Hydrogen 1s-2s transition frequency: Comparison of experiment and theory

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Using the Dirac equation, radiative corrections and finite nuclear size and mass corrections, we calculate the 1s-2s quantum transition frequency $f_{1s,2s}$ of hydrogen and its uncertainty due to the uncertainties $\delta m_e$, $\delta m_p$, $\delta \alpha$, $\delta r_p$, $\delta R_\infty$ of the electron mass $m_e$, proton mass $m_p$, fine structure constant $\alpha$, proton root mean squared charge radius $r_p$, and the Rydberg constant $R_\infty$. We use the 2018 CODATA [E. Tiesinga, P. J. Mohr, D. B. Newell, B. N. Taylor, Rev. Mod. Phys. 93, 025010 (2021)] procedure for the calculation of $f_{1s,2s}$, and the fundamental constants given therein. We find that the value of the experimental frequency lies outside the theoretical uncertainty (the discrepancy between the theoretical and the experimental frequency is $\Delta f_{1s,2s}^{(2018)} = -23.948$ kHz). But, by fitting $r_p$ we obtain a vanishing discrepancy between the calculated and experimental frequencies and a 6.4 kHz theoretical uncertainty, with $r_p = 0.830734$ fm (and a theoretical uncertainty of $\delta r_p = 0.0022$ fm), consistent with a recent measurement [W. Xiong, et al., Nature (London) 575, 147 (2019)].

**Introduction:** The measurement of the 1s-2s atomic hydrogen transition frequency is important for testing the accuracy of quantum mechanics because of hydrogen’s simple structure, combined with the long lifetime of the 2s level and the capability of systematically correcting for the Doppler effect in the two-photon transition frequency. This frequency is among the most precisely measured quantities in science $[1,2]$ and is essential for determining fundamental constants and conversion factors in physics and chemistry $[3,4]$. The electronic energy levels of hydrogen can be calculated with high precision using the Dirac equation, augmented by radiative quantum electrodynamics (QED), finite nuclear size (FNS), and nuclear recoil corrections. Hence, hydrogen spectroscopy is an effective testing-ground for exploring the predictions of QED $[3]$ and determining the proton root mean squared charge radius, $r_p$ (for a recent measurement see Ref. $[4]$). Note that there is still a discrepancy in measurements of $r_p$ using hydrogen and muonic hydrogen, known as the proton radius puzzle $[3,5]$, which has attracted significant attention because it could arise from a violation of lepton universality and existence of interactions not accounted for in the Standard Model. Furthermore, measurements of the 1s-2s transition in anti-hydrogen can be used to test the validity of CPT symmetry and Lorentz invariance $[7,11]$.

The measured frequency $f_{1s,2s}^{(exp)}$ of the 1s-2s two-photon (Doppler-corrected) quantum transition of hydrogen reported in Ref. $[1]$ is

$$f_{1s,2s}^{(exp)} = 246061413187.035(10) \text{ kHz},$$

[the uncertainty in the measured frequency is $\delta f_{1s,2s}^{(exp)} = 10$ Hz]. Moreover, Ref. $[2]$ reported a frequency of 246061413187.018(11) kHz, confirming the above result.

Here we report the results of our calculations and compare them with experiment. Four schemes of refined calculations are employed to calculate the hydrogen 1s-2s transition frequency, which are then compared with the experimental value $[1]$. Specifically: (1) The procedure outlined in Ref. $[3]$ is used to calculate $f_{1s,2s}^{(Eides)}$ and its uncertainty $\delta f_{1s,2s}^{(Eides)}$. (2) The 2002 CODATA of Ref. $[4]$ are used to calculate $f_{1s,2s}^{(2002)}$ and its uncertainty $\delta f_{1s,2s}^{(2002)}$. (3) The 2018 CODATA of Ref. $[3]$ are used to calculate $f_{1s,2s}^{(2018)}$ and its uncertainty $\delta f_{1s,2s}^{(2018)}$, and (4) using scheme (3) but fitting $r_p$ to obtain a best fit to the experimental frequency. The latter procedure yields a vanishing discrepancy from the experimental frequency $f_{1s,2s}^{(exp)}$ and a theoretical accuracy limited only by the accuracy of the fundamental constants (see Fig. $[1]$). Scheme (4) gives $r_p = 0.830734$ fm and a theoretical uncertainty of the proton radius of 0.0022 fm.

1s-2s transition frequency. The frequency $f_{1s,2s}$ of the 1s-2s transition of hydrogen is given by

$$f_{1s,2s} = \frac{1}{\hbar} \left[ \varepsilon_2^{(tot)} - \varepsilon_1^{(tot)} \right],$$

and the frequency $f_{1s-ns}$ of the $1s \rightarrow ns$ transition of hydrogen is,

$$f_{1s-ns} = \frac{\left[ \varepsilon_n^{(tot)} - \varepsilon_1^{(tot)} \right]}{\hbar},$$

where $\varepsilon_n^{(tot)}$ is the energy of the $s$ state of hydrogen with principal quantum number $n = 1, 2, 3, \ldots$,

$$\varepsilon_n^{(tot)} = \varepsilon_n^{(Dirac)} + \varepsilon_n^{(QED,FNS)}.$$

Here $\varepsilon_n^{(Dirac)}$ is the energy eigenvalue of the Dirac equation which takes into account recoil effects due to the finite proton mass, and $\varepsilon_n^{(QED,FNS)}$ are the QED radiative and FNS radiative corrections to the energy. Substituting Eq. $[3]$ into Eq. $[2]$, we have,

$$f_{1s,2s} = f_{1s,2s}^{(Dirac)} + f_{1s,2s}^{(QED,FNS)},$$

where

$$f_{1s,2s}^{(Dirac)} = \frac{1}{\hbar} \left( \varepsilon_2^{(Dirac)} - \varepsilon_1^{(Dirac)} \right),$$

$$f_{1s,2s}^{(QED,FNS)} = \frac{1}{\hbar} \left( \varepsilon_2^{(QED,FNS)} - \varepsilon_1^{(QED,FNS)} \right).$$
Below we calculate these corrections in turn.

**Dirac energy.** The energy eigenvalue of the Dirac equation for hydrogen is given in Eq. (3.5) of Ref. [3]:

\[
\varepsilon_{n}^{(\text{Dirac})} = m_e c^2 + \hbar c R_{\infty} \left[ \frac{2 G(n)}{1 + \mu_{ep}} - \frac{\mu_{ep} \alpha^2 G^2(n)}{(1 + \mu_{ep})^3} \right], \tag{7}
\]

where \( \mu_{ep} = m_e / m_p \) is the electron-proton mass ratio, \( m_e \) is the electron mass, \( m_p \) is the proton mass, and \( c R_{\infty} \) is the Rydberg frequency, which is related to the Hartree energy \( \epsilon_p \) by the equation, \( c R_{\infty} = \frac{\epsilon_p}{2 \hbar} = \left[ \frac{\varepsilon^2 \mu}{2 \epsilon_p} \right] \) in Gaussian units. The dimensionless function \( G(n) \) is

\[
G(n) = \left[ \frac{1 + \frac{\alpha^2}{\sqrt{1 - \alpha^2 + n - 1}}}{\alpha^2 (\sqrt{1 - \alpha^2 + n - 1})^{-1/2}} \right]^{n/2} - 1. \tag{8}
\]

where \( \alpha \) is the fine structure constant.

The Dirac energy in Eq. (7) can be expanded in a power series in \( \alpha^2 \), as in Eq. (3.4) of Ref. [3]:

\[
\varepsilon_{n}^{(\text{Dirac})} = m_e c^2 - \frac{\hbar c R_{\infty}}{1 + \mu_{ep}} \left\{ \frac{1}{n^2} + \frac{\alpha^2}{n^3} \left( 1 - \frac{3}{4n} \right) + \frac{\mu_{ep}}{(1 + \mu_{ep})^2} \frac{1}{4n^2} \right\}. \tag{9}
\]

Equation (9) is a power series expansion of Eq. (7) in \( \alpha^2 \), up to \( \alpha^4 \) (recall that a factor of \( \alpha^2 \) is contained in \( R_{\infty} \)). The 1s energy obtained using (9) differs from that obtained using (7) by about a MHz.

In what follows, the Dirac energies, the QED radiative corrections and the FNS corrections are calculated for (1) The fundamental constant values given in Ref. [4] using the techniques developed in Refs. [4, 5], and (2) the fundamental constant values using technique developed in Ref. [3]. Using Eq. (7) and the techniques developed in Ref. [5] yields a satisfactory result for the hydrogen 1s-2s transition frequency. The discrepancy between the theoretical and the experimental frequency, ~1.387 kHz, is much smaller than the theoretical frequency uncertainty 21 kHz. Using Eq. (9) gives a large discrepancy, 790.780 kHz, between the theoretical and the experimental frequency. Moreover, using Eq. (7) and the technique in Refs. [3, 4] give a huge discrepancy between the theoretical and experimental frequency, whereas using Eq. (9) reduces the discrepancy. Specifically, using Eq. (7) and Ref. [4] gives the discrepancy 808.915 kHz, but using Eq. (9) reduces the discrepancy to 19.522 kHz. Using Eq. (7) and Ref. [3] gives the discrepancy 736.831 kHz, but using Eq. (9) reduces the discrepancy to ~23.948 kHz. Additional fitting of the Rydberg constant and the proton RMS charge radius decreases the discrepancy to 0.009 kHz. The difference between the transition frequency calculated by the techniques developed in Ref. [3] and the frequency calculated using Ref. [4] is due to the different values of the proton RMS charge radius, see Eqs. (19a) and (11) below. The difference between the transition frequencies calculated by the techniques developed in Refs. [4] and [3] is due to the different values of the fundamental constants given in Eqs. (10) and (28) below, and the high-order QED diagrams that are calculated in Ref. [5], but not in Refs. [4, 5].

**Transion frequency using Ref. [4]:** Reference [3] uses the values of the following fundamental physical constants as given in the CODATA-2002 [4]: the Rydberg frequency \( c R_{\infty} \), the electron to proton mass ratio \( \mu_{ep} \), the electron to muon mass ratio \( \mu_{ep} \), the fine structure constant \( \alpha \), the RMS proton radius \( r_p \), and the reduced electron Compton wavelength \( \lambda_C \). Specifically,

\[
\begin{align*}
\varepsilon_{p}^{(\text{QED})} & = 3.289841960360(22) \times 10^{15} \text{ Hz}, \tag{10a} \\
\mu_{ep}^{(\text{QED})} & = 5.4461702173(25) \times 10^{-4}, \tag{10b} \\
\mu_{ep}^{(\text{QED})} & = 4.83633167(13) \times 10^{-3}, \tag{10c} \\
\alpha^{(\text{QED})} & = 7.29735268(24) \times 10^{-3}, \tag{10d} \\
r_{p}^{(\text{QED})} & = 0.8750(68) \times 10^{-15} \text{ m}, \tag{10e} \\
\lambda_{C}^{(\text{QED})} & = 386.1592678(26) \times 10^{-15} \text{ m}. \tag{10f}
\end{align*}
\]

Moreover, Ref. [3] considers two additional values for the proton radius,

\[
\begin{align*}
r_{p}^{(\text{Eides})} & = 0.875(6) \times 10^{-15} \text{ m}, \tag{11} \\
r_{p}^{(\text{Sick})} & = 0.895(18) \times 10^{-15} \text{ m}. \tag{12}
\end{align*}
\]

where the value of the RMS proton radius \( r_{p}^{(\text{Eides})} \) in Ref. [3] was obtained by fitting to the 1s-2s transition frequency obtained experimentally in Ref. [12], and the RMS proton radius \( r_{p}^{(\text{Sick})} \) is taken from Ref. [13].

References [4] and [5] use the same values of \( R_{\infty}^{(2002)}, \mu_{ep}^{(2002)} \), and \( \alpha^{(2002)} \) given in Eq. (10). Using Eqs. (7) and (10) in Eq. (5), we get the Dirac frequency of the quantum transition

\[
f_{1s,2s}^{(\text{Dirac,2002})} = (246608541023.560 \pm 16) \text{ kHz.} \tag{13}
\]

Using Eqs. (11) and (10) in Eq. (4), we get

\[
f_{1s,2s}^{(\text{Dirac,2002})} = (246608540234.168 \pm 16) \text{ kHz}, \tag{14}
\]

where the tilde indicates the use of the power series expression in \( \alpha^2 \) [see Eq. (10)]. The 16 kHz uncertainty of \( f_{1s,2s}^{(\text{Dirac,2002})} \) and \( f_{1s,2s}^{(\text{Dirac,2002})} \) is due to the uncertainties of the fundamental constants in Eq. (10).

The QED radiative and FNS corrections to the hydrogen energies are calculated in Ref. [3] for the proton RMS charge radius in Eq. (11). The correction \( f_{1s,2s}^{(\text{QED,FNS,Eides})} \) is (see the supplementary material (SM) [14] for details):

\[
f_{1s,2s}^{(\text{QED,FNS,Eides})} = (712783 \pm 12) \text{ kHz.} \tag{15}
\]

Using the proton RMS charge radius in Eq. (11) and the Dirac energy in Eq. (13), the hydrogen 1s-2s transition frequency \( f_{1s,2s}^{(\text{Eides})} \) is

\[
f_{1s,2s}^{(\text{Eides})} = (2466061413185.648 \pm 21) \text{ kHz.} \tag{16}
\]
and the discrepancy $\Delta f^{(\text{Eides})}_{1s,2s} = f^{(\text{Eides})}_{1s,2s} - f^{(\text{exp})}_{1s,2s}$ is

$$\Delta f^{(\text{Eides})}_{1s,2s} = -1.387 \text{ kHz}. \quad (17)$$

$|\Delta f^{(\text{Eides})}_{1s,2s}|$ is much larger than the uncertainty of $f^{(\text{Eides})}_{1s,2s}$, $\delta f^{(\text{Eides})}_{1s,2s} = 21 \text{ kHz}$, but is much larger than the experimental uncertainty of $f^{(\text{exp})}_{1s,2s}$, $\delta f^{(\text{exp})}_{1s,2s} = 0.010 \text{ kHz}$.

Using the proton RMS charge radius in Eq. (12) and the Dirac frequency in Eq. (14), the hydrogen 1s-2s transition frequency $f^{(\text{Eides})}_{1s,2s}$ is

$$f^{(\text{Eides})}_{1s,2s} = (2466061412396.255 \pm 21) \text{ kHz}, \quad (18)$$

and the discrepancy $\Delta f^{(\text{Eides})}_{1s,2s} = f^{(\text{Eides})}_{1s,2s} - f^{(\text{exp})}_{1s,2s}$ is

$$\Delta f^{(\text{Eides})}_{1s,2s} = -790.780 \text{ kHz}. \quad (19)$$

$|\Delta f^{(\text{Eides})}_{1s,2s}|$ is much larger than the uncertainty of $f^{(\text{Eides})}_{1s,2s}$, $\delta f^{(\text{Eides})}_{1s,2s} = 20 \text{ kHz}$, but is much larger than the experimental uncertainty of $f^{(\text{exp})}_{1s,2s}$, $\delta f^{(\text{exp})}_{1s,2s} = 0.010 \text{ kHz}$.

The QED radiative and FNS corrections to the hydrogen energies are also calculated in Ref. [5] for the proton RMS charge radius in Eq. (12). The correction $f^{(\text{QED,FNS,Eides,Sick})}_{1s,2s}$ is (see SM [14] for details):

$$f^{(\text{QED,FNS,Eides,Sick})}_{1s,2s} = (-7127886 \pm 44) \text{ kHz}. \quad (20)$$

Moreover, the transition frequency $f^{(\text{Eides,Sick})}_{1s,2s}$ for the proton RMS charge radius in Eq. (12) is

$$f^{(\text{Eides,Sick})}_{1s,2s} = (246606141341 \pm 47) \text{ kHz}, \quad (21)$$

and the difference $\Delta f^{(\text{Eides,Sick})}_{1s,2s} = f^{(\text{Eides,Sick})}_{1s,2s} - f^{(\text{exp})}_{1s,2s}$ is

$$\Delta f^{(\text{Eides,Sick})}_{1s,2s} = -46 \text{ kHz}. \quad (22)$$

$|\Delta f^{(\text{Eides,Sick})}_{1s,2s}|$ is smaller than the uncertainty of $f^{(\text{Eides,Sick})}_{1s,2s}$, $\delta f^{(\text{Eides,Sick})}_{1s,2s} = 47 \text{ kHz}$, but much larger than the experimental uncertainty $\delta f^{(\text{exp})}_{1s,2s} = 0.010 \text{ kHz}$.

**Transition frequency using 2002 CODATA** [4]: The values of the fundamental constants used in Ref. [4] are given in Eq. (10), and the Dirac frequency $f^{(\text{Dirac},2002)}_{1s,2s}$ is given in Eq. (13). Using the technique in Ref. [4] (see SM [14]), we find the following QED radiative and FNS correction $f^{(\text{QED,FNS,2002})}_{1s,2s}$ to the 1s-2s transition frequency:

$$f^{(\text{QED,FNS,2002})}_{1s,2s} = (-7127027.610 \pm 16) \text{ kHz}. \quad (23)$$

Using Eq. (7) in Eq. (4), and the proton RMS charge radius in Eq. (10), we get the transition frequency $f^{(2002)}_{1s,2s}$,

$$f^{(2002)}_{1s,2s} = (2466061413995.950 \pm 23) \text{ kHz}, \quad (24)$$

and the discrepancy $\Delta f^{(2002)}_{1s,2s} = f^{(2002)}_{1s,2s} - f^{(\text{exp})}_{1s,2s}$ is

$$\Delta f^{(2002)}_{1s,2s} = 808.915 \text{ kHz}. \quad (25)$$

$|\Delta f^{(2002)}_{1s,2s}|$ is much larger than the uncertainty of $f^{(2002)}_{1s,2s}$, $\delta f^{(2002)}_{1s,2s} = 23 \text{ kHz}$, and much larger than the uncertainty of $f^{(\text{exp})}_{1s,2s}$, $\delta f^{(\text{exp})}_{1s,2s} = 0.010 \text{ kHz}$.

Using Eq. (9) in Eq. (4), we get

$$f^{(2002)}_{1s,2s} = (2466061413206.557 \pm 23) \text{ kHz}, \quad (26)$$

and the discrepancy $\Delta f^{(2002)}_{1s,2s} = f^{(2002)}_{1s,2s} - f^{(\text{exp})}_{1s,2s}$ is

$$\Delta f^{(2002)}_{1s,2s} = 19.522 \text{ kHz}. \quad (27)$$

$|\Delta f^{(2002)}_{1s,2s}|$ is much larger than the uncertainty of $f^{(2002)}_{1s,2s}$, $\delta f^{(2002)}_{1s,2s} = 23 \text{ kHz}$, but much larger than the uncertainty of $f^{(\text{exp})}_{1s,2s}$, $\delta f^{(\text{exp})}_{1s,2s} = 0.010 \text{ kHz}$.

**Transition frequency using 2018 CODATA** [4]: The values of the Rydberg frequency $cR_{\infty}$, the electron to proton mass ratio $\mu_{ep}$, the electron to muon mass ratio $\mu_{e\mu}$, the fine structure constant $\alpha$, the RMS proton radius $r_p$, and the reduced electron Compton wavelength $\lambda_C$,
from Ref. \[3\] are:

\[
\begin{align*}
\frac{C_{\infty}^{\text{(2018)}}}{c} &= 3.2898419602508(64) \times 10^{15} \text{ Hz}, \\
\mu_{p,c}^{\text{(2018)}} &= 5.44617021487(33) \times 10^{-4}, \\
\mu_{\mu}^{\text{(exp)}} &= 4.83633169(11) \times 10^{-3}, \\
\alpha^{\text{(2018)}} &= 7.2973526693(11) \times 10^{-3}, \\
\lambda_{p}^{\text{(2018)}} &= 0.8414(19) \times 10^{-15} \text{ m}, \\
\lambda_{C}^{\text{(2018)}} &= 3.8615926796(12) \times 10^{-13} \text{ m}.
\end{align*}
\]

Using Eq. (7) in Eq. (4), we get the Dirac frequency

\[
f^{\text{(Dirac,2018)}} = (2466068540913.7 \pm 4.8) \text{ kHz}.
\]

Using Eq. (7) in Eq. (4), we get

\[
f^{\text{(Dirac,2018)}} = (2466068540152.921 \pm 4.8) \text{ kHz}.
\]

Using the technique in Ref. \[3\] (see the SM \[14\]), we find the following QED radiative and FNS correction

\[
f^{\text{(QED,FNS,2018)}} = (-7126679.6 \pm 4.4) \text{ kHz}.
\]

The hydrogen 1s-2s transition frequency \(f^{\text{(2018)}}\) for the proton RMS charge radius in Eq. (23) and the Dirac frequency in Eq. (28a) is

\[
f^{\text{(2018)}} = (2466061413923.866 \pm 6.4) \text{ kHz},
\]

and the discrepancy \(\Delta f^{\text{(2002)}} = f^{\text{(2018)}} - f^{\text{(exp)}}\) is

\[
\Delta f^{\text{(2018)}} = 736.831 \text{ kHz}.
\]

\(|\Delta f^{\text{(2018)}}|\) is much larger than the uncertainty of \(f^{\text{(2018)}}\), \(\delta f^{\text{(2018)}} = 6.4 \text{ kHz}\), and much larger than the experimental uncertainty \(\delta f^{\text{(exp)}} = 0.010 \text{ kHz}\).

The hydrogen 1s-2s transition frequency \(f^{\text{(2018)}}\) using the proton RMS charge radius in Eq. (23) and the Dirac frequency in Eq. (28a) is

\[
f^{\text{(2018)}} = (246606141387.035 \pm 6.4) \text{ kHz},
\]

and the discrepancy \(\Delta \tilde{f}^{\text{(2018)}} = f^{\text{(2018)}} - f^{\text{(exp)}}\) is

\[
\Delta \tilde{f}^{\text{(2018)}} = -23.948 \text{ kHz}.
\]

\(|\Delta \tilde{f}^{\text{(2018)}}|\) is larger than the uncertainty of \(\tilde{f}^{\text{(2018)}}\), \(\delta \tilde{f}^{\text{(2018)}} = 6.4 \text{ kHz}\), and much larger than the experimental uncertainty \(\delta \tilde{f}^{\text{(exp)}} = 0.010 \text{ kHz}\).

Fitting \(r_{p}\) to obtain optimal transition frequency: Next, since \(r_{p}\) is the least well-known of the fundamental constants that enter into the expression for \(\tilde{f}^{\text{(2018)}}\), we fit \(r_{p}\) so as to minimize \(\Delta \tilde{f}_{1s,2s} = \tilde{f}_{1s,2s} - f_{1s,2s}^{\text{(exp)}}\). Here the theoretical transition frequency \(\tilde{f}_{1s,2s}\) is a function of \(R_{\infty}^{\text{(2018)}}\), \(r_{p}\) and other fundamental constants, see Ref. [14] for details. We expand \(\Delta \tilde{f}_{1s,2s}\) in powers of \(\vartheta_{p} = (r_{p} - r_{p}^{\text{(2018)}})/\delta r_{p}^{\text{(2018)}}\), and get

\[
\Delta \tilde{f}_{1s,2s} = \Delta \tilde{f}_{1s,2s}^{\text{(2018)}} - B_{1} \vartheta_{p} - B_{2} \vartheta_{p}^{2},
\]

where \(B_{1} = 429.337 \delta \tilde{f}_{1s,2s}^{\text{(exp)}}\) and \(B_{2} = 0.484751 \delta \tilde{f}_{1s,2s}^{\text{(exp)}}\). We can solve for the value of \(r_{p}\) which gives \(\Delta \tilde{f}_{1s,2s} = 0\) and we find that \(r_{p}^{\text{(fit)}} = 0.830734 \text{ fm}\), so that \(\Delta \tilde{f}_{1s,2s}^{\text{(fit)}} = (r_{p}^{\text{(fit)}} - r_{p}^{\text{(2018)}}) = -5.613 \delta r_{p}^{\text{(2018)}} = -0.01066 \text{ fm}\), where \(\delta r_{p}^{\text{(2018)}}\) is the uncertainty of \(r_{p}^{\text{(2018)}}\) given in Eq. (28c).

An estimate of the uncertainty \(\delta r_{p}^{\text{(fit)}}\) due to the experimental frequency uncertainty \(\delta f_{1s,2s}^{\text{(exp)}} = 10 \text{ Hz}\) can be made by solving the equations \(\Delta \tilde{f}_{1s,2s} = \delta f_{1s,2s}^{\text{(exp)}}\) and \(\Delta \tilde{f}_{1s,2s} = -\delta f_{1s,2s}^{\text{(exp)}}\) for \(r_{p}\); we find \(\delta r_{p}^{\text{(fit)}} = 4.5 \times 10^{-6} \text{ fm}\). Note that \(\delta r_{p}^{\text{(fit)}}\) is much smaller than \(\delta r_{p}^{\text{(2018)}}\). A better estimate of the uncertainty \(\delta r_{p}^{\text{(fit)}}\) can be made as follows. We define the functions \(\Delta \tilde{f}_{1s,2s}^{(\pm)} = \tilde{f}^{(\pm)}_{1s,2s} - f^{(\text{exp})}_{1s,2s}\), where \(f^{(\pm)}_{1s,2s}\) is the theoretical 1s-2s transition frequency calculated with the Rydberg constant equal to \(R_{\infty}^{\text{(2018)}} \pm \delta R_{\infty}^{\text{(2018)}}\), see Ref. [14]. Solving the equations \(\Delta \tilde{f}_{1s,2s}^{(\pm)} = 0\), we find \(r_{p}^{(\pm)}\) which gives an uncertainty \(\delta r_{p}^{(\pm)} = |r_{p}^{(+)} - r_{p}^{(-)}|/2\) due to the uncertainty of the Rydberg constant. We find \(\delta r_{p}^{(\pm)} = 1.1 \delta r_{p}^{\text{(2018)}} = 0.0022 \text{ fm}\). We take this to be the theoretical uncertainty of \(r_{p}\).

Summary and Conclusions: We have calculated the 1s-2s quantum transition frequency of the hydrogen atom using QED radiative and finite nuclear size and mass corrections, and evaluated the uncertainty of the calculated result due to uncertainties in the fundamental constants using four methods. (1) The procedure outlined in Ref. [3] yields \(f_{1s,2s}^{\text{(Eides)}} = (2466061413996 \pm 21) \text{ kHz}\) and its uncertainty \(\delta f_{1s,2s}^{\text{(Eides)}} = 2 \text{ kHz}\). (2) The 2002 CODATA of Ref. [3] yields \(f_{1s,2s}^{\text{(2002)}} = (2466061413996 \pm 23) \text{ kHz}\) and its uncertainty is \(\delta f_{1s,2s}^{\text{(2002)}} = 19.522 \text{ kHz}\). (3) The 2018 CODATA of Ref. [3] yields \(f_{1s,2s}^{\text{(2018)}} = (2466061413638 \pm 6.4) \text{ kHz}\) and its uncertainty \(\delta f_{1s,2s}^{\text{(2018)}} = -23.948 \text{ kHz}\). (4) Using method (3) but fitting the proton RMS charge radius to obtain \(f_{1s,2s}^{\text{(2018,fit)}} = f_{1s,2s}^{\text{(exp)}}\), which has an uncertainty due to the uncertainty of the fundamental constants of \(\delta f_{1s,2s}^{\text{(2018,fit)}} = 6.4 \text{ kHz}\), with \(r_{p}^{\text{(fit)}} = 0.830734 \pm 0.0022 \text{ fm}\). This \(r_{p}\) is consistent with the recently measured value, \(0.831 \pm 0.007_{\text{(stat)}} \pm 0.012_{\text{(syst)}} \text{ fm}\). [7]

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Supplementary Material for “Hydrogen 1s-2s transition frequency: Comparison of experiment and theory using various data sets”

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In this supplementary material we expand the discussion of the main text (MT) \cite{1} and address the following topics: the calculation of the hydrogen 1s-ns transition frequencies using the method introduced by Eides et al. \cite{2}, the method used by CODATA-2002 \cite{2}, and the method used by CODATA-2018 \cite{2}.

Hydrogen 1s-ns transition frequency calculations using Eides et al. \cite{2}: The largest contribution to the energies of hydrogen is the Dirac eigenvalue $\epsilon_{\text{Dirac}}(n)$ for an electron bound to a point-like proton with a finite mass $M$. Here the superscript (2002) indicates that we use the values of the fundamental constants in \cite{2}. In this section, we calculate $\epsilon_{\text{Dirac}}(n) = \epsilon_{\text{Dirac}}(n) - m_c c^2$, which depends on the Rydberg frequency $c R_\infty$, electron to proton mass ratio $\mu_{ep}$, and the fine structure constant $\alpha$ [in this section, we use the values of the fundamental constant from Ref. \cite{2}, but omit the superscript (2002) on the fundamental constants for brevity]. The Dirac energy of the hydrogen ns state is given in Eq. (3.5) of Ref. \cite{2} (see also Refs. \cite{3,5}):

$$
\epsilon_{\text{Dirac}}(n) = \frac{2 c R_\infty}{1 + \mu_{ep}} \frac{G(n)}{1 + \mu_{ep}^3},
$$

where $n = 1, 2, 3, \ldots$ is a principal quantum number. The dimensionless function $G(n)$ is:

$$
G(n) = \frac{1}{\alpha^2} \left[ \left( 1 + \frac{\alpha^2}{\sqrt{1 - \alpha^2} + n - 1/2} \right)^{1/2} - 1 \right].
$$

Alternatively, the power series in powers of $\alpha$ of the Dirac energy is given in Eq. (3.4) of Ref. \cite{2} (see also MT \cite{1}):}

$$
\epsilon_{\text{Dirac}}(n) = -\frac{c R_\infty}{1 + \mu_{ep}} \left\{ \frac{1}{n^2} + \frac{\alpha^2}{n^3} \left( 1 - \frac{3}{4n} \right) \right\}.
$$

Inserting the values of $c R_\infty$, $\alpha$ and $\mu_{ep}$ in Ref. \cite{2} into Eq. (1), we get the following values of the energies $\epsilon_{\text{Dirac}}(n)$ of the hydrogen 1s and 2s states:

$$
\epsilon_{\text{Dirac}}^{(\text{Eides})}(1) = h \times (-32880095028800.076) \text{ kHz}, \quad (4a)
$$

$$
\epsilon_{\text{Dirac}}^{(\text{Eides})}(2) = h \times (-82026488566.908) \text{ kHz}, \quad (4b)
$$

Using the values of $c R_\infty$, $\alpha$ and $\mu_{ep}$ in Ref. \cite{2} into Eq. (3), we get the following values of the energies $\epsilon_{\text{Dirac}}(n)$ of the hydrogen 1s and 2s states:

$$
\epsilon_{\text{Dirac}}^{(\text{Eides})}(1) = h \times (-32880095028800.076) \text{ kHz}, \quad (5a)
$$

$$
\epsilon_{\text{Dirac}}^{(\text{Eides})}(2) = h \times (-82026488566.908) \text{ kHz}, \quad (5b)
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\epsilon_{\text{Dirac}}^{(\text{Eides})}(2) = h \times (-82026488566.908) \text{ kHz}, \quad (5b)
$$

The uncertainties $\delta \epsilon_n^{(\text{R})}$, $\delta \epsilon_n^{(\mu_{ep})}$ and $\delta \epsilon_n^{(\alpha)}$ of $\epsilon_n$ due to the uncertainties of $c R_\infty$, $\mu_{ep}$ and $\alpha$ are:

$$
\delta \epsilon_n^{(\text{R})} = \frac{1}{n^2} h \times 21.988 \text{ kHz}, \quad (6a)
$$

$$
\delta \epsilon_n^{(\mu_{ep})} = \frac{1}{n^2} h \times 0.822 \text{ kHz}, \quad (6b)
$$

$$
\delta \epsilon_n^{(\alpha)} = \frac{4n - 3}{n^4} h \times 0.288 \text{ kHz}. \quad (6c)
$$

The QED and finite nuclear size (FNS) corrections to the 1s ground state energy given before Eq. (12.12) in Ref. \cite{2} are:

$$
E_{L}^{(\text{Eides})}(1) = h \times 1872247(14) \text{ kHz}. \quad (7)
$$

It is calculated with $r_N^{(\text{Eides})}$ in Eq. (10) of the MT \cite{1}. Here the uncertainty, $\delta E^{(\text{Eides})}(1) = 14$ kHz, is determined by estimating the as yet un-calculated QED contributions, and the experimental uncertainty in the measurement of the proton RMS charge radius \cite{2}. The QED and FNS corrections $E_{L}^{(\text{Eides})}(n)$ to the ns state with principal quantum number $n$ is given as $E_{L}^{(\text{Eides})}(n) = \frac{1}{n^2} (E^{(\text{Eides})}(1) + \Delta_n)$, where $\Delta_n$ are tabulated in Table 12.1 of Ref. \cite{2}. Explicitly, for $n = 2$,

$$
\Delta_2 = h \times (1872257.0 \pm 0.05) \text{ kHz}, \quad (8a)
$$

thus

$$
E_{L}^{(\text{Eides})}(2) = h \times (1045009.1 \pm 1.8) \text{ kHz}, \quad (9)
$$

Here the uncertainties are due to the largest of the uncertainties from the proton radius and the (as yet not calculated) QED radiative diagrams.

The theoretical 1s-2s transition frequency from Ref. \cite{2} is

$$
\delta f_{1s,2s}^{(\text{Eides})} = \frac{1}{h} \left[ \epsilon_{\text{Dirac}}^{(\text{Eides})}(2) + E_{L}^{(\text{Eides})}(2) \right.
$$

$$
- \epsilon_{\text{Dirac}}^{(\text{Eides})}(1) - E_{L}^{(\text{Eides})}(1) \right], \quad (10)
$$

...
The experimental frequency $f^{(\text{exp})}_{1s,2s}$ in Ref. [2] is

$$f^{(\text{exp})}_{1s,2s} = (2466061413187.035 \pm 0.010) \text{kHz},$$

(12)

The discrepancy $\Delta f^{(\text{Eides})}_{1s,2s} = f^{(\text{Eides})}_{1s,2s} - f^{(\text{exp})}_{1s,2s}$ is

$$\Delta f^{(\text{Eides})}_{1s,2s} = -1.387 \text{kHz},$$

(13)

which yields

$$f^{(\text{Eides})}_{1s,2s} = (2466061413186.658 \pm 20297) \text{Hz}.$$  

(11)

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(11)

The discrepancy $\Delta f^{(\text{Eides})}_{1s,ns} = f^{(\text{Eides})}_{1s,ns} - f^{(\text{exp})}_{1s,ns}$ is

$$\Delta f^{(\text{Eides})}_{1s,ns} = -0.790780 \text{MHz},$$

(16)

Note that $|\Delta f^{(\text{Eides})}_{1s,2s}|$ is much larger than the uncertainty $\delta f^{(\text{Eides})}_{1s,2s}$ of $f^{(\text{Eides})}_{1s,2s}$ and the experimental uncertainty $\delta f^{(\text{exp})}_{1s,2s}$ of $f^{(\text{exp})}_{1s,2s}$. Hence, we conclude that the non-perturbative expression for the Dirac energy, $\epsilon^{(\text{Dirac})}_{1s,2s}$, taken together with the perturbative expression of the radiative corrections, gives a preferable result to that obtained using the perturbative expression for the Dirac energy, $\epsilon^{(\text{Dirac})}_{1s,2s}$ in Eq. (1). Therefore we use $f^{(\text{Eides})}_{1s,2s}$ as a theoretical $1s \rightarrow 2s$ transition frequency.

Now we use the procedure of Ref. [2] to calculate the QED and FNS corrections $\epsilon^{(\text{Sick})}_{N}$ but instead of using the proton RMS radius in Eq. (10) of the MT, as recommended in Ref. [2], we use the proton RMS radius in Eq. (11) of the MT. The correction $E^{(\text{Eides, Sick})}_{L}(1)$ to the $1s$ state energy is

$$E^{(\text{Eides, Sick})}_{L}(1) = h \times 8172902(6)(50) \text{kHz}.$$  

(17)

The QED and FNS corrections $E^{(\text{Eides, Sick})}_{L}(n)$ to the $s$ state with principal quantum number $n \geq 2$ is given as

$$E^{(\text{Eides, Sick})}_{L}(n) = \frac{1}{n^2} \left( E^{(\text{Eides, Sick})}_{L}(1) + \Delta_n \right),$$

where $\Delta_n$ with $n = 2, 3$ are given in Eq. (3), hence

$$E^{(\text{Eides, Sick})}_{L}(2) = h \times (405016.0 \pm 6.3) \text{kHz}.$$  

(18)

The theoretical frequencies $f^{(\text{Eides, Sick})}_{1s,ns}$ of the hydrogen $1s$-$ns$ transitions are:

$$f^{(\text{Eides, Sick})}_{1s,ns} = \frac{1}{h} \left[ \epsilon^{(\text{Dirac})}_{1s,ns} + E^{(\text{Eides, Sick})}_{L}(n) \right] - \epsilon^{(\text{Dirac})}_{1s,ns} \left( 1 - E^{(\text{Eides, Sick})}_{L}(1) \right),$$

(19)

which yields

$$f^{(\text{Eides, Sick})}_{1s,ns} = (2466061413141 \pm 47) \text{kHz}.$$  

(20)

The discrepancy $\Delta f^{(\text{Eides,2002})}_{1s,ns} = f^{(\text{Eides,2002})}_{1s,ns} - f^{(\text{exp})}_{1s,ns}$ is

$$\Delta f^{(\text{Eides, Sick})}_{1s,ns} = -46 \text{kHz},$$

(21)

which yields

$$f^{(\text{Eides,2002})}_{1s,ns} = (2466061413141 \pm 47) \text{kHz}.$$  

(20)

Note that $|\Delta f^{(\text{Eides})}_{1s,2s}|$ is much larger than the uncertainty $\delta f^{(\text{Eides})}_{1s,2s}$ of $f^{(\text{Eides})}_{1s,2s}$ and the experimental uncertainty $\delta f^{(\text{exp})}_{1s,2s}$ of $f^{(\text{exp})}_{1s,2s}$. Hence, we conclude that the non-perturbative expression for the Dirac energy, $\epsilon^{(\text{Dirac})}_{1s,ns}$ in Eq. (1), taken together with the perturbative expression of the radiative corrections, gives a preferable result to that obtained using the perturbative expression for the Dirac energy, $\epsilon^{(\text{Dirac})}_{1s,ns}$ in Eq. (3). Therefore we use $f^{(\text{Eides})}_{1s,ns}$ as a theoretical $1s \rightarrow ns$ transition frequency.

The largest contribution to the energies of hydrogen is the Dirac eigenvalue for an electron bound to a point-like proton with a finite mass $M$ given in Ref [1]. In this section, we consider $\epsilon^{(\text{Dirac})}_{1s,ns}$ in Eq. (1) and $\epsilon^{(\text{Dirac})}_{1s,ns}$ in Eq. (3), where the superscript (2002) indicates that we take the fundamental constant values from the 2002 CODATA data [2]. Explicitly, $\epsilon^{(\text{Dirac})}_{1s,ns}$ with $n = 1$ and 2 are

$$\epsilon^{(\text{Dirac})}_{1s,ns}(1) = h \times (-328809502996 \pm 22) \text{kHz},$$

(22a)

$$\epsilon^{(\text{Dirac})}_{1s,ns}(2) = h \times (-822026488945.5 \pm 5.5) \text{kHz},$$

(22b)

On the other hand, $\epsilon^{(\text{Dirac})}_{1s,ns}$ with $n = 1$ and 2 are

$$\epsilon^{(\text{Dirac})}_{1s,ns}(1) = h \times (-328809502880 \pm 22) \text{kHz},$$

(23a)

$$\epsilon^{(\text{Dirac})}_{1s,ns}(2) = h \times (-822026488569.5 \pm 5.5) \text{kHz},$$

(23b)

We now apply the technique described in Appendix A of Ref. [2] and calculate the Lamb shift $E^{(\text{Eides,2002})}_{L}(n)$ for the hydrogen $ns$ state energy. We keep the atomic number $Z$ in the equations in order to be able to generalize the results to the case of light hydrogen-like ions in the...
The leading relativistic recoil correction is
\[ E_S(n) = \frac{m^3}{m^2 M} \frac{(Z\alpha)^5}{\pi n^3} m_e c^2 \left( \frac{1}{3} \ln \left( \frac{1}{Z^2 \alpha^2} \right) - \frac{8}{3} \ln k_0(n) - \frac{1}{9} - \frac{7}{3} a_n - \frac{2}{M^2 - m_e^2} \right) \times \left[ M^2 \ln \left( \frac{m_e}{m} \right) - m_e^2 \right] + \cdots, \] (24)
where
\[ a_n = -2 \ln \left( \frac{2}{n} \right) - 2 + \frac{1}{n} - 2 \sum_{i=1}^{n} \frac{1}{i}. \]

Values for the Bethe logarithms \( \ln k_0(n) \) with \( n = 1 \) and 2 are
\[ \ln k_0(1) = 2.984128556, \quad \ln k_0(2) = 2.811769893. \] (25)
The corrections \( E_S(1) \) and \( E_S(2) \) to the 1s and 2s state energies of hydrogen are
\[ E_S(1) = h \times 2409.51 \text{ kHz}, \quad (26a) \]
\[ E_S(2) = h \times 341.29 \text{ kHz}. \] (26b)

The contributions of the next two orders in \( Z\alpha \) can be written as
\[ E_R(n) = m_e \frac{(Z\alpha)^6}{M n^3} m_e c^2 \left[ D_{60} + D_{72} Z\alpha \ln^2(Z\alpha) \right. \]
\[ \left. + \cdots \right], \] (27)
where
\[ D_{60} = 4 \ln 2 - \frac{7}{2}, \quad D_{72} = -\frac{11}{60\pi}. \]

The corrections \( E_R(1) \) and \( E_R(2) \) to the 1s and 2s state energies of hydrogen are
\[ E_R(1) = h \times (-7.811) \text{ kHz}, \quad (28a) \]
\[ E_R(2) = h \times (-0.976) \text{ kHz}. \] (28b)

Another effect involving properties of the nucleus is the nuclear polarization which arises from interactions between the electron and the nucleus in which the nucleus is excited from the ground state to virtual higher-energy states. In other words, the electric field created by the electron causes deformation of the nuclear charge distribution \([3,4]\), and the deformation of the nucleus changes electronic energies of the atom. Reference [4] uses the following nuclear polarization correction to the \( s \) states energies of hydrogen:
\[ E_P(n) = -\frac{0.070(13)}{n^3} h \times \text{kHz}. \] (29)

The corrections \( E_P(1) \) and \( E_P(2) \) to the 1s and 2s state energies of hydrogen are
\[ E_P(1) = h \times (-0.070 \pm 0.013) \text{ kHz}, \quad (30a) \]
\[ E_P(2) = h \times (-0.0088 \pm 0.0016) \text{ kHz}. \] (30b)

The self-energy corrections of order \( \alpha(Z\alpha)^4 \) is
\[ E_{SE}^{(2)}(n) = \frac{\alpha}{\pi} \frac{(Z\alpha)^4}{n^3} F(Z\alpha, n) m_e c^2, \] (31)
where the function \( F(Z\alpha, n) \) is
\[ F(Z\alpha, n) = A_{41} \ln \left( \frac{1}{Z^2 \alpha^2} \right) + A_{40} + A_{50} Z\alpha \]
\[ + A_{62} Z^2 \alpha^2 \ln^2 \left( \frac{1}{Z^2 \alpha^2} \right) \]
\[ + A_{61} Z^2 \alpha^2 \ln \left( \frac{1}{Z^2 \alpha^2} \right) + G_{SE}(Z\alpha, n) Z^2 \alpha^2. \] (32)

The constants \( A \) are:
\[ A_{41} = \frac{4}{3}, \quad A_{40} = -\frac{4}{3} \ln k_0(n) + \frac{10}{9}, \]
\[ A_{50} = \left( \frac{139}{32} - 2 \ln(2) \right) \pi, \quad A_{62} = -1, \]
\[ A_{61} = 4 \sum_{i=1}^{n} \frac{1}{i} + \frac{28}{3} \ln 2 - 4 \ln n - \frac{601}{180} - \frac{77}{45 n^2}. \]

The Bethe logarithm \( \ln k_0(n) \) is given in Eq. (25), and the function \( G_{SE}(\alpha, n) \) for hydrogen atoms in the 1s and 2s states is
\[ G_{SE}(\alpha, 1) = -30.29024(2), \quad G_{SE}(\alpha, 2) = -31.18515(9). \]

Following the convention in Ref. [5], we multiply \( F(Z\alpha, n) \) by a factor \( m^3/m_e^3 \), and replace \( \ln(1/\alpha^2) \) by \( \ln((m_e/m) (1/\alpha^2)) \).

The corrections \( E_{SE}^{(2)}(1) \) and \( E_{SE}^{(2)}(2) \) to the 1s and 2s state energies of hydrogen are
\[ E_{SE}^{(2)}(1) = h \times 8383339.465 \text{ kHz}, \quad (33a) \]
\[ E_{SE}^{(2)}(2) = h \times 1071281.002 \text{ kHz}. \] (33b)

The second-order vacuum polarization level shift, due to the creation of a virtual electron-positron pair in the exchange of photons between the electron and the nucleus, is
\[ E_{VP}^{(2)}(n) = \frac{\alpha}{\pi} \frac{(Z\alpha)^4}{n^3} H(Z\alpha) m_e c^2, \] (34)
where
\[ H(Z\alpha) = H^{(1)}(Z\alpha) + H^{(R)}(Z\alpha), \]
and
\[ H^{(1)}(Z\alpha) = V_{40} + V_{50} Z\alpha + V_{61} (Z\alpha)^2 \ln \left( \frac{1}{Z^2 \alpha^2} \right) \]
\[ + (Z\alpha)^2 G_{VP}^{(1)}(Z\alpha, n), \]
\[ H^{(R)}(Z\alpha) = (Z\alpha)^2 G_{VP}^{(R)}(Z\alpha). \]
Here $V_{40} = -4/15$, $V_{50} = 5\pi/48$ and $V_{61} = -2/15$.

$G^{(1)}_{\nu}(\alpha, n)$ for hydrogen $Z = 1$ is

$$G^{(1)}_{\nu}(\alpha, 1) = -0.618724, \quad G^{(1)}_{\nu}(\alpha, 2) = -0.808872.$$  

Moreover,

$$G^{(R)}_{\nu}(Z\alpha) = \frac{19}{45} \frac{\pi^2}{27} + \left( \frac{1}{16} - \frac{31\pi^2}{2880} \right) \pi Z\alpha + \cdots$$

Following the convention in Ref. [5], we multiply $H(Z\alpha, n)$ by a factor $m^2/m_c^2$, and replace $\ln(1/\alpha^2)$ by $\ln(m_c/(m_c/m))$.

The corrections $E^{(2)}_{\nu}(1)$ and $E^{(2)}_{\nu}(2)$ to the 1s and 2s state energies are:

$$E^{(2)}_{\mu\nu}(1) = h \times (-214816.602) \ \text{kHz}, \quad (35a)$$  

$$E^{(2)}_{\mu\nu}(2) = h \times (-26853.103) \ \text{kHz}. \quad (35b)$$

Vacuum polarization from the muon-antimuon $\mu^+\mu^-$ pair is

$$E^{(2)}_{\mu\nu}(n) = -\frac{4}{15} \frac{\alpha}{\pi} \frac{(Z\alpha)^4}{n^3} \frac{m_e^2}{m_\mu^2} \frac{m_\mu}{m_e} m_e c^2,$$  

and the hadronic vacuum polarization is

$$E^{(2)}_{\text{had\nu\nu}}(n) = 0.671(15)E^{(2)}_{\mu\nu}(n). \quad (37)$$

The muonic and hadronic corrections to the 1s and 2s state energies are

$$E^{(2)}_{\mu\nu}(1) = h \times (-5.068) \ \text{kHz}, \quad (38a)$$  

$$E^{(2)}_{\mu\nu}(2) = h \times (-0.634) \ \text{kHz}, \quad (38b)$$  

$$E^{(2)}_{\text{had\nu\nu}}(1) = h \times (-3.401) \ \text{kHz}, \quad (38c)$$  

$$E^{(2)}_{\text{had\nu\nu}}(2) = h \times (-0.425) \ \text{kHz}. \quad (38d)$$

The corrections from two virtual photons is given by

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

where

$$F^{(4)}(Z\alpha) = B_{40} + B_{50} Z\alpha + B_{63} (Z\alpha)^2 \ln^3 \left( \frac{1}{Z^2\alpha^2} \right) +$$

$$B_{62} (Z\alpha)^2 \ln \left( \frac{1}{Z^2\alpha^2} \right) +$$

$$B_{61} (Z\alpha)^2 \ln \left( \frac{1}{Z^2\alpha^2} \right) + B_{60} (Z\alpha)^2 + \cdots$$

and

$$B_{40} = \frac{3\pi^2}{2} \ln 2 - \frac{10\pi^2}{27} - \frac{2179}{648} - \frac{9}{4} \zeta(3),$$

$$B_{50} = -21.5561(31),$$

$$B_{63} = -\frac{8}{27},$$

$$B_{62} = \frac{16}{9} \left[ \frac{71}{60} - \ln 2 + \psi(n) + \gamma - \ln n - \frac{1}{n} + \frac{1}{4n^2} \right].$$

Here $\zeta(z)$ is the Riemann zeta function, $\gamma$ is the Euler constant and $\psi(n)$ is the psi function,

$$\psi(x) = \frac{\Gamma'(x)}{\Gamma(x)},$$

where $\Gamma(x)$ is the Euler gamma function. The coefficient $B_{61}$ is

$$B_{61} = \frac{39751}{10800} + \frac{4N(ns)}{3} + \frac{55\pi^2}{27} - \frac{616 \ln 2}{135} - \frac{3\pi^2 \ln 2}{4} + \frac{40 \ln^2 2}{9} - \frac{9\zeta(3)}{8} + \left( \frac{304}{135} - \frac{32 \ln 2}{9} \right) \frac{3}{4} + \gamma + \psi(n) - \left( \ln(n) - \frac{1}{n} + \frac{1}{4n^2} \right),$$

where $N(ns)$ and the uncertainties $\delta N(ns)$ of $N(ns)$ for $n = 1$ and 2 are

$$N(1s) = 17.855672(1), \quad N(2s) = 12.032209(1).$$

The constant $B_{60}$ and the uncertainty $\delta B_{60}$ of $B_{60}$ for the ns states with $n = 1$ and 2 are

$$B_{60}(1s) = -61.6(9.2), \quad B_{60}(2s) = -53.2(8.0).$$

The corrections $E^{(4)}(1)$ and $E^{(4)}(2)$ to the 1s and 2s state energies are

$$E^{(4)}(1) = h \times 721.61 \ \text{kHz}, \quad (40a)$$

$$E^{(4)}(2) = h \times 90.67 \ \text{kHz}. \quad (40b)$$

The leading contribution from three virtual photons is

$$E^{(6)}(n) = \frac{\alpha^3}{\pi^3} \frac{(Z\alpha)^4}{n^3} F^{(6)}(Z\alpha) m_e c^2,$$  

where

$$F^{(6)}(Z\alpha) = C_{40} + C_{50} Z\alpha + \cdots .$$

The constant $C_{40}$ is

$$C_{40} = -\frac{5684}{9} + \frac{85\zeta(5)}{24} - \frac{121\pi^2\zeta(3)}{72} - \frac{8407\zeta(3)}{2304} + \frac{71 \ln^4 2}{27} - \frac{239\pi^2 \ln^2 2}{135} + \frac{4787\pi^2 \ln 2}{108} + \frac{1591\pi^4}{3240} - \frac{252251\pi^2}{9720} + \frac{679441}{93312},$$

where

$$\alpha_4 = \sum_{j=1}^{\infty} \frac{1}{j^2} \approx 0.5174790616738993.$$
For low Z, the leading contribution to the s state energy due to FNS is

\[ \mathcal{E}_{\text{FNS}}(n) = \frac{2}{3} \frac{m^3}{m^2_e} \frac{(Z \alpha)^4}{n^4} \frac{r_N^2}{\lambda_C^2} m_e c^2, \]

where \( \lambda_C \) is the reduced electron Compton wavelength in Eq. (9f) of the MT, and \( r_N \) is the RMS nuclear radius. The RMS proton radius is given in Eq. (9e) of the MT.

The leading and next-order corrections are given by

\[ \mathcal{E}_{\text{FNS}}(n) = \frac{2}{3} \frac{m^3}{m^2_e} \frac{(Z \alpha)^4}{n^4} \frac{r_N^2}{\lambda_C^2} m_e c^2, \]

\[ \delta \mathcal{E}_{\text{FNS}}(n) = \left\{ 1 - C_{\eta} \frac{m}{m_e} \frac{r_N}{\lambda_C} Z \alpha \right. \]

\[ \left. - \left[ \ln \left( \frac{m}{m_e} \frac{r_N}{\lambda_C} \frac{Z \alpha}{n} \right) + \psi(n) + \gamma \right] - \frac{5n + 9}{4n^2} - C_\theta \right\} (Z \alpha)^2 \right\}, \]

where \( C_{\eta} \) and \( C_\theta \) are constants that depend on the details of the assumed charge distribution in the nucleus. The values used in Ref. [3] for hydrogen atoms are \( C_{\eta} = 1.7(1) \) and \( C_\theta = 0.47(4) \).

The corrections \( E_{\text{FNS}}(1) \) and \( E_{\text{FNS}}(2) \) to the 1s and 2s state energies of hydrogen are:

\[ E_{\text{FNS}}(1) = h \times 1198.040 \text{ kHz}, \]
\[ E_{\text{FNS}}(2) = h \times 149.762 \text{ kHz}. \]

The uncertainty \( \delta E_{\text{FNS}}(n) \) of \( E_{\text{FNS}}(n) \) due to the uncertainty \( \delta r_N \) of \( r_N \) is:

\[ \delta E_{\text{FNS}}(n) = \frac{4}{3} \frac{(Z \alpha)^4}{n^4} \frac{m^3}{m^2_e} \frac{r_N}{\lambda_C^2} m_e c^2. \]

\( \delta E_{\text{FNS}}(n) \) for \( n = 1 \) and 2 are:

\[ \delta E_{\text{FNS}}(1) = h \times 19 \text{ kHz}, \]
\[ \delta E_{\text{FNS}}(2) = h \times 2.3 \text{ kHz}. \]

**Nuclear-size correction to self-energy and vacuum polarization:** In addition to the direct effect of finite nuclear size on energy levels, its effect on the self-energy and vacuum polarization contributions should also be considered. The additional contribution to the self-energy due to the finite size of the nucleus is [3]

\[ E_{\text{NSE}}(n) = \left( 4 \ln 2 - \frac{23}{4} \right) \alpha Z \alpha \mathcal{E}_{\text{FNS}}(n), \]

where \( \mathcal{E}_{\text{FNS}}(n) \) is given in Eq. (43). The corrections \( E_{\text{NSE}}(n) \) for \( n = 1 \) and 2 are:

\[ E_{\text{NSE}}(1) = h \times (-0.1898) \text{ kHz}, \]
\[ E_{\text{NSE}}(2) = h \times (-0.02373) \text{ kHz}. \]

The additional contribution due to the finite size of the nucleus to the vacuum polarization is

\[ E_{\text{NVP}}(n) = \frac{3}{4} \alpha (Z \alpha) \mathcal{E}_{\text{FNS}}(n). \]

The corrections \( E_{\text{NSE}}(n) \) for \( n = 1 \) and 2 are

\[ E_{\text{NVP}}(1) = h \times 0.0478 \text{ kHz}, \]
\[ E_{\text{NVP}}(2) = h \times 0.0060 \text{ kHz}. \]

The correction to the energy of the nS state of hydrogen due to radiative-recoil effects is

\[ E_{\text{RR}}(n) = \frac{m^3}{m^2_e} \frac{\alpha(Z \alpha)^5}{n^2 \pi^2 n^4} m_e c^2 \left[ -6 \zeta(3) - 2 \pi^2 \ln 2 + \frac{35 \pi^2}{36} \right] \]

\[ - \frac{448}{27} + \frac{2}{3} \pi Z \alpha \ln^2 \left( \frac{1}{Z \alpha^2} \right) + \cdots \].

The corrections \( E_{\text{RR}}(n) \) for \( n = 1 \) and 2 are

\[ E_{\text{RR}}(1) = h \times (-12.328) \text{ kHz}, \]
\[ E_{\text{RR}}(2) = h \times (-1.541) \text{ kHz}. \]

The nucleus self-energy correction to the ns state energy of hydrogen is [3]

\[ E_{\text{SEN}}(n) = \frac{4Z^2 \alpha(Z \alpha)^4}{3\pi n^3} \frac{m^3 c^2}{M^2} \left[ \ln \left( \frac{M}{m} \frac{1}{Z^2 \alpha^2} \right) \right. \]

\[ \left. - \ln k_0(n) \right]. \]

The correction \( E_{\text{SEN}}(1) \) for the 1s state and the correction \( E_{\text{SEN}}(2) \) for the 2s state are

\[ E_{\text{SEN}}(1) = h \times 5.583 \text{ kHz}, \]
\[ E_{\text{SEN}}(2) = h \times 0.698 \text{ kHz}. \]

The theoretical centroid total energy of the ns state of hydrogen, \( \epsilon_n \), is the sum of contributions given in Eqs. (22), (20), (28), (30), (33), (35), (38), (40), (42), (44), (49), (51), (53) and (55). The binding energies \( \epsilon_n = \epsilon_n - m_e c^2 \) with \( n = 1 \) and 2 are

\[ \epsilon_1 = h \times (-3288086858048 \pm 29) \text{ kHz}, \]
\[ \epsilon_2 = h \times (-8220254441.6 \pm 6.0) \text{ kHz}, \]

The binding energy \( \tilde{\epsilon}_n \) is the sum of contributions given in Eqs. (23), (24), (25), (30), (33), (35), (38), (40), (42), (44), (49), (51), (53) and (55):

\[ \tilde{\epsilon}_1 = h \times (-3288086856879 \pm 29) \text{ kHz}, \]
\[ \tilde{\epsilon}_2 = h \times (-822025443672.7 \pm 6.0) \text{ kHz}. \]

Hence, the theoretical frequency \( f_{1s}^{(2002)} = (\epsilon_2 - \epsilon_1)/h \) of the 1s-2s transition is

\[ f_{1s}^{(2002)} = (246601413206.557 \pm 23) \text{ kHz}, \]

and the theoretical frequency \( f_{1s}^{(2002)} = (\tilde{\epsilon}_2 - \tilde{\epsilon}_1)/h \) is

\[ f_{1s}^{(2002)} = (246601413995.950 \pm 23) \text{ kHz}. \]

The experimental frequency \( f_{1s}^{(\text{exp})} \) is given in Eq. (12), and the difference \( \Delta f_{1s,ns}^{(2002)} = f_{1s}^{(2002)} - f_{1s}^{(\text{exp})} \) is

\[ \Delta f_{1s,ns}^{(2002)} = 808.915 \text{ kHz}. \]
and the difference $\Delta \tilde{f}^{(2002)}_1 = \tilde{f}^{(2002)}_1 - f^{(\text{exp})}_1$ is
\[ \Delta \tilde{f}^{(2002)}_1 = 19.522 \text{ kHz}. \] (61)

It is important to notice that $\Delta \tilde{f}^{(2002)}_1$ is much larger than the theoretical uncertainty $\delta f^{(\text{exp})}_1 = 23$ kHz of $f^{(\text{exp})}_1$ and much larger than the experimental uncertainty $\delta f^{(\text{exp})}_1 = 0.010$ kHz of $f^{(\text{exp})}_1$. On the other hand, $\Delta \tilde{f}^{(2002)}_2$ is smaller than $\delta f^{(\text{exp})}_2$, but much larger than $\delta f^{(\text{exp})}_2$. Hence, we conclude that the perturbative expression for the Dirac energy, $\epsilon^{\text{Dirac}}_1(n)$ in Eq. (1), taken together with the perturbative expansion of the radiative corrections yields a better result than using the non-perturbative expression for the Dirac energy, $\epsilon^{\text{Dirac}}_1(n)$ in Eq. (1).

Hydrogen 1s-2s transition frequency calculations using CODATA-2018: Here we use the values of the fundamental physical constants given in Eq. (23) of the MT and the technique developed in Section VII.A of Ref. [1] to calculate the s-state energies of hydrogen and the 1s → ns transition frequencies.

The largest contribution to the energies of hydrogen is the Dirac eigenvalue for an electron bound to a point-like nucleus with a finite mass $M$ given in Ref. [1]. In this section, we consider $\epsilon^{(2018)}_1(n)$ in Eq. (1) and $\epsilon^{(2018)}_2(n)$ in Eq. (3), where the superscript (2018) indicates that we take the fundamental constant values from the 2018 CODATA [5].

Explicitly, $\epsilon^{(2002)}_1(n)$ with $n = 1, 2$
\[ \epsilon^{(2018)}_1(1) = h \times (-3288095029840.8 \pm 6.4) \text{ kHz}, \] (62a)
\[ \epsilon^{(2018)}_1(2) = h \times (-822026488927.1 \pm 1.6) \text{ kHz}. \] (62b)

On the other hand, $\epsilon^{(2002)}_2(n)$ with $n = 1, 2$
\[ \epsilon^{(2018)}_2(1) = h \times (-3288095028691.7 \pm 6.4) \text{ kHz}, \] (63a)
\[ \epsilon^{(2018)}_2(2) = h \times (-822026488538.8 \pm 1.6) \text{ kHz}. \] (63b)

We now apply the technique described in Section VII.A of Ref. [1] and calculate the Lamb shift $E^{(2018)}_L(n)$ of the hydrogen $ns$ state energy. The leading relativistic-recoil correction to the s state energy to lowest order in $Z\alpha$ and all orders in $\mu_{cp}$ is
\[ E_S(n) = \frac{\mu_{cp}}{(1 + \mu_{cp})^3} \frac{(Z\alpha)^5}{\pi n^3} m_e c^2 \left\{ \frac{1}{3} \ln \left( \frac{1}{(Z\alpha)^2} \right) - \frac{8}{3} \ln k_0(n) - \frac{1}{9} - \frac{7}{3} a_n - \frac{2}{1 - \mu_{cp}^2} \times \left[ \ln \left( 1 + \mu_{cp} \right) - \mu_{cp}^2 \ln \left( \frac{1 + \mu_{cp}}{\mu_{cp}} \right) \right] \right\}, \] (64)
where
\[ a_n = -2 \ln \left( \frac{2}{n} \right) - 2 + \frac{1}{n} - 2 \sum_{i=1}^{n} \frac{1}{i}. \]

The corrections $E_S(1)$ and $E_S(2)$ to the 1s and 2s state energies of hydrogen are
\[ E_S(1) = h \times 2409.51 \text{ kHz}, \] (65a)
\[ E_S(2) = h \times 341.29 \text{ kHz}. \] (65b)

Additional contributions to lowest order in the mass ratio $\mu_{cp}$ and of higher order in $Z\alpha$ is [6]
\[ E_R(n) = \mu_{cp} \left( \frac{Z\alpha}{n^3} \right)^6 m_e c^2 \left[ D_{60} + Z\alpha G_{\text{REC}}(n, Z\alpha) \right], \] (66)
where $D_{60} = 4 \ln 2 - 7/2$, and the function $G_{\text{REC}}(Z\alpha)$ is given by
\[ G_{\text{REC}}(n, Z\alpha) = D_{72} \ln \left( \frac{1}{Z^2\alpha^2} \right) + D_{71}(n) \ln \left( \frac{1}{Z^2\alpha^2} \right) + D_{70}(n) + \cdots, \] (67)
where $D_{72} = -11/(60\pi)$. The coefficients $D_{71}(n)$ and $D_{70}(n)$ are not known analytically, leaving only the first term on the right-hand side of Eq. (67), which is independent of $n$. Instead, Ref. [1] uses the following values for $G_{\text{REC}}(n, \alpha)$ which is numerically computed for hydrogen ($Z = 1$) for the $s$ states:
\[ \pi G_{\text{REC}}(1, \alpha) = 9.720(3), \]
\[ \pi G_{\text{REC}}(2, \alpha) = 14.899(3). \]

The corrections $E_R(1)$ and $E_R(2)$ to the 1s and 2s state energies of hydrogen are
\[ E_R(1) = h \times (-7.162) \text{ kHz}, \] (68a)
\[ E_R(2) = h \times (-0.880) \text{ kHz}. \] (68b)

The one-photon self-energy of an electron bound to a point-like nucleus having an infinite mass is
\[ E^{(2)}_{\text{SE}}(n) = \frac{\alpha}{\pi} \frac{(Z\alpha)^4}{n^3} F(Z\alpha, n) m_e c^2, \] (69)
where the function $F(Z\alpha, n)$ is
\[ F(Z\alpha, n) = A_{41} \ln \left( \frac{1}{Z^2\alpha^2} \right) + A_{40} + A_{50} Z\alpha + A_{62} Z^2\alpha^2 \ln^2 \left( \frac{1}{Z^2\alpha^2} \right) + A_{61} Z^2\alpha^2 \ln \left( \frac{1}{Z^2\alpha^2} \right) + G_{\text{SE}}(Z\alpha, n) Z^2\alpha^2, \] (70)
The constants $A$’s are:
\[ A_{41} = \frac{4}{3}, \quad A_{40} = -\frac{4}{3} \ln k_0(n) + \frac{10}{9}, \]
\[ A_{50} = \left( \frac{139}{32} - 2 \ln(2) \right) \pi, \quad A_{62} = -1, \]
\[ A_{61} = 4 \sum_{i=1}^{n} \frac{1}{i} + \frac{28}{3} \ln 2 - 4 \ln n - \frac{601}{180} - \frac{77}{45n^2}. \]
For hydrogen atoms in the $s$ state, the function $G_{SE}(\alpha, n)$ is

$$G_{SE}(\alpha, 1) = -30.290240(20),$$
$$G_{SE}(\alpha, 2) = -31.185150(90).$$

Following the convention in Ref. 3, we multiply $F(Z\alpha, n)$ by a factor $m_e^3/m_e^3$, and replace $\ln(1/\alpha^2)$ by $\ln((m_e/m_e)(1/\alpha^2))$.

The corrections $E^{(2)}_{SE}(1)$, $E^{(2)}_{SE}(2)$ and $E^{(2)}_{SE}(3)$ to the $1s$, $2s$ and $3s$ state energies of hydrogen are

$$E^{(2)}_{SE}(1) = h \times 8383339.47 \text{ kHz},$$
$$E^{(2)}_{SE}(2) = h \times 1071281.00 \text{ kHz}.$$(71a)

The second-order vacuum polarization correction to the $s$ state energy of H or HLI with a point-like nucleus having infinite mass is,

$$E^{(2)}_{VP}(n) = \frac{\alpha}{\pi} \frac{(Z\alpha)^4}{n^3} H(Z\alpha) m_e c^2,$$(72)

where

$$H(Z\alpha) = H^{(1)}(Z\alpha) + H^{(R)}(Z\alpha),$$

and

$$H^{(1)}(Z\alpha) = V_{40} + V_{50} Z\alpha + V_{61} (Z\alpha)^2 \ln \left(\frac{1}{Z^2\alpha^2}\right) + (Z\alpha)^2 G^{(1)}_{VP}(Z\alpha, n).$$

Here $V_{40} = -4/15$, $V_{50} = 5\pi/48$ and $V_{61} = -2/15$. $G^{(1)}_{VP}(\alpha, n)$ for hydrogen, $Z = 1$, is

$$G^{(1)}_{VP}(\alpha, 1) = -0.618724,$$
$$G^{(1)}_{VP}(\alpha, 2) = -0.808872.$$ 

Moreover,

$$H^{(R)}(Z\alpha) = (Z\alpha)^2 G^{(R)}_{VP}(Z\alpha),$$

where

$$G^{(R)}_{VP}(Z\alpha) = \frac{19}{45} \frac{\pi^2}{27} \left[ -\frac{1}{16} \frac{31\pi^2}{2880} \right] \pi Z\alpha + \cdots.$$ 

The corrections $E^{(2)}_{VP}(1)$ and $E^{(2)}_{VP}(2)$ to the $1s$ and $2s$ state energies are:

$$E^{(2)}_{VP}(1) = h \times (-215167.77) \text{ kHz},$$
$$E^{(2)}_{VP}(2) = h \times (-26897.00) \text{ kHz}.$$(73a)

Vacuum polarization from the muon-antimuon $\mu^+\mu^-$ pair is

$$E^{(2)}_{\mu^+\mu^-}(n) = -\frac{4}{15} \frac{\alpha}{\pi} \frac{(Z\alpha)^4}{n^3} \frac{m_\mu^2}{m_e^3} \frac{m_\mu^3}{m_e^3} m_e c^2,$$(74)

and the hadronic vacuum polarization is

$$E^{(2)}_{\text{had VP}}(n) = 0.671(15) E^{(2)}_{\mu^+\mu^-}(n).$$ (75)

The muonic and hadronic corrections to the $1s$ and $2s$ state energies are

$$E^{(2)}_{\mu^+\mu^-}(1) = h \times (-5.068) \text{ kHz},$$
$$E^{(2)}_{\mu^+\mu^-}(2) = h \times (-0.634) \text{ kHz},$$
$$E^{(2)}_{\text{had VP}}(1) = h \times (-3.401) \text{ kHz},$$
$$E^{(2)}_{\text{had VP}}(2) = h \times (-0.425) \text{ kHz}.$$(76a)

The two-photon corrections are

$$E^{(4)}(n) = \frac{\alpha^2}{\pi^2} \frac{(Z\alpha)^4}{n^3} F^{(4)}(Z\alpha) m_e c^2,$$(77)

where

$$F^{(4)}(Z\alpha) = B_{40} + B_{50} Z\alpha + B_{63} (Z\alpha)^2 \ln \left(\frac{1}{Z^2\alpha^2}\right) + B_{62} (Z\alpha)^2 \ln \left(\frac{1}{Z^2\alpha^2}\right) + B_{60} (Z\alpha)^2 + B_{72} (Z\alpha)^3 \ln \left(\frac{1}{Z^2\alpha^2}\right) + B_{71} (Z\alpha)^3 \ln \left(\frac{1}{Z^2\alpha^2}\right) + \cdots,$$

and

$$B_{40} = \frac{3\pi^2}{2} \ln 2 - \frac{10\pi^2}{27} - \frac{2179}{648} - \frac{9}{4} \zeta(3),$$
$$B_{50} = -21.55447(13),$$
$$B_{63} = -\frac{8}{27},$$
$$B_{62} = \frac{16}{9} \left[ \frac{71}{60} - \ln 2 + \psi(n) + \gamma - \ln n \left[ \frac{1}{n} + \frac{1}{4n^2} \right] \right],$$
$$B_{61} = \frac{413581}{64800} \frac{4N(ns)}{3} + \frac{2027\pi^2}{864} - \frac{616\ln 2}{135} - \frac{2\pi^2}{3} \ln 2 + \frac{40\ln^2 2}{9} + \zeta(3) + \left(\frac{304}{135} - \frac{32\ln 2}{9}\right) \left[ \frac{3}{4} + \gamma + \psi(n) \right] - \ln(n) \left[ \frac{1}{n} + \frac{1}{4n^2} \right] - \frac{43}{36} + \frac{133\pi^2}{864},$$

where $N(ns)$ and the uncertainties $\delta N(ns)$ of $N(ns)$ for $n = 1, 2$ are

$$N(1s) = 17.85567203(1),$$
$$N(2s) = 12.03214158(1).$$

The constants $B_{60}$ and $B_{71}$ for the $nS$ states with $n = 1, 2$ are

$$B_{60}(1s) = -78.7(9.3),$$
$$B_{71}(1s) = -116(12),$$
$$B_{60}(2s) = -83.6(9.3),$$
$$B_{71}(2s) = -100(12),$$

where

$$F^{(4)}(Z\alpha) = \frac{\alpha^2}{\pi^2} \frac{(Z\alpha)^4}{n^3} F^{(4)}(Z\alpha) m_e c^2,$$
and the constant $B_{72}$ is

$$B_{72} = \left( -\frac{139}{48} + \frac{4 \ln 2}{3} - \frac{5}{72} \right) \pi.$$ 

The corrections $E^{(4)}(1)$ and $E^{(4)}(2)$ to the $1s$ and $2s$ state energies are

$$E^{(4)}(1) = h \times 728.17 \text{ kHz},$$

$$E^{(4)}(2) = h \times 91.59 \text{ kHz}.$$  

(78a)

(78b)

The three-photon contribution $E^{(6)}(n)$ to the $nS$ state of hydrogen is

$$E^{(6)}(n) = \frac{\alpha^3}{n^3} (Z \alpha)^4 F^{(6)}(Z \alpha) m_e c^2,$$

(79)

where

$$F^{(6)}(Z \alpha) = C_{40} + C_{50} Z \alpha + C_{63} (Z \alpha)^2 \ln^3(Z \alpha) + C_{62} (Z \alpha)^2 \ln^2(Z \alpha) + C_{61} (Z \alpha)^2 \ln(Z \alpha) + C_{60} (Z \alpha)^2.$$ 

The constant $C_{40}$ is

$$C_{40} = \frac{568a_4}{9} + \frac{85\zeta(5)}{24} - \frac{121\pi^2\zeta(3)}{72} - \frac{84071\zeta(3)}{2304},$$

$$- \frac{71\ln^2 2}{27} + \frac{239\pi^2 \ln^2 2}{135} + \frac{4787\pi^2 \ln 2}{108} + \frac{1591\pi^4}{3240},$$

$$- \frac{252251\pi^2}{9720} + \frac{679441}{93312}.$$ 

Reference [9] uses

$$C_{50} = 0, \quad C_{63} = 0, \quad C_{61} = 0, \quad C_{60} = 0.$$ 

The coefficient $C_{62}$ is

$$C_{62} = \frac{2}{3} \left[ - \frac{1523}{648} - \frac{10\pi^2}{27} + \frac{3}{2} \ln^2 2 - \frac{9}{4} \zeta(3) - \frac{82}{81} \right].$$ 

The corrections $E^{(6)}(1)$ and $E^{(6)}(2)$ to the $1s$ and $2s$ state energies are

$$E^{(6)}(1) = h \times (-850.26) \text{ kHz},$$

$$E^{(6)}(2) = h \times (-106.28) \text{ kHz}.$$ 

(80a)

(80b)

Following Ref. [9], we write the FNS and nuclear-polarizability correction $E_{\text{nuc}l}(n)$ to the $nS$ state energies of hydrogen in the form:

$$E_{\text{nuc}l}(n) = \sum_{i=4}^{\infty} E_{\text{nuc}l}^{(i)}(n),$$

(81)

where $E_{\text{nuc}l}^{(i)}(n)$ is proportional to $\alpha^i$. The first and lowest-order contribution is

$$E_{\text{nuc}l}^{(4)}(n) = \frac{2}{3} \frac{(Z \alpha)^4}{n^3} \frac{m^3}{m_e^2} \frac{r_N^2}{\lambda_C^3} m_e c^2.$$ 

(82)

$E_{\text{nuc}l}^{(4)}(n)$ for $n = 1, 2$ are

$$E_{\text{nuc}l}^{(4)}(1) = h \times 1107.15 \text{ kHz},$$

$$E_{\text{nuc}l}^{(4)}(2) = h \times 138.39 \text{ kHz}.$$ 

(83a)

(83b)

The uncertainty $\delta E_{\text{nuc}l}^{(4)}(n)$ of $E_{\text{nuc}l}^{(4)}(n)$ due to the uncertainty $\delta r_N$ of $r_N$ is:

$$\delta E_{\text{nuc}l}^{(4)}(n) = \frac{4}{3} \frac{(Z \alpha)^4}{n^3} \frac{m^3}{m_e^2} \frac{r_N^2}{\lambda_C^3} m_e c^2.$$ 

(84)

$\delta E_{\text{nuc}l}^{(4)}(n)$ for $n = 1, 2$ are

$$\delta E_{\text{nuc}l}^{(4)}(1) = h \times 5.0 \text{ kHz},$$

$$\delta E_{\text{nuc}l}^{(4)}(2) = h \times 0.63 \text{ kHz}.$$ 

(85a)

(85b)

The $\alpha^5$ correction for hydrogen is

$$E_{\text{nuc}l}^{(5)}(n) = -\frac{1}{3} \frac{(Z \alpha)^5}{n^3} \frac{m^3}{m_e^2} \frac{r_N^3}{\lambda_C^3} m_e c^2,$$ 

(86)

where the effective Friar radius of the proton $\approx 0$ is

$$r_{\text{PF}} = 1.947(75) \text{ fm}.$$ 

$E_{\text{nuc}l}^{(5)}(n)$ for $n = 1, 2$ are

$$E_{\text{nuc}l}^{(5)}(1) = h \times (-21.630) \text{ kHz},$$

$$E_{\text{nuc}l}^{(5)}(2) = h \times (-2.704) \text{ kHz}.$$ 

(87a)

(87b)

The $\alpha^6$ correction $E_{\text{nuc}l}^{(6)}(n)$ to the energy has finite-nuclear-size correction $E_{\text{ins}}^{(6)}(n)$, nuclear-polarizability correction $E_{\text{pol}}^{(6)}(n)$, and radiative finite-nuclear-size contribution $E_{\text{rad}}^{(6)}(n)$:

$$E_{\text{nuc}l}^{(6)}(n) = E_{\text{ins}}^{(6)}(n) + E_{\text{pol}}^{(6)}(n) + E_{\text{rad}}^{(6)}(n),$$

(88)

where

$$E_{\text{ins}}^{(6)}(n) = -\frac{2}{3} \frac{(Z \alpha)^6}{n^3} \frac{m^3}{m_e^2} \frac{r_N^2}{\lambda_C^3} m_e c^2 \left[ \frac{9}{4n^2} - 3 + \frac{1}{n} + 2\gamma - \ln \left( \frac{n}{2} \right) + \psi(n) \right] + \ln \left( \frac{m^3}{m_e^2} \frac{r_N^2}{\lambda_C^3} Z \alpha \right),$$

(89)

$$E_{\text{pol}}^{(6)}(n) = h \times \frac{0.393}{n^3} \text{ kHz},$$

(90)

$$E_{\text{rad}}^{(6)}(n) = \frac{2}{3} \frac{\alpha(Z \alpha)^5}{n^3} \frac{m^3}{m_e^2} \frac{r_N^2}{\lambda_C^3} \times (4 \ln 2 - 5) m_e c^2,$$ 

(91)

and

$$r_{N2} = 1.068497 r_N.$$
\( E_{\text{nucl}}^{(6)}(n) \) for \( n = 1, 2 \) are
\[
E_{\text{nucl}}^{(6)}(1) = h \times 0.938 \ \text{kHz}, \quad E_{\text{nucl}}^{(6)}(2) = h \times 0.124 \ \text{kHz}.
\]

The \( n^7 \) correction to the energy is
\[
E_{\text{nucl}}^{(7)}(n) = \frac{2}{3} \frac{\alpha(Z \alpha)^6}{\pi n^3} \frac{m^3 r_N^2}{m^2} \frac{m_e c^2}{\lambda_C^3} \left[ -\frac{2}{3} \ln^2 \left( \frac{1}{Z^2 \alpha^2} \right) + \ln^2 \left( \frac{m}{m_e} \frac{r_N}{\lambda_C} \right) \right]. \tag{93}
\]

\( E_{\text{nucl}}^{(7)}(n) \) for \( n = 1, 2 \) are
\[
E_{\text{nucl}}^{(7)}(1) = h \times (-0.00968) \ \text{kHz}, \quad E_{\text{nucl}}^{(7)}(2) = h \times (-0.00121) \ \text{kHz}. \tag{94a}
\]

The nucleus self-energy correction to the \( nS \) state energy of hydrogen is
\[
E_{\text{SEN}}(n) = \frac{4Z^2 \alpha(Z \alpha)^4}{3\pi n^3} \frac{m^3 c^2}{M^2} \left[ \ln \left( \frac{M}{m} \frac{1}{Z^2 \alpha^2} \right) - \ln k_0(n) \right], \tag{98}
\]

The theoretical total energy of centroid of the \( ns \) state of hydrogen, \( \epsilon_n \), is the sum of the contributions given in Eqs. \( [54a, 55a, 56a, 71, 72, 76, 78, 80, 95, 97] \) and \( [99] \). The binding energies \( \epsilon_n = \epsilon_n - m_e c^2 \) with \( n = 1, 2 \) are
\[
\epsilon_1^{(2018)} = h \times (-3288086857963.0 \pm 8.1) \ \text{kHz}, \tag{100a}
\]
\[
\epsilon_2^{(2018)} = h \times (-82205444039.2 \pm 1.7) \ \text{kHz}. \tag{100b}
\]

\( E_{\text{nucl}}(n) \) for \( n = 1, 2 \) are
\[
E_{\text{nucl}}^{(1)} = h \times 1086.45 \ \text{kHz}, \quad E_{\text{nucl}}^{(2)} = h \times 135.81 \ \text{kHz}. \tag{95a}
\]

The nuclear corrections to the \( nS \) state energy of hydrogen due to radiative-recoil effects is
\[
E_{\text{RR}}(n) = \frac{m^3}{m_e M} \frac{\alpha(Z \alpha)^5}{\pi^2 n^3} m_e c^2 \left[ 6 \zeta(3) - 2 \pi^2 \ln 2 + \frac{35 \pi^2}{36} - \frac{448}{27} + \frac{2}{3} \frac{\pi Z \alpha}{\lambda_C} \ln^2 \left( \frac{1}{Z^2 \alpha^2} \right) + \cdots \right]. \tag{96}
\]

The corrections \( E_{\text{RR}}(1) \) and \( E_{\text{RR}}(2) \) to the 1s and 2s state energies are
\[
E_{\text{RR}}(1) = h \times (-12.328) \ \text{kHz}, \quad E_{\text{RR}}(2) = h \times (-1.541) \ \text{kHz}. \tag{97a}
\]

The theoretical frequency \( \tilde{f}_1^{(2018)} \) of the 1s state is
\[
\tilde{f}_1^{(2018)} = (\epsilon_1^{(2018)} - \epsilon_{1s}^{(1)}) / h = 49661413923.9 \pm 6.4 \ \text{kHz}. \tag{102}
\]

The experimental frequency \( f_1^{(1)} \) is given in Eq. \( [12] \), and the discrepancy \( \Delta f_1^{(1)} = f_1^{(1)} - f_1^{(exp)} \) is
\[
\Delta f_1^{(1)} = 736.8 \ \text{kHz}. \tag{104}
\]

The correction \( E_{\text{SEN}}(1) \) for the 1s state and the correction \( E_{\text{SEN}}(2) \) for the 2s state are
\[
E_{\text{SEN}}(1) = h \times 5.583 \ \text{kHz}, \quad E_{\text{SEN}}(2) = h \times 0.698 \ \text{kHz}. \tag{99a}
\]

The binding energy \( \tilde{\epsilon}_n \) of the \( nS \) state of hydrogen is the sum of the contributions given in Eqs. \( [53a, 53b, 55a, 71, 73, 76, 78, 80, 93, 97] \) and \( [99] \). The binding energy \( \tilde{\epsilon}_n \) with \( n = 1, 2 \) are
\[
\tilde{\epsilon}_1^{(2018)} = h \times (-3288086856814.0 \pm 8.1) \ \text{kHz}, \tag{101a}
\]
\[
\tilde{\epsilon}_2^{(2018)} = h \times (-82205443650.9 \pm 1.7) \ \text{kHz}. \tag{101b}
\]

The theoretical frequency \( f_1^{(1)} = (\tilde{\epsilon}_2^{(1)} - \tilde{\epsilon}_1^{(1)}) / h \) of the 1s-2s transition is
\[
f_1^{(1)} = (2466061413923.9 \pm 6.4) \ \text{kHz}. \tag{103}
\]
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