Precise Calculation of Transition Frequencies of Hydrogen and Deuterium Based on a Least-Squares Analysis

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We combine a limited number of accurately measured transition frequencies in hydrogen and deuterium, recent quantum electrodynamics (QED) calculations, and, as an essential additional ingredient, a generalized least-squares analysis, to obtain precise and optimal predictions for hydrogen and deuterium transition frequencies. Some of the predicted transition frequencies have relative uncertainties more than an order of magnitude smaller than that of the *g* factor of the electron, which was previously the most accurate prediction of QED.

In the past decade there have been significant advances in both the measurement and theory of transition frequencies in hydrogen and deuterium. With the advent of frequency-comb metrology, the progress in measurements has accelerated to the extent that the uncertainty in the experimental value of the 1*S*-2*S* frequency in hydrogen has decreased by 3 orders of magnitude in about ten years [1]. Many other precision measurements of transitions in hydrogen and deuterium with principal quantum number *n* up to 12 have been made and are listed in Table I, together with the 1*S*-2*S* frequency [1–10]. In addition, precise measurements have been made involving states of hydrogen with *n* = 27 to 30 [11]. Further advances may be anticipated from a number of groups currently working to improve measurement accuracy [12–15].

On the theoretical side, there has been progress in the accuracy of quantum electrodynamics (QED) calculations which has led to a significant reduction of the uncertainty of both the one-photon [16–20] and two-photon [21–26] contributions. In addition to this progress, the application of the least-squares method described here makes it possible in some cases to predict transition frequencies with a relative uncertainty that is more than an order of magnitude smaller than the relative uncertainty in the Rydberg constant, which is 6.6×10^{-12}.

It is of interest to have accurate calculations of hydrogen and deuterium transition frequencies for comparison to existing and new experimental values, for both frequency standards applications, and as tests of QED. Also, with sufficiently accurate theory available, it would be possible to consider redefining the SI second in terms of an assigned value of the Rydberg constant. Although this would entail about 3 orders of magnitude improvement in the theory, the recent rate of progress suggests that it may be within reach.

In this Letter, we give theoretical values for a number of transition frequencies that are meant to be best values consistent with currently available experimental and theoretical information. Such calculated values for the transitions in Table I follow from the results of the 2002 CODATA least-squares adjustment of the fundamental constants [27–29], and are listed in that table. Of course, the calculated value of the 1*S*-2*S* transition in hydrogen should not be viewed as a theoretical prediction, because the least-squares adjustment determines values of the adjusted constants (variables or unknowns of the adjustment) so that the calculated frequency is essentially equal to the very precise measured value. The number in parentheses with each value is the standard uncertainty (estimated standard deviation) in the last two figures. Hyperfine structure effects are not included in the quoted numbers.

For hydrogen or deuterium transition frequencies not included in the 2002 CODATA adjustment, we proceed as follows. The energy level E_i of state *i* can be written as a function of the fundamental constants and an additional adjusted constant δ_i which takes into account the uncertainty in the theory [27,30,31]. For example, for the case in which *i* is a state of hydrogen, we have

$$E_i = H_i(R_\infty, \alpha, A_r(e), A_r(p), R_p) + \delta_i, \qquad (1)$$

where the constants that appear as arguments of the function H_i are listed in Table II. Because the values of the constants in Eq. (1), including δ_i, result from a least-squares adjustment, they are correlated, particularly those for R_∞ and R_p, which have a correlation coefficient of 0.996. The uncertainty of the calculated value for the 1*S*-2*S* frequency in hydrogen is increased by a factor of about 500 if such correlations are neglected. The function H_i also depends implicitly on *c* and the Planck constant *h*. However, these constants are not displayed as variables, because *c* is a fixed number, and the frequencies ($E_i - E_{i'}$)/*h* are essentially independent of *h*. Levels in deuterium are given as similar functions with p replaced by d.

TABLE I. Transition frequencies in hydrogen ν_H and in deuterium ν_D used in the 2002 CODATA least-squares adjustment of the values of the fundamental constants and the calculated values. Hyperfine effects are not included in these values.

Experiment	Frequency interval(s)	Reported value $\nu/$kHz	Calculated value $\nu/$kHz
Niering et al. [1]	$\nu_H(1S_{1/2} - 2S_{1/2})$	2 466 061 413 187.103(46)	2 466 061 413 187.103(46)
Weitz et al. [2]	$\nu_H(2S_{1/2} - 4S_{1/2}) - \frac{1}{4}\nu_H(1S_{1/2} - 2S_{1/2})$	4 797 338(10)	4 797 331.8(2.0)
	$\nu_H(2S_{1/2} - 4D_{5/2}) - \frac{1}{4}\nu_H(1S_{1/2} - 2S_{1/2})$	6 490 144(24)	6 490 129.9(1.7)
	$\nu_D(2S_{1/2} - 4S_{1/2}) - \frac{1}{4}\nu_D(1S_{1/2} - 2S_{1/2})$	4 801 693(20)	4 801 710.2(2.0)
	$\nu_D(2S_{1/2} - 4D_{5/2}) - \frac{1}{4}\nu_D(1S_{1/2} - 2S_{1/2})$	6 494 841(41)	6 494 831.5(1.7)
Huber et al. [3]	$\nu_D(1S_{1/2} - 2S_{1/2}) - \nu_H(1S_{1/2} - 2S_{1/2})$	670 994 334.64(15)	670 994 334.64(15)
de Beauvoir et al. [4]	$\nu_H(2S_{1/2} - 8S_{1/2})$	770 649 350 012.0(8.6)	770 649 350 016.1(2.8)
	$\nu_H(2S_{1/2} - 8D_{3/2})$	770 649 504 450.0(8.3)	770 649 504 449.1(2.8)
	$\nu_H(2S_{1/2} - 8D_{5/2})$	770 649 561 584.2(6.4)	770 649 561 578.2(2.8)
	$\nu_D(2S_{1/2} - 8S_{1/2})$	770 859 041 245.7(6.9)	770 859 041 242.6(2.8)
	$\nu_D(2S_{1/2} - 8D_{3/2})$	770 859 195 701.8(6.3)	770 859 195 700.3(2.8)
	$\nu_D(2S_{1/2} - 8D_{5/2})$	770 859 252 849.5(5.9)	770 859 252 845.1(2.8)
Schwob et al. [5]	$\nu_H(2S_{1/2} - 12D_{3/2})$	799 191 710 472.7(9.4)	799 191 710 481.9(3.0)
	$\nu_H(2S_{1/2} - 12D_{5/2})$	799 191 727 403.7(7.0)	799 191 727 409.1(3.0)
	$\nu_D(2S_{1/2} - 12D_{3/2})$	799 409 168 038.0(8.6)	799 409 168 041.7(3.0)
	$\nu_D(2S_{1/2} - 12D_{5/2})$	799 409 184 966.8(6.8)	799 409 184 973.4(3.0)
Bourzeix et al. [6]	$\nu_H(2S_{1/2} - 6S_{1/2}) - \frac{1}{4}\nu_H(1S_{1/2} - 3S_{1/2})$	4 197 604(21)	4 197 600.3(2.2)
	$\nu_H(2S_{1/2} - 6D_{5/2}) - \frac{1}{4}\nu_H(1S_{1/2} - 3S_{1/2})$	4 699 099(10)	4 699 105.4(2.2)
Berkeland et al. [7]	$\nu_H(2S_{1/2} - 4P_{1/2}) - \frac{1}{4}\nu_H(1S_{1/2} - 2S_{1/2})$	4 664 269(15)	4 664 254.3(1.7)
	$\nu_H(2S_{1/2} - 4P_{3/2}) - \frac{1}{4}\nu_H(1S_{1/2} - 2S_{1/2})$	6 035 373(10)	6 035 384.1(1.7)
Hagley and Pipkin [8]	$\nu_H(2S_{1/2} - 2P_{3/2})$	9 911 200(12)	9 911 197.6(2.4)
Lundeen and Pipkin [9]	$\nu_H(2P_{1/2} - 2S_{1/2})$	1 057 845.0(9.0)	1 057 844.0(2.4)
Newton et al. [10]	$\nu_H(2P_{1/2} - 2S_{1/2})$	1 057 862(20)	1 057 844.0(2.4)

The theory included in the function H_i in Eq. (1) is described in detail in Appendix A of Ref. [27], which provides a review of the relevant calculations. Much of that information is in the form of equations that are valid for any state, with the exception of tables of data that only have entries for the levels included in the 2002 CODATA adjustment [32]. Estimates of the theoretical uncertainties of the function H_i, represented by the constant δ_i in Eq. (1), are also given in Appendix A of Ref. [27]. The *a priori* estimated value of δ_i is $\delta_i(\text{th}) = 0$, because the theoretical expression for the levels includes all known contributions. However, the estimated uncertainty $u[\delta_i(\text{th})]$ is not zero, and there are significant covariances between the various δ's that take into account the expected patterns in the uncertainties. For example, for S states there are components of uncertainty with the functional form C/n^3, where C is a common unknown constant, and there are components of uncertainty common to hydrogen and deuterium levels with the same quantum numbers. The theoretical uncertainties and covariances are included in the least-squares adjustment as input data for the adjusted variables δ_i.

A generalized least-squares adjustment is formulated here along the lines described in Refs. [28,29]. Symbols that refer to data used in the 2002 CODATA adjustment of the constants are also defined in Ref. [28]. New energy levels E_l to be determined are added to the adjustment,

along with the corresponding theoretical expressions of the form in Eq. (1), and for each added level not among those in Table I, a new adjusted variable δ_l is added. The updated column vector of input data Q_u, matrix of their covariances V_u, and column vector of variables Z_u are written in block form as

$$Q_u = \begin{pmatrix} Q \\ Q_\delta \\ Q_E \end{pmatrix}; \quad V_u = \begin{pmatrix} V & T & 0 \\ T^\top & S & 0 \\ 0 & 0 & V_E \end{pmatrix}; \quad Z_u = \begin{pmatrix} Z \\ Z_\delta \end{pmatrix}, \quad (2)$$

where Q, V, and Z are the corresponding sets of quantities used in the 2002 CODATA least-squares adjustment, Q_δ is the set of theoretical data $\delta_l(\text{th}) = 0$ for the new variables

TABLE II. The 2002 CODATA values of the constants used in the evaluation of the spectrum of hydrogen and deuterium.

Constant	Value
Speed of light	$c = 299\,792\,458$ m s^{-1}
Rydberg constant	$R_\infty = 10\,973\,731.568\,525(73)$ m^{-1}
Fine-structure constant	$\alpha = 1/137.035\,999\,11(46)$
Electron relative atomic mass	$A_r(e) = 5.485\,799\,094\,5(24) \times 10^{-4}$
Proton relative atomic mass	$A_r(p) = 1.007\,276\,466\,88(13)$
Deuteron relative atomic mass	$A_r(d) = 2.013\,553\,212\,70(35)$
Proton rms charge radius	$R_p = 0.8750(68)$ fm
Deuteron rms charge radius	$R_d = 2.1394(28)$ fm

δ_l, Z_δ is the new set of adjusted variables δ_l, and Q_E is input data for the new energy levels E_l. In V_u, where $V_{uik} = \text{cov}(Q_{ui}, Q_{uk})$, S and T are the sets of theoretical covariances involving the new δ's, and V_E is the set of covariances of the new levels E_l. Since the input data for the new levels are unknown, we simply assume that the uncertainties are very large and that there are no correlations among them or with the rest of the input data. This yields the blocks of zeros in V_u and results in V_E being diagonal.

The input data and adjusted variables are related by the set of observational equations given by

$$Q_u \doteq F_u(Z_u); \qquad \begin{pmatrix} Q \\ Q_\delta \\ Q_E \end{pmatrix} \doteq \begin{pmatrix} F(Z) \\ Z_\delta \\ E(Z_u) \end{pmatrix}, \qquad (3)$$

where the dot over the equal sign indicates that the equation represents the ideal relations between the input data and the adjusted constants which are not simultaneously satisfied, since the set of equations is overdetermined. In Eq. (3), F is the set of functions in the observational equations of the 2002 CODATA adjustment, and E is the set of expressions for the new energy levels of the form in Eq. (1). The observational equations are linearized by writing the Taylor series

$$Q_u \doteq F_u(Z_u^{(0)}) + A_u(Z_u - Z_u^{(0)}) + \cdots, \qquad (4)$$

where A_u is the matrix of derivatives

$$A_{uij} = \frac{\partial F_{ui}(Z_u^{(0)})}{\partial Z_{uj}^{(0)}}; \qquad A_u = \begin{pmatrix} A & 0 \\ 0 & I \\ B & C \end{pmatrix}, \qquad (5)$$

and neglecting higher-order terms. In Eq. (5), A is the matrix of derivatives from the 2002 CODATA adjustment, I is the identity matrix, and B and C are derivatives of the new energy levels with respect to the old and new variables, respectively. The truncated expression in Eq. (4) corresponds to

$$Y_u \doteq A_u X_u, \qquad (6)$$

where $Y_u = Q_u - F_u(Z_u^{(0)})$ and $X_u = Z_u - Z_u^{(0)}$.

The update adjustment starts with

$$Z_u^{(0)} = \begin{pmatrix} \hat{Z} \\ 0 \end{pmatrix}, \qquad (7)$$

where $\hat{Z}$ is the final vector of constants from the 2002 CODATA adjustment and

$$Y_u = \begin{pmatrix} \hat{Y} \\ Y_\delta \\ Y_E \end{pmatrix} = \begin{pmatrix} Q - F(\hat{Z}) \\ Q_\delta - Z_\delta^{(0)} \\ Q_E - E(Z_u^{(0)}) \end{pmatrix}, \qquad (8)$$

where $\hat{Y}$ is the final value of Y from the 2002 CODATA adjustment and $Y_\delta = 0$. The solution $\hat{X}_u$ to Eq. (6), the value of X_u that minimizes $(Y_u - A_u X_u)^\top V_u^{-1}(Y_u - A_u X_u)$, is

$$\hat{X}_u = G_u A_u^\top V_u^{-1} Y_u; \qquad G_u = (A_u^\top V_u^{-1} A_u)^{-1}. \quad (9)$$

The covariance matrix of the solution $\hat{X}_u$ is G_u, and its calculation is the key to the update. The Schur-Banachiewicz inverse formula [33,34] applied to the upper-left four blocks of the matrix V_u in Eq. (2) gives

$$V_u^{-1} = \begin{pmatrix} V^{-1} + V^{-1}TRT^\top V^{-1} & -V^{-1}TR & 0 \\ -RT^\top V^{-1} & R & 0 \\ 0 & 0 & V_E^{-1} \end{pmatrix}, \qquad (10)$$

where $R = (S - T^\top V^{-1}T)^{-1}$. For increasing uncertainties of the unknown input data for the new levels E_l, we have $V_E^{-1} \to 0$, and we work in this limit. A direct calculation from Eqs. (5), (9), and (10), with $V_E^{-1} = 0$, yields

$$G_u^{-1} = \begin{pmatrix} G^{-1} + G^{-1}URU^\top G^{-1} & -G^{-1}UR \\ -RU^\top G^{-1} & R \end{pmatrix}, \qquad (11)$$

where $G = (A^\top V^{-1}A)^{-1}$ is the matrix from the 2002 CODATA adjustment and $U = GA^\top V^{-1}T$. Evidently, Eq. (11) is the Schur-Banachiewicz inverse expression for

$$G_u = \begin{pmatrix} G & U \\ U^\top & P \end{pmatrix}, \qquad (12)$$

provided $R = (P - U^\top G^{-1}U)^{-1}$, that is, if

$$P = S - T^\top V^{-1}T + U^\top G^{-1}U = S + DT, \qquad (13)$$

where $D = T^\top V^{-1}(AGA^\top V^{-1} - I)$. This result for G_u in terms of G means that the exact result of the enlarged least-squares adjustment can be obtained from results of the 2002 CODATA least-squares adjustment with a relatively simple calculation. That is, the matrix inversions needed for the enlarged adjustment have effectively been carried out exactly, with the results explicitly expressed in terms of the matrices and vectors of the 2002 CODATA adjustment. In particular,

$$G_u A_u^\top V_u^{-1} = \begin{pmatrix} GA^\top V^{-1} & 0 & 0 \\ D & I & 0 \end{pmatrix}, \qquad (14)$$

so that

$$\hat{X}_u = \begin{pmatrix} GA^\top V^{-1}[Q - F(\hat{Z})] \\ D[Q - F(\hat{Z})] \end{pmatrix} = \begin{pmatrix} 0 \\ D\hat{Y} \end{pmatrix}, \qquad (15)$$

TABLE III. Calculated transition frequencies in hydrogen and deuterium from the $1S$ state to the $3S$ and $3D$ excited states.

Excited state	Hydrogen ν_H/kHz	Deuterium ν_D/kHz
$3S_{1/2}$	2 922 743 278 671.6(1.4)	2 923 538 534 391.8(1.4)
$3D_{3/2}$	2 922 746 208 551.40(70)	2 923 541 464 741.75(72)
$3D_{5/2}$	2 922 747 291 888.61(70)	2 923 542 548 374.66(72)

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TABLE IV. Examples of calculated transition frequencies in hydrogen and deuterium from the $2S$ state to various S and D excited states.

Excited state	Hydrogen ν_H/kHz	Deuterium ν_D/kHz
$3S_{1/2}$	456 681 865 484.5(1.4)	456 806 126 870.1(1.4)
$3D_{3/2}$	456 684 795 364.30(69)	456 809 057 220.01(69)
$3D_{5/2}$	456 685 878 701.51(69)	456 810 140 852.91(69)
$4S_{1/2}$	616 520 150 628.5(2.0)	616 687 903 590.7(2.0)
$4D_{3/2}$	616 521 386 393.3(1.7)	616 689 139 553.8(1.7)
$4D_{5/2}$	616 521 843 426.7(1.7)	616 689 596 711.9(1.7)

or for the adjusted constants

$$\hat{Z}_u = Z_u^{(0)} + \hat{X}_u = \begin{pmatrix} \hat{Z} \\ D\hat{Y} \end{pmatrix} \qquad (16)$$

with covariance matrix $\mathrm{cov}(\hat{Z}_u) = G_u$. More importantly, Eqs. (12) and (16) show that both the values and uncertainties of the new levels being calculated are influenced by their covariances with the levels in the 2002 CODATA least-squares adjustment, while the values and uncertainties of the variables from that adjustment are not changed at all. Also, since the only adjusted variables that change in the update appear linearly in Eq. (3), no iteration of the update is needed to reach the final result.

The energy levels and their covariances are thus given by

$$\begin{aligned} \hat{Q}_E &= E(\hat{Z}_u), \\ \mathrm{cov}(\hat{Q}_E) &= BGB^\top + CU^\top B^\top + BUC^\top + CPC^\top, \end{aligned} \qquad (17)$$

where the latter result is the lower-right block of the relation $\mathrm{cov}(\hat{Q}_u) = A_u G_u A_u^\top$. The result from Eq. (17) for a transition frequency ν_{lm} and its standard uncertainty $u(\nu_{lm})$ for the transition $l \rightarrow m$ is given by

$$\begin{aligned} h\nu_{lm} &= \hat{Q}_{El} - \hat{Q}_{Em}, \\ hu(\nu_{lm}) &= [u^2(\hat{Q}_{El}) - 2\mathrm{cov}(\hat{Q}_{El}, \hat{Q}_{Em}) + u^2(\hat{Q}_{Em})]^{1/2}, \end{aligned} \qquad (18)$$

where $u^2(\hat{Q}_{Ei}) = \mathrm{cov}(\hat{Q}_{Ei}, \hat{Q}_{Ei})$, $i = l, m$.

Examples of calculated transition frequencies in hydrogen and deuterium based on this update, starting from the results of the 2002 CODATA least-squares adjustment, are given in Tables III and IV [35]. The frequencies in Tables III and IV all have relative uncertainties that are smaller than the relative uncertainty of the Rydberg constant, mainly as a result of the correlations between R_∞, R_p, and R_d. In some cases, these values are nearly 5 orders of magnitude more accurate than the corresponding best previous values [36]. A database that gives the frequency of any transition between levels with $n \leq 200$ based on the calculations described here is maintained on the web site [32].

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