-widths (so that no indication of a double peaked pattern is present), the observed peak is at the center of gravity of the complex; while if two lines are well separated, one of them may cause an asymmetry in the wings of the other but there will be only a negligible shift in the peak. Fortunately, a clear separation between "close" lines and "far" lines is possible in the patterns being considered. The last column of Table I lists the position of the observed peak as the center of gravity of the components which, as indicated by the braces, fall close enough together so as to be unresolved.

OBSERVATIONAL DATA

The pertinent observations on the fine structure of hydrogen, deuterium, and helium are the data of

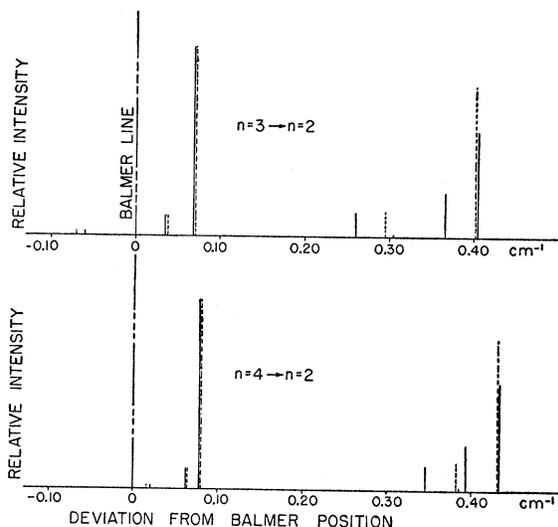


FIG. 1. Fine structure pattern for hydrogen. A comparison of the pattern with and without the Lamb-Retherford shift. The dotted lines represent positions and intensities of the Dirac-Sommerfeld pattern. The solid lines represent the positions and intensities including the line-splitting which results from the new electrostatics.

Houston,¹⁸ Drinkwater, Richardson, and Williams,¹⁹ and Chu.²⁰ We have gone back to Houston's original paper and have decided to use all of Houston's data rather than merely the long wavelength components in calculating the Rydberg. Houston himself points out, "the asymmetry in the short wavelength component is so pronounced that it is possible to determine the position of the third component which is causing it (i.e., this third component is the $3P_{1/2}-2S_{1/2}$ transition). This is the component predicted by the theory of Sommerfeld and Unsöld and which has previously been inferred from the displacement of the maximum. . . . Because of this asymmetry, only the long wavelength component is used in the computation of the Rydberg constant." The theory of the hydrogen fine structure, however, seems to be adequately well confirmed by experiment that we feel no concern in using *all* of the experimental data, in connection with the theoretical predictions of the fine structure pattern, in the present analysis. Even the previous discrepancy in the doublet separation, in which the observed separation is less than the theoretical value, has now been fully explained. The conclusion that the discrepancy could be resolved by an arbitrary *ad hoc* shift in the energy of the n^2S levels^{21,22} has been completely confirmed by the measurements of this shift (the Lamb-Retherford shift), which is the reason for the present re-examination of the entire question.

We have similarly reviewed the data of Drinkwater, Richardson, and Williams and feel confident in using both components of the doublet in our analysis. The reproducibility in the individual measurements of DRW leads, however, to probable errors which are unrealistic. This can best be seen if we compare the separation of the two main peaks with its theoretical value. DRW measure $0.3198 \pm 0.0010 \text{ cm}^{-1}$ to be the separation between what they call line 14 and line 2 in $H\alpha$ and $0.3205 \pm 0.0010 \text{ cm}^{-1}$ for the corresponding separation in $D\alpha$. The theoretical value, including the effects of the blending of components 1 and 4 and the Lamb splitting of component 2 is 0.3230 cm^{-1} for $H\alpha$ and 0.3231 cm^{-1} for $D\alpha$. The extent of the disagreement can also be exhibited in terms of the value of α which would be implied by the measured separations. We find $1/\alpha = 137.72 \pm 0.15$ from hydrogen and $1/\alpha = 137.44 \pm 0.15$ from deuterium, compared with the value given by DuMond and Cohen²³ as 137.043. (It might be pointed out that if we had tried to calculate $1/\alpha$ from the measured separations on the basis of the Dirac theory without the Lamb shift we would have obtained $1/\alpha = 139.65$.) For this reason we have used the quoted errors only to determine relative weights to be assigned

¹⁸ W. V. Houston, Phys. Rev. **30**, 608 (1927).

¹⁹ Drinkwater, Richardson, and Williams, Proc. Roy. Soc. (London) **174**, 164 (1940).

²⁰ D. Y. Chu, Phys. Rev. **55**, 175 (1939).

²¹ E. C. Kemble and R. D. Present, Phys. Rev. **44**, 1031 (1932).

²² S. Pasternack, Phys. Rev. **54**, 1113 (1938).

²³ J. W. DuMond and E. R. Cohen, Phys. Rev. **82**, 555 (1951).

TABLE II. Observational data for the calculation of the Rydberg constant.^a

Wavelength (air) angstroms	Wave number (vacuum) cm^{-1}	Balmer line cm^{-1}	Rydberg cm^{-1}	Source
6562.7110 ± 0.0018	15233.3972 ± 0.0041	15233.0049 ± 0.0041	109677.635 ± 0.030	$H\alpha_1$, Houston
6562.8473 ± 0.0009	15233.0811 ± 0.0021	15233.0117 ± 0.0021	109677.684 ± 0.015	$H\alpha_2$, Houston
	15233.3868 ± 0.0016	15232.9945 ± 0.0016	109677.560 ± 0.012	$H\alpha_1$, DRW
	15233.0670 ± 0.0014	15232.9976 ± 0.0014	109677.583 ± 0.010	$H\alpha_2$, DRW
	15233.2551 ± 0.0021	15232.9921 ± 0.0021	109677.543 ± 0.015	$H\alpha_3$, DRW
4861.2800 ± 0.0013	20564.9695 ± 0.0055	20564.5520 ± 0.0055	109677.610 ± 0.029	$H\beta_1$, Houston
4861.3578 ± 0.0022	20564.6405 ± 0.0092	20564.5643 ± 0.0092	109677.676 ± 0.049	$H\beta_2$, Houston
	15237.5317 ± 0.0014	15237.1393 ± 0.0014	109707.403 ± 0.010	$D\alpha_1$, DRW
	15237.2112 ± 0.0013	15237.1418 ± 0.0013	109707.421 ± 0.009	$D\alpha_2$, DRW
	15237.4127 ± 0.0021	15237.1496 ± 0.0021	109707.477 ± 0.015	$D\alpha_3$, DRW
4685.7030 ± 0.0012	21335.5431 ± 0.0055	21334.8905 ± 0.0055	109722.294 ± 0.028	He, Houston
4685.8030 ± 0.0026	21335.0879 ± 0.0118	21334.8911 ± 0.0118	109722.297 ± 0.060	He, Houston
4685.7017 ± 0.0014	21335.5490 ± 0.0063	21334.8964 ± 0.0063	109722.324 ± 0.033	He, Chu
4685.8012 ± 0.0020	21335.0961 ± 0.0090	21334.8993 ± 0.0090	109722.339 ± 0.048	He, Chu
4685.5313 ± 0.0032	21336.3247 ± 0.0145	21334.8874 ± 0.0145	109722.278 ± 0.074	He, Chu

^a As indicated by the errors associated with these observations, retaining 4 decimal places in the wave numbers cannot be justified in all cases. The measurements have all been carried through with four decimal places as a matter of consistency and to be certain that rounding-off errors would not build up additional uncertainties.

to the data and have made use of the external consistency to define the actual errors.

Chu's measurements are taken as he reported them. Birge¹ raises the question of excluding one of Chu's four plates on the basis that the doublet separation measured there is inconsistent with the separation measured on the other three plates. Birge, however, does not notice this inconsistency in the original data but finds it only when he has computed $1/\alpha$ from each of the four plates separately. It then appears that plate 126 yields $1/\alpha = 139.790$, compared to the other three values 137.314, 136.971, and 136.971. (These are the actual figures quoted by Birge and calculated in his 1941 paper. They do not include corrections for the Lamb shift,²⁴ but the discussion would not be affected if this refinement were made since we are not interested here in the value of the fine structure constant but only in the consistency of the data.) On this basis, then, Birge questions retaining plate 126, but he does not actually exclude it. If, however, we look at the errors involved in these determinations of $1/\alpha$, we see a different picture. The values are $1/\alpha = 139.8 \pm 1.8$, compared to $1/\alpha = 137.3 \pm 1.2$, 137.0 ± 1.2 , 137.0 ± 1.4 . Plate 126 therefore differs from the other three by an amount

²⁴ Corrected for the modification in fine structure pattern due to the Lamb shift, these values would all be raised by 0.076.

which is less than twice the error in this difference, and it would seem unwise to exclude it since the results would, in such a case, appear to have much better consistency than should reasonably be ascribed to them.

The data from all three sources are tabulated in Table II. Houston's and Chu's measurements of wavelengths in air have been corrected to vacuum using Barrell and Sears' formula²⁵ for refractive index:

$$(\mu-1)\times 10^6 = 272.581 + 1.5453/\lambda^2 + 0.01268/\lambda^4,$$

with λ in microns. This formula gives μ correctly to better than 1 part in 10^8 . The data of DRW are given by them directly in terms of vacuum wave numbers using this expression for index of refraction, so that their results require no further correction.

Houston's measurements, as well as Chu's, are based on the value 5015.6750A for the He line. This line was measured relative to the cadmium line 6438.4696A, which is the defining standard of length, by Merrill²⁶ who gave the wavelength as 5015.675A and to which he appends the comments, "From the number and internal agreement of the individual determinations it seems that an error larger than 0.003A is scarcely to be expected."²⁷ Merrill's actual data list seven observations ranging from 0.673 to 0.677 for the fractional part of the wavelength, with a mean of 0.6752 ± 0.0008 . In a survey of other measurements, however, he quotes a value of 0.678 measured by Lord Rayleigh and 0.679 by Priest. Now an increase of one milliangstrom in the accepted wavelength of this line will reduce the value of the Rydberg as inferred from the data of Houston or Chu, who use this line as their standard of length, by 0.022 cm^{-1} , and this is neither a negligible nor an improbable correction. Therefore, it is evident that in our analysis of the measurements of the Rydberg constant we cannot exclude the possibility that Houston and Chu used a wavelength standard which is different than that used by Drinkwater, Richardson, and Williams merely due to the fact that, relative to the cadmium line whose *defined* wavelength in air is 6438.4696A, the helium line actually has a wavelength which is somewhat different than 5015.6750A. We shall use as the measured wavelength of this line relative to the cadmium line

$$\lambda = 5015.6752 \pm 0.0015 \quad (\text{standard deviation}),$$

where the error has been somewhat arbitrarily chosen to allow for possible systematic errors in Merrill's measurements. In our least squares analysis of all of the pertinent experimental data, it will now be necessary

²⁵ H. Barrell and J. E. Sears, Jr., *Trans. Phil. Soc.* **238**, 1 (1949).

²⁶ P. W. Merrill, *Astrophys. J.* **46**, 357 (1917).

²⁷ In a recent private communication Dr. Merrill informed the author that he would now say that a correction of 0.002A or 0.003A might not be at all inconceivable. It was his feeling, furthermore, that with present day techniques (the original measurements were made in 1917) improved accuracy for the wavelength of this line could easily be attained and that on the basis of this discrepancy such a measurement should probably be undertaken.

to include this as an observational equation and to include as part of the results of our least squares fitting the "best" value of this wavelength.

In addition to these measurements of wavelengths, measurements of the isotopic shift are useful in determining the atomic mass of the electron, although they give no direct information on the value of the Rydberg constant. The separation between the $H\alpha$ lines and the $D\alpha$ lines has been carefully measured by several investigators. The $H\alpha$ Balmer line is given by

$$\bar{\nu}_H = \frac{5}{36}R_H = \frac{5}{36}R_\infty \frac{H-m}{H},$$

and the $D\alpha$ Balmer line is given by

$$\bar{\nu}_D = \frac{5}{36}R_D = \frac{5}{36}R_\infty \frac{D-m}{D},$$

where m =atomic mass of the electron, H =atomic mass of the hydrogen atom, and D =atomic mass of the deuterium atom. These expressions give us

$$m = \frac{36HD}{5(D-H)} \frac{\bar{\nu}_D - \bar{\nu}_H}{R_\infty}.$$

Using the values of Li, Whaling, Fowler, and Lauritsen²⁸ for the atomic masses $H=1.008142$ and $D=2.014735$, we find (note that it is adequate here to use an approximate value of $R_\infty=109737.3$)

$$m = (13.2393 \times 10^{-5})(\bar{\nu}_D - \bar{\nu}_H)$$

for the atomic mass of the electron, when the isotopic shift is measured in vacuum wave numbers. The error in this coefficient due to the errors in the atomic masses is approximately 6 parts per million. A correction for the fact that the measured lines are at slightly larger wave number than the theoretical "Balmer line" would decrease the factor $36/5$ by five parts per million. Both these quantities are completely negligible with respect to the accuracy of the measurements.

The pertinent data are those of Shane and Spedding,²⁹ Robinson,³⁰ and Williams.³¹ In the case of Shane and Spedding it has been necessary to compute their value of the separation by working backwards from their quoted values of e/m , the Faraday, and the atomic masses. They give $e/m=1.7579 \times 10^7$ emu, which is calculated from the formula

$$\frac{e}{m} = \frac{FR_H(D-H)}{(R_D - R_H)D(H-m)},$$

²⁸ Li, Whaling, Fowler, and Lauritsen, *Phys. Rev.* **83**, 512 (1951).

²⁹ C. D. Shane and F. H. Spedding, *Phys. Rev.* **47**, 33 (1935).

³⁰ C. F. Robinson, *Phys. Rev.* **55**, 423 (1939). See also R. T. Birge, *Phys. Rev.* **60**, 766 (1941).

³¹ R. C. Williams, *Phys. Rev.* **54**, 558 (1938).

using the values: $H=1.007775$, $D=2.01363$, $R_H=109677.759$, $F=9651.1$. From this we may calculate $R_D-R_H=29.86276 \text{ cm}^{-1}$ and

$$\bar{\nu}_D - \bar{\nu}_H = (5/36)(29.86276) = 4.147605 \text{ cm}^{-1}.$$

Since a correction for index of refraction was omitted³² in the original paper, this value is the separation measured in air.

Robinson's measurements were made on the most intense component of $H\alpha$ and $D\alpha$ in air and the separation is $\Delta\bar{\nu}=4.1453\pm 0.0010 \text{ cm}^{-1}$. This becomes $4.14415\pm 0.0010 \text{ cm}^{-1}$ when reduced to vacuum. (Apparently the only published data on Robinson's work is an abstract in the Bulletin of the American Physical Society. The values quoted here are reported by R. T. Birge in his 1941 paper and were communicated to him privately by Professor Houston.)

Williams measured the interference patterns of $H\alpha$ and $D\alpha$ with a 3-mm étalon. The measured peak-to-peak interval is given as $\Delta\bar{\nu}=4.14716\pm 0.00040 \text{ cm}^{-1}$ in air. This value, however, must be corrected because of differential effects due to the influence of components 3 and 4 on the position of the center of component 1. The major source of this correction is due to the fact that Williams' experimental conditions were such that the Doppler broadening of the lines is less for D than for H; component 3 has an appreciable overlap with component 1 in $H\alpha$ but a negligible effect in $D\alpha$. He evaluates this net correction as 0.00090 cm^{-1} so that the true isotopic shift in air is $\Delta\bar{\nu}=4.14806 \text{ cm}^{-1}$. Williams' correction to vacuum appears, however, to be in error; from his published figures one would calculate an index of refraction for air $\mu=1.0002557$, whereas Barrell and Sears' value at this wavelength is $\mu=1.0002762$. Apparently this can be ascribed only to a numerical error on Williams' part. We therefore find (using Barrell and Sears' value for index of refraction) that the wave-number separation in vacuum is $\Delta\bar{\nu}=4.14691\pm 0.00040 \text{ cm}^{-1}$.

The data from the three sources and their probable errors are given in Table III.

TREATMENT OF EXPERIMENTAL DATA

In combining all these independent results it is important that the weights assigned to each individual value shall be consistent with the weights assigned to the other data, in order that the relative accuracy of the several measurements be properly represented. The errors listed in Table II are the errors reported by the respective authors, although we shall not use these values by themselves to determine the weights. It is felt that there is too much variation among the results of different observers (compared with the errors quoted by them) to believe their quoted accuracy as representing much more than an indication of the reproducibility of the measurement under a given set of experimental conditions.

³² R. C. Williams and R. C. Gibbs, Phys. Rev. 48, 971 (1935).

TABLE III. $D\alpha-H\alpha$ isotopic shift and calculated atomic mass of the electron.

Source	$\bar{\nu}_D - \bar{\nu}_H$ (in air) cm^{-1}	$\bar{\nu}_D - \bar{\nu}_H$ (in vacuum) cm^{-1}	$m \times 10^5$ amu
C. H. Shane and F. H. Spedding	4.14761	4.14646	54.8961 ± 0.0074
C. F. Robinson	4.1453	4.14415	54.8655 ± 0.0132
R. C. Williams	4.14806	4.14691	54.9020 ± 0.0053

If we consider the measurements on a given Balmer pattern to constitute a single determination of the Rydberg we have six independent observations: (Houston, $H\alpha$, $H\beta$, He; DRW, $H\alpha$, $D\alpha$; Chu, He). These independent values are obtained by taking a mean value of the Rydberg as computed from each of the lines in the pattern. The error assigned shall be the larger of the two values computed by internal and external consistency.

The procedure now is to carry out a least squares solution to determine the most consistent values for the Rydberg constants and the electron mass. In order to handle the equations conveniently we introduce approximate values for R_∞ and m and then calculate the necessary corrections to these numbers. Therefore let M_i be the atomic mass of an arbitrary nucleus and R_i the associated Rydberg constant; we can write

$$R_\infty = \left(1 + \frac{m}{M_i}\right) R_i.$$

We must also take into account the fact that Houston and Chu both used the helium $\lambda 5015$ line as their standard of length and hence their computed Rydberg values are to be corrected if a change is made in the wavelength standard which they used. We shall therefore write

$$R_\infty' = \left(1 + \frac{m}{M_i}\right) R_i,$$

when the equation refers to the data of either Houston or Chu. We now let

$$R_\infty = R_0 + x, \quad R_\infty' = R_0 + y, \quad m = m_0 + z \times 10^{-5},$$

where $R_0 = 109737.3000 \text{ cm}^{-1}$, $m_0 = 54.9000 \times 10^{-5} \text{ amu}$, and $M_1 = 1.007593$, $M_2 = 2.014186$, $M_4 = 4.002775$. Thus we obtain two linear equations

$$x - (R_i \times 10^{-5} / M_i)z = (m_0 R_i / M_i) + R_i - R_0$$

(for the data of Drinkwater, Richardson and Williams);

$$y - (R_i \times 10^{-5} / M_i)z = (m_0 R_i / M_i) + R_i - R_0$$

(for the data of Houston or Chu).

Now because we admit that the He wavelength may be in error, we shall write the correct wavelength as

$$\lambda = 5015.6750 + \delta,$$

where δ is the correction (measured in angstroms) to be applied to the assumed value to obtain the actual value.

(Of course we cannot find the true value of δ but we can make a "best estimate" of this quantity.) Since Houston's standard value was 5015.6750, and the calculated value of the Rydberg constant is inversely proportional to this, we must write

$$(5015.6750)R_{\infty}' = (5015.6750 + \delta)R_{\infty},$$

which reduces to the relation

$$y = x + 21.88\delta.$$

The measurements of Drinkwater, Richardson, and Williams on the wavelength of $H\alpha$ and $D\alpha$, tabulated in Table II, yield a mean value $R_1 = 109677.567 \pm 0.011 \text{ cm}^{-1}$ for $H\alpha$ and $R_2 = 109707.424 \pm 0.018$ for $D\alpha$. The linearized equations are therefore

$$x - 1.088z = 0.026 \pm 0.011 \quad \text{wt} = 83, \quad (\text{a})$$

$$x - 0.544z = 0.027 \pm 0.018 \quad \text{wt} = 31. \quad (\text{b})$$

Houston's measurements on $H\alpha$, $H\beta$, and He yield mean values, respectively, of $R_1 = 109677.674 \pm 0.020 \text{ cm}^{-1}$; $R_2 = 109677.626 \pm 0.037 \text{ cm}^{-1}$; $R_4 = 109722.295 \pm 0.038 \text{ cm}^{-1}$, and therefore yield, respectively, the equations

$$y - 1.088z = 0.133 \pm 0.020, \quad \text{wt} = 25, \quad (\text{c})$$

$$y - 1.088z = 0.085 \pm 0.037, \quad \text{wt} = 8, \quad (\text{d})$$

$$y - 0.274z = 0.044 \pm 0.038, \quad \text{wt} = 7. \quad (\text{e})$$

Chu's measurements on He yield $R_4 = 109722.322 \pm 0.038$, which gives us

$$y - 0.274z = 0.070 \pm 0.038, \quad \text{wt} = 7. \quad (\text{f})$$

Merrill's measurement of the wavelength of the He 5015 line gives, according to the previous discussion of this measurement, $\delta = 0.0002 \pm 0.0015\text{A}$, so that we have a further equation

$$x - y = -0.004 \pm 0.033, \quad \text{wt} = 9. \quad (\text{g})$$

Finally the spectroscopic determinations of the atomic mass of the electron by Shane and Spedding, Robinson, and Williams give three additional equations:

$$z = -0.004 \pm 0.011, \quad \text{wt} = 83, \quad (\text{h})$$

$$z = -0.035 \pm 0.020, \quad \text{wt} = 25, \quad (\text{i})$$

$$z = 0.002 \pm 0.008, \quad \text{wt} = 150. \quad (\text{j})$$

The errors assigned to the numerical quantities in these equations are standard deviations, and the associated weights are taken to be proportional to the reciprocal of the square of the standard deviation, an error of ± 0.100 being assigned unit weight. The least squares procedure is now to set up, in the usual way, the normal equations for the system. These equations are

$$123x - 9y - 107.168z = 2.959,$$

$$-9x + 56y - 39.740z = 4.839,$$

$$-107.168x - 39.74y + 405.539z = 8.2863,$$

and the solution of these equations is

$$x = 0.0261, \quad y = 0.0870, \quad z = -0.00502, \quad \chi^2 = 11.94.$$

The quantity χ^2 is the sum of the squares of the normalized residuals (which it is the purpose of "least squares" to make "least"). For 7 degrees of freedom—10 equations minus 3 unknowns—the expectation value of χ^2 is just equal to 7 and there is a probability of 0.10 that in a normally distributed universe χ^2 would be larger than 12.0. Therefore, considering the uncertainty with which the errors in the observational equations (a)–(j) can be assigned, the agreement is quite reasonable. Expressing this in a slightly different way we can compute the ratio of internal to external consistency as used by Birge³³; this quantity is $r_e/r_i = 1.3$. Using the larger measure of error the final answers are

$$x = 0.0261 \pm 0.0140, \quad y = 0.0870 \pm 0.0188,$$

$$z = -0.00502 \pm 0.0079, \quad \delta = 0.0028 \pm 0.0007.$$

The correlation coefficients for these adjusted variables are

$$r(x, y) = 0.277, \quad r(y, z) = 0.362, \quad r(z, x) = 0.530,$$

$$r(\delta, x) = -0.333, \quad r(\delta, z) = -0.044.$$

The purely spectroscopic values therefore become

$$R_{\infty} = 109737.326 \pm 0.014 \text{ cm}^{-1},$$

$$m = (54.895 \pm 0.008) \times 10^{-5} \text{ amu},$$

$$\lambda = 5015.6778 \pm 0.0007\text{A}.$$

The consistency of the observed data is shown graphically in Fig. 2. In order to be able to draw a two-dimensional picture of the actual three-dimensional manifold, we represent in Fig. 2 only the projection onto the x - z plane of the intersection of the surfaces of the observational equation with the surface $y = x + 0.0609$. This procedure is the geometrical equivalent of recomputing the data of Houston and of Chu on the assumption that the correct value of the wavelength of the helium green line is equal to the least squares "best" value. The ellipse at the center of the plot is the projection on the x - z plane of the ellipsoid of error. This ellipsoid is such that its projected semidiameter on any axis is the standard error of the corresponding variable.³⁴

The value of m obtained here is to be compared with the value computed from the data reported by DuMond and Cohen^{23, 35} on the very accurate microwave results which yield a measurement of the atomic mass of the

³³ R. T. Birge, Phys. Rev. **40**, 207 (1932).

³⁴ J. W. M. DuMond and E. R. Cohen, Revs. Modern Phys. **20**, 82 (1948).

³⁵ In the present paper m is used for the atomic mass of the electron. DuMond and Cohen use this letter for the physical mass of the electron, so that in their notation the atomic mass is Nm , where N is Avogadro's constant. Since there is no need in the present analysis to consider Avogadro's constant explicitly and since the numerical values for m are always followed by an indication of the units (amu), the present simplified notation should produce no ambiguity.

electron. Hipple, Sommer, and Thomas³⁶ and Bloch and Jeffries³⁷ have measured the ratio of the proton "cyclotron" frequency to the proton resonance frequency in the same magnetic field and a weighted average of these results is $\omega_e/\omega_p = 0.358071 \pm 0.000007$. Gardner and Purcell³⁸ have measured the ratio of the proton resonance frequency to the electron cyclotron frequency in the same field and find $\omega_p/\omega_e = (1.52101 \pm 0.00002) \times 10^{-3}$. Thus the ratio of electron mass to proton mass is simply $(0.358071)(1.52101) \times 10^{-3} = 54.4630 \times 10^{-6}$; and using 1.007593 for the mass of the proton we find $m = (54.8785 \pm 0.0013) \times 10^{-6}$, the error quoted being a probable error, which is smaller than the spectroscopic value by 0.016 ± 0.008 .

If we use this value and neglect the spectroscopic mass determinations the Rydberg constant is $R_\infty = 109737.311 \pm 0.012 \text{ cm}^{-1}$, a decrease of 0.015 which is just slightly larger than the standard deviation. This value is indicated in Fig. 2 by the small circle and the vertical line.

The over-all picture appears to be fairly consistent, although it must be remembered that there is some area of uncertainty. The assignment of a correction to the wavelength of the helium green line is certainly an assumption which should not be accepted without stronger evidence than that offered at present. Our least squares "best" value of the helium wavelength, $5015.6778 \pm 0.0007 \text{ \AA}$, is larger than the value given by Merrill, 5015.675 \AA , by 0.0028 ± 0.0007 , which is a significant correction with respect to its standard deviation and at the same time is not too great a correction with respect to the accuracy with which the spectroscopic determination was carried out. It would therefore be well worth while to redetermine the ratio of the wavelength of this line to the fundamental cadmium wavelength standard. In the absence of this, all we have actually done is to use the data of Houston and Chu as a determination of the atomic mass of the electron and determine the Rydberg constant entirely from the measurements of Drinkwater, Richardson, and Williams. The discrepancy between the spectroscopic determination and the "microwave" determination of the atomic mass of the electron may appear annoyingly large, but the difference is not statistically improbable and we shall therefore adopt as the best available present value of the Rydberg constant

$$R_\infty = 109737.311 \pm 0.012 \text{ cm}^{-1}.$$

This value is consistent with an electron mass

$$m = (54.8785 \pm 0.0013) \times 10^{-6} \text{ atomic mass units,}$$

and if this is subsequently changed by methods which are independent of the Rydberg constant, a correction factor can be specified. By comparing these values with the purely spectroscopic results, we find that an increase

³⁶ Hipple, Sommer, and Thomas, *Phys. Rev.* **76**, 1877 (1949); **80**, 487 (1950).

³⁷ F. Bloch and C. D. Jeffries, *Phys. Rev.* **80**, 305 (1950).

³⁸ J. H. Gardner and E. M. Purcell, *Phys. Rev.* **76**, 1262 (1949).

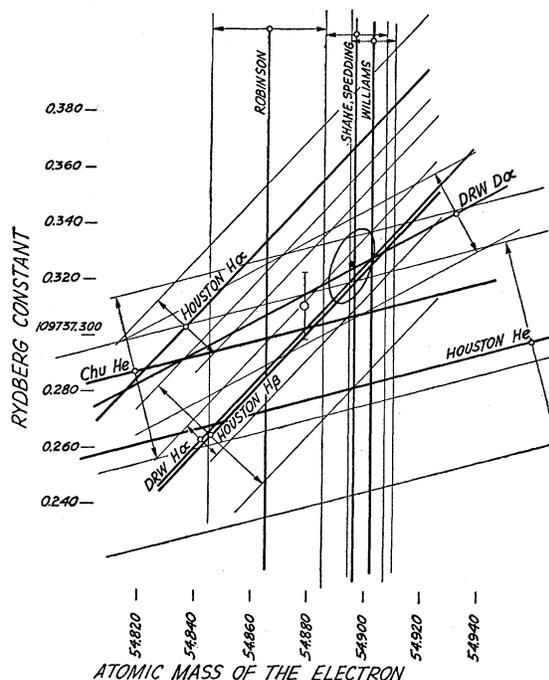


FIG. 2. A consistency diagram for the spectroscopic data determining the Rydberg constant. Each heavy line represents an experimental result. The light lines on either side of each heavy line indicate the standard deviation of the measurement. The black dot at the center of the ellipse is the least squares "best" value for the Rydberg constant and the atomic mass of the electron. The ellipse itself is the projection of the standard error ellipsoid onto the plane of the diagram and the standard error of any variable is given in turn by the projection of this ellipse on the corresponding axis. The small open circle and the vertical line to the left of, and slightly below, the ellipse is the value of the Rydberg constant if the microwave data is used to determine the electron atomic mass.

of 1 part per million in the electron mass will produce an increase of 0.0005 cm^{-1} in the Rydberg. It is important to point out, however, that there is nothing particularly fundamental in this coefficient; its value is dependent upon the values and weights of the Rydbergs for different atoms and reflects only the way in which the present data determine an observational relationship between R_∞ and m . With a different set of observational data this relationship will change.

The value given here, $109737.311 \text{ cm}^{-1}$, for the Rydberg constant is only slightly larger than R. T. Birge's 1941 value. This is the result of various compensating effects. If we do not use the "microwave" value for the electron mass, but restrict ourselves entirely to optical spectroscopic data the Rydberg is $109737.326 \text{ cm}^{-1}$ or 0.023 cm^{-1} larger than Birge's value. Except for a small effect due to the difference in the treatment of the data, this change is a result of the Lamb shift corrections to the energy levels. Using the smaller "microwave" mass reduces this difference by 0.015 cm^{-1} , so that the result is only 0.008 cm^{-1} larger than Birge's value. On the other hand, if the wavelength of the green helium line is not to be changed from

Merrill's value and if no other reason can be given for choosing Drinkwater, Richardson, and Williams over Houston and Chu, then the value of the Rydberg, which would then have to be calculated from consideration of all of these data, would be increased significantly since Houston's and Chu's data in combination with the spectroscopic mass determinations yield $R_\infty = 109737.387 \text{ cm}^{-1}$. In fact, a least squares solution of the present observational data, excluding Eq. (g) and putting in its place, $x=y$, gives $109737.346 \pm 0.019 \text{ cm}^{-1}$. The larger error in this case is a reflection of the larger spread in the data because of the inconsistency between the cadmium and helium wavelength standards.

We shall conclude by listing the Rydberg constant for the four lightest stable nuclei. In addition to the previously quoted mass we use the value 3.015899 ± 0.000011 for the mass of the He^3 nucleus (the probable errors quoted for the nuclear masses have negligible effect on the error of the results)

$$\begin{aligned} R_\infty &= 109737.311 \pm 0.012 \text{ cm}^{-1}, \\ R_{\text{H}} &= 109677.575 \pm 0.012, \\ R_{\text{D}} &= 109707.420 \pm 0.012, \\ R_{\text{He}^3} &= 109717.346 \pm 0.012, \\ R_{\text{He}^4} &= 109722.268 \pm 0.012. \end{aligned}$$

Proposed Method for Producing Short Intense Monoenergetic Ion Pulses*

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A method is outlined whereby suitable periodic deflection over the range of possible path lengths between foci of an appropriate focusing magnet is utilized to convert a continuous monoenergetic ion beam at one focus into very short duration high intensity monoenergetic ion pulses at the other focus. Time-of-flight analysis of reaction particle pulses resulting from the interaction of the ion pulses with stationary target nuclei is discussed, and the application of this method to the elastic and inelastic scattering of neutrons is considered briefly.

IN principle the interaction of a beam of high intensity short duration monoenergetic ion pulses with stationary target nuclei and time-of-flight analysis of the resultant reaction particle pulses is a form of spectroscopy applicable to all types of nuclear particles. Spatially separated, by differing times of flight from target or scatterer to an appropriately placed detector, the energy and angular distribution of any particular group of particles could then be determined without interference from other groups or in the case of scattering without interference from the source particles except for elastic scattering in the forward direction.

The problem of an appropriate method of producing a beam of high intensity, short duration, monoenergetic ion pulses appears, however, to have hindered application of this technique. One approach to this problem, which it is felt may be of sufficient general interest to warrant publication in its present design stage, is outlined in the accompanying diagram (Fig. 1).

It consists in principle of deflecting successive portions of a continuous monoenergetic ionbeam, such as that from an electrostatic generator, over progressively shorter paths between foci a and g of magnet M in a manner such that all portions of the beam so deflected arrive at g essentially simultaneously in a high intensity,

short duration current pulse. These ion pulses incident in turn on an appropriate target at g produce similar short duration, high intensity, reaction particle pulses. In more detail, magnet M is a focusing magnet with an ion deflector at focus a , a target at focus g , and the property that path lengths from a to g become progressively shorter for paths entering the magnetic field at successive points from k to e . When swept at an appropriate rate from c to e by the deflector at a , all ions successively crossing line ce in one edge of the monoenergetic ion beam can be made to emerge from the magnetic field on a cylindrical surface which collapses to a focus on its axis through g . Under these circumstances a sharply focused, relatively low intensity, long duration ion pulse entering the field of magnet M emerges greatly foreshortened along its direction of motion and arrives at g as a very short duration, high intensity pulse.

As a consequence of the quite arbitrary choice of geometry shown, the path length from c to d , due to the selection of 45° for angles cbj and dbj , is approximately $2S$ longer than the path length from e to f . The rate at which the ion beam must be swept along line ce on entering the field of magnet M to fulfill the above requirement is then approximately one-half the velocity of the incident beam. Swept at this rate, a segment of the deflected and chopped incident ion beam x thick and approximately $2S$ long becomes a pulse ap-

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