

Fundamental Constants and the Hydrogen Atom^{*}

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Abstract. A review is given of the latest adjustment of the values of the fundamental constants. The new values are recommended by the Committee on Data for Science and Technology (CODATA) for international use. Most of the fundamental constants are obtained by the comparison of the results of critical experiments and the corresponding theoretical expressions based on quantum electrodynamics (QED). An important case is the Rydberg constant which is determined primarily by precise frequency measurements in hydrogen and deuterium.

1 Introduction

The 1998 adjustment of the values of the fundamental physical constants has been carried out by the authors under the auspices of the CODATA Task Group on Fundamental Constants [1,2]. The purpose of the adjustment is to determine “best” values of various fundamental constants such as the fine-structure constant, Rydberg constant, Avogadro constant, Planck constant, electron mass, muon mass, as well as many others, that provide the greatest consistency among the most critical experiments based on relationships derived from condensed matter theory and quantum electrodynamics (QED) theory. The 1998 CODATA recommended values of the constants also may be found on the Web at: physics.nist.gov/constants.

2 1998 Least Squares Adjustment

We first recall the method of least squares as it is applied to the adjustment of values of the fundamental constants. The experimental results, or possibly theoretical results, form the observational data q_1, q_2, \dots, q_N . A selected set of the fundamental constants z_1, z_2, \dots, z_M ($M \leq N$), are the “unknowns” or variables (also called adjusted constants) of the adjustment and are related to the data by observational equations of the form

$$q_i \doteq f_i(z) \equiv f_i(z_1, z_2, \dots, z_M) ; \quad i = 1, 2, \dots, N . \quad (1)$$

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The symbol \doteq is employed, because, in general, the system of equations is overdetermined and an equality is not possible for all of the data.

The equations are nonlinear, and we make a linear approximation about starting values s for z :

$$q_i \doteq f_i(s) + \sum_{j=1}^M \frac{\partial f_i(s)}{\partial s_j} (z_j - s_j) + \cdots, \quad (2)$$

or

$$y_i \doteq \sum_{j=1}^M a_{ij} x_j + \cdots, \quad (3)$$

where $y_i = q_i - f_i(s)$, $x_j = z_j - s_j$, and

$$a_{ij} = \frac{\partial f_i(s)}{\partial s_j}. \quad (4)$$

In terms of matrices (where X denotes a matrix with elements x_j , etc.) we have

$$Y \doteq AX \quad (5)$$

with *covariance matrix* $V = \text{cov}(Y)$, where the elements $\text{cov}(Y)_{ii}$ are the variances of the q_i and the elements $\text{cov}(Y)_{ij} = \text{cov}(Y)_{ji}$ are the covariances of the q_i and q_j . The least-squares solution \hat{X} for X that minimizes

$$(Y - AX)^\top V^{-1} (Y - AX) \quad (6)$$

with respect to X is given by

$$\hat{X} = (A^\top V^{-1} A)^{-1} A^\top V^{-1} Y \quad (7)$$

$$\text{cov}(\hat{X}) = (A^\top V^{-1} A)^{-1} \quad (8)$$

and

$$\hat{Z} = S + \hat{X} \quad (9)$$

$$\text{cov}(\hat{Z}) = \text{cov}(\hat{X}) \quad (10)$$

$$\hat{Y} = A\hat{X} \quad (11)$$

$$\hat{q}_i = f_i(s) + \hat{y}_i. \quad (12)$$

If the observational data Y are uncorrelated, then we have

$$(Y - AX)^\top V^{-1} (Y - AX) = \sum_{i=1}^N \frac{(Y - AX)_i^2}{\text{cov}(Y)_{ii}}. \quad (13)$$

Some of the adjusted constants used in the 1998 least-squares adjustment are given in Table 1. In that table, the relative atomic masses are defined by

$$A_r(x) = \frac{m_x}{\frac{1}{12}m(^{12}\text{C})}, \quad (14)$$

where $m(^{12}\text{C})$ is the mass of the carbon 12 atom. The quantities a_e and a_μ are the magnetic moment anomalies of the electron and muon, respectively, $\Delta\nu_{\text{Mu}}$ is the ground-state hyperfine splitting in muonium, and $E_{\text{H}}(nL_j)$ and $E_{\text{D}}(nL_j)$ are the energies of the nL_j levels in hydrogen and deuterium, respectively. (Here, n is the principal quantum number, L is the nonrelativistic orbital angular momentum symbol, and j is the total angular momentum quantum number of the level.) The corrections δ_e , $\delta_{\text{H}}(nL_j)$, and $\delta_{\text{D}}(nL_j)$ are discussed below.

Table 1. Some of the adjusted constants used in the 1998 least-squares adjustment of the values of the constants

Adjusted constant	Symbol
electron relative atomic mass	$A_r(\text{e})$
proton relative atomic mass	$A_r(\text{p})$
deuteron relative atomic mass	$A_r(\text{d})$
fine-structure constant	α
additive correction in theoretical expression for a_e	δ_e
additive correction in theoretical expression for a_μ	δ_μ
additive correction in theoretical expression for $\Delta\nu_{\text{Mu}}$	δ_{Mu}
electron-muon mass ratio	m_e/m_μ
Planck constant	h
molar gas constant	R
Rydberg constant	R_∞
bound-state proton rms charge radius	R_{p}
additive correction in theoretical expression for $E_{\text{H}}(nL_j)$	$\delta_{\text{H}}(nL_j)$
bound-state deuteron rms charge radius	R_{d}
additive correction in theoretical expression for $E_{\text{D}}(nL_j)$	$\delta_{\text{D}}(nL_j)$

Examples of the observational equations are given in Table 2. In that table, ν_{H} and ν_{D} are transition frequencies in hydrogen and deuterium such as those given in Table 3 below, K_{J} is the Josephson constant, which is characteristic of the Josephson effect, and R_{K} is the von Klitzing constant, which is characteristic of the quantum Hall effect. Note that $E_{\text{X}}(nL_j)/h$ is proportional to cR_∞ and independent of h , hence h is not an adjusted constant in these equations.

Table 2. Some observational equations that express the input data as functions of the adjusted constants

$\nu_{\text{H}}(n_1\text{L}_{1j_1} - n_2\text{L}_{2j_2}) \doteq \left[E_{\text{H}}\left(n_2\text{L}_{2j_2}; R_{\infty}, \alpha, A_{\text{r}}(\text{e}), A_{\text{r}}(\text{p}), R_{\text{p}}, \delta_{\text{H}}(n_2\text{L}_{2j_2})\right) \right. \\ \left. - E_{\text{H}}\left(n_1\text{L}_{1j_1}; R_{\infty}, \alpha, A_{\text{r}}(\text{e}), A_{\text{r}}(\text{p}), R_{\text{p}}, \delta_{\text{H}}(n_1\text{L}_{1j_1})\right) \right] / h$
$R_{\text{p}} \doteq R_{\text{p}}$
$\nu_{\text{D}}(n_1\text{L}_{1j_1} - n_2\text{L}_{2j_2}) \doteq \left[E_{\text{D}}\left(n_2\text{L}_{2j_2}; R_{\infty}, \alpha, A_{\text{r}}(\text{e}), A_{\text{r}}(\text{d}), R_{\text{d}}, \delta_{\text{D}}(n_2\text{L}_{2j_2})\right) \right. \\ \left. - E_{\text{D}}\left(n_1\text{L}_{1j_1}; R_{\infty}, \alpha, A_{\text{r}}(\text{e}), A_{\text{r}}(\text{d}), R_{\text{d}}, \delta_{\text{D}}(n_1\text{L}_{1j_1})\right) \right] / h$
$R_{\text{d}} \doteq R_{\text{d}}$
$\delta_{\text{H}}(n\text{L}_j) \doteq \delta_{\text{H}}(n\text{L}_j)$
$\delta_{\text{D}}(n\text{L}_j) \doteq \delta_{\text{D}}(n\text{L}_j)$
$a_{\text{e}} \doteq a_{\text{e}}(\alpha, \delta_{\text{e}})$
$\delta_{\text{e}} \doteq \delta_{\text{e}}$
$\Delta\nu_{\text{Mu}} \doteq \Delta\nu_{\text{Mu}}\left(R_{\infty}, \alpha, \frac{m_{\text{e}}}{m_{\mu}}, \delta_{\mu}, \delta_{\text{Mu}}\right)$
$\delta_{\text{Mu}} \doteq \delta_{\text{Mu}}$
$K_{\text{J}} \doteq \left(\frac{8\alpha}{\mu_0 ch}\right)^{1/2}$
$R_{\text{K}} \doteq \frac{\mu_0 c}{2\alpha}$
$K_{\text{J}}^2 R_{\text{K}} \doteq \frac{4}{h}$

3 Electron Magnetic Moment Anomaly

One of the most important constants is the fine-structure constant α . It is determined primarily by comparison of measurement and theory for the electron magnetic moment anomaly a_{e} defined by

$$g_{\text{e}} = -2(1 + a_{\text{e}}),$$

where $g_{\text{e}}(\text{Dirac}) = -2$. Measurements by the University of Washington group [3] have yielded

$$\begin{aligned} a_{\text{e}-}(\text{exp}) &= 1\,159\,652\,188.4(4.3) \times 10^{-12} \\ a_{\text{e}+}(\text{exp}) &= 1\,159\,652\,187.9(4.3) \times 10^{-12}. \end{aligned} \tag{15}$$

(Here and throughout this paper, all uncertainties are standard uncertainties, i.e., one standard deviation estimates.) Assuming CPT invariance holds, we take

a weighted average of these values and obtain

$$a_e = 1\,159\,652\,188.3(4.2) \times 10^{-12}, \quad (16)$$

where the covariance of the two values has been taken into account.

The complete theoretical expression for a_e can be written as

$$a_e(\alpha, \delta_e) = C_e^{(2)} \left(\frac{\alpha}{\pi} \right) + C_e^{(4)} \left(\frac{\alpha}{\pi} \right)^2 + C_e^{(6)} \left(\frac{\alpha}{\pi} \right)^3 + C_e^{(8)} \left(\frac{\alpha}{\pi} \right)^4 \\ + a_e(\text{had}) + a_e(\text{weak}) + \delta_e, \quad (17)$$

where $C_e^{(2)} = \frac{1}{2}$, the $C_e^{(2i)}$ with $i \geq 2$ are numerical constants that depend only weakly on m_e/m_μ and m_e/m_τ , $a_e(\text{had})$ is the predominantly hadronic vacuum polarization contribution, $a_e(\text{weak})$ is the predominantly electroweak contribution, and δ_e is the additive correction that takes into account the uncertainties of all known and unknown contributions. The numerical values of these contributions are summarized in the article on the 1998 adjustment [1,2]. Also given there is the estimate $\delta_e = 0.0(1.1) \times 10^{-12}$, for which the corresponding observational equation is $0.0 \doteq \delta_e$, with the associated variance $(1.1 \times 10^{-12})^2$.

The 1998 recommended value of α^{-1} based on all the available data, but which is primarily influenced by the comparison of theory and experiment for the anomalous magnetic moment of the electron, is

$$\alpha^{-1} = 137.035\,999\,76(50). \quad (18)$$

4 Rydberg Constant

The Rydberg constant is evaluated by the comparison of theory and experiment for energy levels in hydrogen and deuterium. The measured transition frequencies used in the 1998 adjustment are given in Table 3.

4.1 Theory Relevant to the Rydberg Constant

The contributions that have been considered in order to obtain precise theoretical expressions for hydrogenic energy levels are as follows: the Dirac eigenvalue with reduced mass, relativistic recoil, nuclear polarization, self energy, vacuum polarization, two-photon corrections, three-photon corrections, finite nuclear size, nuclear size correction to self energy and vacuum polarization, radiative-recoil corrections, and nucleus self energy.

For example, the $1S - 2S$ transition frequency for hydrogen is given by the expression

$$\nu_H(1S_{1/2} - 2S_{1/2}) = \frac{3}{4} R_\infty c \left[1 - \frac{A_r(e)}{A_r(p)} + \frac{11}{48} \alpha^2 \right. \\ \left. - \frac{28}{9} \frac{\alpha^3}{\pi} \ln \alpha^{-2} - \frac{14}{9} \left(\frac{\alpha R_p}{\lambda_C} \right)^2 + \dots \right], \quad (19)$$

Table 3. Summary of measured transition frequencies ν considered in the 1998 constants adjustment for the determination of the Rydberg constant R_∞ (H is hydrogen and D is deuterium)

Transition frequency	Lab ^a -year
$\nu_{\text{H}}(1\text{S}_{1/2} - 2\text{S}_{1/2}) = 2\,466\,061\,413\,187.34(84) \text{ kHz}$	MPQ-97 [4]
$\nu_{\text{H}}(2\text{S}_{1/2} - 8\text{S}_{1/2}) = 770\,649\,350\,012.1(8.6) \text{ kHz}$	LKB/LPTF-97 [5]
$\nu_{\text{H}}(2\text{S}_{1/2} - 8\text{D}_{3/2}) = 770\,649\,504\,450.0(8.3) \text{ kHz}$	LKB/LPTF-97 [5]
$\nu_{\text{H}}(2\text{S}_{1/2} - 8\text{D}_{5/2}) = 770\,649\,561\,584.2(6.4) \text{ kHz}$	LKB/LPTF-97 [5]
$\nu_{\text{H}}(2\text{S}_{1/2} - 12\text{D}_{3/2}) = 799\,191\,710\,472.7(9.4) \text{ kHz}$	LKB/LPTF-99 [6]
$\nu_{\text{H}}(2\text{S}_{1/2} - 12\text{D}_{5/2}) = 799\,191\,727\,403.7(7.0) \text{ kHz}$	LKB/LPTF-99 [6]
$\nu_{\text{H}}(2\text{S}_{1/2} - 4\text{S}_{1/2}) - \frac{1}{4}\nu_{\text{H}}(1\text{S}_{1/2} - 2\text{S}_{1/2}) = 4\,797\,338(10) \text{ kHz}$	MPQ-95 [7]
$\nu_{\text{H}}(2\text{S}_{1/2} - 4\text{D}_{5/2}) - \frac{1}{4}\nu_{\text{H}}(1\text{S}_{1/2} - 2\text{S}_{1/2}) = 6\,490\,144(24) \text{ kHz}$	MPQ-95 [7]
$\nu_{\text{H}}(2\text{S}_{1/2} - 6\text{S}_{1/2}) - \frac{1}{4}\nu_{\text{H}}(1\text{S}_{1/2} - 3\text{S}_{1/2}) = 4\,197\,604(21) \text{ kHz}$	LKB-96 [8]
$\nu_{\text{H}}(2\text{S}_{1/2} - 6\text{D}_{5/2}) - \frac{1}{4}\nu_{\text{H}}(1\text{S}_{1/2} - 3\text{S}_{1/2}) = 4\,699\,099(10) \text{ kHz}$	LKB-96 [8]
$\nu_{\text{H}}(2\text{S}_{1/2} - 4\text{P}_{1/2}) - \frac{1}{4}\nu_{\text{H}}(1\text{S}_{1/2} - 2\text{S}_{1/2}) = 4\,664\,269(15) \text{ kHz}$	Yale-95 [9]
$\nu_{\text{H}}(2\text{S}_{1/2} - 4\text{P}_{3/2}) - \frac{1}{4}\nu_{\text{H}}(1\text{S}_{1/2} - 2\text{S}_{1/2}) = 6\,035\,373(10) \text{ kHz}$	Yale-95 [9]
$\nu_{\text{H}}(2\text{S}_{1/2} - 2\text{P}_{3/2}) = 9\,911\,200(12) \text{ kHz}$	Harvard-94 [10]
$\nu_{\text{H}}(2\text{P}_{1/2} - 2\text{S}_{1/2}) = 1\,057\,845.0(9.0) \text{ kHz}$	Harvard-86 [11]
$\nu_{\text{H}}(2\text{P}_{1/2} - 2\text{S}_{1/2}) = 1\,057\,862(20) \text{ kHz}$	Sussex-79 [12]
$\nu_{\text{D}}(2\text{S}_{1/2} - 8\text{S}_{1/2}) = 770\,859\,041\,245.7(6.9) \text{ kHz}$	LKB/LPTF-97 [5]
$\nu_{\text{D}}(2\text{S}_{1/2} - 8\text{D}_{3/2}) = 770\,859\,195\,701.8(6.3) \text{ kHz}$	LKB/LPTF-97 [5]
$\nu_{\text{D}}(2\text{S}_{1/2} - 8\text{D}_{5/2}) = 770\,859\,252\,849.5(5.9) \text{ kHz}$	LKB/LPTF-97 [5]
$\nu_{\text{D}}(2\text{S}_{1/2} - 12\text{D}_{3/2}) = 799\,409\,168\,038.0(8.6) \text{ kHz}$	LKB/LPTF-99 [6]
$\nu_{\text{D}}(2\text{S}_{1/2} - 12\text{D}_{5/2}) = 799\,409\,184\,966.8(6.8) \text{ kHz}$	LKB/LPTF-99 [6]
$\nu_{\text{D}}(2\text{S}_{1/2} - 4\text{S}_{1/2}) - \frac{1}{4}\nu_{\text{D}}(1\text{S}_{1/2} - 2\text{S}_{1/2}) = 4\,801\,693(20) \text{ kHz}$	MPQ-95 [7]
$\nu_{\text{D}}(2\text{S}_{1/2} - 4\text{D}_{5/2}) - \frac{1}{4}\nu_{\text{D}}(1\text{S}_{1/2} - 2\text{S}_{1/2}) = 6\,494\,841(41) \text{ kHz}$	MPQ-95 [7]
$\nu_{\text{D}}(1\text{S}_{1/2} - 2\text{S}_{1/2}) - \nu_{\text{H}}(1\text{S}_{1/2} - 2\text{S}_{1/2}) = 670\,994\,334.64(15) \text{ kHz}$	MPQ-98 [13]

^a MPQ: Max-Planck-Institut für Quantenoptik, Garching.

LKB: Laboratoire Kastler-Brossel, Paris.

LPTF: Laboratoire Primaire du Temps et des Fréquences, Paris.

where only the leading contributions of the reduced mass, relativistic correction contained in the Dirac eigenvalue, self energy, and finite nuclear size are shown. Three contributions of particular interest here are considered in the following paragraphs.

4.2 Self Energy

A recent calculation has substantially reduced the uncertainty of the contribution of the second-order one-photon electron self energy to the energy level of the 1S state. In general, this contribution can be expressed as

$$E_{\text{SE}}^{(2)} = \frac{\alpha}{\pi} \frac{(Z\alpha)^4}{n^3} F(Z\alpha) m_e c^2 . \quad (20)$$

The leading terms for the 1S state are given by

$$F(\alpha) = A_{41} \ln(\alpha)^{-2} + A_{40} + \dots , \quad (21)$$

where the coefficients A_{41} and A_{40} , as well as some of the higher-order coefficients A_{ij} , are known. A complete numerical calculation has yielded

$$F(\alpha) = 10.316\,793\,650(1) , \quad (22)$$

where the uncertainty corresponds to a frequency of 0.8 Hz, which is currently negligible [14]. The calculation incorporated new methods of convergence acceleration that reduced the time required for the calculation by about three orders of magnitude. The best estimate of $F(\alpha)$ from a truncated power series evaluation alone, which stands little chance of improvement, yields a result that differs by more than 10 kHz from this value.

4.3 Two-Photon Corrections

At present, contributions from two-photon corrections and finite nuclear size introduce the largest uncertainty in the theoretical expressions for energy levels. Corrections from two virtual photons, of order α^2 , have been calculated as a power series in $Z\alpha$:

$$E^{(4)} = \left(\frac{\alpha}{\pi}\right)^2 \frac{(Z\alpha)^4}{n^3} m_e c^2 F^{(4)}(Z\alpha) , \quad (23)$$

where

$$\begin{aligned} F^{(4)}(Z\alpha) &= B_{40} + B_{50}(Z\alpha) + B_{63}(Z\alpha)^2 \ln^3(Z\alpha)^{-2} \\ &\quad + B_{62}(Z\alpha)^2 \ln^2(Z\alpha)^{-2} + \dots \\ &= B_{40} + (Z\alpha)G^{(4)}(Z\alpha) . \end{aligned} \quad (24)$$

The final portion of B_{40} was first correctly obtained numerically nearly 30 years ago [15], and was subsequently calculated analytically. The result is

$$B_{40} = \left[2\pi^2 \ln 2 - \frac{49}{108}\pi^2 - \frac{6131}{1296} - 3\zeta(3) \right] \delta_{l0} \\ + \left[\frac{1}{2}\pi^2 \ln 2 - \frac{1}{12}\pi^2 - \frac{197}{144} - \frac{3}{4}\zeta(3) \right] \frac{1}{\kappa(2l+1)} , \quad (25)$$

where κ is the Dirac angular momentum-parity quantum number and l is the nonrelativistic orbital angular momentum quantum number. The next coefficient has been calculated only recently, with the result [16,17,18,19]

$$B_{50} = -21.5561(31)\delta_{l0} . \quad (26)$$

There is some information about the higher-order coefficients [20,21]:

$$B_{63} = -\frac{8}{27}\delta_{l0} \quad (27)$$

$$B_{62} = \frac{16}{9} \left(C + \psi(n) - \ln n - \frac{1}{n} + \frac{1}{4n^2} \right) ; \quad \text{for S states} \quad (28)$$

$$B_{62} = \frac{4}{27} \frac{n^2 - 1}{n^2} ; \quad \text{for P states} , \quad (29)$$

where $\psi(n)$ is the logarithmic derivative of the gamma function [22]. Other coefficients such as B_{61} and B_{60} are not known. There have also been numerical calculations of one of the two-photon diagrams which are not in agreement with each other [23,24]. However, the largest single uncertainty of the two-photon corrections comes from the unknown constant C in Eq. (28), which is estimated to be $C = 0(5)$. This value is mainly responsible for the 90 kHz uncertainty of the theoretical energy level of the 1S state. An important fact is that although C is unknown, its contribution to energy levels has a known dependence on n , namely $1/n^3$. Hence, the theoretical expressions for the energy levels are highly correlated with known covariances. For example, the correlation coefficient of the theoretical expressions for the 1S and 2S energy levels in hydrogen is 0.999.

4.4 Finite Nuclear Size

At low Z , the leading contribution due to the finite size of the nucleus is

$$E_{\text{NS}} = \frac{2}{3} \frac{(Z\alpha)^2}{n^3} m_e c^2 \left(\frac{Z\alpha R_N}{\lambda_C} \right)^2 , \quad (30)$$

where R_N is the bound-state root-mean-square (rms) charge radius of the nucleus and λ_C is the Compton wavelength of the electron divided by 2π . The bound-state rms charge radius R_N is defined by the above equation and, except for the proton, differs from the scattering rms charge radius r_N [25]. Relativistic corrections to this expression are known, but are comparatively small. As in the

case of the two-photon corrections, the uncertainty in the energy levels due to uncertainty in the rms charge radius has a known dependence on n , which is also $1/n^3$. Since the bound-state nuclear radius is an adjusted constant, uncertainty in its value does not contribute to the uncertainty explicitly assigned to the theoretical expression for an energy level. This is in contrast to the case of the two-photon corrections, e.g., the uncertainty associated with the constant C above. In the case of R_N , the effect of its uncertainty on the theoretical expressions for the energy levels is taken into account automatically through the least-squares adjustment.

A comprehensive analysis of the relevant existing low- and high-energy e-p scattering data and low-energy neutron-atom scattering data based on dispersion relations, together with various theoretical constraints, has yielded the result for the proton scattering radius $r_p = 0.847(8)$ fm [26]. This value differs somewhat from the earlier value $r_p = 0.862(12)$ fm [27]. Although this earlier result is based solely on low-energy data, such data are the most critical in determining the value of r_p . [We do not consider still earlier values, for example $r_p = 0.805(11)$ fm [28], because the more recent results had available a larger set of data and improved methods of analysis.] The authors of Ref. [26] have stressed the importance of simultaneously fitting both the proton and neutron data and note that if the value of 0.862 fm is used, one cannot simultaneously fit both sets of data in their dispersion-theoretical analysis. Clearly, to obtain a more accurate value of r_p , improved low-energy data are necessary. In the absence of additional information, for the purpose of the 1998 adjustment we took $r_p = 0.8545(120)$ fm, which is simply the unweighted mean of the values of Ref. [26] and Ref. [27] with the larger of the two uncertainties.

For hydrogen, in the context of the theoretical expressions we employ for the energy levels, R_p is the same as r_p , and hence

$$R_p = 0.8545(120) \text{ fm} . \quad (31)$$

For deuterium, we employ the value [1,2,29,25]

$$R_d = 2.130(10) \text{ fm} . \quad (32)$$

[Note that for both the proton and deuteron the interpretation of the quoted value obtained from the scattering data depends on whether muonic and/or hadronic vacuum polarization has been included as a correction to the data [30]. However, at the level of uncertainty of current interest, such vacuum polarization effects may be neglected.]

4.5 Total Energy and Uncertainty

The total energy $E_X(nL_j)$ of a particular level (where $L = S, P, \dots$ and $X = H, D$) is just the sum of the various contributions mentioned above plus an additive correction $\delta_X(nL_j)$ that accounts for the uncertainty in the theoretical expression for $E_X(nL_j)$. Our theoretical estimate of the value of $\delta_X(nL_j)$ for a particular level is zero with a variance equal to the sum of the variances of the

individual contributions, since the contributions to the energy of a given level are independent. (Uncertainties associated with the adjusted constants are not explicitly included, because the least-squares adjustment determines the values and uncertainties of these constants, as well as the effect of both on the energy levels.) For a given isotope, the covariance of any two δ 's is obtained by summing the variances that are common to the two levels.

As an example, we consider the nS states of hydrogen, with the slight change of notation $E_H(nS_{1/2}) \rightarrow E_{nS}$ and $\delta_H(nS_{1/2}) \rightarrow \delta_{nS}$. The energy levels are of the form $E_{nS} + \delta_{nS}$ with variance

$$\text{var}(E_{nS}) = \text{var}(\delta_{nS}) = \left(\frac{a_S}{n^3}\right)^2 + \left(\frac{b_{nS}}{n^3}\right)^2, \quad (33)$$

and covariance

$$\text{cov}(E_{n_1S}, E_{n_2S}) = \text{cov}(\delta_{n_1S}, \delta_{n_2S}) = \frac{a_S^2}{n_1^3 n_2^3}. \quad (34)$$

The quantity a_S corresponds to the contribution to the uncertainty that is proportional to $1/n^3$ in the theory for energy level nS , and the quantity b_{nS} corresponds to the remainder of the uncertainty. When calculating the covariances between states of different n , we treat the quantities b_{nS} as statistically independent. In general, $|a_S| \gg |b_{nS}|$. This disparity leads to a considerable reduction in uncertainty in the theoretical expressions for the relative positions of the S-state energy levels. For example, for the difference $E_{1S} - 8E_{2S}$, the variance is

$$\begin{aligned} \text{var}(E_{1S} - 8E_{2S}) &= \text{var}(E_{1S}) + 8^2 \text{var}(E_{2S}) - 2 \cdot 8 \text{cov}(E_{1S}, E_{2S}) \\ &= a_S^2 + b_{1S}^2 + a_S^2 + b_{2S}^2 - 2a_S^2 \\ &= b_{1S}^2 + b_{2S}^2. \end{aligned} \quad (35)$$

Since we include the covariances of the expressions for the energy levels in the least-squares analysis, such cancellations are automatically taken into account. However, this is only a special case of a more general phenomenon. Even though the theory determines the individual S levels with an uncertainty of the order of a_S/n^3 , the relative positions of the S levels are determined with an uncertainty of the order of b_{nS}/n^3 , because information about any particular S level essentially determines the unknown constant a_S .

4.6 Result of LSA for the Rydberg Constant

Based on the above discussion of experiment and theory, we consider the relationship of the proton and deuteron radii, two-photon corrections, and the Rydberg constant in the 1998 least-squares adjustment. If the values of R_p and R_d given in Eqs. (31) and (32) as derived from scattering data are included as input data together with the data on which the 1998 adjustment of the constants

is based, then the least-squares adjustment yields the values labeled as LSA A in Table 4. For this adjustment, the normalized residual

$$r_i = \frac{(x - \hat{x})}{u(x)} \quad (36)$$

of each $\delta_X(nS_{1/2})$, $n = 1, 2, 3, 4, 6, 8$, is in the range $-1.410 < r_i < -1.406$, which shows an average deviation between theory and experiment corresponding to $126/n^3$ kHz for $nS_{1/2}$ states [$u(x)$ is the standard uncertainty of x].

The most likely sources for this difference are a deviation of the value of the proton charge radius and/or the deuteron charge radius predicted by the spectroscopic data from the values deduced from scattering experiments, an uncalculated contribution to the energy levels from the two-photon QED correction that exceeds the estimated uncertainty for this term, or a combination of these.

To allow for either or both of these possibilities, we consider a second least-squares adjustment in which both R_p and R_d are treated as free variables, i.e., the scattering input values for these quantities are not included. This is the approach taken in the final 1998 least-squares adjustment, and yields the values labeled LSA B in Table 4. In this case, $|r_i| < 0.0001$ for the δ 's.

Table 4. Results of least-squares adjustments A and B

LSA	R_∞	R_p	R_d
A	10 973 731.568 521(81) m ⁻¹	0.859(10) fm	2.1331(42) fm
B	10 973 731.568 549(83) m ⁻¹	0.907(32) fm	2.153(14) fm

5 Conclusion

Because of limitations in the theory of the energy levels of hydrogen and deuterium, full advantage can not yet be taken of the existing measurements of H and D transition frequencies to deduce a value of R_∞ . Since the uncertainty in the theory is dominated by the uncertainty of the two-photon corrections, reducing this uncertainty is crucial for continued progress. Of comparable importance are improved experimental determinations of the rms charge radii of the proton and deuteron. Such a result for the proton radius is expected from the determination of the Lamb shift in muonic hydrogen by an international group at PSI [31]. Of course, results from high-precision measurements of the proton and deuteron elastic form factors at low momentum transfer as well as additional high-accuracy measurements of transition frequencies in H and D would be of value.

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