Short Communication

Deuteron charge radius and Rydberg constant from spectroscopy data in atomic deuterium

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Abstract

We give a pedagogical description of the method to extract the charge radii and Rydberg constant from laser spectroscopy in regular hydrogen (H) and deuterium (D) atoms, that is part of the CODATA least-squares adjustment (LSA) of the fundamental physical constants. We give a deuteron charge radius $r_d$ from D spectroscopy alone of 2.1415(45) fm. This value is independent of the measurements that lead to the proton charge radius, and five times more accurate than the value found in the CODATA Adjustment 10. The improvement is due to the use of a value for the $1S \rightarrow 2S$ transition in atomic deuterium which can be inferred from published data or found in a PhD thesis.

Keywords: deuteron radius, proton radius, Rydberg constant

(Some figures may appear in colour only in the online journal)
The discrepancy of \( \sim 7 \sigma \) between these two values has been coined the ‘proton radius puzzle’ [4, 5].

The CREMA collaboration has just published a value of the deuteron charge radius \( r_d \) from laser spectroscopy of muonic deuterium (\( \mu D \)) [6]

\[
\rho_d(\mu D) = 2.1256 (8) \text{ fm},
\]

again more than \( 7 \sigma \) smaller than the CODATA-2010 value of \( r_d \)

\[
r_d(\text{CODATA-2010}) = 2.1424 (21) \text{ fm}.
\]

However, comparison of the new \( \rho_d(\mu D) \) value with the CODATA-2010 value may be considered inadequate or redundant, because the CODATA values of \( r_d \) and \( \rho_d \) are highly correlated, with a correlation coefficient \( c(r_d, \rho_d) = 0.9989 \) (see [3], equation (92)). This large correlation is the result of the very precisely measured isotope shift of the \( 1S \rightarrow 2S \) transition in atomic hydrogen (H) and deuterium (D) [7, 8], which yields a very accurate value for the difference of the (squared) deuteron and proton charge radii [9]

\[
r_d^2 - \rho_p^2 = 3.82007(65) \text{ fm}^2.
\]

One could thus argue that the CODATA deuteron charge radius is larger than the muonic deuteron value only because the correlated, and very accurately determined, proton charge radius is larger than the muonic value.

Here we use the available data on spectroscopy of atomic deuterium to deduce a precise value of \( r_d \) which does not depend on \( \rho_p \) through equation (5). In our analysis we use a value of the \( 1S \rightarrow 2S \) transition in atomic deuterium (see table 6) that has not been used by CODATA. Its value can either be inferred from published data or found in a PhD thesis [10]. This \( 1S \rightarrow 2S \) value helps improve the accuracy of the deuteron charge radius by a factor of five, compared to the CODATA partial adjustment 10 [3].

1.1. CODATA partial adjustments

The final CODATA-2010 recommended values of the fundamental constants are deduced in the so-called ‘Adjustment 3’. As detailed in section XIII.B.2 on page 1577 ff. of the CODATA-2010 report [3], there are additional adjustments that use only a subset of the available input data. ‘Adjustments 6–12’ are the ones relevant for \( r_p, \rho_p \) and the Rydberg constant \( R_{\infty} \), and the results are summarized in table XXXVIII of [3].

These auxiliary partial adjustments serve two purposes: on the one hand, they verify the internal consistency of the CODATA LSA, as results from different subsets of the data are in good agreement with each other. On the other hand, these adjustments provide uncorrelated values of \( r_p \) and \( r_d \). These can then be compared with their muonic counterparts to obtain a clearer picture of the issues surrounding the ‘proton radius puzzle’.

For the proton, the value of \( r_p \) that is deduced from data obtained by precision spectroscopy in atomic hydrogen alone (omitting both elastic electron–proton (e–p) scattering results and measurements in deuterium) is determined in Adjustment 8, see table XXXVIII of [3]:

\[
r_p(\text{H spectr., CODATA}) = 0.8764(89) \text{ fm}.
\]

This value is in excellent agreement with equation (2), and only slightly less accurate, see figure 1. The ‘atomic physics’ part of the proton radius puzzle is the 4.0\( \sigma \) discrepancy between equations (1) and (6). It is unaffected by the problems that may exist in the analysis of e–p scattering data [11–15].

The situation is somewhat less favorable for the deuteron charge radius \( r_d \). The CODATA-2010 value from the full Adjustment 3 given in equation (4) is very precise:

\[
r_d(\text{CODATA}) = 2.1424(21) \text{ fm}.
\]

This value is not accurate enough for a useful comparison with the new result from muonic deuterium, see figure 2.

\[
\text{CODATA}
\]

\[
\text{H avg.}
\]

\[
\mu H
\]

\[
\mu D + \text{iso}
\]

\[
2S \rightarrow 2P_{\mu D}
\]

\[
2S \rightarrow 2P_{\mu H}
\]

\[
2S \rightarrow 2P_{diso}
\]

\[
1S \rightarrow 2S + 2S \rightarrow 4S_{1/2}
\]

\[
1S \rightarrow 2S + 2S \rightarrow 4D_{5/2}
\]

\[
1S \rightarrow 2S + 2S \rightarrow 4D_{3/2}
\]

\[
1S \rightarrow 2S + 2S \rightarrow 12D_{3/2}
\]

\[
1S \rightarrow 2S + 2S \rightarrow 12D_{5/2}
\]

\[
0.82 \quad 0.84 \quad 0.86 \quad 0.88 \quad 0.9 \quad 0.92
\]

Proton charge radius \( r_p \) [fm]

Figure 1. Proton rms charge radii from muonic hydrogen (\( \mu H \), the stripe includes the uncertainty) and muonic deuterium [6] (‘\( \mu D + \text{iso} \)’, obtained using equation (5)), in comparison with the CODATA-2010 value (equation (2)), the value from hydrogen spectroscopy alone (equation (19)), and the alternative value from using the \( 1S \rightarrow 3S \) measurement in hydrogen instead of the \( 1S \rightarrow 2S \) transition, see text. Also shown are the individual values from \( 2S \rightarrow 2P \) and from combining \( 1S \rightarrow 2S \) and \( 2S \rightarrow n\ell \), see table 4.

7 The CODATA-2010 report quotes 2.121(25) fm, but we list all charge radii with 4 decimal figures to make the different accuracies immediately obvious. The numbers in equation (7) were provided by Taylor and Newell from CODATA/NIST.
12. The ‘missing’ $1S\rightarrow 2S$ measurement in D

The reason for this significantly worse accuracy of $r_d$ in equation (7) is the apparent lack of a precise measurement of the $1S\rightarrow 2S$ transition in atomic deuterium. Only the isotope shift, i.e. the difference of the $1S\rightarrow 2S$ transitions in H and D, is used in the CODATA LSA, see [3], table XI.

This is perfectly valid for the ‘full’ CODATA Adjustment 3 using all available input data. However, for Adjustment 10 of spectroscopy data in D, the lack of a precise value for the $1S\rightarrow 2S$ transition in D results in a much larger uncertainty.

In this note we argue that the $1S\rightarrow 2S$ transition frequency in atomic deuterium has been measured very accurately by some of the authors at MPQ. The published isotope shifts [7, 8] are in fact the calculated differences of the measured $1S\rightarrow 2S$ transition in atomic deuterium and hydrogen.

We can thus proceed to deduce a precise value of the deuteron radius from deuterium spectroscopy alone, combining the $1S\rightarrow 2S$ transition in D, measured by some of the authors at MPQ, with the $1S\rightarrow 8S$, $8D$, and $12D$ transitions in D, measured by some of the authors at LKB. The new value is five times more precise as the one in equation (7), and can be usefully compared to the muonic deuterium value of [6] ($\mu D$) is $3.5\sigma$ smaller than the average value from deuteron spectroscopy (equation (20)).

The first term on the right hand side is the famous Bohr result for the energy levels of an electron orbiting an infinitely heavy nucleus $-R_s/m_e^2$, corrected for the leading order nuclear motion by the reduced mass ratio $m_{red}/m_e$. Here, $R_s$ denotes the Rydberg constant, $c$ is the speed of light in vacuum, and $m_e$ is the reduced mass of the atom with an electron of mass $m_e$ and a nucleus of mass $m_N$ is given by

$$m_{red} = \frac{m_e m_N}{m_e + m_N} \approx \frac{m_e}{1 + \frac{m_N}{m_e}}.$$ (9)

The mass ratios $m_{red}/m_N$ are tabulated in [3].

The second term in equation (8) is the finite nuclear size correction, whose leading order is given in kHz by [3, 16]

$$E_{NS}^{(0)} = \frac{2}{3\hbar} \left( \frac{m_{red}}{m_e} \right)^4 \left( \frac{Z_\alpha}{\lambda_or} \right)^2 \left( \frac{r_N}{\alpha or} \right)^2.$$ (10)

Here, $\alpha \approx 1/137.036$ is the fine structure constant, $Z = 1$ is the nuclear charge for H and D, $\lambda_or = 386.16$ fm is the reduced Compton wavelength of the electron, and $r_N$ is the rms charge radius of the nucleus, i.e. $r_d$ for H and $r_d$ for D.

The charge radius contribution $E_{NS}$ is significant only for S-states ($\ell = 0$), as indicated by the Kronecker symbol $\delta_{00}$ in equation (8).

The $1/n^3$ dependence of $E_{NS}$ in equation (8) originates from the overlap of the electron’s wave function with the extended nuclear charge distribution. For our purposes it is convenient to sum $E_{NS}^{(0)}$ and all other finite nuclear size effects that are proportional to $1/n^3$. These higher-order nuclear size corrections are $2 \times 10^{-4}$ of $E_{NS}$ and thus very small, see [3] equations (75), (77) and (78). We obtain

$$E_{NS}(H) = 1564.60 \times r_p^2 \text{ kHz fm}^{-2},$$ (11)

$$E_{NS}(D) = 1565.72 \times r_p^2 \text{ kHz fm}^{-2},$$ (12)

both with negligible uncertainty on the level of a few Hz fm$^{-2}$. For reference, $E_{NS}$ amounts to approx. 1100 kHz and 7100 kHz for the 1S ground state in H and D, respectively.
Table 1. Values of $\Delta(n, \ell, j)$ in kHz for relevant energy levels in atomic hydrogen. $\Delta(n, \ell, j)$ includes all relevant corrections to the energy levels from fine structure splittings and QED effects. The uncertainties are taken from [3], table XVIII. They arise mostly from the estimated uncertainty of uncalculated two-loop corrections [16]. An uncertainty of ‘(0)’ denotes ‘negligibly small’.

| n  | $S_{1/2}$       | $P_{1/2}$       | $P_{3/2}$         | $D_{3/2}$       | $D_{5/2}$       |
|----|----------------|----------------|------------------|----------------|----------------|
| 1  | −35626637.5(2.5)| −13693861.67(3)| −2724820.10(3)  | −1622832.29(0) | −539495.09(0)  |
| 2  | −12636167.73(31)| −2224408.70(0) | −853278.87(0)   | −855566.25(0)  | −398533.10(0)  |
| 3  | 4552757.02(9)   | −138996.24(0)  | 81867.09(0)      |                |                |
| 4  | −2091350.05(4) | 44349.61(0)    | 27422.46(0)      |                |                |
| 5  | −293431.56(1)  |                |                  |                |                |

Table 2. Values of $\Delta(n, \ell, j)$ in kHz for relevant energy levels in atomic deuterium. The caption of table 1 applies.

| n  | $S_{1/2}$       | $P_{1/2}$       | $P_{3/2}$         | $D_{3/2}$       | $D_{5/2}$       |
|----|----------------|----------------|------------------|----------------|----------------|
| 1  | −35621512.1(2.3)| −13696839.80(3)| −2724804.25(3)  | −1623126.89(0) | −539493.99(0)  |
| 2  | −12638504.55(29)| −1057845.0(9.0)| 9911200(12)      | 8.5 × 10^{-6}  | Harvard 1994   |
| 3  | 4553743.34(9)   | 12 × 10^{-6}   | Harvard 1994     |                |                |
| 4  | −2091828.14(4) | 770649.305012(8.6)| 1.1 × 10^{-11} | LKB 1997       | [30]*          |
| 5  | 770649.504450(8.3)| 1.1 × 10^{-11} | LKB 1997       |                |                |
| 6  | 770649.561584(2.6)| 8.3 × 10^{-12} | LKB 1997       | [30]*          |
| 7  | 799191710472(7.9)| 1.1 × 10^{-11} | LKB 1999       | [31]*          |
| 8  | 799191727403(7.7)| 8.7 × 10^{-12} | LKB 1999       |                |                |
| 9  | 2466061413187.103(46)| 1.9 × 10^{-14} | MPQ 2000       | [32]           |
| 10 | 2466061413187.080(34)| 1.4 × 10^{-14} | MPQ 2004       | [33]*          |
| 11 | 2466061413187.035(10)| 4.2 × 10^{-15} | MPQ 2011       | [34]           |
| 12 | 2466061413187.018(11)| 4.5 × 10^{-15} | MPQ 2013       | [35]           |
| 13 | 2922743278678(13)| 4.4 × 10^{-12} | LKB 2010       | [36]*          |
| 14 | 2922743278659(17)| 5.8 × 10^{-12} | MPQ 2016       | [37]           |

The third ingredient of equation (8), $\Delta(n, \ell, j)$, summarizes all the remaining corrections. The largest part of $\Delta(n, \ell, j)$ is due to the use of the Dirac equation instead of the simple Bohr formula. Other contributions are the fine- and hyperfine-splittings, the relativistic, QED, radiative, recoil and Darwin–Foldy corrections, fine size corrections for $P$-states, nuclear polarizability, and many higher-order corrections. These are listed in section IV.A.1 of [3].

The $\Delta(n, \ell, j)$ can be calculated very accurately using the detailed formulas found e.g. in [3, 17, 18]. We list in tables 1 and 2 the values of $\Delta(n, \ell, j)$ for relevant states in H and D, respectively. For reference, the sum of all so-called QED corrections, included in $\Delta(1, 0, 1/2)$ of the 1S ground state in H and D amount to 8171 663.8 ± 2.5 kHz and 8176 795.7 ± 2.3 kHz, respectively. The dominant uncertainties arise from the two-loop corrections [16], and they are responsible for almost all of the uncertainties of the $\Delta(n, \ell, j)$. The hyperfine splittings of the 1S and 2S states have been measured very accurately [19–21].

All constants except $R_\infty$ and the radii $r_N$ in equations (8)–(12) are known with sufficient accuracy [3] from measurements other than H or D spectroscopy. This leaves $R_\infty$ and $r_N$ to be determined from H or D spectroscopy. Note that we will later only be concerned with transition frequencies between different energy levels, so the Planck constant $\hbar$ on the left hand side of equation (8) drops out.

The Rydberg constant $R_\infty$ appears in equation (8) explicitly only for the 1S (Bohr) term. This is to emphasize that the full accuracy of $\sim 10^{-12}$ is required only for the Bohr term, because only the measurements of optical transitions between levels with different principal quantum number $n$ are accurate on the $10^{-12}$ level or better, see table 3. These measurements achieve accuracies in the kHz range or better, for transitions frequencies of a several hundred THz.
Table 4. Proton charge radii from hydrogen. The row labeled ‘CODATA Adjustment 8’ is the value using all hydrogen data, listed in [3], table XXXVIII. Also given are the radii from combining the 2S → nℓ transitions in H with either 1S → 2S or 1S → 3S. All values agree very well. ‘avg’ denotes the average of all values in the rows above, also considering correlations.

| #  | Transition(s) | \( r_p \) (fm) |
|----|---------------|----------------|
| H1 | 2S → 2P₁/₂     | 0.9270 ± 0.0553 |
| H2 | 2S → 2P₃/₂     | 0.8788 ± 0.0262 |
| H3 | 2S → 2P₅/₂     | 0.8688 ± 0.0354 |
| H10 + H4 | 1S → 2S + 2S → 8S₁/₂ | 0.8666 ± 0.0211 |
| H10 + H5 | 1S → 2S + 2S → 8D₁/₂ | 0.8789 ± 0.0204 |
| H10 + H6 | 1S → 2S + 2S → 8D₃/₂ | 0.8911 ± 0.0155 |
| H10 + H7 | 1S → 2S + 2S → 12D₅/₂ | 0.8551 ± 0.0222 |
| H10 + H8 | 1S → 2S + 2S → 12D₇/₂ | 0.8641 ± 0.0164 |
| IS → 2S (H10) + all H(2S → nℓ) | 0.8747 ± 0.0091 Avg. |
| IS → 3S (H13 + H14) + all H(2S → nℓ) | 0.8780 ± 0.0108 |
| CODATA Adj. 8 | 0.8764 ± 0.0089 Equation (19) |

3.1. Radio-frequency measurements within \( n = 2 \)

The first block in table 3, items H1–H3, are radio-frequency measurements of 2S → 2P transition frequencies in H. Modifying the measured frequencies by \( \Delta(2S₁/₂) − \Delta(2P_j) \) from table 1, each of these three measurements can be used individually to determine a value of the proton charge radius \( r_p \) from equation (11)

\[
\tilde{\nu}(2S₁/₂ → 2P₁/₂) = \frac{1}{8} E_{NS}. \tag{16}
\]

Each of these three measurements H1–H3 thus yields, a value of \( r_p \), listed in table 4.

As explained above, these three \( r_p \) values are in fact independent of the exact value of the Rydberg constant: the relative uncertainties of the radio-frequency measurements are on the order of \( 10^{-8} \), so only the 6 most significant digits of \( R_\infty \) enter the calculation. The ‘proton radius puzzle’ could ultimately require a change of \( R_\infty \) by 7σ, or \( 10^{-11} \), as explained below. But such a change would not affect the \( r_p \) values obtained from items H1–H3.

3.2. Optical measurements between levels with different \( n \)

The 2nd block in table 3, items H4–H8, lists the five most accurate measurements of transition frequencies between the metastable 2S state and higher-\( n \) ‘Rydberg’ states with \( n = 8 \) or 12. Because these transitions are between levels with different principal quantum number \( n \), one has to combine each of these measurements with a 2nd measurement to obtain a pair of values for \( r_p \) and \( R_\infty \), using equation (8). Ideally, one combines each of the items H4–H8 with a measurement of the 1S → 2S transition from block 3 in table 3, solving pairs of equations like

\[
\tilde{\nu}(1S → 2S) = \frac{3}{4} cR_\infty - \frac{7}{8} E_{NS} \tag{17}
\]

\[
\tilde{\nu}(2S → 8S) = \frac{15}{64} cR_\infty - \frac{63}{512} E_{NS}. \tag{18}
\]

Considering the uncertainties of the experimental values in table 3 and of the \( \Delta(n, ℓ, j) \) in table 1 one sees immediately, that the dominant uncertainty is always given by the 2S → nℓ measurements with their experimental uncertainty of the order of \( \sim 7 \) kHz. Several measurements of the 1S → 2S transition exist with uncertainties of much less than 1 kHz. Hence one can choose any of the items H9–H12 to reach the same conclusion.

We choose the 2004 measurement [33] H10 with an uncertainty of 0.034 kHz, which was also used in CODATA-2010. The results are summarized in table 4.

A trivial weighted average of all individual \( r_p \) values in table 4 yields \( r_p \) from H spectroscopy alone, of \( r_p(H) = 0.8746 ± 0.0076 \) fm, 4.4σ larger than the \( \mu p \) value. This number is in good agreement with a recent evaluation [18], which finds a 0.035(7) fm, or 4.9σ, difference between H and \( \mu p \).

However, relevant correlations exist between the various measurements of block 2, see [3], table XIX. These correlations increase the uncertainty of the derived \( r_p(H) = 0.8747(91) \) fm.

Technically, also the 2nd (finite size) and 3rd (\( \Delta(n, ℓ,j) \)) terms contain the Rydberg constant, acting as a ‘unit converter’ between atomic units, used in the calculation of \( E_{NS} \) and \( \Delta(n, ℓ,j) \), and the SI unit of frequency, in which the measurements are done. The accuracy required in the latter terms is much lower, on the order of a few times \( 10^{-8} \). This becomes obvious from kHz-accuracy required for the \( E_{NS} \) (1100 kHz and 7100 kHz for H and D, respectively), or for the \( \Delta(1S) \) (\(-35.6 \times 10^6\) kHz). Thus, these terms do not require the full \( 10^{-12} \) accuracy in \( R_\infty \). Instead, one can calculate \( R_\infty \) with an accuracy of a few \( 10^5 \) from the definition

\[
R_\infty = \frac{\alpha^2 m_e c}{2\hbar}, \tag{13}
\]

and the values of \( \alpha, m_e \) and \( h \) from measurements other than spectroscopy of H or D [22–26].

The CODATA-2010 report lists 24 transition frequencies in H and D that enter the LSA, see [3], table XI. We reproduce the most relevant numbers, and a few more, in tables 3, 5 and 6. In particular, we list several measurements of the 1S → 2S transition frequency in D.

Next we introduce the modified transition frequencies

\[
\tilde{\nu}[(n, ℓ,j) → (n', ℓ',j') = v_{meas} + \Delta(n, ℓ,j) − \Delta(n', ℓ',j')] \tag{14}
\]

where all fine-, hyperfine-, and QED contributions (except for the finite size effect of 5 states) have been removed. These modified transition frequencies can then be used to extract \( r_N \) and \( R_\infty \) using

\[
\tilde{\nu}[(n, ℓ,j) → (n', ℓ',j')] = cR_\infty \frac{m_{red}}{m_e} \frac{1}{n^2} - \frac{1}{n'^2} - E_{NS} \left( \frac{\nu_{0}}{n^3} - \frac{\delta_{0}}{n'^3} \right), \tag{15}
\]

which of course follows from equation (8).

3. Proton radius from hydrogen spectroscopy

Table 3 lists 14 transition frequencies in atomic hydrogen. These can be separated in three blocks.
Table 5. Some recent measurements of the H–D isotope shift. An asterisk following the reference denotes items considered in the most recent CODATA-2010 report.

| #  | Transitions                  | Frequency (kHz) | Rel. unc. | Source | References |
|----|-----------------------------|-----------------|-----------|--------|------------|
| 1  | D(1S1/2 $\rightarrow$ 2S1/2) - H(1S1/2 $\rightarrow$ 2S1/2) | 670994334.64(15) | 2.2 $\times$ 10^{-10} | MPQ 1998 | [7]        |
| 2  | D(1S1/2 $\rightarrow$ 2S1/2) - H(1S1/2 $\rightarrow$ 2S1/2) | 670994334.606(15) | 2.2 $\times$ 10^{-11} | MPQ 2010 | [8]        |

Table 6. Some recent measurements in atomic deuterium. An asterisk following the reference denotes items considered in the most recent CODATA-2010 report. Items D9 and D10 are direct measurements using a CH4 stabilized He:Ne laser as a transfer oscillator, while D11 and D12 have been measured using the IS $\rightarrow$ 2S transition in hydrogen and a hydrogen maser as transfer oscillators.

| #  | (n, ℓ, j) – (n', ℓ', j') | $\nu_{\text{max}}$ (kHz) | Rel. unc. | Source | References |
|----|--------------------------|--------------------------|-----------|--------|------------|
| D4 | 2S1/2 $\rightarrow$ 8S1/2 | 770859041.245.7 (6.9) | 8.9 $\times$ 10^{-12} | LKB 1997 | [30]        |
| D5 | 2S1/2 $\rightarrow$ 8D3/2 | 770859195.701.8 (6.3) | 8.2 $\times$ 10^{-12} | LKB 1997 | [30]        |
| D6 | 2S1/2 $\rightarrow$ 8D5/2 | 770859252.849.5 (5.9) | 7.7 $\times$ 10^{-12} | LKB 1997 | [30]        |
| D7 | 2S1/2 $\rightarrow$ 12D3/2 | 799409168.038.0 (8.6) | 1.1 $\times$ 10^{-11} | LKB 1999 | [31]        |
| D8 | 2S1/2 $\rightarrow$ 12D5/2 | 799409184.966.8 (6.8) | 8.5 $\times$ 10^{-12} | LKB 1999 | [31]        |
| D9 | 1S1/2 $\rightarrow$ 2S1/2 | 2466732407.521.8 (1.5) | 6.1 $\times$ 10^{-13} | MPQ 1997 | [10]        |
| D10| 2466732407.522.88 (91) | 3.7 $\times$ 10^{-13} | MPQ 1997 | [10] |
| D11| 2466732407.521.74 (20) | 7.9 $\times$ 10^{-14} | MPQ 1998/2000 | H9 + H11 |
| D12| 2466732407.521.641(25) | 1.0 $\times$ 10^{-14} | MPQ 2010/2011 | H11 + H12 |

Alternatively, one can, instead of the 1S $\rightarrow$ 2S transition (H10) combine the 1S $\rightarrow$ 3S transitions (H13 and H14) with all 2S $\rightarrow$ nℓ transitions. This yields (including correlations) $r_p(\text{H}) = 0.8780(108)$ fm, in very good agreement with the value above, and only slightly less accurate.

A reliable value for the proton rms charge radius deduced from H data alone, which takes into account all data in H listed in table XI of [3], as well as the correlations between all input parameters, is given in Adjustment 8 of the CODATA-2010 LSA, see [3], table XXXVIII.

$$r_p(\text{H spectroscopy}) = 0.8764(89) \text{ fm.} \quad (19)$$

This value is 4.0σ larger than the value from muonic hydrogen, see figure 1.

Considering elastic electron–proton (e–p) scattering data together with H spectroscopy, as done in Adjustment 9 of the CODATA-2010 LSA, yields $r_p(\text{H and e–p}) = 0.8796(56)$ fm, which is 6.9σ larger than the μp value. This is the ‘proton radius puzzle’ between measurements with electrons and muonic hydrogen.

4. Deuteron radius from deuterium spectroscopy alone

The principle of determining the deuteron radius from deuterium spectroscopy is exactly analogous to the one described for hydrogen above. However, not all measurements were done for deuterium. Table 6 lists the relevant deuterium data.

First, we note that there are no radio-frequency measurements of 2S $\rightarrow$ 2P transitions (i.e. no ‘block 1’). Thus there are no ‘Rydberg-free’ $r_q$ values such as the $r_p$ values H1–H3.

Moreover, no measurement of the 1S $\rightarrow$ 2S transition in ‘deuteron only’ is listed in the CODATA list of measurements, see [3], table XI. Only the 1S $\rightarrow$ 2S isotope shift, i.e. the difference of the 1S $\rightarrow$ 2S transition in D and H, is listed there. We give the two most recent values of the H/D isotope in table 5.

This apparent lack of a precise measurement of the 1S $\rightarrow$ 2S transition in D seems to make it impossible to apply the procedure outlined above for hydrogen, in which pairs of ($R_\infty$, $r_q$) obtained by combining 1S $\rightarrow$ 2S and 2S $\rightarrow$ nℓ measurements. CODATA instead performs their Adjustment 10 of all ‘deuteron only’ measurements using only 2S $\rightarrow$ nℓ measurements (plus some much less accurate differences of 2S $\rightarrow$ 4S/D and 1/4 of the 1S $\rightarrow$ 2S transition [38], which we omit here for brevity).

Any frequency measurement is nothing more than a frequency comparison. The so-called ‘absolute frequency measurements’ are characterized by a comparison to a Cs clock [39]. Technically, all these comparisons between H and Cs involve intermediate comparisons with ‘transfer oscillators’.

For example, items I1, D9 and D10 used a CH4 stabilized HeNe laser, which was then transported to the German Standards Institute PTB for comparison with a Cs clock. In between, a plethora of local oscillators were used in two ‘frequency chains’ [10]. More recently, items H9–H12 used a hydrogen maser as a transfer oscillator. This maser was then compared to a Cs fountain clock [39].

The isotope shift measurement I2 is a frequency comparison between D(1S $\rightarrow$ 2S) and the same hydrogen maser,
Table 7. Deuteron charge radii from deuterium. The value labeled ‘equation (20)’ is our result. It is the average of the individual values above it, taking into account the known correlations between the $2S \rightarrow nl'$ measurements. The next two values use items D9 and D10, which have not been measured using atomic hydrogen as a transfer oscillator (see text).

| # | Transitions | $r_d$ (fm) |
|---|-------------|------------|
| D12 + D4 | $1S \rightarrow 2S \rightarrow 8S_{1/2}$ | 2.1451 ± 0.0068 |
| D12 + D5 | $1S \rightarrow 2S \rightarrow 8D_{3/2}$ | 2.1435 ± 0.0064 |
| D12 + D6 | $1S \rightarrow 2S \rightarrow 8D_{3/2}$ | 2.1465 ± 0.0059 |
| D12 + D7 | $1S \rightarrow 2S \rightarrow 12D_{3/2}$ | 2.1385 ± 0.0081 |
| D12 + D8 | $1S \rightarrow 2S \rightarrow 12D_{3/2}$ | 2.1358 ± 0.0064 |
| D12 + all D(2S $\rightarrow nl'$) | 2.1415 ± 0.0045 | Equation (20) |
| D9 + all D(2S $\rightarrow nl'$) | 2.1414 ± 0.0045 |
| D10 + all D(2S $\rightarrow nl'$) | 2.1411 ± 0.0045 |

using GPS calibration. The maser was then compared to the hydrogen $1S \rightarrow 2S$ transition. The practical reason to use hydrogen as an intermediate transfer oscillator to the Cs SI clock was that it did not require the availability of a primary Cs frequency standard at MPQ.

Thus, we combine items H9 and I1, and H11 and I2, to obtain two values for the $D(1S \rightarrow 2S)$ transition frequency, D11 and D12. This avoids double-counting, because item H10 has been used above to determine the proton radius. For simplicity, we add the uncertainties linearly, although a more rigorous evaluation of the combined uncertainty, including all correlations, would certainly yield a smaller uncertainty of the $D(1S \rightarrow 2S)$ transition frequency.

If one wishes, one could also use the values D9 or D10 which can be found in the PhD thesis of Th. Udem [10]. These values are ‘absolute’ frequency measurements without the use of hydrogen as a transfer oscillator.

All of the four values D9...D12 are sufficiently accurate to proceed with the determination of $r_d$ values from combining $1S \rightarrow 2S$ and $2S \rightarrow nl'$ for $n = 8,12$, see table 7.

The trivial weighted average of the values in table 7 is $r_d = 2.1422(30)$ fm, i.e. 5.3σ larger than the µd value. Again, however, correlations between the $2S \rightarrow nl'$ measurements increase the uncertainty. Taking into account these correlations we obtain

$$r_d(\text{D spectroscopy}) = 2.1415(45) \text{ fm}. \quad (20)$$

This value is 3.5σ larger than the new value from muonic deuterium.

For comparison, using instead of D12, the $1S \rightarrow 2S$ measurements D9 or D10, yields $r_d = 2.1414(45)$ fm and $r_d = 2.1411(45)$ fm, respectively, including the correlations. The agreement of these three values shows that it is not important which of the available D($1S \rightarrow 2S$) measurements is chosen (see table 7).

Moreover, this ‘D spectroscopy’ value is in excellent agreement with the global CODATA value from Adjustment 3, $r_d = 2.1424 \pm 0.0021$ fm. This is a strong indication for the internal consistency of CODATA LSA. This agreement is also evident in the agreement of the Rydberg constants from

4 See [3], table XIX.

H spectroscopy on the one hand, and D spectroscopy on the other. This is further discussed in section 6.

We emphasize again that this 3.5σ discrepancy between muonic and electronic deuterium spectroscopy measurements is as independent as possible of any measurement used in the proton charge radius determination. Correlations may exist because of unidentified systematic shifts in any of the electronic or muonic measurements, or missing or wrong theory contributions in electronic or muonic atoms. In the absence of any indication for such an unknown correlation, the new µd measurement [6] constitutes an independent discrepancy.

5. The deuteron structure radius

In the preceding sections we were concerned with hidden or implicit correlations between the (CODATA) values of $r_p$ and $r_d$, which originate from the nature of performing a least-squares adjustment using all available input data in H and D. Here, we could provide values of $r_p$ and $r_d$ which are as uncorrelated as possible by separating the analysis of H and D data.

Physics, on the other hand, is also the source of an explicit correlation between $r_p$ and $r_d$, simply because the deuteron contains a proton. The deuteron charge radius is related to the proton charge radius by [9, 40]

$$r_d^2 = r_{\text{struct}}^2 + r_p^2 + r_n^2 + \frac{3\hbar^2}{4mc^2}, \quad (21)$$

where $r_{\text{struct}} = 1.97507(78)$ fm [9] is the deuteron structure radius, i.e. the proton-neutron separation, $r_n$ is the neutron mean square charge radius ($r_n^2 = -0.114(3)$ fm [41, 42], and the rightmost term is the Darwin–Foldy correction of 0.0331 fm² due to the zitterbewegung of the proton, see [9] and also the appendix of [43].

The 0.8% smaller deuteron charge radius from muonic deuterium in equation (3) is very consistent with the 4% smaller proton radius from muonic deuterium equation (1), inserted in equation (21). This is the reason why the new $r_d(\mu \text{d})$ is understood to confirm the smaller proton radius from muonic hydrogen [6].

6. The Rydberg constant

The correlation coefficient of the proton radius $r_p$ and the Rydberg constant $R_\infty$ is as large as 0.989 in the CODATA LSA. Therefore, a change of $r_p$ by ±σ will normally result in a change of $R_\infty$ by almost the same ±σ. This can be understood by considering equation (8), and the accuracy of the measurements in H listed in table 3:

The accuracy of each of the $2S \rightarrow nl'$ transitions ($n = 8,12$), which determine the accuracy of $R_\infty$, is about 1 part in 10^11. As a consequence, the uncertainty of the Rydberg constant in CODATA-2010 is about 6 parts in 10^12. The $1S \rightarrow 2S$ transition, on the other hand, has been measured with an uncertainty of 4 parts in 10^15, i.e. a factor of 1000 more accurately.

A look at equation (17) reveals the correlation: the left side is measured with an accuracy of 0.010 kHz. The 1st term on
The right side is known only to \( \sim 10 \text{kHz} \) (3/4 of the 17 kHz uncertainty of the CODATA value of \( cR_e \)) [3].

Adopting the muonic values of \( r_p \) and \( r_d \) in \( E_{\text{NS}} \) will thus shift the central value of \( E_{\text{NS}} \), which must immediately be compensated by a corresponding change in \( R_\infty \) because of the 1000-fold more precisely determined left side of equation (17). At the same time, the smaller uncertainty of the muonic charge radii will yield more accurate values of \( R_\infty \), when combined with the electronic 1S \( \rightarrow \) 2S transitions:

\[
R_\infty [H(1S \rightarrow 2S); r_p(\mu p)] = 3.289 \, 841 \, 960 \, 249(3) \times 10^{12} \text{kHz c}^{-1}
\]

from electronic and muonic hydrogen [2], and

\[
R_\infty [D(1S \rightarrow 2S); r_\mu (\mu d)] = 3.289 \, 841 \, 960 \, 234(6) \times 10^{12} \text{kHz c}^{-1}
\]

from electronic and muonic deuterium [6].

The value in equation (22) is in good agreement with the one from CODATA Adjustment 11,

\[
R_\infty (\text{Adjustment 11}) = 3.289 \, 841 \, 960 \, 255(4) \times 10^{12} \text{kHz c}^{-1}
\]

see table XXXVIII of [3], which includes \( r_p \) from muonic hydrogen in the global LSA. Because of its tiny uncertainty, the muonic \( r_p \) value dominates Adjustment 11, yielding \( r_p \) (Adjustment 11) = 0.84225(65) fm, and this change of \( r_p \) is accompanied by a change of \( R_\infty \), as described above.

For reference, the CODATA recommended value of the Rydberg constant is

\[
R_\infty (\text{CODATA} - 2010) = 3.289 \, 841 \, 960 \, 364(17) \times 10^{12} \text{kHz c}^{-1}
\]

which is 7\( \sigma \) larger.

For completeness, the values of the Rydberg constant from hydrogen data alone, taken from CODATA Adjustment 8, is

\[
R_\infty (\text{H spectroscopy}) = 3.289 \, 841 \, 960 \, 361(28) \times 10^{12} \text{kHz c}^{-1}.
\]

The one we deduce from deuterium data alone, including the 1S \( \rightarrow \) 2S transition is

\[
R_\infty (D \text{ spectroscopy}) = 3.289 \, 841 \, 960 \, 357(35) \times 10^{12} \text{kHz c}^{-1}.
\]

A measurement of transition frequencies between high-lying circular Rydberg states of atomic H, with \( n = 27...30 \), circular Rydberg states of atomic hydrogen [45], equation (28).

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Rydberg constant from CODATA-2010 [3], equation (25) and CODATA-2014 [44], from spectroscopy of regular H and D, equations (26) and (27), respectively, and from combining the muonic charge radius of the proton and the deuteron and the measurement of the 1S \( \rightarrow \) 2S transition in H and D, equations (22) and (23), respectively. Also shown is the result from spectroscopy of high-lying \( n = 27...30 \) circular Rydberg states of atomic hydrogen [45], equation (28).

This result is unfortunately not accurate enough to discriminate the muonic and the ‘purely electronic’ values, see figure 3.

New insight into the ‘proton radius puzzle’ is expected from several new atomic physics measurements: the 2S \( \rightarrow \) 4P transitions in H [46, 47] will yield an independent value of the Rydberg constant. A new measurement of the classical Lamb shift in H [48] will yield a proton charge radius that is independent of the exact value \( R_\infty \), see section 3.1. Improved measurements of the 1S \( \rightarrow \) 3S transition in H are underway at MPQ and LKB [49, 50]. Measurements of the 1S-2S transition in H-like He\(^+\) ions [51–53] will, when combined with a new value of the alpha particle charge radius from muonic helium spectroscopy [54], yield a Rydberg constant or test higher-order QED contributions. The Rydberg constant can also be determined from high-precision spectroscopy of molecules and molecular ions of hydrogen isotopes [55–59], combined with improved calculations [60]. One-electron ions in circular Rydberg states [61, 62] will also yield a Rydberg constant free from nuclear radius effects.

As a final remark, we may attribute the small 2.2\( \sigma \) difference between the two Rydberg values using the muonic radii (equations (22) and (23)) to the deuteron polarizability contribution [63–67], summarized in [6].

7. **Conclusions**

The most accurate value of the deuteron rms charge radius from laser spectroscopy of regular (electronic) deuterium...
only is \( r_D = 2.1415(45) \) fm. It is obtained using a value for the \( 1S \rightarrow 2S \) transition in atomic deuterium which can be inferred from published data [8, 34], or found in a PhD thesis [10]. Our value is in excellent agreement with the CODATA value [3], and only twice less accurate.

In contrast to the CODATA value, the deuteron radius above is as uncorrelated as possible to measurements that determine the proton rms charge radius \( r_p \). The CODATA Adjustment 10, which is also independent of \( r_p \), is five times less accurate than the value above, because of a more conservative treatment of the deuterium \( 1S \rightarrow 2S \) measurements.

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Note added. After the submission of this manuscript, the updated CODATA-2014 paper was published [44]. The numbering of the partial Adjustments remained the same. What was table XXXVIII in CODATA-10 is now table XXIX on page 54 of CODATA-14.

The partial Adjustments 8 (H spectroscopy) and 10 (D spectroscopy) yield identical values compared to CODATA-10, our equations (6) and (7), respectively. The only new input data is our item H12, the 2013 measurement of the \( 1S \rightarrow 2S \) transition from MPQ.

The change of the recommended values of \( r_p, r_D \), and \( R_\infty \) from the full Adjustment 3) is exclusively from a reassessment of the uncertainty of the electron scattering data [68]. None of the conclusions of the present manuscript are changed.

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