PHYSICAL REVIEW A **93**, 022513 (2016)

Tabulation of the bound-state energies of atomic hydrogen

M. Horbatsch and E. A. Hessels[*]
Department of Physics and Astronomy, York University, Toronto, Ontario, Canada M3J 1P3

(Received 5 January 2016; published 26 February 2016)

We present tables for the bound-state energies for atomic hydrogen. The tabulated energies include the hyperfine structure and thus this work extends the work of Mohr *et al.* [P. J. Mohr *et al.*, Rev. Mod. Phys. **84**, 1527 (2012)], which excludes the hyperfine structure. The tabulation includes corrections of the hyperfine structure due to the anomalous moment of the electron, due to the finite mass of the proton, and due to off-diagonal matrix elements of the hyperfine Hamiltonian. These corrections are treated incorrectly in most other works. Simple formulas valid for all quantum numbers are presented for the hyperfine corrections. The tabulated energies have uncertainties of less than 1 kHz for all states. This accuracy is possible because of the recent precision measurement [R. Pohl *et al.*, Nature (London) **466**, 213 (2010)] of the proton radius. The effect of this radius on the energy levels is also tabulated and the energies are compared to precision measurements of atomic hydrogen energy intervals.

DOI: 10.1103/PhysRevA.93.022513

I. INTRODUCTION

The current state of the theoretical knowledge of the bound-state energy levels of atomic hydrogen has been presented in the CODATA analysis of Ref. [1]. Here we expand on that work, by also including the hyperfine structure. Because of a recent precise determination [2,3] of the rms proton charge radius R_p, obtained from measurements of the $n = 2$ intervals in muonic hydrogen, all of the atomic hydrogen energy levels can now be determined to an accuracy of better than 1 kHz. In this work we present tables for the energies $E_{n\ell jf}$ of $|nljfm_f\rangle$ bound states of atomic hydrogen. These tables also indicate how the energy of each state is affected by the value of R_p and by the determination of the Rydberg constant that results from this R_p value.

The present work was performed because of the need for precision energy levels for the analysis of an ongoing measurement of the hydrogen $n = 2$ Lamb shift, for which the hyperfine structure and fine structure must be carefully considered. The tabulation is mostly based on the theoretical and experimental work of others and is intended as a practical resource.

II. OVERVIEW

To date, only three intervals in atomic hydrogen have been measured to an accuracy of better than 1 kHz:

$$\begin{aligned} &\nu(1S_{1/2}f = 1 \\ &\quad\to 2S_{1/2}f = 1) : 2\,466\,061\,102\,474.806(10)\ \text{kHz}, \\ &\nu(1S_{1/2}f = 0 \to 1S_{1/2}f = 1) : 1\,420\,405.751\,768(1)\ \text{kHz}, \\ &\nu(2S_{1/2}f = 0 \to 2S_{1/2}f = 1) : 177\,556.8343(67)\ \text{kHz}, \end{aligned} \tag{1}$$

where the first and the last values were measured [4,5] by Hänsch and co-workers and the $1S_{1/2}$ hyperfine interval is based on an analysis by Karshenboim [6] of all measurements of this interval. The uncertainties in Eq. (1), and in all other quantities in this work, are given in parentheses and represent one-standard-deviation uncertainties in the final digits.

All other measurements of intervals in atomic hydrogen have uncertainties of greater than 6 kHz. The energies tabulated in this work (and their uncertainties) are given to an accuracy of 0.1 kHz. This accuracy is more than sufficient for comparing to current measurements and foreseeable future improvements of these measurements. None of our tabulated values, except those directly derived from Eq. (1), are given to an accuracy of less than 0.1 kHz, both because it is not necessary at this time and because, given the experimental uncertainties, some terms in the atomic hydrogen energies may not have been fully considered at a higher level of accuracy.

Precise theoretical predictions are needed to determine all other intervals [other than those of Eq. (1)] to an accuracy of less than 1 kHz. In addition, precise values of fundamental constants are required. The most important constant needed is the Rydberg constant R_∞. As will be discussed in Sec. V, this constant can be obtained from a combination of the theoretical predictions for the hydrogen atom and the measurements of Eq. (1).

The second most important constant is the fine-structure constant α, the value of which is known from a comparison between theory and measurements of the magnetic moment of the electron. For this work, we use the CODATA [7] value of

$$\alpha = 1/137.035\,999\,139(31), \tag{2}$$

which is derived almost entirely from the electron magnetic moment. The proton's mass, magnetic moment, and rms charge radius are also needed. The CODATA values for these quantities are

$$m_\mathrm{p}/m_\mathrm{e} = 1836.152\,673\,89(17), \tag{3}$$

$$g_\mathrm{p} = 5.585\,694\,702(17), \tag{4}$$

$$R_\mathrm{p} = 0.8751(61)\ \text{fm}. \tag{5}$$

A more precise determination of the rms charge radius has been obtained using measurements [2,3] of the $n = 2$ levels of muonic hydrogen by Antognini and co-workers:

$$R_\mathrm{p} = 0.840\,87(39)\ \text{fm}. \tag{6}$$

---

[*] hessels@yorku.ca

This value differs significantly from the CODATA determination. We use this more precise determination of R_p in this work, but also tabulate the shifts in the bound-state hydrogen energies that would result if the CODATA value were used. The other two required constants are the Compton wavelength λ_C and the muon mass m_μ, which have CODATA values of

$$\lambdabar_C = \frac{\lambda_C}{2\pi} = 386.159\,267\,64(18)\ \mathrm{fm}, \tag{7}$$

$$m_\mu/m_\mathrm{e} = 206.768\,2826(46). \tag{8}$$

The constants of Eqs. (2)–(4) and (6)–(8) are all determined using physical systems other than atomic hydrogen and therefore should be considered to be external inputs to the theory. Equations (2)–(4), (7), and (8) are known with sufficient precision as to lead to uncertainties in the hydrogen energies of much less than 0.1 kHz. The proton charge radius R_p of Eq. (6), however, despite its more precise determination, is still one of the leading causes for uncertainty in the hydrogen energies.

The binding energy of an $|n\ell j f m_f\rangle$ state of hydrogen can be written as

$$E_{n\ell jf} = E_n^{(\mathrm{g})} + E_{n\ell j}^{(\mathrm{fs})} + E_{n\ell jf}^{(\mathrm{hfs})}, \tag{9}$$

where

$$E_n^{(\mathrm{g})} = -\frac{\mathcal{R}}{n^2}\frac{m_\mathrm{r}}{m_\mathrm{e}} \tag{10}$$

is the gross structure, $E_{n\ell j}^{(\mathrm{fs})}$ is the fine-structure contribution, and $E_{n\ell jf}^{(\mathrm{hfs})}$ is the hyperfine-structure contribution. The energies are of course independent of m_f in the absence of an external field. Here $\mathcal{R} = cR_\infty$, c is the speed of light, R_∞ is the Rydberg constant, $m_\mathrm{r} = m_\mathrm{e}m_\mathrm{p}/M$ is the reduced mass, $M = m_\mathrm{e} + m_\mathrm{p}$, and m_e and m_p are the electron and proton masses, respectively. For this work, Planck's constant h is suppressed and all energies are given in frequency units.

III. FINE-STRUCTURE ENERGY CONTRIBUTIONS

The values of $E_{n\ell j}^{(\mathrm{fs})}$ are discussed in detail in Ref. [1]:

$$E_{n\ell j}^{(\mathrm{fs})} = \Delta E_M + E_S + E_\mathrm{R} + E_\mathrm{SE}^{(2)} + E_\mathrm{VP}^{(2)} + E^{(4)} + E^{(6)} + E_\mathrm{RR} + E_\mathrm{SEN} + E_\mathrm{NS}, \tag{11}$$

where ΔE_M gives the mass-corrected Dirac fine structure, E_S and E_R are relativistic recoil corrections, $E_\mathrm{SE}^{(2)}$ and $E_\mathrm{VP}^{(2)}$ are self-energy and vacuum polarization quantum-electrodynamics (QED) corrections, respectively, $E^{(4)}$ and $E^{(6)}$ are higher-order QED corrections, E_RR and E_SEN are small QED corrections due to the finite mass of the proton, and E_NS is the correction for the size (rms charge radius) of the proton. For completeness, we include the formulas given in Ref. [1] that give contributions that are significant to this work, leaving out energy terms and corrections that lead to contributions of less than 0.025 kHz to our tabulated values. Because of the precisely measured $1S$-$2S$ interval of Eq. (1), $E^{(\mathrm{fs})}$ for the $1S$ state energy needs to be determined less accurately and is only necessary for the determination of the Rydberg constant, as will be discussed in Sec. V.

From Ref. [1], we obtain

$$\Delta E_M = E_M - Mc^2 - E_n^{(\mathrm{g})} = \frac{2[f_{nj}-1] - [f_{nj}-1]^2\frac{m_\mathrm{r}}{M}}{\alpha^2}\frac{\mathcal{R}m_\mathrm{r}}{m_\mathrm{e}} + \frac{\mathcal{R}}{n^2}\frac{m_\mathrm{r}}{m_\mathrm{e}} + \frac{1-\delta_{\ell 0}}{2\ell+1}\frac{\alpha^2\mathcal{R}m_\mathrm{e}^2}{\kappa_{\ell j}n^3m_\mathrm{p}^2}, \tag{12}$$

$$E_S = \frac{2m_\mathrm{r}^3\alpha^3\mathcal{R}}{m_\mathrm{e}^2m_\mathrm{p}\pi n^3}\left\{\frac{\delta_{\ell 0}}{3}\lambda - \frac{8}{3}\beta_{n\ell} - \frac{\delta_{\ell 0}}{9} - \frac{7}{3}a_{n\ell} - 2\delta_{\ell 0}\frac{m_\mathrm{e}}{m_\mathrm{p}}\right\}, \tag{13}$$

$$E_\mathrm{R} = \frac{2m_\mathrm{e}\alpha^4\mathcal{R}}{m_\mathrm{p}\pi n^3}\left\{D_{60}^{(n\ell)} - \frac{11\delta_{\ell 0}}{60}\alpha\lambda^2 + D_{71}^{(n\ell j)}\alpha\lambda\right\}, \tag{14}$$

$$E_\mathrm{SE}^{(2)} = \frac{2m_\mathrm{r}^3\alpha^3\mathcal{R}}{m_\mathrm{e}^3\pi n^3}\left\{\frac{4\delta_{\ell 0}}{3}\lambda - \frac{4\beta_{n\ell}}{3} + \frac{10\delta_{\ell 0}}{9} - \frac{(1-\delta_{\ell 0})}{2\kappa_{\ell j}(2\ell+1)}\frac{m_\mathrm{e}}{m_\mathrm{r}} + \left(\frac{139}{32} - 2\ln 2\right)\pi\delta_{\ell 0}\alpha - \delta_{\ell 0}\alpha^2\lambda^2 + A_{61}^{(n\ell j)}\alpha^2\lambda + G_\mathrm{SE}^{(n\ell j)}\alpha^2\right\}, \tag{15}$$

$$E_\mathrm{VP}^{(2)} = \frac{2m_\mathrm{r}^3\alpha^3\mathcal{R}}{m_\mathrm{e}^3\pi n^3}\left\{\left[-\frac{4}{15}\left(1 + 1.67\frac{m_\mathrm{e}^2}{m_\mu^2}\right) + \frac{5\pi}{48}\alpha - \frac{2}{15}\alpha^2\lambda + \left(\frac{19}{45} - \frac{\pi^2}{27}\right)\alpha^2\right]\delta_{\ell 0} + G_\mathrm{VP}^{(1)(n\ell j)}\alpha^2\right\}, \tag{16}$$

$$E^{(4)} = \frac{2m_\mathrm{r}^3\alpha^4\mathcal{R}}{m_\mathrm{e}^3\pi^2n^3}\left\{0.53894\delta_{\ell 0} + \frac{0.3285(1-\delta_{\ell 0})}{\kappa_{\ell j}(2\ell+1)}\frac{m_\mathrm{e}}{m_\mathrm{r}} - 21.554\delta_{\ell 0}\alpha - \frac{8\delta_{\ell 0}}{27}\alpha^2\lambda^3 + B_{62}^{(n\ell)}\alpha^2\lambda^2 + B_{61}^{(n\ell j)}\alpha^2\lambda + B_{60}^{(n\ell j)}\alpha^2\right\}, \tag{17}$$

$$E^{(6)} = \frac{2m_\mathrm{r}^3\alpha^5\mathcal{R}}{m_\mathrm{e}^3\pi^3n^3}\left\{0.418\delta_{\ell 0} - \frac{1.2(1-\delta_{\ell 0})}{\kappa_{\ell j}(2\ell+1)}\frac{m_\mathrm{e}}{m_\mathrm{r}} + C_{50}\alpha\right\}, \tag{18}$$

$$E_\mathrm{NS} = \frac{4m_\mathrm{r}^3\alpha^2R_\mathrm{p}^2\mathcal{R}}{3m_\mathrm{e}^3\lambdabar_C^2n^3}\left\{1 - \alpha^2\ln\frac{\alpha R_\mathrm{p}}{n\lambdabar_C} - 1.8\alpha^2\right\}\delta_{\ell 0}, \tag{19}$$

$$E_\mathrm{RR} = \frac{2m_\mathrm{r}^3\alpha^4\mathcal{R}}{m_\mathrm{p}m_\mathrm{e}^2\pi^2n^3}\delta_{\ell 0}\left\{-13.47 + \frac{2}{3}\pi\alpha\lambda^2 + \Delta^\mathrm{RR}\alpha\lambda\right\}, \tag{20}$$

and

$$E_\mathrm{SEN} = \frac{8m_\mathrm{r}^3\alpha^3\mathcal{R}}{3m_\mathrm{p}^2m_\mathrm{e}\pi n^3}\left\{\delta_{\ell 0}\ln\frac{m_\mathrm{p}}{m_\mathrm{e}\alpha^2} - \beta_{n\ell}\right\}. \tag{21}$$

Here $\lambda = \ln(\alpha^{-2}m_\mathrm{e}/m_\mathrm{r})$, $\delta_{\ell 0}$ is the Kronecker delta, $\kappa_{\ell j} = (\ell - j)(2j+1)$, $f_{nj} = [1 + \alpha^2(n-\delta)^{-2}]^{-1/2}$ in Eq. (12) (with $\delta = j + \frac{1}{2} - [(j+\frac{1}{2})^2 - \alpha^2]^{1/2}$), $\beta_{n\ell}$ are the Bethe logarithms (tabulated in Ref. [8]),

$$a_{n\ell} = -2\left[\ln\frac{2}{n} + \sum_{i=1}^{n}\frac{1}{i} + 1 - \frac{1}{2n}\right]\delta_{\ell 0} + \frac{1-\delta_{\ell 0}}{\ell(\ell+1)(2\ell+1)}, \tag{22}$$

$$D_{60}^{(n\ell)} = \left(4\ln 2 - \frac{7}{2}\right)\pi\delta_{\ell 0} + \frac{\left[3 - \frac{\ell(\ell+1)}{n^2}\right]2\pi(1-\delta_{\ell 0})}{(4\ell^2-1)(2\ell+3)}, \tag{23}$$

$$\begin{aligned} A_{61}^{(n\ell j)} = {} & \left[\left(\sum_{i=1}^{n}\frac{4}{i}\right) + \frac{28}{3}\ln 2 - 4\ln n - \frac{601}{180} - \frac{77}{45n^2}\right]\delta_{\ell 0} \\ & + \left(1 - \frac{1}{n^2}\right)\left(\frac{2}{15} + \frac{\delta_{j(1/2)}}{3}\right)\delta_{\ell 1} \\ & + \frac{8[3n^2 - \ell(\ell+1)](1-\delta_{\ell 0})}{3n^2\ell(4\ell^2-1)(\ell+1)(2\ell+3)}, \end{aligned} \tag{24}$$

and

$$\begin{aligned} B_{62}^{(n\ell)} = {} & \frac{16}{9}\left[1.067 + \psi(n) - \ln n - \frac{1}{n} + \frac{1}{4n^2}\right]\delta_{\ell 0} \\ & + \frac{4\delta_{\ell 1}}{27}\frac{n^2-1}{n^2}, \end{aligned} \tag{25}$$

with ψ being the digamma function. The values of $G_{\mathrm{SE}}^{(n\ell j)}$ of Eq. (15), $G_{\mathrm{VP}}^{(1)(n\ell j)}$ of Eq. (16), and $B_{61}^{(n\ell j)}$ and $B_{60}^{(n\ell j)}$ of Eq. (17) are discussed in Ref. [1] and the tabulated values (along with values given in Refs. [9–13] and simple extrapolations and interpolations) are sufficiently precise for the present work. The values of $D_{71}^{(n\ell j)}$ are needed only for the lowest-lying states and have recently been calculated in Ref. [14].

Although many uncertainties to the fine-structure energy contributions $E_{n\ell j}^{(\mathrm{fs})}$ are detailed in Ref. [1], only four uncertainties dominate and need to be considered in this work. The first comes from an uncertainty of ± 19.7 in the $\ell = 0$ coefficients $B_{60}^{(n\ell j)}$ of Eq. (17), which leads to an uncertainty of $\delta_{\ell 0}(2.0\ \mathrm{kHz})/n^3$. The second comes from the uncertainty in R_{p} [of Eq. (6)] in Eq. (19), which contributes $\delta_{\ell 0}(1.0\ \mathrm{kHz})/n^3$. The third comes from the coefficient C_{50} of Eq. (18), which is presumed to be $\pm 30\delta_{\ell 0}$ and leads to an uncertainty of $\delta_{\ell 0}(1.0\ \mathrm{kHz})/n^3$. The fourth comes from the Δ^{RR} coefficient of Eq. (20), which is presumed to be ± 10, thus leading to an uncertainty of $\delta_{\ell 0}(0.7\ \mathrm{kHz})/n^3$. An additional uncertainty in Eq. (14) has now been resolved by Ref. [14] and does not need to be included. These four dominant uncertainties all have the same dependence on n and ℓ and therefore can be added in quadrature to give a combined uncertainty of $\delta_{\ell 0}(2.6\ \mathrm{kHz})/n^3$. All other uncertainties listed in Ref. [1] are more than an order of magnitude smaller. The values of $E_{n\ell j}^{(\mathrm{fs})}$ for the lowest-lying states, along with their uncertainties, are listed in Table I.

TABLE I. Fine-structure energies $E_{n\ell j}^{(\mathrm{fs})}$ for the lowest-lying states of atomic hydrogen. Uncertainties in units of the final digit of the value are shown in parentheses. Values given without uncertainties have uncertainties of less than 0.1 kHz. The values in this table are determined using the Rydberg constant obtained in Sec. V; however, using the CODATA value instead would not change the values, since the resulting changes would be at the level of 1 Hz or less.

State	$E_{n\ell j}^{(\mathrm{fs})}$ (kHz)	State	$E_{n\ell j}^{(\mathrm{fs})}$ (kHz)
$1S_{1/2}$	−35 625 530.5(26)		
$2S_{1/2}$	−12 636 029.4(3)		
$2P_{1/2}$	−13 693 861.6	$2P_{3/2}$	−2 724 820.1
$3S_{1/2}$	−4 552 716.0(1)		
$3P_{1/2}$	−4 867 590.3	$3P_{3/2}$	−1 617 501.0
$3D_{3/2}$	−1 622 832.7	$3D_{5/2}$	−539 495.5
$4S_{1/2}$	−2 091 332.8		
$4P_{1/2}$	−2 224 408.7	$4P_{3/2}$	−853 278.9
$4D_{3/2}$	−855 566.5	$4D_{5/2}$	−398 533.1
$4F_{5/2}$	−399 342.4	$4\mathrm{F}_{7/2}$	−170 827.1
$5S_{1/2}$	−1 123 202.3		
$5P_{1/2}$	−1 191 397.0	$5P_{3/2}$	−489 379.3
$5D_{3/2}$	−490 561.2	$5D_{5/2}$	−256 560.1
$5F_{5/2}$	−256 977.8	$5F_{7/2}$	−139 977.9
$5G_{7/2}$	−140 196.4	$5G_{9/2}$	−69 996.6
$6S_{1/2}$	−670 236.8		
$6P_{1/2}$	−709 720.8	$6P_{3/2}$	−303 461.0
$6D_{3/2}$	−304 148.6	$6D_{5/2}$	−168 731.3
$6F_{5/2}$	−168 974.3	$6F_{7/2}$	−101 266.0
$6G_{7/2}$	−101 393.0	$6G_{9/2}$	−60 768.1
$6H_{9/2}$	−60 846.8	$6H_{11/2}$	−33 763.6

IV. HYPERFINE STRUCTURE

The hyperfine contributions to the energies are given by

$$\begin{aligned} E_{n\ell jf}^{(\mathrm{hfs})} = {} & \delta_{\ell 0}\left(f - \frac{3}{4}\right)\frac{\Delta E_{1S}^{\mathrm{hfs}} + \Delta_n}{n^3} \\ & + (1-\delta_{\ell 0})\left(E_{\mathrm{diag}}^{\mathrm{hfs}} + \Delta E^{\mathrm{hfs}}\right). \end{aligned} \tag{26}$$

For $\ell = 0$ states, where the structure of the nucleus affects the hyperfine structure, $E_{n\ell jf}^{(\mathrm{hfs})}$ is determined using the precise measurement of the ground-state hyperfine interval $\Delta E_{1S}^{\mathrm{hfs}}$ of Eq. (1). For $n = 2$, $\Delta_2 = 48.922(27)$ kHz can be determined directly from the measured interval of Eq. (1). For higher n, the correction Δ_n is discussed in detail in Ref. [15] and to the accuracy required here is given by

$$\Delta_n = \frac{8}{3}g_{\mathrm{p}}\alpha^4\mathcal{R}\frac{m_{\mathrm{e}}}{m_{\mathrm{p}}}\left(\frac{1}{3} + \frac{3}{2n} - \frac{11}{6n^2}\right). \tag{27}$$

For $\ell \neq 0$, nuclear effects are not significant and the dominant diagonal term $E_{\mathrm{diag}}^{\mathrm{hfs}}$ of the atomic hydrogen hyperfine Hamiltonian

$$\begin{aligned} H_{\mathrm{hfs}} = {} & g_{\mathrm{p}}\alpha^2\mathcal{R}\frac{m_{\mathrm{e}}}{m_{\mathrm{p}}}\frac{a_0^3}{\hbar^2}\left\{\left(1 + \frac{g_{\mathrm{p}}-1}{g_{\mathrm{p}}}\frac{m_{\mathrm{e}}}{m_{\mathrm{p}}}\right)\frac{\vec{I}\cdot\vec{L}}{r^3}\right. \\ & \left. + (1+a_{\mathrm{e}})\left[\frac{3\vec{I}\cdot\hat{r}\vec{S}\cdot\hat{r}}{r^3} - \frac{\vec{I}\cdot\vec{S}}{r^3} + \frac{8\pi}{3}\delta(\vec{r})\vec{I}\cdot\vec{S}\right]\right\} \end{aligned} \tag{28}$$

is given by

$$\begin{aligned} E_{\mathrm{diag}}^{\mathrm{hfs}} = {} & g_{\mathrm{p}}\frac{\alpha^2\mathcal{R}}{n^3}\frac{m_{\mathrm{r}}^3}{m_{\mathrm{e}}^3}\frac{m_{\mathrm{e}}}{m_{\mathrm{p}}}\frac{f(f+1) - j(j+1) - \frac{3}{4}}{(2\ell+1)j(j+1)}\left\{1 + \frac{a_{\mathrm{e}}}{2\kappa_{\ell j}}\right. \\ & + \frac{g_{\mathrm{p}}-1}{g_{\mathrm{p}}}\frac{m_{\mathrm{e}}}{m_{\mathrm{p}}}\frac{2\kappa_{\ell j}-1}{2\kappa_{\ell j}} + \alpha^2\left[\frac{3(2j+1)^2-1}{2(2j+1)^2 j(j+1)}\right. \\ & \left.\left. + \frac{3}{n(2j+1)} + \frac{3-8\kappa_{\ell j}}{2n^2(2\kappa_{\ell j}-1)}\right]\right\}. \end{aligned} \tag{29}$$

The $a_{\mathrm{e}} = (g_{\mathrm{e}}-2)/2$ electron anomalous moment corrections do not apply to the $\vec{I}\cdot\vec{L}$ term in the hyperfine

TABLE II. Hyperfine-structure energies $E^{(\mathrm{hfs})}_{n\ell jf}$ for the lowest-lying states of atomic hydrogen. All values are uncertain by less than 0.1 kHz. The precisely measured values are given for the $1S$ and $2S$ states.

State	f	$E^{(\mathrm{hfs})}_{n\ell jf}$ (kHz)	f	$E^{(\mathrm{hfs})}_{n\ell jf}$ (kHz)
$1S_{1/2}$	0	−1 065 304.313 8260(8)	1	355 101.437 9420(3)
$2S_{1/2}$	0	−133 167.6257(51)	1	44 389.2086(17)
$2P_{1/2}$	0	−44 379.0	1	14 790.5
$2P_{3/2}$	1	−14 781.3	2	8870.3
$3S_{1/2}$	0	−39 457.0	1	13 152.3
$3P_{1/2}$	0	−13 149.4	1	4382.4
$3P_{3/2}$	1	−4379.7	2	2628.2
$3D_{3/2}$	1	−2629.2	2	1577.4
$3D_{5/2}$	2	−1576.9	3	1126.4
$4S_{1/2}$	0	−16 645.9	1	5548.6
$4P_{1/2}$	0	−5547.4	1	1848.8
$4P_{3/2}$	1	−1847.7	2	1108.8
$4D_{3/2}$	1	−1109.2	2	665.5
$4D_{5/2}$	2	−665.3	3	475.2
$4F_{5/2}$	2	−475.3	3	339.5
$4F_{7/2}$	3	−339.4	4	264.0

Hamiltonian and this leads to the $2\kappa_{\ell j}$ denominator of the a_e term. The a_e correction is included (for the $2P$ states) in Ref. [16], is included to first order in α in Ref. [17], but is included incorrectly (without the $2\kappa_{\ell j}$ in the denominator) in Ref. [18]. The tabulation of Ref. [19] correctly includes the a_e correction for the P states (following the prescription of Ref. [16]), but, because this prescription is specific to P states, gives only an estimate (along with an estimated uncertainty) for higher-ℓ states. Given the size of the hyperfine structure, it is sufficient for this work to approximate a_e by its lowest-order term: $\alpha/2\pi$.

The correction proportional to $[(g_\mathrm{p}-1)/g_\mathrm{p}](m_\mathrm{e}/m_\mathrm{p})$ results from the interaction of the proton's orbital motion with its spin. This term is included (for the $2P$ states) in Ref. [16], but is given incorrectly for the $2P$ state in Eqs. (27) and (28) of Ref. [20] for muonic hydrogen, where the term is even more important. The term is correctly included for muonic hydrogen in Table II of Ref. [20] and in Ref. [21]. The term is omitted in Ref. [17], Ref. [22], and Ref. [18]. This mass-correction term contributes 13 kHz to the $2P_{1/2}$ hyperfine structure and thus must certainly be included at the accuracy of this work. The correction is included correctly for P states in the tabulation of Ref. [19] (following the prescription of Ref. [16]), but, since this prescription is specific to P states, only an estimate (along with an estimated uncertainty) is given for higher-ℓ states. The general form for this correction (as a function of n, ℓ, and j) does not seem to appear previously in the literature.

The correction proportional to α^2 in Eq. (29) is a relativistic correction that is given in Ref. [17]. Higher-order corrections are also considered in that work, but are insignificant at the level of this work.

The smaller ΔE^hfs contribution comes from an off-diagonal element of the hyperfine Hamiltonian. This element causes a very slight mixing between the $|n,\ell,j=\ell-\frac{1}{2},f=\ell,m_f\rangle$ state and the $|n,\ell,j=\ell+\frac{1}{2},f=\ell,m_f\rangle$ state and its contribution to the energy can be determined to sufficient accuracy by the expression from second-order perturbation theory

$$\begin{aligned}\Delta E^\mathrm{hfs} &= \frac{|\langle n\ell jf=\ell m_f|H_\mathrm{hfs}|n\ell j'f=\ell m_f\rangle|^2}{E^{(\mathrm{fs})}_{n\ell j}-E^{(\mathrm{fs})}_{n\ell j'}}\\ &= \frac{2\alpha^2\mathcal{R}}{n^3}\frac{m_\mathrm{e}^2}{m_\mathrm{p}^2}g_\mathrm{p}^2\frac{(j-\ell)\delta_{f\ell}}{(2\ell+1)^4}.\end{aligned} \tag{30}$$

This expression for ΔE^hfs was first given (for the $2P$ states) in Ref. [16]. This expression differs from the one given there in that it is generalized to allow for any value of n, ℓ, and j and is simplified using analytic expressions for the 6-J symbols. The general form does not appear to be presented in the literature and an incorrect form (with an incorrect dependence on ℓ) is used in the tabulation of Ref. [19]. The magnitude of the off-diagonal contributions calculated in Ref. [19] is too large by a factor of $\ell^2(\ell+1)^2(2\ell+1)^2/36$ (a factor of 25, 196, 900, and 3025 for D, F, G, and H states, respectively).

The values of $E^{(\mathrm{hfs})}_{n\ell jf}$ of Eq. (26) are listed in Table II. The tabulated values include the contributions of Eq. (30). In all cases the values can be determined to an uncertainty of less than the 0.1 kHz accuracy tabulated in this work.

V. GROSS STRUCTURE

The gross structure $E^{(\mathrm{g})}$ of Eq. (10) requires a precise value for the Rydberg constant. This value can be obtained by equating the precise measured value of Eq. (1) for the $1S_{1/2}f=1\rightarrow 2S_{1/2}f=1$ interval to Eq. (9), with the values of $E^{(\mathrm{fs})}_{n\ell j}$ and $E^{(\mathrm{hfs})}_{n\ell jf}$ obtained in the previous sections:

$$\begin{aligned}&2\,466\,061\,102\,474.806(10)\text{ kHz}\\ &\quad=\frac{3}{4}\mathcal{R}\frac{m_\mathrm{r}}{m_\mathrm{e}}+22\,989\,501.2(2.2)\text{ kHz}\\ &\quad\quad-310\,712.2294(17)\text{ kHz}.\end{aligned} \tag{31}$$

The number in the second line of Eq. (31) is due to the difference of $E^{(\mathrm{fs})}_{n\ell j}$ for the two states and includes the correlated error for the difference. The second term is due to the difference of $E^{(\mathrm{hfs})}_{n\ell jf}$ for the two states and is given by the difference of the $1S$ and $2S$ hyperfine-interval measurements of Eq. (1) divided by 4. Solving for the Rydberg constant gives

$$\mathcal{R}=cR_\infty=3\,289\,841\,960\,248.9(3.0)\text{ kHz}, \tag{32}$$

where the 3.0 kHz uncertainty is dominated by the uncertainty in the $E^{(\mathrm{fs})}$ term. Equation (32) differs considerably from the CODATA value of 3 289 841 960 355(19) kHz. The difference is almost entirely due to the fact that the value from Antognini and co-workers of R_p [Eq. (6)] is used, whereas the CODATA compilation uses the value of Eq. (5). A very small contribution to the difference comes from the recent improvement [14] in the determination of $E^{(\mathrm{fs})}$ from the determination of $D^{(n\ell j)}_{71}$. The uncertainty in the value from Antognini and co-workers of R_p [Eq. (6)] contributes 1.2 kHz to the 3.0 kHz uncertainty in Eq. (32), with the rest of the uncertainty resulting from the other (theoretical) uncertainties discussed in the last paragraph of Sec. III.

TABLE III. Total binding energies for the lowest-lying S ($\ell = 0$) states, with uncertainties in the last digits given in parentheses. Values given without uncertainties have uncertainties of less than 0.1 kHz. The last column gives the change δ_R in the binding energy that would result if R_p is increased by 0.034 23 fm (the difference between the CODATA value and that of Antognini and co-workers [2,3]).

n	$E(nS_{1/2}\,f=0)$ (kHz)	$E(nS_{1/2}\,f=1)$ (kHz)	δ_R(kHz)
1	−3 288 087 922 416.0(4)	−3 288 086 502 010.2(4)	−15.3
2	−822 025 577 092.2(4)	−822 025 399 535.4(4)	−15.3
3	−365 343 617 904.3(2)	−365 343 565 294.9(2)	−8.5
4	−205 505 309 952.5(1)	−205 505 287 757.9(1)	−5.3
5	−131 523 180 988.2(1)	−131 523 169 624.6(1)	−3.6
6	−91 335 431 601.7(1)	−91 335 425 025.6(1)	−2.6
7	−67 103 520 641.6(1)	−67 103 516 500.4(1)	−1.9
8	−51 376 096 003.6	−51 376 093 229.3	−1.5
9	−40 593 435 126.6	−40 593 433 178.1	−1.2
10	−32 880 666 896.5	−32 880 665 476.0	−1.0
11	−27 174 094 155.3	−27 174 093 088.1	−0.8
12	−22 833 779 830.0	−22 833 779 008.0	−0.7
13	−19 455 996 185.2	−19 455 995 538.7	−0.6
14	−16 775 829 289.9	−16 775 828 772.2	−0.5
15	−14 613 608 126.8	−14 613 607 705.9	−0.4
16	−12 843 989 064.0	−12 843 988 717.2	−0.4
17	−11 377 372 464.9	−11 377 372 175.8	−0.4
18	−10 148 333 775.8	−10 148 333 532.3	−0.3
19	−9 108 198 599.8	−9 108 198 392.7	−0.3
20	−8 220 148 221.6	−8 220 148 044.1	−0.3

VI. TOTAL BINDING ENERGIES

Using Eq. (9), along with the Rydberg constant of Eq. (32), the values of $E^{(\mathrm{fs})}_{n\ell j}$ of Sec. III, and $E^{(\mathrm{hfs})}_{n\ell jf}$ of Sec. IV, allows for a determination of the energies of all bound states of atomic hydrogen. Energies for $\ell = 0$, 1, and 2 are given in Tables III, IV, and V, respectively, with higher-ℓ energies given in Table VI. The uncertainties listed are dominated by the uncertainties in $E^{(\mathrm{fs})}$ (both due to the fine structure of the state and due to the effect of $E^{(\mathrm{fs})}$ on the determination of the Rydberg constant). The uncertainties listed take into account the correlation between these two ways that $E^{(\mathrm{fs})}$ enters the determination of the energies.

The final column in the tables gives the shift that the energy levels would experience if the CODATA value of R_p were used instead of the value from Antognini and co-workers. In referring to Eq. (19), one might assume that the value of R_p would affect only $\ell = 0$ states. However, this is not the case, since the value of R_p also affects the determination of the Rydberg constant [see Eq. (31)] and therefore the energies of all states are affected.

VII. COMPARISON TO MEASURED VALUES

Table VII gives a compilation of the most precise measurements to date of atomic hydrogen intervals. Many of these measurements reported values that were corrected for the hyperfine structure. Given the inconsistency of hyperfine corrections applied in the literature (including inconsistent or incorrect application of anomalous moment corrections, of finite mass corrections, and of corrections due to off-diagonal hyperfine-structure contributions), we have, where possible, given the actual intervals (or linear combination of intervals) measured.

Note that the hyperfine structure for the $4P_{1/2}$, $4P_{3/2}$, $4D_{5/2}$, $6D_{5/2}$, $8D_{3/2}$, $8D_{5/2}$, $12D_{3/2}$, and $12D_{5/2}$ states (with splittings of 7396.2, 2956.5, 1140.5, 337.9, 221.8, 142.6, 65.7, and 42.2 kHz, respectively) is not resolved in the measurements of Table VII and therefore it is crucial to know both the hyperfine splittings and the relative strength of transitions to determine the energy splittings. References [18,23] give explicit values for the expected strength of the two hyperfine transitions ($\frac{2}{9}$ and $\frac{7}{9}$) and give an explicit correction for how much this linear combination differs from the hyperfine centroid of the D states. References [25,26,29] do not give such explicit corrections since their fits include the hyperfine structure. We therefore list the hyperfine centroid values given in those works. A further analysis of the work of Ref. [29] may be necessary, as they appear to use a simplified form for the presumed hyperfine intervals for their fits [33].

TABLE IV. Continuation of Table III for the lowest-lying P ($\ell = 1$) states.

n	$E(nP_{1/2}\,f=0)$ (kHz)	$E(nP_{1/2}\,f=1)$ (kHz)	$E(nP_{3/2}\,f=1)$ (kHz)	$E(nP_{3/2}\,f=2)$ (kHz)	δ_R (kHz)
2	−822 026 546 135.9(7)	−822 026 486 966.4(7)	−822 015 547 496.7(7)	−822 015 523 845.1(7)	−26.8
3	−365 343 906 471.0(3)	−365 343 888 939.2(3)	−365 340 647 611.9(3)	−365 340 640 604.0(3)	−11.9
4	−205 505 431 929.9(2)	−205 505 424 533.7(2)	−205 504 057 100.4(2)	−205 504 054 143.9(2)	−6.7
5	−131 523 243 500.5(1)	−131 523 239 713.6(1)	−131 522 539 588.6(1)	−131 522 538 074.9(1)	−4.3
6	−91 335 467 797.2(1)	−91 335 465 605.8(1)	−91 335 060 441.3(1)	−91 335 059 565.3(1)	−3.0
7	−67 103 543 442.8(1)	−67 103 542 062.8(1)	−67 103 286 915.7(1)	−67 103 286 364.0(1)	−2.2
8	−51 376 111 281.9	−51 376 110 357.4	−51 375 939 428.9	−51 375 939 059.3	−1.7
9	−40 593 445 858.7	−40 593 445 209.3	−40 593 325 160.9	−40 593 324 901.3	−1.3
10	−32 880 674 721.0	−32 880 674 247.6	−32 880 586 732.3	−32 880 586 543.1	−1.1
11	−27 174 100 034.5	−27 174 099 678.8	−27 174 033 927.3	−27 174 033 785.2	−0.9
12	−22 833 784 358.7	−22 833 784 084.8	−22 833 733 439.4	−22 833 733 329.9	−0.7
13	−19 455 999 747.3	−19 455 999 531.9	−19 455 959 697.9	−19 455 959 611.8	−0.6
14	−16 775 832 142.0	−16 775 831 969.5	−16 775 800 076.2	−16 775 800 007.3	−0.5
15	−14 613 610 445.7	−14 613 610 305.5	−14 613 584 375.1	−14 613 584 319.0	−0.5

TABLE V. Continuation of Tables III and IV for the lowest-lying D ($\ell = 2$) states.

n	$E(nD_{3/2} f=1)$ (kHz)	$E(nD_{3/2} f=2)$ (kHz)	$E(nD_{5/2} f=2)$ (kHz)	$E(nD_{5/2} f=3)$ (kHz)	δ_R (kHz)
3	−365 340 651 193.1(3)	−365 340 646 986.5(3)	−365 339 566 803.7(3)	−365 339 564 100.3(3)	−11.9
4	−205 504 058 649.5(2)	−205 504 056 874.8(2)	−205 503 601 172.2(2)	−205 503 600 031.7(2)	−6.7
5	−131 522 540 392.4(1)	−131 522 539 483.7(1)	−131 522 306 163.9(1)	−131 522 305 580.0(1)	−4.3
6	−91 335 060 910.1(1)	−91 335 060 384.3(1)	−91 334 925 361.2(1)	−91 334 925 023.3(1)	−3.0
7	−67 103 287 212.4(1)	−67 103 286 881.3(1)	−67 103 201 852.2(1)	−67 103 201 639.4(1)	−2.2
8	−51 375 939 628.3	−51 375 939 406.5	−51 375 882 443.7	−51 375 882 301.1	−1.7
9	−40 593 325 301.3	−40 593 325 145.5	−40 593 285 138.7	−40 593 285 038.6	−1.3
10	−32 880 586 834.9	−32 880 586 721.3	−32 880 557 556.4	−32 880 557 483.4	−1.1
11	−27 174 034 004.5	−27 174 033 919.1	−27 174 012 007.1	−27 174 011 952.2	−0.9
12	−22 833 733 498.9	−22 833 733 433.2	−22 833 716 555.3	−22 833 716 513.1	−0.7

The third column of Table VII gives the prediction of this work for each of the measured intervals (or linear combination of intervals). Eleven of the 15 entries in the table show agreement to within 1.5 standard deviations with the values given in this work. Three more of the entries agree to within 2 standard deviations. One measurement (the $2S$ to $8D_{5/2}$ interval, which is the most precise measurement in the table) disagrees by more than 3 standard deviations. The overall level of agreement between the measured values and the values of this work can be assessed by calculating a χ^2 value for the agreement for the 15 entries in the table. The resultant χ^2 of 30.6 shows that the agreement is not good. The χ^2 distribution for 15 degrees of freedom has a probability of 0.10% for χ^2 being 30.6 or larger. This discrepancy is dominated by the $2S$ to $8D_{5/2}$ interval. If it were not included, the χ^2 value would be 20.7.

The discrepancy between column 2 and column 3 of Table VII could be eliminated if either the measurement or theoretical uncertainties are underestimated. In order to make the agreement acceptable, the theoretical uncertainty of column 3 could be increased by a factor of 30. This could be achieved by assuming an uncertainty (cf. the last paragraph of Sec. III) of (80 kHz)$\delta_{\ell 0}/n^3$. An overlooked contribution of this size seems unlikely given the many decades of careful work on atomic hydrogen theory. In order to get acceptable agreement, the measurement uncertainties could be increased by a factor of 1.5. An increase in experimental uncertainties by a factor of 1.5 is far more plausible than an increase in theoretical uncertainties by a factor of 30, especially given the large contribution of systematic effects in the measurements and given the fact that the measurement uncertainty is, in all cases, a very small fraction of the natural width of the transition. Karshenboim [34] discusses the tension between the most precise measurements in Table VII (including similar measurements in deuterium) and suggests that the tension might indicate an underestimation of experimental uncertainties.

Another way to analyze the discrepancy between column 2 and column 3 of Table VII is to determine the required change

TABLE VI. Continuation of Tables III–V for the lowest-lying ($\ell \geqslant 3$) states.

n	ℓ	$E(n\ell j = \ell - \frac{1}{2} f = \ell - 1)$	$E(n\ell j = \ell - \frac{1}{2} f = \ell)$	$E(n\ell j = \ell + \frac{1}{2} f = \ell)$	$E(n\ell j = \ell + \frac{1}{2} f = \ell + 1)$	δ_R (kHz)
4	3	−205 503 601 791.5(2)	−205 503 600 976.7(2)	−205 503 373 140.3(2)	−205 503 372 536.9(2)	−6.7
5	3	−131 522 306 484.4(1)	−131 522 306 067.2(1)	−131 522 189 415.0(1)	−131 522 189 106.0(1)	−4.3
6	3	−91 334 925 548.0(1)	−91 334 925 306.5(1)	−91 334 857 799.4(1)	−91 334 857 620.6(1)	−3.0
7	3	−67 103 201 970.3(1)	−67 103 201 818.3(1)	−67 103 159 306.5(1)	−67 103 159 193.9(1)	−2.2
8	3	−51 375 882 523.1	−51 375 882 421.2	−51 375 853 941.6	−51 375 853 866.2	−1.7
9	3	−40 593 285 194.6	−40 593 285 123.0	−40 593 265 120.9	−40 593 265 067.9	−1.3
5	4	−131 522 189 594.9(1)	−131 522 189 354.5(1)	−131 522 119 365.0(1)	−131 522 119 173.9(1)	−4.3
6	4	−91 334 857 904.1(1)	−91 334 857 765.0(1)	−91 334 817 261.8(1)	−91 334 817 151.2(1)	−3.0
7	4	−67 103 159 372.6(1)	−67 103 159 285.1(1)	−67 103 133 778.7(1)	−67 103 133 709.0(1)	−2.2
8	4	−51 375 853 986.1	−51 375 853 927.4	−51 375 836 840.1	−51 375 836 793.4	−1.7
9	4	−40 593 265 152.2	−40 593 265 111.0	−40 593 253 110.0	−40 593 253 077.2	−1.3
6	5	−91 334 817 329.4(1)	−91 334 817 238.9(1)	−91 334 790 237.1(1)	−91 334 790 161.9(1)	−3.0
7	5	−67 103 133 821.4(1)	−67 103 133 764.4(1)	−67 103 116 760.4(1)	−67 103 116 713.0(1)	−2.2
8	5	−51 375 836 868.8	−51 375 836 830.6	−51 375 825 439.2	−51 375 825 407.5	−1.7
9	5	−40 593 253 130.2	−40 593 253 103.4	−40 593 245 102.8	−40 593 245 080.6	−1.3
7	6	−67 103 116 790.3(1)	−67 103 116 750.2(1)	−67 103 104 604.6(1)	−67 103 104 570.3(1)	−2.2
8	6	−51 375 825 459.3	−51 375 825 432.5	−51 375 817 295.9	−51 375 817 272.9	−1.7
9	6	−40 593 245 117.0	−40 593 245 098.1	−40 593 239 383.5	−40 593 239 367.4	−1.3
8	7	−51 375 817 310.8	−51 375 817 290.9	−51 375 811 188.4	−51 375 811 171.0	−1.7
9	7	−40 593 239 394.0	−40 593 239 380.0	−40 593 235 094.1	−40 593 235 081.9	−1.3
9	8	−40 593 235 102.2	−40 593 235 091.4	−40 593 231 757.9	−40 593 231 748.3	−1.3

TABLE VII. Comparison to measurements. Column 2 gives the measured interval (or linear combination of intervals) and column 3 gives the predicted interval from this work. The final column gives the amount by which the proton radius would have to change in order to give agreement between column 2 and 3. Uncertainties in units of the final digit of the value are shown in parentheses.

Interval (or combinations of intervals)	Measurement (kHz)	This work (kHz)	ΔR_p (fm)
$(2S_{1/2}\,f=1 \rightarrow 4S_{1/2}\,f=1) - \frac{1}{4}(1S_{1/2}\,f=1 \rightarrow 2S_{1/2}\,f=1)$	4 836 176(10)[a]	4 836 158.8(3)	+0.059(34)
$\frac{2}{9}(2S_{1/2}\,f=1 \rightarrow 4D_{5/2}\,f=2) + \frac{7}{9}(2S_{1/2}\,f=1 \rightarrow 4D_{5/2}\,f=3)$ $-\frac{1}{4}(1S_{1/2}\,f=1 \rightarrow 2S_{1/2}\,f=1)$	6 523 655(24)[b]	6 523 631.6(2)	+0.093(95)
$2S_{1/2}\,f=1 \rightarrow 8S_{1/2}\,f=1$	770 649 306 316.4(86)[c]	770 649 306 306.1(4)	+0.025(21)
$\frac{3}{8}(2S_{1/2}\,f=1 \rightarrow 8D_{3/2}\,f=1) + \frac{5}{8}(2S_{1/2}\,f=1 \rightarrow 8D_{3/2}\,f=2)$	770 649 460 060.8(83)[d]	770 649 460 045.7(4)	+0.038(21)
$\frac{5}{12}(2S_{1/2}\,f=1 \rightarrow 8D_{5/2}\,f=2) + \frac{7}{12}(2S_{1/2}\,f=1 \rightarrow 8D_{5/2}\,f=3)$	770 649 517 195.0(64)[e]	770 649 517 174.9(4)	+0.051(16)
$\frac{3}{8}(2S_{1/2}\,f=1 \rightarrow 12D_{3/2}\,f=1) + \frac{5}{8}(2S_{1/2}\,f=1 \rightarrow 12D_{3/2}\,f=2)$	799 191 666 083.5(93)[f]	799 191 666 077.6(4)	+0.014(22)
$\frac{5}{12}(2S_{1/2}\,f=1 \rightarrow 12D_{5/2}\,f=2) + \frac{7}{12}(2S_{1/2}\,f=1 \rightarrow 12D_{5/2}\,f=3)$	799 191 683 014.5(70)[g]	799 191 683 004.7(4)	+0.023(16)
$1S_{1/2}\,f=1 \rightarrow 3S_{1/2}\,f=1$	2 922 742 936 729(13)[h]	2 922 742 936 715.0(2)	+0.069(65)
$(2S_{1/2}\,f=1 \rightarrow 6S_{1/2}\,f=1) - \frac{1}{4}(1S_{1/2}\,f=1 \rightarrow 3S_{1/2}\,f=1)$	4 240 346(21)[i]	4 240 331.0(3)	+0.047(65)
$\frac{5}{12}(2S_{1/2}\,f=1 \rightarrow 6D_{5/2}\,f=2) + \frac{7}{12}(2S_{1/2}\,f=1 \rightarrow 6D_{5/2}\,f=3)$ $-\frac{1}{4}(1S_{1/2}\,f=1 \rightarrow 3S_{1/2}\,f=1)$	4 740 197(11)[j]	4 740 192.5(3)	+0.015(35)
$\frac{1}{4}(2S_{1/2}\,f=1 \rightarrow 4P_{1/2}\,f=0) + \frac{3}{4}(2S_{1/2}\,f=1 \rightarrow 4P_{1/2}\,f=1)$ $-\frac{1}{4}(1S_{1/2}\,f=1 \rightarrow 2S_{1/2}\,f=1)$	4 697 560.0(149)[k]	4 697 534.0(2)	+0.104(59)
$\frac{3}{8}(2S_{1/2}\,f=1 \rightarrow 4P_{3/2}\,f=1) + \frac{5}{8}(2S_{1/2}\,f=1 \rightarrow 4P_{3/2}\,f=2)$ $-\frac{1}{4}(1S_{1/2}\,f=1 \rightarrow 2S_{1/2}\,f=1)$	6 068 664.0(105)[l]	6 068 664.1(2)	−0.001(42)
$2S_{1/2}\,f=0 \rightarrow 2P_{3/2}\,f=1$	10 029 586(12)[m]	10 029 595.6(3)	+0.029(36)
$2P_{1/2}\,f=1 \rightarrow 2S_{1/2}\,f=0$	909 887(9)[n]	909 874.2(3)	+0.038(27)
$2P_{1/2}\,f=1 \rightarrow 2S_{1/2}\,f=0$	909 904(20)[o]	909 874.2(3)	+0.089(60)

[a] Reference [18] with its hfs correction of −38 838 kHz subtracted out to give the original measured value.
[b] References [18,23] with their hfs correction of −33.511 kHz subtracted out. The $4D_{5/2}$ hfs is not resolved in the measurement.
[c] References [24,25] with their hfs correction of 43 695.6 kHz subtracted out to give the original measured value.
[d] References [24,25] with their hfs correction of 44 389.2 kHz subtracted out. The $8D_{3/2}$ hfs is not resolved in the measurement.
[e] References [24,25] with their hfs correction of 44 389.2 kHz subtracted out. The $8D_{5/2}$ hfs is not resolved in the measurement.
[f] References [25,26] with their hfs correction of 44 389.2 kHz subtracted out. The $12D_{3/2}$ hfs is not resolved in the measurement.
[g] References [25,26] with their hfs correction of 44 389.2 kHz subtracted out. The $12D_{5/2}$ hfs is not resolved in the measurement.
[h] Reference [27].
[i] References [25,28] with their hfs correction of −42 742.1 kHz subtracted out to give the original measured value.
[j] References [25,28] with their hfs correction of −41 098.1 kHz subtracted out. The $8D_{5/2}$ hfs is not resolved in the measurement.
[k] Reference [29] with its hfs correction of −33 291 kHz subtracted out. The $4P_{1/2}$ hfs is not resolved in the measurement.
[l] Reference [29] with its hfs correction of −33 291 kHz subtracted out. The $4P_{3/2}$ hfs is not resolved in the measurement.
[m] Reference [30] with its hfs correction of −118 386 kHz subtracted out to give the original measured value.
[m] Reference [31].
[o] Reference [32].

ΔR_p in the proton radius (from its value from Antognini and co-workers) that would lead to agreement between the values in these columns. These ΔR_p values are given in the final column of Table VII, along with their uncertainties (which are dominated by the measurement uncertainties of column 2). The listed values of ΔR_p are almost all positive and their weighted average (with an acceptable χ^2 value of 7.3 for 14 degrees of freedom) is 0.035(7) fm (which is 4.9 standard deviations from zero). Thus, the atomic hydrogen data would be consistent with the theoretical predictions if R_p were 4% larger than the value from Antognini and co-workers.

This 4% discrepancy has been the topic of great interest since the muonic measurement of R_p was published [3]. A similar discrepancy has been found between the value for R_p from Antognini and co-workers and that obtained from electron proton scattering [35–37] (although our recent analysis [38] of the scattering data does not support the notion of this discrepancy). The 4% discrepancy for R_p is often referred to as the proton size puzzle and many works have discussed the puzzle (see Refs. [39–41] for reviews of this body of work).

VIII. SUMMARY

We presented clear formulas and tabulations of the bound-state energy levels for atomic hydrogen. The tabulation includes a more precise value for the proton charge radius. The hyperfine structure corrections due to the anomalous moment and the finite mass of the proton and due to off-diagonal matrix elements of the hyperfine Hamiltonian were clearly laid out, along with general formulas for their dependence on n, ℓ, j, and f. The energy of all bound states of atomic hydrogen can now be determined to a precision of better than 1 kHz.

ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada and the Canada Research Chairs program.

---

[1] P. J. Mohr, B. N. Taylor, and D. B. Newell, J. Phys. Chem. Ref. Data **41**, 043109 (2012).
[2] A. Antognini, F. Nez, K. Schuhmann, F. D. Amaro, F. Biraben, J. M. Cardoso, D. S. Covita, A. Dax, S. Dhawan, M. Diepold *et al.*, Science **339**, 417 (2013).
[3] R. Pohl, A. Antognini, F. Nez, F. D. Amaro, F. Biraben, J. M. Cardoso, D. S. Covita, A. Dax, S. Dhawan, L. M. Fernandes *et al.*, Nature (London) **466**, 213 (2010).
[4] C. G. Parthey, A. Matveev, J. Alnis, B. Bernhardt, A. Beyer, R. Holzwarth, A. Maistrou, R. Pohl, K. Predehl, T. Udem *et al.*, Phys. Rev. Lett. **107**, 203001 (2011).
[5] N. Kolachevsky, A. Matveev, J. Alnis, C. G. Parthey, S. G. Karshenboim, and T. W. Hänsch, Phys. Rev. Lett. **102**, 213002 (2009).
[6] S. G. Karshenboim, Phys. Rep. **422**, 1 (2005).
[7] P. J. Mohr, D. B. Newell, and B. N. Taylor, arXiv:1507.07956v1 (2015).
[8] G. W. F. Drake and R. A. Swainson, Phys. Rev. A **41**, 1243 (1990).
[9] U. D. Jentschura, Phys. Rev. A **74**, 062517 (2006).
[10] U. D. Jentschura and P. J. Mohr, Phys. Rev. A **72**, 014103 (2005).
[11] U. D. Jentschura and P. J. Mohr, Phys. Rev. A **69**, 064103 (2004).
[12] U. D. Jentschura, J. Phys. A **36**, L229 (2003).
[13] S. Kotochigova, P. J. Mohr, and B. N. Taylor, Can. J. Phys. **80**, 1373 (2002).
[14] V. A. Yerokhin and V. M. Shabaev, Phys. Rev. Lett. **115**, 233002 (2015).
[15] U. D. Jentschura and V. A. Yerokhin, Phys. Rev. A **73**, 062503 (2006).
[16] S. J. Brodsky and R. G. Parsons, Phys. Rev. **163**, 134 (1967).
[17] B. J. Wundt and U. D. Jentschura, Phys. Rev. A **83**, 052501 (2011).
[18] M. Weitz, A. Huber, F. Schmidt-Kaler, D. Leibfried, W. Vassen, C. Zimmermann, K. Pachucki, T. W. Hänsch, L. Julien, and F. Biraben, Phys. Rev. A **52**, 2664 (1995).
[19] A. Kramida, At. Data Nucl. Data Tables **96**, 586 (2010).
[20] A. Martynenko, Phys. At. Nucl. **71**, 125 (2008).
[21] U. D. Jentschura, Ann. Phys. (N.Y.) **326**, 500 (2011).
[22] B. J. Wundt and U. D. Jentschura, J. Phys. B **43**, 115002 (2010).
[23] M. Weitz, F. Schmidt-Kaler, and T. W. Hänsch, win *Solid State Lasers: New Developments and Applications*, edited by M. Inguscio and R. Wallenstein, NATO Advanced Studies Institute, Series B: Physics (Plenum, New York, 1993), Vol. 317, p. 331.
[24] B. de Beauvoir, F. Nez, L. Julien, B. Cagnac, F. Biraben, D. Touahri, L. Hilico, O. Acef, A. Clairon, and J.-J. Zondy, Phys. Rev. Lett. **78**, 440 (1997).
[25] B. de Beauvoir, C. Schwob, O. Acef, L. Jozefowski, L. Hilico, F. Nez, L. Julien, A. Clairon, and F. Biraben, Eur. Phys. J. D **12**, 61 (2000).
[26] C. Schwob, L. Jozefowski, B. de Beauvoir, L. Hilico, F. Nez, L. Julien, F. Biraben, O. Acef, J.-J. Zondy, and A. Clairon, Phys. Rev. Lett. **82**, 4960 (1999).
[27] O. Arnoult, F. Nez, L. Julien, and F. Biraben, Eur. Phys. J. D **60**, 243 (2010).
[28] S. Bourzeix, B. de Beauvoir, F. Nez, M. D. Plimmer, F. de Tomasi, L. Julien, F. Biraben, and D. N. Stacey, Phys. Rev. Lett. **76**, 384 (1996).
[29] D. J. Berkeland, E. A. Hinds, and M. G. Boshier, Phys. Rev. Lett. **75**, 2470 (1995).
[30] E. W. Hagley and F. M. Pipkin, Phys. Rev. Lett. **72**, 1172 (1994).
[31] S. R. Lundeen and F. M. Pipkin, Phys. Rev. Lett. **46**, 232 (1981).
[32] G. Newton, D. Andrews, and P. Unsworth, Philos. Trans. R. Soc. London Ser. A **290**, 373 (1979).
[33] D. J. Berkeland, Ph.D. Thesis, Yale University, 1995.
[34] S. G. Karshenboim, Phys. Rev. A **91**, 012515 (2015).
[35] J. C. Bernauer *et al.*, Phys. Rev. Lett. **105**, 242001 (2010).
[36] J. Bernauer, M. Distler, J. Friedrich, T. Walcher, P. Achenbach, C. A. Gayoso, R. Böhm, D. Bosnar, L. Debenjak, L. Doria *et al.*, Phys. Rev. C **90**, 015206 (2014).
[37] G. Lee, J. R. Arrington, and R. J. Hill, Phys. Rev. D **92**, 013013 (2015).
[38] M. Horbatsch and E. A. Hessels, Phys. Rev. C **93**, 015204 (2016).
[39] R. Pohl, R. Gilman, G. A. Miller, and K. Pachucki, Annu. Rev. Nucl. Part. Sci. **63**, 175 (2013).
[40] J. C. Bernauer and R. Pohl, Sci. Am. **310** (2), 32 (2014).
[41] C. E. Carlson, Prog. Part. Nucl. Phys. **82**, 59 (2015).