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Least-Squares Adjustment of the Atomic Constants, 1952

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1. THE GROUP KNOWN AS THE ATOMIC CONSTANTS

THIS review is concerned with the determination of the numerical values of an interesting subgroup of the general constants and conversion factors of physics and chemistry known as the atomic constants. No clear-cut definition of this subgroup exists, and, indeed, with the passage of time it has been found convenient to include in it more and more members of the parent group because of the improvements (partly theoretical and partly in the form of increased experimental precision) in our knowledge of the interrelations between the members. As of the present date we may, perhaps somewhat arbitrarily, enumerate the following six interrelated constants as the primary atomic constants: N, Avogadro's number; e, the electronic charge; m, the electronic rest-mass;[1] h, Planck's constant; c, the velocity of light; and λ_g/λ_s, the important conversion factor which converts x-ray wavelengths from the arbitrary Siegbahn x units (in which at 18° C the grating constant of the cleavage planes of calcite is $d_{18}=3029.45$ x units) to milliangstrom units. (We shall call this latter conversion factor for brevity simply λ.) Certain important constants such as $R_\infty=2\pi me^4h^{-3}c^{-1}$, the Rydberg fundamental wave number of spectroscopy; $F=Ne$, the Faraday constant of electrochemistry; $\alpha=2\pi e^2/(hc)$, Sommerfeld's fine-structure constant; $a_0=h^2/(4\pi^2me^2)$, Bohr's fundamental radius, and many others are closely related to the six named above by well-established formulas. In a few cases, certain rather accurately known "auxiliary constants" such as R_0, the gas constant, must be combined with these, as, for example, to compute the Stefan-Boltzman radiation constant $\sigma=(2/15)\pi^5R_0^4c^{-2}h^{-3}N^{-4}$ in the Stefan-Boltzman σT^4 law.

Thus there is a large group of very important fundamental numerical values, which are so interlaced and interconnected by known, well-established relationships that a precise knowledge of only about five of them, together with five or six very accurately known auxiliary constants, is all that is needed to establish the values of the entire group with considerable certainty. The choice of which particular set of five atomic constants we shall call our primary ones is to some extent arbitrary or dictated by mathematical convenience. Once they are selected, these primary constants are the "unknowns" whose values it shall be our object to determine by the method of least-squares, so as to form a consistent set which does the least violence to all our known sources of information with as much accuracy as the present state of our knowledge permits as regards both the values themselves and their standard errors. From the "best" (least-squares adjusted) values of these unknowns, combined with whatever auxiliary constants may be needed, all the other atomic constants and conversion factors will be computed. In the present instance, we have selected α, c, e, N, and λ as the five primary unknowns.

The reader accustomed to the textbook accounts of how such atomic constants as e, h, and m were measured for the first time in famous and historically important experiments such as R. A. Millikan's oil-drop experiment or his studies of the photoelectric effect, Planck's interpretation of the experimental curves of blackbody radiation, or J. J. Thomson's deflection experiments on cathode rays, may be surprised to see how little remains of these traditional methods in the present high precision evaluation. These earlier methods, which were of great value for the progress of knowledge at the time and which still possess immense historical importance, are now so greatly surpassed in accuracy by more modern, though sometimes less direct, methods that, although the earlier results are not inconsistent with the later ones, they would carry no significant weight if included in a least-squares solution.

2. RECENT HIGH PRECISION EXPERIMENTAL DATA

Undoubtedly the greatest single contribution to the progress of our knowledge of the atomic constants is to be found in the monumental pioneer work of R. T. Birge,[2] who by his painstaking and persistent life-long effort has certainly done more than any other person to separate truth from error and bring order out of chaos

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[1] We omit the usual subscript zero since we shall need to use this later with a different meaning.

[2] R. T. Birge, Revs. Modern Phys. **1**, 1 (1929); Phys. Rev. **40**, 207 (1932); Phys. Rev. **40**, 228 (1932); Phys. Rev. **42**, 736 (1932); Nature **133**, 648 (1934); Nature **134**, 771 (1934); Phys. Rev. **48**, 918 (1935); Nature **137**, 187 (1936); Phys. Rev. **54**, 972 (1938); Am. Phys. Teacher **7**, 351 (1939); Phys. Rev. **55**, 1119 (1939); Phys. Rev. **57**, 250 (1940); Phys. Rev. **58**, 658 (1940); Phys. Rev. **60**, 766 (1941); Repts. Progr. Phys. **VIII**, 90 (1942); Am. J. Phys. **13**, 63 (1945).

in this field. His 1929 and 1942 general reviews are all-time models of meticulous care in studying a huge mass of primary data, searching out errors, sifting and evaluating to separate the chaff from the wheat, and they are required reading for a proper understanding of this subject.

Rapid evolution in the direction of much higher accuracy of the data bearing on the atomic constants has occurred since 1947; undoubtedly partly the result of the stimulus given the subject by the many analyses of Birge and others during the preceding two decades, but chiefly made possible by the intense development since World War II of microwave and atomic beam techniques for the study of proton resonance in magnetic fields, the fine structure of energy levels in hydrogen and deuterium, the magnetic moments, spin gyromagnetic ratios, nuclear magnetic resonance frequencies, and cyclotron frequencies of fundamental particles such as protons and electrons, etc. Great improvements have also been made thanks to microwave cavity resonance and high frequency Kerr cell techniques in the measurement of the velocity of light. Unfinished work is also under way at the National Bureau of Standards to improve the accuracy of the electrochemical evaluations of the Faraday: (1) by the electrolysis of silver in which both the *anodic silver lost* and the *cathodic silver deposited* are weighed and compared and re-solution of the silver in the electrolyte is minimized by using for that medium a solution of silver perchlorate in perchloric acid, and (2) by anodically oxidizing sodium oxalate. Finally, a great advance in the accuracy of our knowledge of the atomic weights of light atoms has been gained through the determination of these by the measurement of nuclear reaction energies.

Of these modern experiments those used in the least-squares adjustment of this review are (1) the precision determination at the U. S. National Bureau of Standards of γ, the gyromagnetic ratio of the proton by Thomas, Driscoll, and Hipple; (2) the magnetic moment of the proton expressed in nuclear magnetons (ratio ω_c/ω_p of the cyclotron frequency to the magnetic resonance frequency of the proton in a given magnetic field) as obtained, (a) with the U. S. National Bureau of Standards "Omegatron" of Sommer, Thomas, and Hipple and also (b) at Stanford University with the inverse cyclotron of Bloch and Jeffries; (3) the fine structure separation ΔE_D of the $2^2P_{\frac{3}{2}}-2^2P_{\frac{1}{2}}$ levels in deuterium using the atomic beam magnetic resonance method performed by Dayhoff at Columbia; and (4) the ratio of the electron magnetic moment to the proton magnetic moment measured by Koenig, Kusch, and Prodell, also at Columbia University. References and numerical results for all the above work are given in Secs. 6 and 7. No attempt will be made here to describe experimental details of the techniques.

Since the discovery by Willis Lamb of the slight shift in the hydrogen levels, as a result of a remarkable program[3] of studies at Columbia University of the fine and hyperfine structure of the hydrogen spectrum, a complete reexamination and recalculation of the experimental data on which the determinations of R_∞, R_H, and R_D are based becomes necessary. A very thorough and complete study of the masses of the light atoms based on measurements of nuclear reaction energies has been made by Li, Whaling, Fowler, and Lauritsen at California Institute of Technology. For references and results of these studies see Sec. 7.

The all important velocity of light has received much attention in the period during and following World War II, with greatly improved accuracy resulting. Several excellent and concise reviews[4–7] of the situation concerning this constant at different epochs have been given of which that of Mulligan is to be recommended. The recent important high precision measurements of this constant are those of Hansen and Bol[8] at Stanford, using microwave cavity resonance with a cavity of fixed length; Bergstrand[9–10] in Norway, using Kerr cell-modulated visible light (the "Geodimeter"); cavity resonance work with a cavity of variable length by Essen;[11] at National Physical Laboratory, Teddington, England, using cavity resonance in a cavity of variable length; Froome,[12] also at NPL, using a free-space microwave interferometer; and Aslakson[13] using Shoran.

All the measurements just cited indicate quite unequivocally that the earlier weighted average value arrived at by Birge,[4] based chiefly on earlier measurements by Michelson, Pease, and Pearson[14] with the rotating mirror method in an evacuated tube and by Anderson,[15] using Kerr cell modulation, namely, 299 776 km/sec, was low by about 15 or 16 km/sec. As a matter of fact, if the Michelson, Pease, and Pearson and the Anderson values had been excluded from Birge's weighted average, the remainder of the data he considered, which included the remarkably accurate determination of the ratio of the electrical units by Rosa and

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[3] Willis E. Lamb, Jr., and Robert C. Retherford, "Fine structure of the hydrogen atom," Part I, Phys. Rev. **79**, 549 (1950); Part II, Phys. Rev. **81**, 222 (1951); Part III, Phys. Rev. **85**, 259 (1952); Part IV, Phys. Rev. **86**, 1014 (1952); Part V and Part VI (unpublished Columbia reports at the date of writing).

[4] R. T. Birge, Reps. Progr. Phys. **VIII**, 92–101 (1941).

[5] L. Essen, Nature **165**, 582 (1950).

[6] J. F. Mulligan, Am. J. Phys. **20**, 165 (1952).

[7] E. S. Dayhoff, Survey of Microwave Interferometers and Measurements of the Velocity of Light for the National Bureau of Standards Office of Basic Instrumentation, September 2, 1952, OBI Project 7507, 14.9 Project 1459.

[8] Kees Bol, thesis, Stanford University, 1950; Phys. Rev. **80**, 298 (1950). Unfortunately W. W. Hansen's untimely death came before this experiment was finished.

[9] Erik Bergstrand, Nature **163**, 338 (1949); **165**, 405 (1950).

[10] Erik Bergstrand, Arkiv Fysik **2**, 119 (1950); **3**, 479 (1951).

[11] L. Essen, Proc. Roy. Soc. (London) **A204**, 260 (1950); Nature **167**, 258 (1951).

[12] K. D. Froome, Proc. Roy. Soc. (London) **A213**, 123 (1952).

[13] C. I. Aslakson, Nature **164**, 711 (1949); Trans. Am. Geophys. Union **30**, 475 (1949).

[14] Michelson, Pease, and Pearson, Astrophys. J. **82**, 26 (1935).

[15] W. C. Anderson, J. Opt. Soc. Am. **31**, 187 (1941).

Dorsey,[16] would have yielded a weighted average not inconsistent with the present newer values.[17] These newer values are not all of equal reliability or accuracy, however, and in particular the Hansen and Bol result disagrees with the others by being some 3 kilometers per sec too low, a disagreement which, though small judged by earlier standards, is uncomfortably large relative to the claimed probable errors.

E. S. Dayhoff, in a privately circulated report,[7] criticizes the Hansen and Bol measurements because the resonant frequencies of not enough different modes of vibration were measured to obtain the requisite amount of information (especially as regards the skin depth) for an experiment otherwise so carefully and ingeniously designed to give such high precision. In Essen's (1950) results his cavity appeared to be about 2×10^{-4} cm larger in electrical diameter than it actually was mechanically because of the effective skin depth, and this was 2.8 times the calculated skin depth. Dayhoff concludes that this was probably because of polishing the silvered surface whose conductivity close to the surface, it appears, can be thus greatly decreased by the effect of cold working associated with polishing. Such an effect would increase Hansen and Bol's estimated skin depth correction of 3 km/sec to 8 km/sec and would bring their value of c into substantial agreement with the others. Table I lists these recent results with their estimated standard errors.

Note added in proof.—Dr. E. L. Ginzton of Stanford has recently pointed out to us that the above-mentioned interpretation of Essen's results as transmitted to us by Dr. Dayhoff is open to some question. Dr. Ginzton is of the opinion that the effect of possible variations in the diameter of Essen's cavity as a function of axial position are not properly taken into account in the Teddington measurements and that this might account for part of the discrepancy between the NPL and the Stanford results. This work on c is being continued at Stanford by Ginzton.

3. THE METHOD OF LEAST SQUARES

The first man to apply the method of least squares in a thoroughgoing way to obtain a consistent set of "best" adjusted values for the atomic constants was a former student of Birge, Frank G. Dunnington.[18] There are two uses which can be made of a least-squares solution of this sort: (1) It may be used on a fairly consistent overdetermined set of equations to determine the adjusted best values of the constants. (2) It may be used on an inconsistent set of equations as a tool to ascertain, if possible, which of the equations contains the concealed systematic error. At the time of Dunnington's work, because progress in refining the experiment of Duane and Hunt on the short-wavelength limit of the continuous x-ray spectrum was still not very advanced and for other reasons, there was a disturbing lack of consistency among the equations for determining the atomic constants. Dunnington's chief preoccupation in his paper was with this question of locating the cause of inconsistency. His attack consisted in performing a series of least-squares adjustments in each of which one item was omitted in an effort to see which item was the cause of inconsistency. Other least-squares solutions,[19–22] on the other hand, made subsequent to Dunnington's have been performed chiefly to determine "best" compromise values of the constants from a reasonably consistent set of data.

TABLE I. Experimental values of the velocity of light in vacuum.

Author	Date of publication	Reference	Method[a]	Velocity km/sec
Aslakson	1949	13	Shoran	299 792 ±3.5
Hansen and Bol	1950	8	FLCR	299 789.3±1.2
Essen	1950	11	VLCR	299 792.5±4.5
Bergstrand	1951	10	Geodimeter	299 793.1±0.32
Froome	1952	12	FSMWI	299 792.6±0.7

[a] FLCR = Fixed length cavity resonance. VLCR = Variable length cavity resonance. FSMWI = Free space microwave interferometer.

It is clear that in the quest for the "best" consistent set of values of the constants the entire situation of their complicated interrelatedness requires the application of some unbiased analytic technique. That is to say, one must (1) decide which if any of the quantities which we have chosen to call the primary atomic constants are known with sufficient accuracy relative to the rest, so that they can be practically eliminated from the category of "unknowns" and treated as known numbers (merely to save labor); (2) set up as many independent equations as there are reliable determinations of functions of the unknowns; and finally, (3) solve for the "best" compromise values of the unknowns. Considerably more such equations can be set up than the number of unknowns. Because of both random and systematic errors in the experimental determinations represented by the different equations, these latter may, in general, be expected to be more or less incompatible. The method of least squares then supplies a well-known mathematical technique for obtaining the "best compromise" values of the unknowns to satisfy all the equations approximately.

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[16] E. B. Rosa and N. E. Dorsey, Bull. Bur. Standards **3**, 433 (1907).

[17] *A posteriori* reasons to account for systematic errors in the Michelson, Pease, and Pearson and the Anderson determinations are not hard to find. The base line of the first mentioned determination was on very unstable alluvial soil, while the different transit times of the electrons in the detecting tube in Anderson's work constituted a possible source of systematic error which he recognized clearly himself. This latter objection is avoided in Bergstrand's "Geodimeter."

[18] F. G. Dunnington, Revs. Modern Phys. **11**, 68 (1939).

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

[20] J. W. M. DuMond and E. R. Cohen, Report to National Research Council, Committee on Constants and Conversion Factors of Physics, December, 1950.

[21] J. A. Bearden and H. M. Watts, Phys. Rev. **81**, 73 (1951); **81**, 160 (1951).

[22] J. W. M. DuMond and E. R. Cohen, Am. Sci. **40**, 447 (1952).

If we examine all the different experiments described in the previous section, we find that in the majority of cases the individual measurements do not measure one of the primary unknown quantities, but rather some function of several of them. Furthermore, the function whose numerical value is determined by such an experiment can be expressed in most cases (except for quantities which can be considered as accurately calculable correction factors) as a simple product of powers, positive or negative, of the primary variables of the form

$$N^{i_\mu}e^{j_\mu}m^{k_\mu}\cdots=A_\mu(1-r_\mu),\quad \mu=1,2,3,\cdots,N_{Eq}, \tag{3.1}$$

wherein A_μ is the numeric which results from the measurement and N, e, m, etc., are the primary variables. If we were to put true values of these variables (which we do not know) into the left-hand side of Eq. (3.1) we would, in general, not obtain the number A_μ, since it is the result of measurement and therefore subject to error. We must include the factor $1-r_\mu$ in order that Eq. (3.1) shall be a valid equation. We do not know the true values of the primary variables so that we cannot compute r_μ from this. The quantity r_μ is the actual relative error in the measured quantity A_μ, and this is, of course, beyond our ken. We know only an estimate of some of the parameters of its probability distribution. The most probable value of the error is zero, since the numeric quoted as the result of an experiment is, to the best of knowledge, the number which is most likely to be the correct value of the quantity being measured. Furthermore, we have an estimate of the root-mean-square deviation of the relative error σ_μ, and we shall restrict ourselves momentarily to a Gaussian[23] distribution for the errors such that the probability of the error r_μ lying between the values r and $r+dr$ is

$$P_\mu\{r<r_\mu<r+dr\}=\frac{1}{(2\pi)^{\frac{1}{2}}\sigma_\mu}\exp(-r^2/2\sigma_\mu^2)dr. \tag{3.2}$$

When we omit the factors $1-r_\mu$ from Eqs. (3.1) the system is, in general, overdetermined; we have N_{Eq} equations and only q variables $(q<N_{Eq})$, so that a solution is impossible (except for the very improbable situation in which all of the experimental data are exactly compatible). When we introduce the quantities r_μ, we increase the number of unknowns to $q+N_{Eq}$, there being one residual for each observational equation, and we are able to satisfy the equations in infinitely many ways. It is now necessary to find some additional conditions which will allow us to choose that one solution, from the infinitely many which are available to us, which represents the "best" choice. This "best" choice can be based on the Axiom of Maximum Likelihood:

"Of all the possible choices for the set of residuals (r_μ), the best choice is that whose probability of occurrence is maximum."

The probability of obtaining simultaneously the set of values, $r_1, r_2, r_3, \cdots, r_{N_{Eq}}$ is the product of the probabilities of obtaining each value separately, provided these errors are all independent. (The importance of this proviso will soon become evident.) Therefore,

$$\begin{aligned}P(r_1,r_2,r_3,\cdots)&=(2\pi)^{-\frac{1}{2}N_{Eq}}[\sigma_1\sigma_2\sigma_3\cdots\sigma_{N_{Eq}}]^{-1}\\&\quad\times\exp\left\{-\tfrac{1}{2}\left(\frac{r_1^2}{\sigma_1^2}+\frac{r_2^2}{\sigma_2^2}+\frac{r_3^2}{\sigma_3^2}+\cdots\right)\right\}.\end{aligned} \tag{3.3}$$

This probability will be a maximum when the sum in the exponent is a minimum. This then is the "least-squares" condition: The N_{Eq} equations (3.1) are solved for the residuals r_μ written as functions of the unknown variables $N, e, m, \cdots$ and we seek that set of values for the variables which minimizes the sum of the squares of the quotient of each residual divided by its standard deviation.

If the distribution of the errors is other than Gaussian, it is difficult to formulate an analytic procedure based on the condition of Maximum Likelihood but it has been shown[24] that, independent of any assumptions about the exact distribution of the errors of the A_μ save that the σ_μ exist (i.e., are finite) in each case, this least-squares condition is equivalent to the condition that the resultant solution shall be that set which has minimum root-mean-square deviations. [See following article by E. R. Cohen; Revs. Modern Phys. **25**, 709 (1953).]

For convenience in effecting the least-squares adjustment, the system of Eqs. (3.1) is "linearized." We adopt origin values N_0, e_0, m_0, etc., which have been chosen sufficiently close to our expected solution that any set of values N, e, m, in which we are likely to be interested will differ from these individual origin values by only small relative amounts; that is, $N_0, e_0, m_0, \cdots$ are so chosen that $x_N=(N-N_0)/N_0$, $x_e=(e-e_0)/e_0$, $x_m=(m-m_0)/m_0, \cdots$ are always small, and we then express the experimental measurements in terms of these dimensionless variables $x_N, x_e, x_m, \cdots$. To each type of experimental determination of a function of the type (3.1) there corresponds a hyperplane

$$i_\mu x_N+j_\mu x_e+k_\mu x_m+\cdots=a_\mu-r_\mu, \tag{3.4}$$

which is tangent to the curved surface (3.1). The constant a_μ is given by $a_\mu=(A_\mu-A_{\mu0})/A_{\mu0}$, in which $A_{\mu0}$ is the value of the function f when the origin values $N_0, e_0, m_0, \cdots$ are inserted. The orientation of this plane in the hyperspace depends on the exponents $i_\mu, j_\mu, k_\mu, \cdots$ of (3.1) [i.e., the coefficients $i_\mu, j_\mu, k_\mu, \cdots$

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[23] The Gaussian distribution is not uniquely implied by these two parameters, A_μ and σ_μ, and the least-squares procedure can, in fact, be justified *without recourse to any presumed probability distribution of errors*. The introduction of such a distribution is convenient and makes possible a more direct development.

[24] E. Whittaker and G. Robinson, *Calculus of Observations* (Blackie & Sons, London, 1944), fourth edition, p. 224.

of (3.4)], while the origin distance of the plane depends on a_μ. The entire status of our knowledge regarding the "best" values of e, m, and h to fit the data is contained in the way these various planes intersect each other to define some compromise point, taking into consideration the relative reliability of the positioning of each plane, i.e., the magnitude of the standard error, σ_μ. The function $Q=\sum(r_\mu^2/\sigma_\mu^2)$, which is to be minimized, is therefore an expression of the second degree in the variables x_N, x_e, x_m, etc., and the minimum condition is obtained by equating to zero each of the partial derivatives of Q taken with respect to each variable in turn. It is easy to show that this process is equivalent to the following simple recipe for forming the so-called "normal equations": Write down the system of eqs. (3.4) omitting the residue r_μ in each case. Assign to each equation a weight

$$p_\mu=C/\sigma_\mu^2, \tag{3.5}$$

where the constant C may have any convenient numerical value. To obtain the normal equation associated with a given variable (i.e., the one which expresses the condition that the partial derivative of Q with respect to that variable shall vanish), multiply each of the linearized observational equations (with r_μ omitted!) by the coefficient of the variable in question in that equation and by the weight assigned to that equation. These individual expressions are then added together to give a single "normal" equation. Repeat for each variable, and in this way construct a set of q simultaneous equations for the q unknown quantities x_N, x_e, x_m, etc.

The solution is completed by inserting the values obtained for the x's into the original set of observational equations (3.4) and finding the associated residuals; the values of the residuals computed using the solution of the normal equations we shall denote as R_μ (a number) to be distinguished from r_μ which is a function of the variables x_N, x_e, $\cdots$. The minimum value of the quadratic expression Q is usually denoted by the symbol χ^2

$$\chi^2=\sum(R_\mu^2/\sigma_\mu^2). \tag{3.6}$$

An important measure of the consistency of the entire set of equations is given by χ^2 divided by the difference between the number of equations N_{Eq} and the number of unknowns q. The expectation value of $[\chi^2/(N_{Eq}-q)]^{\frac{1}{2}}$ is unity; this quantity is the generalization to multidimensional space of R. T. Birge's[25] ratio of the measures of external and internal consistency. The difference $N_{Eq}-q$ is known as the "number of degrees of freedom" of the system.

A word of caution about the actual method of formulating the equations of least-squares from the data as applied to the atomic constants is in place at this point. The general form of the primitive equations of observation is given in Eq. (3.1) above. In each such equation A_μ is a number with an estimated relative standard error σ_μ, the result of reduction of some particular experimental observations, which, if care to avoid it has not been exercised, *may be correlated observationally* with some of the other A_μ by reason of the fact that one and the same error-contributing component (such as, for example, c) may have been used in reducing the data to arrive at both A_μ's.

Now, it is an important point, which has never been emphasized in even the most advanced texts on least squares, that the observational equations must be observationally independent, if the above classical procedure of effecting least-squares adjustment is to be followed. This is because one cannot otherwise assign simple independent weights to the different equations. If, on the contrary, the equations are observationally correlated, the standard errors of the a's can only be measured by an error matrix involving correlation coefficients corresponding to all possible pairs of a's as well as individual standard errors for each a, and the weights must be replaced by a "weight matrix," the inverse of the error matrix, to express the situation fully. The process of least-squares adjustment can then be formulated[26] in matrix algebra in a manner quite analogous to the simpler case of independent a's but with considerable increase in labor.

The easy and obvious way out of this difficulty is to recast the entire system of equations in such a way as to remove the observational correlations between the a's. This amounts to finding a transformation which diagonalizes the error and weight matrices. It may be impossible to do this, however, without transferring some of the quantities with larger standard errors from the category of the known a's to the category of the unknown x's and also to write for each of these an extra observational equation in which the new unknown x is equated to its appropriate input datum a, the numerical result of direct measurements. This, of course, complicates the problem by increasing the number of unknowns to be adjusted, but it in no way affects the original overdetermination $(N_{Eq}-q)$ of the set, since an additional observational equation is added for each new unknown introduced.

4. CALCULATION OF STANDARD ERRORS AND CORRELATION COEFFICIENTS

The reliability of the output values of any least-squares adjustment must, in general, be described not only by stating the standard deviation for each numerical result but also by specifying certain quantities known as *correlation coefficients*, r_{ij} *for each pair of results*. The numerical output values, of e, m, h, c, etc., are of little use unless functions of these can be combined to compute other derived values. Now the standard devia-

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[25] R. T. Birge, Phys. Rev. **40**, 213–224 (1932).

[26] This formulation was, we believe, given for the first time by J. W. M. DuMond and E. R. Cohen, Report to the National Research Council on the Atomic Constants, December, 1950. See also E. R. Cohen, Phys. Rev. **81**, 162 (1951).

tions of such derived values must be computed, as we shall show in this section, by formulas which involve not only the standard deviations of the values entering into the function but also the correlation coefficients r_{ij} connecting all possible pairs of those values.

The calculation of error estimates in such a situation may be unfamiliar to many physicists. There is no escape from this added complication in the computation of precision measures, however, since it reflects the complexity inherent in the sources of our knowledge of the adjusted values. A comprehension of the content of this section is, therefore, essential to the correct use of the adjusted output values given here.

Each quantity subject to random or accidental error (frequently known as a "random variable") may conveniently be thought of as a sample taken at random from a group or "universe" of values which group themselves around a mean value according to some frequency law. This frequency law we shall usually assume to be the normal or Gaussian law. For each such random variable x_i, one is to think then of the implied universe of values in the background which it is presumed would be obtained by repeated measurements on it. This universe may be described by giving some of its parameters. Thus, if the universe is known to be Gaussian, for example, then prescription of its first and second moments, i.e., its mean value $\mathbf{x}_i$ and its variance σ_i^2 are sufficient. (The standard deviation σ_i is the root-mean-square deviation from the mean of this universe of values.)

Two such random quantities are observationally independent, if the random selection of a sample value from one universe in no wise affects or biases the free selection of a sample from the other universe. If, however, two variables are connected by a strict functional relationship so that the value of *either one is uniquely determined by the other*, the variables are completely correlated and the correlation coefficient connecting them has the absolute value unity. Random samples can no longer be selected freely and independently from the two universes because of the functional condition which ties the selections rigidly together. Having selected a sample value from one universe at random, the second selection is now completely dictated in value. On the other hand, if one of the two random variables is a function of the other *and also of still other completely independent random variables*, then the first two will be partially but not completely correlated, and the correlation coefficient connecting them will have an absolute value somewhere between zero and unity. The problem of correlated errors has been pointed up in a previous article in this journal[27] (q.v.), and it was shown there that, in general, the distribution in probability of the possible solutions of the set of eqs. (3.4) is represented by a hyperellipsoid of probability in the constants space whose major axes are skew to the coordinate axes. Because of this the probability distribution of a particular variable is dependent upon the specification of the values of all the other variables. The extent of this dependence is expressed by correlation coefficients. There exists then in the hyperspace of our primary variables a hyperellipsoid of error whose principal axes will lie, in general, oblique to the axes of any of the primary variables in a way which depends on the precision (and consequent weights) to be attached to the various input data. The various standard deviations σ_i of the different linearized unknowns x_i together with the correlation coefficients r_{ij} connecting all possible pairs of unknowns can be systematized in the form of a square matrix whose derivation from the normal equations we shall now describe.

For definiteness, let us now consider a system with four unknowns. We shall write the (linearized) observationally independent equations in the form

$$i_\mu x_1 + j_\mu x_2 + k_\mu x_3 + l_\mu x_4 = a_\mu - r_\mu, \qquad \mu = 1, 2, 3 \cdots N_{Eq}, \tag{4.1}$$

and to each of the N_{Eq} equations we assign a weight $p_\mu = C/\sigma_\mu^2$ (see Eq. 3.5), in which σ_μ is the standard error of the constant term a_μ. We construct the normal equations in accord with the instructions of the previous section and these can be written in the form

$$\begin{aligned} b_{11}x_1 + b_{12}x_2 + b_{13}x_3 + b_{14}x_4 &= c_1, \\ b_{21}x_1 + b_{22}x_2 + b_{23}x_3 + b_{24}x_4 &= c_2, \\ b_{31}x_1 + b_{32}x_2 + b_{33}x_3 + b_{34}x_4 &= c_3, \\ b_{41}x_1 + b_{42}x_2 + b_{43}x_3 + b_{44}x_4 &= c_4. \end{aligned} \tag{4.2}$$

The quantities b_{ij} are symmetric, $(b_{ij} = b_{ji})$;

$$b_{11} = \sum_\mu p_\mu i_\mu^2, \quad b_{12} = b_{21} = \sum_\mu p_\mu i_\mu j_\mu, \quad b_{22} = \sum_\mu p_\mu j_\mu^2, \tag{4.3}$$

and it should be apparent from the form of these four quantities exactly how the other twelve b_{ij} may be constructed. The constant terms of the normal equation c_j are calculated in a similar way:

$$c_1 = \sum_\mu p_\mu i_\mu a_\mu, \quad c_2 = \sum_\mu p_\mu j_\mu a_\mu, \text{ etc.}, \cdots \tag{4.4}$$

It is well known that the solution of the set of eqs. (4.2) can be written in the form

$$\begin{aligned} x_1 &= d_{11}c_1 + d_{12}c_2 + d_{13}c_3 + d_{14}c_4, \\ x_2 &= d_{21}c_1 + d_{22}c_2 + d_{23}c_3 + d_{24}c_4, \\ x_3 &= d_{31}c_1 + d_{32}c_2 + d_{33}c_3 + d_{34}c_4, \\ x_4 &= d_{41}c_1 + d_{42}c_2 + d_{43}c_3 + d_{44}c_4, \end{aligned} \tag{4.5}$$

in which the sixteen numbers d_{ij} bear an inverse relationship to the set of numbers b_{ij}; the element d_{ij} is equal to the minor of b_{ji} in the determinant of the b's divided by the determinant itself. All the information

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[27] J. W. M. DuMond and E. R. Cohen, Revs. Modern Phys. **20**, 91–94 (1948).

required for the complete solution of the problem of least squares is contained in the sixteen b's (or equivalently in the sixteen d's) and the four c's. In addition to the "best" values of the x's, we are equally interested in determining the precision measures which must be assigned to them. The x's are not accurately determined quantities, since they are computed from numbers which are the results of experiments and therefore are subject to error. Using the definition of the c's from Eq. (4.4) in Eq. (4.5) allows us to express our solution in terms of the directly observed quantities a_μ. There is some error associated with each quantity a_μ. This error, which we shall call E_μ, is unknown (if it were known we should remove the error by correcting the quantity a_μ); we know an estimate of the mean square value of this error, however, and we can, therefore, make an estimate of the mean square error in a function of the a_μ. The error ϵ_i in x_i, which is produced by errors E_1 in a_1, E_2 in a_2, E_3 in a_3, etc., can be calculated from the partial derivative of x_i taken with respect to a_μ:

$$\epsilon_i=\frac{\partial x_i}{\partial a_1}E_1+\frac{\partial x_i}{\partial a_2}E_2+\frac{\partial x_i}{\partial a_3}E_3+\cdots. \tag{4.6}$$

The errors E_μ are to be considered as random variables; they may be positive or negative. Since the numeric a_μ is presumably the best estimate available for this quantity, we expect E_μ to be zero. On the other hand, the mean value of E_μ^2 is estimated to be σ_μ^2, so that σ_μ is an estimate of root mean square error in a_μ.

If we calculate the mean value of ϵ_i^2 we find

$$\begin{aligned}\sigma_{x_i}^2=\langle\epsilon_i^2\rangle=&\left(\frac{\partial x_i}{\partial a_1}\right)^2\sigma_1^2+\left(\frac{\partial x_i}{\partial a_2}\right)^2\sigma_2^2\\&+\left(\frac{\partial x_i}{\partial a_3}\right)^2\sigma_3^2+\cdots+2\left(\frac{\partial x_i}{\partial a_1}\frac{\partial x_i}{\partial a_2}\right)\langle E_1E_2\rangle\\&+2\left(\frac{\partial x_i}{\partial a_1}\frac{\partial x_i}{\partial a_3}\right)\langle E_1E_3\rangle+\cdots,\end{aligned} \tag{4.7}$$

in which the $\langle\ \rangle$ about a quantity denotes the operation of taking the average value of that quantity. Since the a's have been assumed to be observationally independent, the errors in two different a's are in no way related to each other, and the average value of the product of two different errors vanishes, since for any value of one error the other may be averaged out to zero. Thus, in such a case, the cross product terms in Eq. (4.7) disappear, and we have the law of the propagation of independent errors

$$\sigma_{x_i}^2=\langle\epsilon_i^2\rangle=\sum_\mu\left(\frac{\partial x_i}{\partial a_\mu}\right)^2\sigma_\mu^2. \tag{4.8}$$

When the differentiations are actually carried out we find, after some straightforward but somewhat lengthy algebraic manipulation, that the mean square error in x_i is given simply by Cd_{ii}. Thus, the diagonal elements of the matrix (d) are directly related to the standard errors of the solution. It may also be shown that the off-diagonal elements of matrix (d) are similarly related to the mean value of the product of the errors in two different variables:

$$\langle\epsilon_i\epsilon_j\rangle=Cd_{ij}. \tag{4.9}$$

For this reason we refer to the matrix (d_{ij}) as the "error matrix" of the solution. It is important to realize that the mean value of the product of the errors of two different x's does not vanish, because these quantities are not independent in terms of the observational quantities a_μ, each x_i being expressed ultimately in the least-squares procedure by some linear combination of the a_μ.

The extent of this correlation can be best expressed by defining the "correlation coefficient" r_{ij} connecting the two variables x_i and x_j by the relationship

$$r_{ij}=d_{ij}/(d_{ii}d_{jj})^{\frac{1}{2}}. \tag{4.10}$$

It can be shown that r_{ij} must lie between the limits -1 and $+1$. If the two variables are uncorrelated, in the sense that an error in one is completely independent of an error in the other, $r_{ij}=0$; at the other extreme, if the two variables are functionally related to the extent that an error in one completely determines the error in the other $r_{ij}=\pm 1$, the sign depending on whether a positive error in one variable is associated with a positive or a negative error in the other. Once we have calculated the error matrix, it is no longer necessary to express a function of the x's in terms of the independent quantities a_μ in order to calculate its standard error, as long as we realize that the errors in the x's are correlated. If we have any function $f(x_1, x_2, x_3, x_4)$, the error in the function arising from specified errors ϵ_1, ϵ_2, ϵ_3, ϵ_4 in the x's is

$$\epsilon_f=\alpha_1\epsilon_1+\alpha_2\epsilon_2+\alpha_3\epsilon_3+\alpha_4\epsilon_4, \tag{4.11}$$

where $\alpha_i=\partial f/\partial x_i$, and the mean square error (variance) of f is given by

$$\sigma_f^2=\langle\epsilon_f^2\rangle=\sum_{ij}\alpha_i\alpha_j\langle\epsilon_i\epsilon_j\rangle=C\sum_{ij}\alpha_i\alpha_jd_{ij}. \tag{4.12}$$

The quantity C is the constant relating the "weight" of an observation to its variance; our *a priori* choice for this constant (its value by "internal consistency") is

$$C_I=p_\mu\sigma_\mu^2\ \text{(internal)}. \tag{4.13}$$

It is possible also to make an *a posteriori* estimate of C (its value by "external consistency") based on the statistical agreement of the least-squares solution. We expect the quantity $\chi^2/(N_{Eq}-q)$ to be equal to unity; if this is not so, we make an *a posteriori* readjustment in the scale of our standard deviation and define

$$C_E=C_I\chi^2/(N_{Eq}-q)=\sum_\mu p_\mu R_\mu^2/(N_{Eq}-q)\quad\text{(external)}. \tag{4.14}$$

Equation (4.12) gives us the generalized law of the propagation of errors; written out in terms of the standard deviation and the correlation coefficients of the variables it becomes

$$\sigma_f^2=\sum_{i=1}^{4}\alpha_i^2\sigma_{x_i}^2+2\sum_{i<j}r_{ij}\alpha_i\sigma_{x_i}\alpha_j\sigma_{x_j}, \tag{4.15}$$

and this form must be used rather than an expression of the form (4.8), if we are dealing with correlated variables (i.e., if the correlation coefficients r_{ij} do not vanish).

As an example of the importance of the correlation coefficient, let us consider now an extreme case. We can write the function $f(x)=x^{s+t}$ as $f(x)=x^s x^t$ and in this latter form, if we consider the two factors to be independent, we would calculate the relative standard error of f to be $(s^2+t^2)^{\frac{1}{2}}$ times the relative standard error of x, whereas in the original form the relative error in f is $(s+t)$ times the relative error in x. However, we have neglected the effect of the correlation coefficient which is this case is $r=+1$ so that the correct expression for the relative error in f, when written in the second form, is $(s^2+t^2+2st)^{\frac{1}{2}}$, and *not* $(s^2+t^2)^{\frac{1}{2}}$, times the relative error in x, and we have thereby resolved the paradox. This method of computing errors (Eq. 4.15) will be called the method of the ellipsoid of error, because it is the analytical equivalent of constructing two parallel planes tangent to either side of the ellipsoid of error and normal to a given axis in the hyperspace of the unknowns (the axis for the linear function, f) to find the domain of standard deviation $\pm\sigma_f$ cut off by those planes on that axis.

The generalized formula of errors is the one used in calculating the error measures of all the derived quantities in obtaining our least-squares adjusted general table of output values in this paper. Now, it is true that a certain valid objection could be raised to the practice of giving only the standard deviations of the derived output values, for these values are definitely *not* observationally independent, in general. To give, however, a complete matrix of standard deviations *and correlation coefficients* connecting all possible pairs of all the derived values would obviously be too cumbersome. We must emphasize, however, that when any of these output values are used in formulas to compute other quantities, it is strictly *incorrect* to compute the probable error of the resultant quantities by the ordinary formula of propagation of errors for observationally independent quantities. The correct probable error may be either greater or less than this because of the cross-product terms. When two correlated quantities are to be combined, the standard error of the resultant can be calculated only if the correlation coefficient is also known or if the quantities are re-expressed in terms of variables whose correlation coefficients are known. A numerical example of such a computation is given in Sec. 10.

5. REJECTION OF CERTAIN INPUT DATA FOR THE PRESENT LEAST-SQUARES ADJUSTMENT

Two criteria have been followed in selecting data for use in the present adjustment. (1) Reject data of such low numerical accuracy that the corresponding weight of the observational equation would imply negligible influence on the entire solution. (2) Reject data which, even though accurately measured, suffer from uncertainties in theoretical interpretation.

The hyperfine structure shift of hydrogen in the $^2S_{\frac{1}{2}}$ state, $\Delta\nu_H$ would furnish an important datum connecting the quantities α, c, R_∞, and μ_p/μ_e, the ratio of the magnetic moments of proton and electron, were it not for the uncertainty regarding a certain correction term. The shift $\Delta\nu_H$ has been measured by the atomic beam magnetic resonance method with a precision of 6 ppm in 1947 at Columbia University by Nafe and Nelson,[28,29] but more recently, and much more accurately, with a probable error of only 0.2 ppm by the same method by Prodell and Kusch[30] at the same laboratory. This remarkable measurement is absolute in the sense that a microwave frequency which can be directly compared to a fundamental time standard is resonated with an atomic energy level difference. The relationship which is originally due to Fermi[31] is

$$\Delta\nu_H=\frac{16\alpha^2}{3}cR_\infty\left(\frac{\mu_p}{\mu_e}\right)\left(\frac{\mu_e}{\mu_0}\right)^2 \times(1+\tfrac{3}{2}\alpha^2)\left(1+\frac{m}{m_p}\right)^{-3}\mathcal{E}\mathcal{P}. \tag{5.1}$$

In this formula μ_p is the magnetic moment of the proton and μ_e that of the electron; μ_e/μ_0 is the ratio[32] of the electron moment to the Bohr magneton. The factor $(1+\frac{3}{2}\alpha^2)$ is Breit's relativistic correction term, and the next parenthesis is the reduced mass correction term. The last two factors $\mathcal{E}$ and $\mathcal{P}$, whose importance was first pointed out by Bethe and Longmire,[33] correct for the finite extension of the electron and proton dipoles; the magnitude of the former effect has been calculated by Karplus and Klein,[34] but there has only been an order of magnitude estimate for the latter which could be in error by a few parts in 10^5. The present state of meson theory holds little promise that a better estimate will be soon forthcoming. Thus, although the accuracy of the measurement is better than 1 part in 10^6, the theoretical uncertainty is sufficiently large that we have no recourse for the present but to reject this datum.

Under the direct measurements of the Faraday by electrochemical methods we have felt obliged to omit the provisional values obtained from the measurements

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[28] J. E. Nafe and E. B. Nelson, Phys. Rev. **73**, 718 (1948).
[29] E. B. Nelson and J. E. Nafe, Phys. Rev. **75**, 1194 (1949).
[30] A. G. Prodell and P. Kusch, Phys. Rev. **79**, 1009 (1950).
[31] E. Fermi, Z. Physik **60**, 320 (1930).
[32] R. Karplus and N. M. Kroll, Phys. Rev. **77**, 536 (1950).
[33] H. A. Bethe and C. Longmire, Phys. Rev. **75**, 306 (1949).
[34] R. Karplus and A. Klein, Phys. Rev. **85**, 972 (1952).

by Craig and Hoffman with sodium oxalate and with silver. In a preliminary least-squares adjustment we have found that the recently revised values of the sodium oxalate measurements (revised chiefly because of revisions in the chemists international atomic weights) fall considerably out of line with the other observational equations. This by itself would constitute insufficient reason for omitting this datum but a letter from D. N. Craig, dated August 29, 1952, clearly states that work is still in progress to establish (1) the exactness of the assumed chemical reaction, (2) the isotopic composition of the sodium oxalate, and (3) the purity of the sodium oxalate. Dr. Craig concludes, "Consequently, we are not in a position to change the preliminary value which appeared in the Physical Review." We reject the silver value of Craig and Hoffman, because it is presumed also to be only preliminary.

The Faraday values for silver and for iodine which have been kindly furnished by Dr. Vinal based on earlier work are definitive, and hence we have retained them, although they disagree by more than 3 times the internally estimated probable error of the difference between them.

The items listed as Eqs. (6.9) to (6.11) are obtained from measurements of the short wavelength limit of the continuous x-ray spectrum. These measurements have traditionally been called measurements of h/e, whereas what is measured is the dc voltage applied to an x-ray tube and the wavelength in Siegbahn x units of the emitted continuous x-ray spectrum quantum limit. Factors like c and λ_g/λ_s, which were once treated as auxiliary fixed constants, have in the present adjustment acquired the status of unknown variables, and we must, therefore, be careful to recognize exactly what the observed quantity in this experiment really is. Clearly this experiment measures, after appropriate corrections, the conversion constant between the energy in electron volts and the wavelength (in Siegbahn x units) of electromagnetic quanta.

6. CHOICE OF THE UNKNOWNS AND THE PRIMITIVE OBSERVATIONAL EQUATIONS

Wherever more than one important determination of a given datum exists and is deemed worthy of inclusion in our adjustment, *we write a separate observational equation for each of the determinations* instead of following the almost universal past practice of taking a weighted average of all similar determinations and treating this as a single datum for which only one observational equation need be written. This method is the more logical one, since it permits the determination of separate normalized residues for each separate datum and gives a more correct measure of χ^2. Clearly with this method $N_{Eq}-q$, the number of "degrees of freedom" (or of overdetermination) in the least-squares solution will be larger and should give a truer picture of the real consistency situation. Also (and of more direct utility) the separate normalized residues for each determination can be independently computed and assessed.

In order to avoid hidden observational correlations, care has been taken in formulating the primitive equations of observation (6.1) to (6.13) to see that the numeric, the right-hand member of each equation, is the result of a single determination and not the combined result of two or more determinations. For example, Dayhoff quotes in his recent report on the fine structure of hydrogen and deuterium a value of the fine structure constant α. What he actually measured, however, was the frequency separation ΔE_D between the levels $2^2P_{\frac{3}{2}}$ and $2^2P_{\frac{1}{2}}$ in deuterium and his value of α was computed from ΔE_D by the use of a formula involving R_∞, c, and correction factors depending on α and on the ratio M_d/D of the mass of the deuteron to the mass of the deuterium atom. Consequently, in Eq. (6.13) we have equated his measured numeric ΔE_D to the appropriate function of all the quantities involved along with α.

The precision measures given are standard errors σ (as distinguished from "probable error," equal to $0.6745\,\sigma$ for a Gaussian distribution). The absolute standard error is given immediately following each numerical value and the relative standard error in parts per million (ppm) is given in parentheses after this. When experimenters report "limits of error," we have followed the rule of dividing these by two to obtain the standard error.

The physical scale of atomic weights is used throughout in quoting numerical values.

The primitive equations of observation are the following, Eqs. (6.1) to (6.13):

The *velocity of light* as obtained by K. D. Froome[12] at the British National Physical Laboratory with a microwave interferometer:

$$c=(299792.6\pm0.7)\times10^5 \text{ cm sec}^{-1} \text{ (2.3 ppm)}. \quad (6.1)$$

The same constant as obtained by Bergstrand[9,10] with visible light over long base lines using his "geodimeter" (Kerr cell modulation)

$$c=(299793.1\pm0.32)\times10^5 \text{ cm sec}^{-1} \text{ (1.1 ppm)}. \quad (6.2)$$

The results of determinations of the *Faraday* by the electrolysis of iodine and of silver, respectively, as recently recomputed from old data[35] by G. W. Vinal,[36] utilizing the latest international atomic weights (chemical scale) and conversion factors for the absolute electrical units.

$$\text{(Iodine) } Ne/c=9652.15\pm0.13 \text{ emu (g mole)}^{-1} \text{ (phys. scale) (13 ppm)}. \quad (6.3)$$

$$\text{(Silver) } Ne/c=9651.29\pm0.19 \text{ emu (g mole)}^{-1} \text{ (phys. scale) (20 ppm)}. \quad (6.4)$$

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[35] G. W. Vinal and S. J. Bates, Bull. Bur. Standards **10**, 425 (1914); G. W. Vinal and W. M. Bouvard, Bull. Bur. Standards **13**, 147 (1916).

[36] G. W. Vinal, November 22, 1949 and corrected for new atomic mass of iodine (1951) (private communication by J. A. Hipple, December 14, 1951).

The *magnetic moment of the proton* μ' (uncorrected for diamagnetism), expressed in nuclear magnetons $\mu_n = eh/4\pi m_p c$, as obtained by Bloch and Jeffries,[37] using the method of the inverse cyclotron,

$$\mu' = 2.792365 \pm 0.00010 \text{ (36 ppm)} \qquad (6.5)$$

and the same constant as obtained by Sommer, Thomas, and Hipple,[38] using the "omegatron,"

$$\mu' = 2.792685 \pm 0.00003 \text{ (11 ppm)}. \qquad (6.6)$$

The *gyromagnetic ratio for the proton* γ, as obtained at the U. S. National Bureau of Standards by Thomas, Driscoll, and Hipple[39] before making the diamagnetic correction,

$$\gamma = \mu' Ne/(M_p c) = (2.67523 \pm 0.00006) \times 10^4 \text{ sec}^{-1} \text{ gauss}^{-1} \text{ (23 ppm)}. \qquad (6.7)$$

The *conversion factor* $\lambda = \lambda_g/\lambda_s$ from the Siegbahn nominal scale of x-ray wavelengths (expressed in x units) to milliangstroms as recommended for general adoption by Sir Lawrence Bragg[40] after consultation with Professor Manne Siegbahn, Professor B. E. Warren (of the Massachusetts Institute of Technology), and Dr. H. Lipson (of the College of Technology, Manchester, England), and with due consideration given to the analysis of the various sources of primary data by R. T. Birge (see last article of reference 2).

$$\lambda = \lambda_g/\lambda_s = 1.002020 \pm 0.000030 \text{ (30 ppm)}. \qquad (6.8)$$

Three recent precision determinations[41–43] of the *short wavelength limit* of the continuous x-ray spectrum (a) by G. Felt at 24 500 volts, (b) by Bearden, Johnson, and Watts at 10 000 volts and at 6000 volts, and (c) by Bearden and Schwarz at 8000, 9800, and 19600 volts, to obtain the conversion constant from wavelengths in x units on the Siegbahn nominal scale to quantum energy in electron volts, emu:

(G. Felt)

$$hc^2/(\lambda e) = (12370.02 \pm 0.63) \text{ emu cm (51 ppm)}, \qquad (6.9)$$

(B. J. and W.)

$$hc^2/(\lambda e) = (12371.03 \pm 0.48) \text{ emu cm (40 ppm)}, \qquad (6.10)$$

(B. and S.)

$$hc^2/(\lambda e) = (12370.77 \pm 1.03) \text{ emu cm (83 ppm)}. \qquad (6.11)$$

The value of *Avogadro's number multiplied by* λ^2 as obtained by R. T. Birge[2] from his analysis of a considerable number of measurements of the densities of crystals, the geometry of their unit cells and their grating constants expressed on the Siegbhan nominal scale of x units:

$$N\lambda^3 = (6.06179 \pm 0.00023) \times 10^{23} \text{ (g mole)}^{-1} \text{ (physical) (38 ppm)}. \qquad (6.12)$$

The *fine-structure separation in deuterium*, $2^2P_{\frac{3}{2}} - 2^2P_{\frac{1}{2}}$, ΔE_D, measured in frequency units by Dayhoff,[44] using the atomic beam magnetic resonance method,

$$\Delta E_D = (1/16)\alpha^2 R_\infty c \left[1 + (5/8)\alpha^2 + (\alpha/\pi)\left(1 - 5.946\frac{\alpha}{\pi}\right)\right] M_d/D$$
$$= (10971.59 \pm 0.10) 10^6 \text{ sec}^{-1} \text{ (9 ppm)}. \qquad (6.13)$$

7. AUXILIARY CONSTANTS AND EQUATIONS

It will be noted that the quantities[45] involved in expressing the above thirteen primitive observational equations are N, e, m, h, c, α, μ', λ, R_∞, and the masses M_p, D, and M_d on the physical scale of atomic masses. Certain of these quantities are so accurately known from measurements that they can be safely regarded as fixed auxiliary constants, since their relative standard errors are so small as to contribute negligibly when combined in formulas along with the other quantities. These are (a) the masses on the physical scale of atomic masses M_p, D, and M_d along with which we list also H, since it will be needed in computing derived quantities, (b) the Rydberg fundamental wave number R_∞, (c) the ratio of the electron magnetic moment to the proton magnetic moment very recently measured to 0.6 ppm at Columbia by Koenig, Kusch, and Prodell.

The four atomic masses are obtained with great accuracy by the method of measuring nuclear reaction energies:[46]

$$H = 1.008142 \pm 0.000003 \text{ (Physical Scale) (3 ppm)}, \qquad (7.1)$$

$$H/M_p = 1.00054461 \text{ (Computed using } Nm = 0.00054875\text{) (Physical Scale)}, \qquad (7.2)$$

$$D = 2.014735 \pm 0.000006 \text{ (Physical Scale) (3 ppm)}, \qquad (7.3)$$

$$D/M_d = 1.00027244 \text{ (Computed using } Nm = 0.00054875\text{) (Physical Scale)}. \qquad (7.4)$$

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[37] F. Bloch and C. D. Jeffries, Phys. Rev. **80**, 305 (1950); C. D. Jeffries, Phys. Rev. **81**, 1040 (1951).

[38] Sommer, Thomas, and Hipple, Phys. Rev. **82**, 697 (1951).

[39] Thomas, Driscoll, and Hipple, J. Research Natl. Bur. Standards **44**, 569 (1950); Phys. Rev. **78**, 787 (1950).

[40] Sir Lawrence Bragg, Acta Cryst. **1**, 46 (1948); J. Sci. Instr. **24**, 27 (1947).

[41] G. Felt, thesis, California Institute of Technology (1951).

[42] Bearden, Johnson, and Watts, Phys. Rev. **81**, 70 (1951).

[43] J. A. Bearden and G. Schwarz, Phys. Rev. **79**, 674 (1950).

[44] Edward S. Dayhoff, Preprinted Report No. VI on Fine Structure of the Hydrogen Atom, Columbia University (1952).

[45] All the quantities enumerated here appear explicitly in Eqs. (6.1) to (6.13) except m. Because of the Rydberg relationship (R_∞ being so accurately known that we treat it as an exact auxiliary constant) the value of m is implied by the other quantities through the equation $m = 4\pi e^2 R_\infty \alpha^{-3} c^{-2}$, and we therefore list m along with the rest.

[46] Li, Whaling, Fowler, and Lauritsen, Phys. Rev. **83**, 512 (1951).

The numerical value of R_∞ has recently been recomputed[47] taking into consideration the modifications required by the Lamb shift:

$$R_\infty = 109737.311 \pm 0.012 \text{ cm}^{-1} \text{ (0.11 ppm)}. \quad (7.5)$$

The measurement at Columbia by Koenig, Prodell, and Kusch[48] of the ratio of the electron magnetic moment to the proton magnetic moment μ' (without diamagnetic correction) is so accurate as to warrant its inclusion in the category of auxiliary fixed constants

$$[M_p/(Nm\mu')](1+\alpha/2\pi-2.973\ \alpha^2/\pi^2) = 658.2288 \pm 0.0004 \text{ (0.6 ppm)}. \quad (7.6)$$

In addition to the above, there are available two exact auxiliary equations connecting the quantities involved which can be used to reduce the number of variables of the least-squares adjustment. These are the equation expressing α in terms of e, h, and c and the equation for the Rydberg expressed in terms of e, α, c, and m. Solving these for h and m, respectively, we have

$$h = 2\pi e^2/(\alpha c) \quad (7.7)$$

$$m = 4\pi e^2 R_\infty/(\alpha^3 c^2). \quad (7.8)$$

Using the value $1/\alpha = 137.04$, the correction factor μ_e/μ_0 for the anomalous magnetic moment of the electron can be computed with amply sufficient accuracy (less than 0.1 ppm) and it is, therefore, also treated as an auxiliary constant

$$\mu_e/\mu_0 = (1+\alpha/2\pi-2.973\ \alpha^2/\pi^2) = 1.0011453. \quad (7.9)$$

8. FORMATION OF THE LINEARIZED EQUATIONS OF OBSERVATION IN FIVE VARIABLES

We now use Eqs. (7.3)–(7.9) to reduce the number of variables in our solution. None of the original error measures of Eqs. (6.1) to (6.13) are appreciably influenced by the introduction of these very much more accurate auxiliary constants. Hence, the numerics of the new transformed set can be considered to be essentially just as uncorrelated with each other as were the original ones. The new set (with the physical units suppressed) is given below. With these we show on the left the numbers of the earlier equations involved in obtaining each equation. The equations in square brackets are those which contribute negligibly to the error:

(6.1)		$c = 2.997926 \times 10^{10}$	(2.3 ppm)	(8.1)
(6.2)		$c = 2.997931 \times 10^{10}$	(1.1 ppm)	(8.2)
(6.3)		$Ne/c = 9652.15$	(13 ppm)	(8.3)
(6.4)		$Ne/c = 9651.29$	(20 ppm)	(8.4)
(6.5)	[7.5] [7.6] [7.8] [7.9]	$Ne^2/(\alpha^3 c^2) = 3.979879 \times 10^{-10}$	(36 ppm)	(8.5)
(6.6)	[7.5] [7.6] [7.8] [7.9]	$Ne^2/(\alpha^3 c^2) = 3.979423 \times 10^{-10}$	(11 ppm)	(8.6)
(6.7)	[7.5] [7.6] [7.8] [7.9]	$\alpha^3 c/e = 2.425517 \times 10^{13}$	(23 ppm)	(8.7)
(6.8)		$\lambda = 1.002020$	(30 ppm)	(8.8)
(6.9)	[7.7]	$ec/(\lambda\alpha) = 1968.750$	(51 ppm)	(8.9)
(6.10)	[7.7]	$ec/(\lambda\alpha) = 1968.911$	(40 ppm)	(8.10)
(6.11)	[7.7]	$ec/(\lambda\alpha) = 1968.869$	(83 ppm)	(8.11)
(6.12)		$N\lambda^3 = 0.606179 \times 10^{24}$	(38 ppm)	(8.12)
(6.13)	[7.3] [7.4] [7.5]	$\alpha^2 c = 1.596412 \times 10^6$	(9 ppm)	(8.13)

We adopt the following origin values:

$$\alpha_0 = 0.007297000 \qquad (\alpha^2 c)_0 = 1.596268 \times 10^6$$
$$c_0 = 2.997900 \times 10^{10} \qquad (Ne/c)_0 = 9651.174$$
$$e_0 = 4.802200 \times 10^{-10} \qquad (\alpha^3 c/e)_0 = 2.425548 \times 10^{13}$$
$$N_0 = 0.6025000 \times 10^{24} \qquad (Ne^2/\alpha^3 c^2)_0 = 3.978966 \times 10^{-10}$$
$$\lambda_0 = 1.0020200 \qquad (ec/\lambda\alpha)_0 = 1968.959$$
$$(N\lambda^3)_0 = 0.6061585 \times 10^{24}:$$

and define the linearized unknowns $x_1 \cdots x_5$ as follows

$$\alpha = \alpha_0(1+10^{-6}\ x_1)$$
$$c = c_0(1+10^{-6}\ x_2)$$
$$e = e_0(1+10^{-6}\ x_3)$$
$$N = N_0(1+10^{-6}\ x_4)$$
$$\lambda = \lambda_0(1+10^{-6}\ x_5),$$

so that the x's are the relative deviations of the primitive variables from the origin values expressed in ppm.

---

[47] E. R. Cohen, Phys. Rev. **88**, 353 (1952).

[48] Koenig, Prodell, and Kusch, Phys. Rev. **88**, 191 (1952).

We can now write our linearized equations of observation as follows:

$$
\begin{array}{rrrrrlll}
\multicolumn{6}{c}{\text{Linearized Equations of Observation}} & \text{Weight}=1/\sigma^2 & \\
 & x_2 & & & & = 8.7\pm\ 2.3 & 0.198 & (8.14)\\
 & x_2 & & & & = 10.3\pm\ 1.1 & 0.830 & (8.15)\\
 & -x_2 & +x_3 & +x_4 & & = 101\ \pm 13 & 0.0058 & (8.16)\\
 & -x_2 & +x_3 & +x_4 & & = 12\ \pm 20 & 0.0025 & (8.17)\\
-3x_1 & -2x_2 & +2x_3 & +x_4 & & = 229\ \pm 36 & 0.0008 & (8.18)\\
-3x_1 & -2x_2 & +2x_3 & +x_4 & & = 115\ \pm 11 & 0.0083 & (8.19)\\
3x_1 & +x_2 & -x_3 & & & = -\ 13\ \pm 23 & 0.0019 & (8.20)\\
 & & & & x_5 & = 0\ \pm 30 & 0.0011 & (8.21)\\
-x_1 & +x_2 & +x_3 & & -x_5 & = -106\ \pm 51 & 0.0004 & (8.22)\\
-x_1 & +x_2 & +x_3 & & -x_5 & = -\ 24\ \pm 40 & 0.0006 & (8.23)\\
-x_1 & +x_2 & +x_3 & & -x_5 & = -\ 46\ \pm 83 & 0.00015 & (8.24)\\
 & & & x_4 & +3x_5 & = 35\ \pm 38 & 0.0007 & (8.25)\\
2x_1 & +x_2 & & & & = 90\ \pm\ 9 & 0.0123 & (8.26)
\end{array}
$$

9. THE LEAST-SQUARES SOLUTION

The normal equations are now formed from the equations of observation (8.14) to (8.26), according to the classical rule. They are:

$$
\begin{array}{lrrrrrrl}
 & \multicolumn{6}{c}{\text{Normal Equations}} & \\
 & \alpha & c & e & N & \lambda & \text{Const} & \\
\alpha & 0.14935x_1 & +0.08375x_2 & -0.06145x_3 & -0.02730x_4 & +0.00115x_5= & -1.2095 & (9.1)\\
c & 0.08375x_1 & +1.08605x_2 & -0.04545x_3 & -0.02650x_4 & -0.00115x_5= & 8.3784 & (9.2)\\
e & -0.06145x_1 & -0.04545x_2 & +0.04775x_3 & +0.02650x_4 & -0.00115x_5= & 2.8522 & (9.3)\\
N & -0.02730x_1 & -0.02650x_2 & +0.02650x_3 & +0.01810x_4 & +0.00210x_5= & 1.7780 & (9.4)\\
\lambda & 0.00115x_1 & -0.00115x_2 & -0.00115x_3 & +0.00210x_4 & +0.00855x_5= & 0.13720 & (9.5)
\end{array}
$$

The solution of this system of linear equations gives the least-squares adjusted values of the unknowns. The solution together with the corresponding values of the primitive variables are given in Table II.

Substituting these values of the x's into the linearized equations of observation (8.14) to (8.26), one obtains the residues R_i by which each of these thirteen equations fails to balance. Dividing each of these residues by the standard deviation assigned to the observed constant in the equation, we obtain the column of "normalized residues" labeled Case I in Table III, together with the value of $\chi^2=(\Sigma R_i^2/\sigma_i^2)$ and of $r_e/r_i=[\chi^2/(N-q)]^{\frac{1}{2}}$, the ratio of external to internal consistency.

The expectation value of χ^2 for Case I is $N-q=13-5=8$. The actual value 52.1 is seen to be much larger. This corresponds to a ratio of error by external consistency to error by internal consistency of $r_e/r_i=(52.1/8)^{\frac{1}{2}}=2.55$. This large value of χ^2 we interpret as probably meaning that the estimated uncertainties (standard deviations) attached to the various input measurements were throughout somewhat too small. We have used the values given by the experimenters themselves, reduced whenever necessary to the scale of standard deviation. We tend to this view rather than to the alternative possibility that systematic errors are present (though, of course, such a possibility cannot be completely refuted) for the following reason. We have plotted the normalized residues on probability integral graph paper to see if they conform satisfactorily to a normal probability integral distribution curve, which

TABLE II. Least-squares adjusted values.

Linearized unknowns	Primitive variables
$x_1=\ 36.1$	$\alpha=0.007297264$
$x_2=\ 9.80$	$c=2.9979294\times10^{10}$ cm sec^{-1}
$x_3=\ 142.1$	$e=4.802882\times10^{-10}$ esu
$x_4=-45.9$	$N=0.6024723\times10^{24}$ (g mole)$^{-1}$ (Phys.)
$x_5=\ 42.9$	$\lambda=1.002063$

TABLE III. Normalized residues of observational equations.

	R_i/σ_i Case I	R_i/σ_i Case II	R_i/σ_i Case III	R_i/σ_i Case IV
(8.14) c, Froome	0.49	0.49	0.58	0.58
(8.15) c, Bergstrand	−0.46	−0.45	−0.27	−0.28
(8.16) F, Vinal (I)	−1.11		−1.42	
(8.17) F, Vinal (Ag)	3.72		3.51	
(8.18) μ', B J	−3.36	−3.06	−3.12	−2.92
(8.19) μ', STH	−0.44	0.52	0.35	0.96
(8.20) γ, TDH	−0.47	1.29	−1.03	0.21
(8.21) λ, Bragg	1.42	0.53	1.01	0.42
(8.22) h/e, Felt	3.58	3.34		
(8.23) h/e, BJW	2.37	2.09		
(8.24) h/e, BS	1.45	1.31		
(8.25) $N\lambda^3$, Birge	1.26	1.47	−0.42	−0.18
(8.26) ΔE_D, Dayhoff	−0.88	−0.68	−0.15	−0.06
$\chi^2=$	52.1	31.9	26.9	10.15
$r_e/r_i=$	2.55±0.90	2.31±0.95	2.32±1.04	1.84±1.06

on such paper would appear as a straight line.[49] If one or two of the observational equations were subject to a large systematic error, one would expect these to exhibit residues inconsistent with the rest, i.e., departing markedly from the curve for the normal distribution. Fig. 1 shows this plot, and the fluctuations from the normal do not appear to be larger than one would expect for a sample with eight degrees of freedom. We have also performed three additional least-squares adjustments designated as Case II, Case III, and Case IV. In Case II Eqs. (8.16) and (8.17), the two Faraday determinations by electrochemistry, were omitted. In Case III Eqs. (8.22), (8.23), and (8.24), the three x-ray determinations of the quantum limit of the continuous spectrum, were omitted. In Case IV both complete sets of determinations were omitted. Table III gives the normalized residues for these four cases together with the resulting values of χ^2. The normalized residues for each of the four cases are shown in Figs. 1 to 4, and all are approximately equally satisfactory. The values of χ^2 and of r_e/r_i also are not significantly more plausible or satisfactory for Cases II, III, and IV than for Case I. For these reasons, then, we think that the large value of r_e/r_i in Case I probably does not reflect any single large isolated case of systematic error among the thirteen input data. We are basing our adjusted output values on Case I, because it reflects the results of more input data than the other cases.

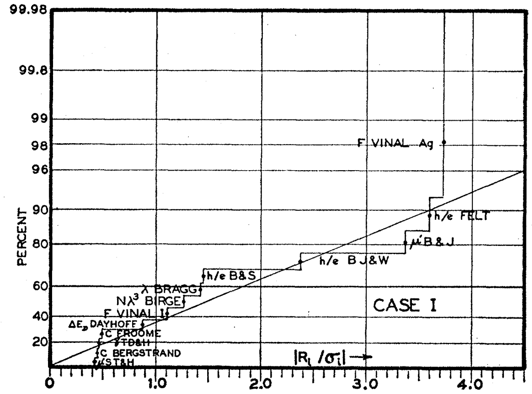

FIG. 1. The normalized residues $|R_i/\sigma_i|$ for a least squares adjustment of the entire thirteen input observational data are here shown as abscissas plotted without regard to algebraic sign in order of increasing absolute magnitude on probability graph paper whose ordinates are so distorted from a linear scale of percent as to rectify probability integral graphs for Gaussian distributions into straight lines of different slopes for different values of χ^2. The straight line shown corresponds to $\chi^2=52.1$, the result for this case in which there are thirteen input equations and eight degrees of freedom. The ratio of the error by external to that by internal consistency is $R_E/R_I=2.55\pm0.90$.

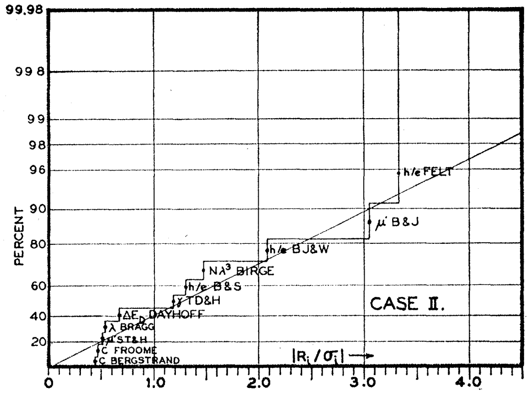

FIG. 2. The normalized residues $|R_i/\sigma_i|$ for a least squares adjustment of all input data save the two electrochemical measurements of the Faraday plotted in similar manner to those of Fig. 1. The straight line shown corresponds to $\chi^2=31.9$, the result for this case in which there are eleven input equations and six degrees of freedom. The ratio of the error by external to that by internal consistency is $R_E/R_i=2.31\pm0.95$.

Adopting the error by external consistency as the measure of error we obtain the error elements shown in Table IV.

In computing the standard deviation of any function of α, c, e, N, and λ, the appropriate elements of the error matrix must be used in Eq. (4.15) as explained in Sec. 4. The tables of atomic constants and conversion factors have been computed using the least squares adjusted values of α, c, e, N, and λ given above together with the auxiliary constants given in the tables, and the standard deviation of derived values following each (±) sign has been computed from Eq. (4.15), using values from the error matrix of Table IV. The reader must realize that if he uses any of these values (either the unknowns α, c, e, N, λ, or tabular values derived

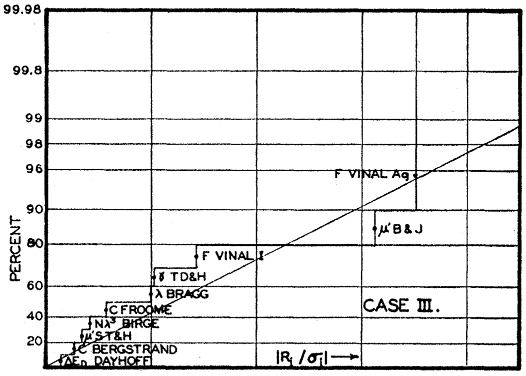

FIG. 3. The normalized residues $|R_i/\sigma_i|$ for a least squares adjustment of all input data save the three x-ray measurements of the short wavelength limit of the continuous spectrum plotted in similar manner to those of Fig. 1. The straight line shown corresponds to $\chi^2=26.9$, the result for this case in which there are ten input equations and five degrees of freedom. The ratio of the error by external to that by internal consistency is $R_E/R_i=2.3\pm1.0$.

---

[49] We are indebted to Professor John Tukey of Princeton for pointing out to us that for the case of a small number of degrees of freedom it is very unlikely that the residuals should be exactly normally distributed. In the present instance let it be understood therefore that we are merely *comparing* the actual distribution of residuals with a normal distribution as a type-form but without any implication as to what precisely their expected distribution *should* be.

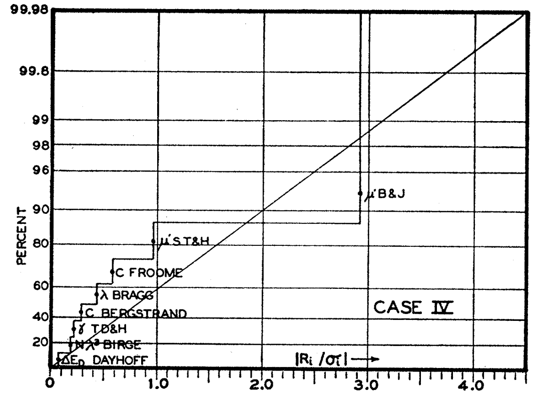

FIG. 4. The normalized residues $|R_i/\sigma_i|$ for a least squares adjustment of all input data save the three x-ray measurements of the short wavelength limit of the continuous spectrum and the two electrochemical measurements of the Faraday plotted in similar manner to those of Fig. 1. The straight line shown corresponds to $\chi^2=10.2$, the result for this case in which there are eight input equations and three degrees of freedom. The ratio of the error by external to that by internal consistency is $R_E/R_i=1.8\pm1.1$.

from these) in further computations, he *must* compute the standard deviation of his results by this more generalized method. We give the following example as an illustration.

10. ILLUSTRATIVE EXAMPLE OF COMPUTATION OF THE STANDARD DEVIATION OF A FUNCTION OF TABULAR VALUES OBTAINED IN THE PRESENT LEAST-SQUARES ANALYSIS

Compute the standard deviation for the ionization energy $I_0=e^2/(2a_0)$ of a hydrogen atom. The Bohr radius is $a_0=h^2/(4\pi^2me^2)$. This is expressed as a function of two variables h and m which are not explicit members of our set of unknowns α, c, e, N, and λ. We have, however, relations (7.7) and (7.8) which relate h and m to those unknowns,

$$(7.7)\quad h=2\pi e^2/(\alpha c)$$
$$(7.8)\quad m=4\pi e^2R_\infty/(\alpha^3c^2),$$

and upon substitution we find that $a_0=\alpha/(4\pi R_\infty)$ so that our desired quantity is $I_0=2\pi R_\infty e^2/\alpha$. The standard deviation in R_∞ (0.11 ppm, see Eq. 7.5) is completely negligible as against contributions of e^2 and α. In terms of the linearized variables the function $\varphi=e^2/\alpha$ whose standard deviation we seek then is

$$f=2x_3-x_1, \tag{10.1}$$

in which we see that the values of the coefficients are $\alpha_3=2$ and $\alpha_1=-1$. (In general, whatever the form of the primitive function φ the α_j's are determined from it by the formula $\alpha_j=(\partial\varphi/\partial u_j)(u_j/\varphi)$, wherein u_j is one of the primitive unknowns, i.e., in the present solution α, c, e, N, or λ). It remains then simply to apply formula (4.15) to obtain σ_f^2 which, written out for this case, is

$$\sigma_f^2=\alpha_1^2\sigma_1^2+\alpha_3^2\sigma_3^2+2\alpha_1\alpha_3\sigma_1\sigma_3r_{13} \tag{10.2}$$
$$=\sigma_1^2+4\sigma_3^2-4\sigma_1\sigma_3r_{13}. \tag{10.3}$$

From the error matrix given in Table IV, we find

$$\sigma_1^2=128;\quad \sigma_3^2=1981;\quad \sigma_1\sigma_3r_{13}=365$$
$$\sigma_f^2=128+7924-1460=6592$$
$$\sigma_f=(6592)^{\frac{1}{2}}=81.1\text{ ppm}.$$

11. DISCUSSION OF THE RESULTS

It is of interest to examine the results of the various analyses for "best" values of the atomic constants made over the last quarter century to obtain an impression as to what progress toward precision and stabilization of the values has been accomplished. Accordingly, we have plotted in Fig. 5 the relative deviations from the present values of h, α^{-1}, e, m, and N and also the estimated probable errors for determinations by various authors in different years: R. T. Birge, 1929; R. T. Birge, 1932; F. G. Dunnington, 1939; R. T. Birge, 1941; R. T. Birge, 1944; DuMond and Cohen, 1947; DuMond and Cohen, 1950; DuMond and Cohen, 1952. The marked instability from 1929 to 1939 is chiefly to be ascribed to the discrepancy arising from R. A. Millikan's use of the incorrect value of the viscosity of air (Harrington's determination) in reducing the data of his oil-drop experiment to determine e. Numerous lesser discrepancies connected with e/m and with h/e which existed at that time have since been discovered and eliminated also.

The improvement as regards both stability and precision has been so great after 1939 that we have felt it worthwhile also to represent the last thirteen years in Fig. 6 to a scale of deviation fivefold that in Fig. 5.

Examination of these charts, especially Fig. 6, shows that the adjusted "best" values have changed in the last two years by from five to nine times the estimated probable errors of the December 1950 evaluation.

TABLE IV. Error elements (external consistency), Case I.

Error matrix, $v_{ij}=\sigma_i\sigma_jr_{ij}$ (in ppm^2)

	α	c	e	N	λ
α	128	−3.30	365	−355	118
c	−3.30	6.34	−4.13	10.47	−1.82
e	365	−4.13	1981	−2454	820
N	−355	10.47	−2454	3568	−1158
λ	118	−1.82	820	−1158	1140

Standard errors σ_i (in ppm)

α	c	e	N	λ
11.33	2.52	444	59.7	33.8

Correlation coefficients r_{ij}

	α	c	e	N	λ
α	1.000	−0.116	0.714	−0.521	0.308
c	−0.116	1.000	−0.036	0.070	−0.021
e	0.714	−0.036	1.000	−0.923	0.546
N	−0.521	0.070	−0.923	1.000	−0.574
λ	0.308	0.021	0.546	−0.574	1.000

Although the changes are small in the absolute sense (the largest being 224 ppm, for h) they are, at first sight, disturbingly large relative to the estimated probable errors of December, 1950. However, we believe the explanation for this is not hard to find, if we recall that the December, 1950 values, unlike the present ones, were afflicted with a systematic uncertainty because of the two uncertain Bethe-Longmire correction terms for the finite spatial extension of the nuclear and electronic dipoles, in the formula connecting $\Delta\nu_H$, the hydrogen hyperfine structure shift, with the Sommerfeld constant α. We supplied each numerical output value in the solution with a so-called Γ-coefficient to facilitate revising the numerical values when more accurate information became available regarding the exact magnitude of the Bethe-Longmire correction terms. We find that if we assign the value $\Gamma=86.2\pm9$ ppm, that is to say if we increase G^2 in the formula

$$\Delta\nu_H=\frac{\alpha^2}{4\pi^2}(\mu_p/\mu_0)R_\infty cG^{-2}, \qquad (11.1)$$

by 86.2 ppm[50] (see p. 180 ff of the December, 1950 report), then the application of the resulting corrections to the five variables depicted in Fig. 6 simultaneously brings all of them fairly satisfactorily into agreement with the values obtained in the present adjustment. This is shown with the dotted lines in Fig. 6.

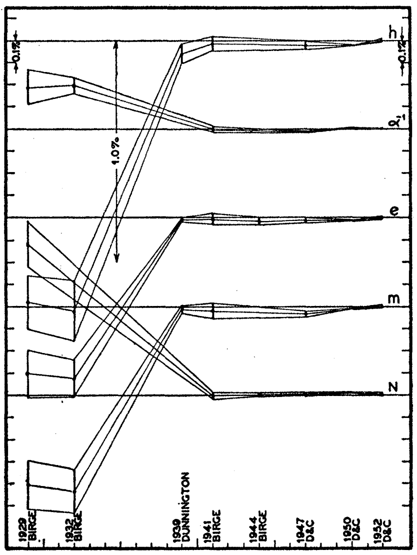

FIG. 5. History of relative fluctuations in the best adjusted values and probable errors of five atomic constants h, α^{-1}, e, m, and N over a 23-year interval. Fluctuations plotted as percent deviations from the present 1952 values. Probable errors rather than standard deviations are plotted to conform with the older usage prevailing through most of the interval. The large fluctuations in the first decade are chiefly due to the effects of Millikan's use of Harrington's erroneous value of the viscosity of air in reducing his oil-drop data to calculate e.

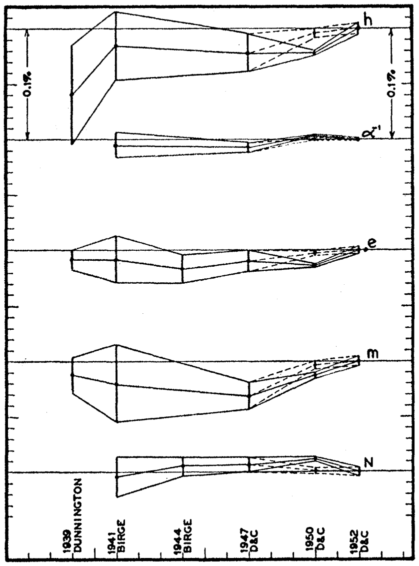

FIG. 6. History of relative fluctuations in the best adjusted values and probable errors of five atomic constants h, α^{-1}, e, m, and N over a 13 year interval plotted to five times larger scale of fluctuation than in Fig. 5. The fluctuations plotted are the percent deviations from the present 1952 values. As in Fig. 5, probable errors rather than standard deviations are plotted as the indices of precision. The full lines are plotted through the December, 1950 values and their probable errors as they were stated in the tables without applying any Γ-coefficient correction for the then uncertain Bethe-Longmire dipole correction terms. The dotted lines are plotted through the revisions required in the December, 1950 values, if these are modified by applying a Γ-coefficient correction to each output value with $\Gamma=86.2$ ppm, as explained in the text.

In addition to the shift in the values of the constants, a change of 86.2 ppm in G^2 increases the probable errors of the 1950 output data by a factor of 1.48, if one uses external consistency (which has now become the larger measure of error) in place of the internal consistency used in the 1950 report. The evaluation of the variation of χ^2 and, hence, of the measure of the errors by external consistency is contained in Table XXXVII of that report.

The general conclusion seems to be a reassuring one, namely, that the constants are settling down to stable values and that successive determinations, even though many quite new and different types of data may enter, not only exhibit smaller and smaller precision measures by external consistency but also yield values which remain reasonably close to the limits set by preceding precision measures.

The Bethe-Longmire correction factor for the spatial

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[50] This increase of 86.2 ppm was computed by solving for a new value of G^2 to compare with the 1950 value, $G^2=0.004751364$. The new value G^2 was obtained from Eq. (11.1), using our present new adjusted best values of α and c and a value of μ_p/μ_0 consistent with the results of Koenig, Kusch, and Prodell (reference 60) Eq. 7.6, corrected for diamagnetism using Ramsey's correction (1.000027). The new value of G^2 thus is not afflicted with any uncertainty regarding the Bethe-Longmire nuclear correction term as was the 1950 value. We regret to point out a misprint in the cited formula for $\Delta\nu_H$ near the bottom of p. 180 of the December, 1950 report (reference 33), in which a factor $c/4\pi^2$ was omitted. It should read as does Eq. 11.1.

extension of the electronic dipole has been computed by R. Karplus and A. Klein,[34] who conclude that this part of the correction alone requires a Γ value of 96.2 ppm to be applied to the results of the December, 1950 report. The conclusion seems to be that the factor correcting for the spatial extension of the nuclear dipole must be of the order of the uncertainties in the above calculations, or only a few ppm at most.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge our indebtedness to the various research workers who have been so kind as to furnish us with their results in advance of publication or to clarify for us doubtful points about which we have inquired. Our grateful appreciation is given to Mrs. Melba Nead of North American Aviation, Incorporated (Downey, California) for her careful and diligent assistance in the computations. We are deeply indebted to Professor John Tukey of Princeton, who has read our manuscript with care from the viewpoint of a mathematical statistician and has made a number of helpful suggestions for its correction and improvement. The work has been carried out as part of the activity of a contract financially supported by the U. S. Office of Naval Research and the U. S. Atomic Energy Commission.

TABLE OF LEAST SQUARES—ADJUSTED OUTPUT VALUES (NOVEMBER, 1952)

I. Auxiliary Constants Used

These auxiliary constants are quantities which are uncorrelated (observationally) with the variables of the least-squares adjustment.

Rydberg wave number for infinite mass[51]

$R_\infty = 109737.309 \pm 0.012$ cm^{-1}

Rydberg wave numbers for the light nuclei

$R_{\mathrm{H}} = 109677.576 \pm 0.012$ cm^{-1}
$R_{\mathrm{D}} = 109707.419 \pm 0.012$ cm^{-1}
$R_{\mathrm{He}^3} = 109717.345 \pm 0.012$ cm^{-1}
$R_{\mathrm{He}^4} = 109722.267 \pm 0.012$ cm^{-1}

Atomic mass of neutron

$\mathrm{n} = 1.008982 \pm 0.000003$

Atomic mass of hydrogen

$\mathrm{H} = 1.008142 \pm 0.000003$

Atomic mass of deuterium

$\mathrm{D} = 2.014735 \pm 0.000006$

Gas constant per mole (physical scale)

$R_0 = (8.31662 \pm 0.00038) \times 10^7$ erg mole^{-1} deg^{-1} C.

Standard volume of a perfect gas (physical scale)

$V_0 = 22420.7 \pm 0.6$ cm^3 atmos mole^{-1}

II. Least-Squares Adjusted Output Values

(The quantity following each ± sign is the standard error by external consistency)

Velocity of light

$c = 299792.9 \pm 0.8$ km sec^{-1}

Avogadro's constant (physical scale)

$N = (6.02472 \pm 0.00036) \times 10^{23}$ (g mole)$^{-1}$

Loschmidt's constant (physical scale)

$L_0 = N/V_0 = (2.68713 \pm 0.00016) \times 10^{19}$ cm^{-3}

Electronic charge

$e = (4.80288 \pm 0.00021) \times 10^{-10}$ esu
$e' = e/c = (1.60207 \pm 0.00007) \times 10^{-20}$ emu

Electron rest mass

$m = (9.1085 \pm 0.0006) \times 10^{-28}$ g

Proton rest mass

$m_p = M_p/N = (1.67243 \pm 0.00010) \times 10^{-24}$ g

Neutron rest mass

$m_n = n/N = (1.67474 \pm 0.00010) \times 10^{-24}$ g

Planck's constant

$h = (6.6252 \pm 0.0005) \times 10^{-27}$ erg sec
$\hbar = h/(2\pi) = (1.05444 \pm 0.00009) \times 10^{-27}$ erg sec

Conversion factor from Siegbahn x units to milliangstroms

$\lambda_g/\lambda_s = 1.002063 \pm 0.000034$

Faraday constant (physical scale)

$F = Ne = (2.89360 \pm 0.00007) \times 10^{14}$ esu (g mole)$^{-1}$
$F' = Ne/c = (9652.01 \pm 0.25)$ emu (g mole)$^{-1}$

Charge-to-mass ratio of the electron

$e/m = (5.27299 \pm 0.00016) \times 10^{17}$ esu g^{-1}
$e'/m = e/(mc) = (1.75888 \pm 0.00005) \times 10^7$ emu g^{-1}

Ratio h/e

$h/e = (1.37943 \pm 0.00005) \times 10^{-17}$ erg sec (esu)$^{-1}$

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[51] This differs from the value $R_\infty = 109737.311 \pm 0.012$ cm^{-1} given by E. R. Cohen (reference 47) and which was used in the least squares adjustment. In reference 47 a tentative value $Nm = 5.48785 \times 10^{-4}$ for the atomic mass of the electron was used with the proviso (page 359) that "an increase of 1 part per million in the electron mass will produce an increase of 0.00005 cm^{-1} in the Rydberg." (The coefficient 0.0005 cm^{-1} in the text is a typographical error.) The present value has, therefore, been revised using this coefficient to accord with our present output value of Nm and similar modifications have been made in the Rydberg values of the light nuclei.

Fine structure constant

$$\alpha = e^2/(\hbar c) = (7.29726 \pm 0.00008) \times 10^{-3}$$
$$1/\alpha = 137.0377 \pm 0.0016$$
$$\alpha/2\pi = (1.161396 \pm 0.000013) \times 10^{-3}$$
$$\alpha^2 = (5.32501 \pm 0.00012) \times 10^{-5}$$
$$1-(1-\alpha^2)^{\frac{1}{2}} = (0.266254 \pm 0.000006) \times 10^{-4}$$

Atomic mass of the electron (physical scale)

$$Nm = (5.48760 \pm 0.00013) \times 10^{-4}$$

Ratio of mass of hydrogen to mass of proton[52]

$$H/H^+ = \left[1 - \frac{Nm}{H}\left(1 - \tfrac{1}{2}\alpha^2\right)\right]^{-1}$$
$$= 1.000544610 \pm 0.000000013$$

Atomic mass of proton

$$H^+ = 1.007593 \pm 0.000003$$

Ratio of proton mass to electron mass

$$H^+/Nm = 1836.13 \pm 0.04$$

Reduced mass of electron in hydrogen atom

$$\mu = mH^+/H = (9.1035 \pm 0.0006) \times 10^{-28} \text{ g}$$

Schrödinger constant for a fixed nucleus

$$2m/\hbar^2 = (1.63844 \pm 0.00016) \times 10^{27} \text{ erg}^{-1} \text{ cm}^{-2}$$

Schrödinger constant for the hydrogen atom

$$2\mu/\hbar^2 = (1.63755 \pm 0.00016) \times 10^{27} \text{ erg}^{-1} \text{ cm}^{-2}$$

First Bohr radius

$$a_0 = \hbar^2/(me^2) = (5.29171 \pm 0.00006) \times 10^{-9} \text{ cm}$$
$$= \alpha/(4\pi R_\infty)$$

Radius of electron orbit in normal H^1, referred to center of mass

$$a_0' = a_0(1-\alpha^2)^{\frac{1}{2}} = (5.29157 \pm 0.00006) \times 10^{-9} \text{ cm}$$

Separation of proton and electron in normal H^1

$$a_0'' = a_0' R_\infty / R_H = (5.29445 \pm 0.00006) \times 10^{-9} \text{ cm}$$

Compton wavelength of the electron

$$\lambda_{ce} = h/(mc) = (24.2625 \pm 0.0006) \times 10^{-11} \text{ cm}$$
$$= \alpha^2/(2R_\infty)$$
$$\bar{\lambda}_{ce} = \lambda_{ce}/(2\pi) = (3.86150 \pm 0.00009) \times 10^{-11} \text{ cm}$$
$$= \alpha^2/(4\pi R_\infty)$$

Compton wavelength of the proton

$$\lambda_{cp} = h/m_p c = (13.2139 \pm 0.0004) \times 10^{-14} \text{ cm}$$
$$\bar{\lambda}_{cp} = \lambda_{cp}/(2\pi) = (2.10307 \pm 0.00007) \times 10^{-14} \text{ cm}$$

Compton wavelength of the neutron

$$\lambda_{cn} = h/m_n c = (13.1958 \pm 0.0004) \times 10^{-14} \text{ cm}$$
$$\bar{\lambda}_{cn} = \lambda_{cn}/(2\pi) = (2.10017 \pm 0.00007) \times 10^{-14} \text{ cm}$$

Classical electron radius

$$r_0 = e^2/(mc^2) = (2.81784 \pm 0.00010) \times 10^{-13} \text{ cm}$$
$$= \alpha^3/(4\pi R_\infty)$$
$$r_0^2 = (7.9402 \pm 0.0005) \times 10^{-26} \text{ cm}^2$$

Thompson cross section

$$\frac{8}{3}\pi r_0^2 = (6.65196 \pm 0.0005) \times 10^{-25} \text{ cm}^2$$

Fine structure doublet separation in hydrogen

$$\Delta E_H = \frac{1}{16} R_H \alpha^2 \left[1 + \frac{\alpha}{\pi} + \left(\frac{5}{8} - \frac{5.946}{\pi^2}\right)\alpha^2\right]$$
$$= 0.365869 \pm 0.000008 \text{ cm}^{-1}$$
$$= 10968.49 \pm 0.25 \text{ Mc sec}^{-1}$$

Fine structure separation in deuterium

$$\Delta E_D = \Delta E_H R_D / R_H = 0.365969 \pm 0.000008 \text{ cm}^{-1}$$
$$= 10971.48 \pm 0.25 \text{ Mc/sec}^{-1}$$

Zeeman displacement per gauss

$$(e/mc)/(4\pi c) = (4.66879 \pm 0.00015) \times 10^{-5} \text{ cm}^{-1} \text{ gauss}^{-1}$$

Boltzmann's constant

$$k = R_0/N = (1.38042 \pm 0.00010) \times 10^{-16} \text{ ergs deg}^{-1}$$
$$k = (8.6164 \pm 0.0004) \times 10^{-5} \text{ ev deg}^{-1}$$
$$1/k = 11605.7 \pm 0.5 \text{ deg ev}^{-1}$$

First radiation constant

$$c_1 = 8\pi hc = (4.9919 \pm 0.0004) \times 10^{-15} \text{ erg cm}$$

Second radiation constant

$$c_2 = hc/k = (1.43884 \pm 0.00008) \text{ cm deg}$$

Atomic specific heat constant

$$c_2/c = (4.79946 \pm 0.00027) \times 10^{-11} \text{ sec deg}$$

Wein displacement law constant[53]

$$\lambda_{\max} T = c_2/(4.96511423) = 0.28979 \pm 0.00005 \text{ cm deg.}$$

Stefan-Boltzmann constant

$$\sigma = (\pi^2/60)(k^4/\hbar^3 c^2) = (0.56686 \pm 0.00005) \times 10^{-4} \text{ erg cm}^{-2} \text{ deg}^{-4} \text{ sec}^{-1}$$

Sackur-Tetrode constant

$$S_0/R_0 = \tfrac{5}{2} + \ln\left\{(2\pi R_0)^{\frac{3}{2}} h^{-3} N^{-4}\right\}$$
$$= -5.57324 \pm 0.00011$$
$$S_0 = -(46.3505 \pm 0.0017) \times 10^{7} \text{ erg mole}^{-1} \text{ deg}^{-1}$$

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[52] The binding energy of the electron in the hydrogem atom has been included in the quantity. The mass of the electron when found in the hydrogen atom is not m, but more correctly $m(1-\frac{1}{2}\alpha^2+\cdots)$.

[53] The numerical constant 4.96511423 is the root of the transcendental equation $x=5(1-e^{-x})$.

Bohr magneton

$$\mu_0 = he/(4\pi mc) = \tfrac{1}{2}e\lambda\!\!\!^{-}_{ce} = (0.92732 \pm 0.00006) \times 10^{-20} \text{ erg gauss}^{-1}$$

Anomalous electron moment correction

$$\left[1 + \frac{\alpha}{2\pi} - 2.973\frac{\alpha^2}{\pi^2}\right] = \mu_e/\mu_0 = 1.001145356 \pm 0.000000013$$

Magnetic moment of the electron

$$\mu_e = (0.92838 \pm 0.00006) \times 10^{-20} \text{ erg gauss}^{-1}$$

Nuclear magneton

$$\mu_n = he/(4\pi m_p c) = \mu_0 Nm/\mathrm{H}^+ = (0.505038 \pm 0.000036) \times 10^{-23} \text{ erg gauss}^{-1}$$

Proton moment

$$\mu = 2.79277 \pm 0.00006 \text{ nuclear magnetons}$$
$$= (1.41045 \pm 0.00009) \times 10^{-23} \text{ erg gauss}^{-1}$$

Gyromagnetic ratio of the proton in hydrogen, uncorrected for diamagnetism

$$\gamma' = (2.67520 \pm 0.00008) \times 10^4 \text{ radians sec}^{-1} \text{ gauss}^{-1}$$

Gyromagnetic ratio of the proton (corrected)

$$\gamma = (2.67527 \pm 0.00008) \times 10^4 \text{ radians sec}^{-1} \text{ gauss}^{-1}$$

Multiplier of (Curie constant)$^{\frac{1}{2}}$ to give magnetic moment per molecule

$$(3k/N)^{\frac{1}{2}} = (2.62178 \pm 0.00017) \times 10^{-20} (\text{erg mole deg}^{-1})^{\frac{1}{2}}$$

Mass-Energy conversion factors

$$1 \text{ g} = (5.60999 \pm 0.00025) \times 10^{26} \text{ Mev}$$
$$1 \text{ electron mass} = 0.510984 \pm 0.000016 \text{ Mev}$$
$$1 \text{ atomic mass unit} = 931.162 \pm 0.024 \text{ Mev}$$
$$1 \text{ proton mass} = 938.232 \pm 0.024 \text{ Mev}$$
$$1 \text{ neutron mass} = 939.526 \pm 0.024 \text{ Mev}$$

Quantum energy conversion factors

$$1 \text{ ev} = (1.60207 \pm 0.00007) \times 10^{-12} \text{ erg}$$
$$E/\tilde{\nu} = (1.98620 \pm 0.00016) \times 10^{-16} \text{ erg cm}$$
$$E\lambda_g = (12397.8 \pm 0.5) \times 10^{-8} \text{ ev-cm}$$
$$E\lambda_s = 12372.2 \pm 0.4 \text{ kilovolt } x \text{ units}$$
$$E/\nu = (6.6252 \pm 0.0005) \times 10^{-27} \text{ erg sec}$$
$$E/\nu = (4.13544 \pm 0.00015) \times 10^{-15} \text{ ev-sec}$$
$$\tilde{\nu}/E = (5.0347 \pm 0.0004) \times 10^{15} \text{ cm}^{-1} \text{ erg}^{-1}$$
$$\tilde{\nu}/E = (8065.98 \pm 0.30) \text{ cm}^{-1} \text{ ev}^{-1}$$
$$\nu/E = (1.50938 \pm 0.00012) \times 10^{26} \text{ sec}^{-1} \text{ erg}^{-1}$$
$$\nu/E = (2.41812 \pm 0.00009) \times 10^{14} \text{ sec}^{-1} \text{ ev}^{-1}$$

de Broglie wavelengths, λ_D of elementary particles[54]

Electrons

$$\lambda_{De} = (7.27373 \pm 0.00016) \text{ cm}^2 \text{ sec}^{-1}/v$$
$$= (1.55226 \pm 0.00008) \times 10^{-13} \text{ cm } (\text{erg})^{\frac{1}{2}}/(E)^{\frac{1}{2}}$$
$$= (1.226377 \pm 0.000032) \times 10^{-7} \text{ cm } (\text{ev})^{\frac{1}{2}}/(E)^{\frac{1}{2}}$$

Protons

$$\lambda_{Dp} = (3.96145 \pm 0.00013) \times 10^{-3} \text{ cm}^2 \text{ sec}^{-1}/v$$
$$= (3.62261 \pm 0.00020) \times 10^{-15} \text{ cm } (\text{erg})^{\frac{1}{2}}/(E)^{\frac{1}{2}}$$
$$= (2.86208 \pm 0.00012) \times 10^{-9} \text{ cm } (\text{ev})^{\frac{1}{2}}/(E)^{\frac{1}{2}}$$

Neutrons

$$\lambda_{Dn} = (3.95599 \pm 0.00013) \times 10^{-3} \text{ cm}^2 \text{ sec}^{-1}/v$$
$$= (3.62005 \pm 0.00020) \times 10^{-15} \text{ cm } (\text{erg})^{\frac{1}{2}}/(E)^{\frac{1}{2}}$$
$$= (2.86005 \pm 0.00012) \times 10^{-9} \text{ cm } (\text{ev})^{\frac{1}{2}}/(E)^{\frac{1}{2}}$$

Energy of 2200 m/sec neutron

$$E_{2200} = 0.0252977 \pm 0.0000006 \text{ ev}$$

Velocity of 1/40 ev neutron

$$v_{0.025} = 2187.017 \pm 0.028 \text{ m/sec}$$

The Rydberg and related derived constants

$$R_\infty = 109737.309 \pm 0.012 \text{ cm}^{-1}$$
$$R_\infty c = (3.289847 \pm 0.000008) \times 10^{15} \text{ sec}^{-1}$$
$$R_\infty hc = (2.17961 \pm 0.00018) \times 10^{-11} \text{ erg}$$
$$\frac{R_\infty hc^2 \times 10^{-8}}{e} = 13.6050 \pm 0.0005 \text{ ev}$$

Hydrogen ionization potential

$$I_0 = 13.5978 \pm 0.0005 \text{ ev}$$
$$= R_H \frac{hc^2}{e}\left[1 + \frac{\alpha^2}{4} + \cdots\right] \times 10^{-8}$$

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[54] These formulas apply only to nonrelativistic velocities. If the velocity of the particle is not negligible compared to the velocity of light c or the energy not negligible compared to the rest mass energy, we must use $\lambda_D = \lambda_c[\epsilon(\epsilon+2)]^{-\frac{1}{2}}$, where λ_c is the appropriate Compton wavelength and ϵ is the kinetic energy measured in units of the particle rest mass.