

Nonresonant effects in precision atomic spectroscopy

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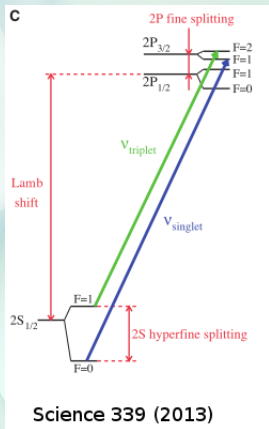
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Prerequisites: hydrogen and muonic hydrogen spectroscopy

Muonic hydrogen

The size of the proton, Nature 466, 213-216 (2010)



The measured transition frequencies

$$\nu_s = 54611.16(1.00)^{\text{stat}}(30)^{\text{sys}} \text{ GHz},$$

$$\nu_t = 49881.35(57)^{\text{stat}}(30)^{\text{sys}} \text{ GHz},$$

$$\begin{aligned} \frac{1}{4}h\nu_s + \frac{3}{4}h\nu_t &= \Delta E_L + 8.8123(2) \text{ meV}, \\ h\nu_s - h\nu_t &= \Delta E_{HFS} - 3.2480(2) \text{ meV} \end{aligned}$$

The numerical terms include: the $2p$ fine structure, the $2p_{3/2}$ hyperfine splitting, and the mixing of the $2p$ states

$$\Delta E_L^{\text{exp}} = 202.3706(23) \text{ meV}, \Delta E_{HFS}^{\text{exp}} = 22.8089(51) \text{ meV}:$$

$$\Delta E_L^{\text{exp}} \approx 206.0336(15) - 5.2275(10)r_E^2,$$

$$\Delta E_{HFS}^{\text{exp}} \approx 22.9763(15) - 0.1621(10)r_Z.$$

$$r_E = 0.84087(39) \text{ fm},$$

$$r_Z = 1.082(37) \text{ fm}.$$

Sustainable value since 2010

Prerequisites: hydrogen and muonic hydrogen spectroscopy

Hydrogen

Theoretical evaluation of hydrogen energies is performed according to the formula

$$E_{nlj} = R_{\infty} \left(-\frac{1}{n^2} + f_{nlj} \left(\alpha, \frac{m_e}{m_p}, r_p \dots \right) \right). \quad (1)$$

$R_{\infty} = m_e \alpha^2 c / 2h$ is the Rydberg constant and $r_p = r_E$ - proton charge radius, f_{nlj} includes all necessary corrections.

Assuming all others are known, the energy depends on two parameters R_{∞}, r_E
 \Rightarrow at least two transition frequencies such that

$$h\nu^{exp} = E_{nlj} - E_{n'l'j'}$$

Most accurately measured frequencies: 1s-2s and 1s-3s - the correction for finite nuclear size
Two-photon absorption transition frequencies: 2s-ns/nd - Rydberg constant

Until 2017, from experiments on hydrogen
proton charge radius $r_p = 0.8759(77)$ fm
Rydberg constant $R_{\infty} = 10973731.568508(65)$ m⁻¹.

CODATA: P. J. Mohr, D. B. Newell, and B. N. Taylor, J. Phys. Chem. Ref. Data 45, 043102 (2016)

The role of line profile asymmetry in precision spectroscopy

The theory was established as early as 2002:
U.D. Jentschura and P.J. Mohr Can. J. Phys. 80, 633-644 (2002)

$$\frac{C}{x^2 + \Gamma^2/4} \rightarrow \frac{C}{x^2 + \Gamma^2/4} + ax + \frac{bx}{x^2 + \Gamma^2/4} \approx \frac{C}{[x - \Delta(x)]^2 + \Gamma^2/4} \quad (2)$$

2s – 4p transition in hydrogen

Line profile asymmetry was observed and taken into account - Science 358, 79 (2017)

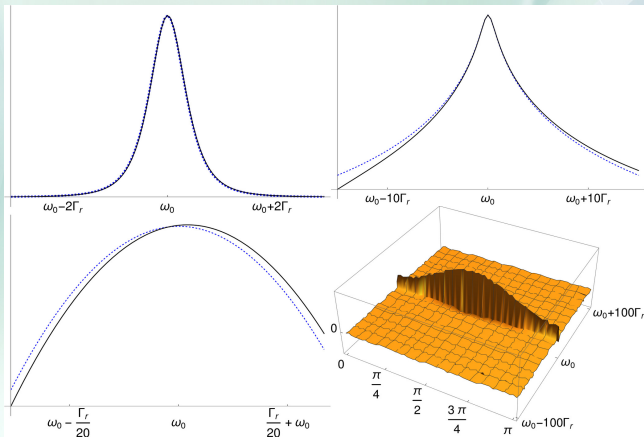
- The theory predicts the asymmetry of the observed line profile (2)
- The process of photon scattering should be examined more carefully
⇒ beyond the resonance approximation
- The differential cross section of one-photon scattering gives at low order the Fano profile
- The asymmetry depends on the angle between the incident and emitted photons
- Using profile symmetrization the "line center" was more neatly determined ("magic angle")
-

$$R_\infty = 10973731.568076(96) \text{ m}^{-1}, r_p = 0.8335(95) \text{ fm}. \quad (3)$$

- "Proton radius puzzle" is almost solved
- Phys. Rev. Lett. 128, 023001 (2022): $r_p = 0.8584(51) \text{ fm}$, $R_\infty = 10973731.568332(52) \text{ m}^{-1}$

Qualitative description of NR effects in hydrogen

The effect of line profile asymmetry can be schematically illustrated as



Spectral line profile asymmetry and NR effects: amplitude and Lorentz profile

- One-photon scattering amplitude of a photon on an atom

$$U_{\bar{f}i}^{(2)} = e^2 \left[\sum_n \frac{(\alpha \mathbf{A}_{k_2, e_2}^*)_{\bar{f}n} (\alpha \mathbf{A}_{k_1, e_1})_{ni}}{E_n(1 - i0) - E_i - \omega_1} + \sum_n \frac{(\alpha \mathbf{A}_{k_1, e_1})_{\bar{f}n} (\alpha \mathbf{A}_{k_2, e_2}^*)_{ni}}{E_n(1 - i0) - E_f + \omega_1} \right]. \quad (4)$$

$\alpha \mathbf{A}_{k, e}$ and $\alpha \mathbf{A}_{k, e}^*$ - photon absorption and emission operators $\Rightarrow (\mathbf{ep})e^{ikr}$

- QED derivation of the Lorentz profile for the atomic spectral line (the regularisation is performed according to F. Low, Phys. Rev. 88, 53 (1952))

$$U_{ba}^{\text{em}} = \frac{\langle b | \alpha \mathbf{A}_{k_2, e_2}^* | a \rangle}{E_b - E_a - \omega + \langle b | \hat{\Sigma}(E_a + \omega) | b \rangle}, \quad (5)$$

imaginary part $\Im \langle b | \hat{\Sigma}(E_b) | b \rangle = -\Gamma_b/2$, the real contributions in E_b and E_a .

- Then the standard expression for the Lorentz profile is:

$$\phi_L(\omega) d\omega = \frac{1}{\aleph} \sum_e \int \frac{\omega d\omega d\mathbf{n}_k}{(2\pi)^3} |U_{ba}^{\text{em}}|^2 = \frac{1}{\aleph} \frac{W_{ba} d\omega}{(\omega_0 - \omega)^2 + \frac{1}{4} \Gamma_b^2}, \quad (6)$$

$$W_{ba} = \frac{4}{3} e^2 \omega_0 |\langle b | \mathbf{p} | a \rangle|^2, \quad \Gamma_b = \sum_{a < b} W_{ba}. \quad (7)$$

Spectral line profile asymmetry and NR effects

Lorentz profile - resonant line contour, frequency distribution

- A careful calculation of $\Im\langle b|\hat{\Sigma}(E_b)|b\rangle = -\Gamma_b/2$, see L. Labzowsky, G. Klimchitskaya, Yu. Dmitriev book 1993, leads to the expression:

$$\Gamma_b(\omega) = -2e^2 \sum_{E_n < E_b} \langle bn| \frac{1 - \alpha_1 \alpha_2}{r_{12}} \sin((E_b - E_n + \omega)r_{12}) |nb\rangle. \quad (8)$$

- The natural level width is represented as:

$$\Gamma_b(\omega) = \Gamma'_b(\omega) + \Gamma''_b(\omega) = 2e^2 \omega \left[\omega_0^2 - \frac{1}{3} \omega^2 \right] |\langle b|r|a\rangle|^2 = \frac{3}{2} \frac{\omega}{\omega_0} \left(1 - \frac{1}{3} \frac{\omega^2}{\omega_0^2} \right) \Gamma_b^{(0)}. \quad (9)$$

Consistent with PRL 108, 043005 (2012); $\Gamma_b^{(0)} = \frac{4}{3} \omega_0^3 |\langle b|r|a\rangle|^2$ at the resonance point.

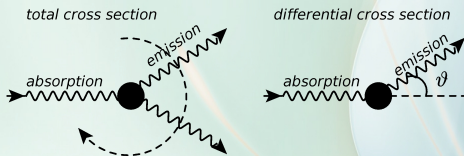
- The extended Lorentz profile:

$$\phi_E(x) = \frac{1}{\pi} \frac{x \Gamma_{ba}^{(0)}}{\omega_0^2 (x-1)^2 + \frac{9}{16} x^2 \left(1 - \frac{1}{3} x^2 \right)^2 \left(\Gamma_b^{(0)} \right)^2}, \quad x = \omega/\omega_0. \quad (10)$$

Differential and total cross sections

Total cross section when the squared amplitude is integrated over all angles
 Differential cross section: the dependence on the angle between the incident and emitted photons

$$d\sigma_{fi}(\omega) \sim \left| \frac{(\alpha A_{k_2, e_2}^*)_{fa} (\alpha A_{k_1, e_1})_{ai}}{E_a - E_i - \omega - \frac{i}{2}\Gamma_a} + \sum_{n \neq a} \frac{(\alpha A_{k_2, e_2}^*)_{fn} (\alpha A_{k_1, e_1})_{ni}}{E_n - E_i - \omega} + \sum_n \frac{(\alpha A_{k_1, e_1})_{fn} (\alpha A_{k_2, e_2}^*)_{ni}}{E_n - E_f + \omega} \right|^2.$$



The shift of the resonant frequency can be determined from the extremum condition:

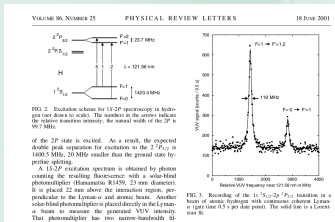
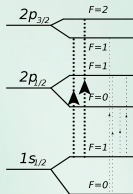
$$d\sigma_{fi}(\omega) = d\sigma_{fi}^{(0)}(\omega) + d\sigma_{fi}^{(1)}(\omega). \quad (12)$$

$$\frac{d(d\sigma_{fi}(\omega))}{d\omega} = 0 \quad \Rightarrow \quad \omega = \omega_0 + \delta_{NR} \quad (\omega_0 = E_a - E_i). \quad (13)$$

NR effects for the total cross section: Ly $_{\alpha}$ line

The transition frequency Ly $_{\alpha}$, 2466060015.04 MHz, is determined with accuracy of ~ 0.5 MHz.

Nonresonant correction for hyperfine structure



$$\phi_{\text{HFS}}(\omega) \approx \frac{f(F, F')}{(\omega - \omega_0)^2 + \frac{1}{4}\Gamma_{2p}^2} + \frac{f(F, F'')}{(\omega - \omega_0 - \Delta_{\text{HFS}})^2 + \frac{1}{4}\Gamma_{2p}^2} + 2\Re \frac{g(F, F', F'')}{(\omega - \omega_0 - \frac{1}{2}\Gamma_{2p})(\omega - \omega_0 - \Delta_{\text{HFS}} - \frac{1}{2}\Gamma_{2p})}$$

$f(1, 2) : f(1, 1) : g(1, 2, 1) = 181 : 1 : 0.307$. The asymmetry due to the interference term $0.307/181 \approx 0.17\%$:

$$\delta_{\text{NR}}^{E(2p_{3/2}) - E(1s_{1/2}, F=1)} \approx 0.0017\Gamma_{2p} \approx 0.17 \text{ MHz.}$$

Other calculated NR corrections to the total cross section are negligible

U.D. Jentschura and P.J. Mohr *Can. J. Phys.* 80, 633-644 (2002) - at MHz level for differential cross section

NR corrections to $1s - 2s$ transition frequency

The $1s - 2s$ transition frequency is the most accurately determined in hydrogen, with an experimental error of ~ 10 Hz at present, 10^{-15} relative value
NR corrections to the $1s - 2s$ transition frequency: spontaneous and in an external electric field decays

NR correction can be estimated as $|\delta| = \frac{\Gamma_{2s,2\gamma}^2}{\Delta E} \sim \frac{[m\alpha^2(\alpha Z)^6]^2}{m(\alpha Z)^2} = m\alpha^4(\alpha Z)^{10} \sim 10^{-14}$ Hz.

For a weak electric field, the Stark (mixing) parameter is $\xi_S = \langle 2s | d\mathcal{E} | 2p \rangle / \Delta E_L \ll 1$:

$|\delta| = \frac{\Gamma_{\text{exp}}^2}{\Delta E_L} \sim 10^{-3}$ Hz.

For the differential scattering cross section one can find

$$|\delta| = \frac{1}{2} \left(\frac{\Gamma_{2p',2\gamma} \Gamma_{2p,1\gamma}}{\Gamma_{2s,2\gamma} \Gamma_{\text{exp}}} \right)^{\frac{1}{2}} \frac{\Gamma_{\text{exp}}^2}{\Delta E_L} \sim 10^{-2} \text{ Hz.} \quad (15)$$

The absorption and emission regions are spatially separated in the experiment
Fradkin E.S., Gitman D.M., Shvartsman Sh.M. *Quantum electrodynamics with unstable vacuum*, 1991

The experimental situation is very successful

The quantum interference effect (QIE)

Differential scattering cross section: two close resonances

NR correction was derived by Jentschura U.D., Mohr P.J., Can. J. Phys. 80, 633 (2002) (fine structure):

$$d\sigma \sim \frac{C}{x^2 + \frac{\Gamma_a^2}{4}} + ax + \frac{xb}{x^2 + \frac{\Gamma_a^2}{4}} = \frac{C}{[x - \Delta(x)]^2 + \frac{\Gamma_a^2}{4}}, \quad (16)$$

$$\Delta(x) = \frac{a}{2C} \left(x^2 + \frac{\Gamma_a^2}{4}\right)^2 + \frac{b}{2C} \left(x^2 + \frac{\Gamma_a^2}{4}\right) \quad \text{Fano profile} \quad (17)$$

Then the frequency shift ($x = \omega_0 - \omega$, $a \sim 1/\Delta_{\text{fs}}^3$, $b \sim 1/\Delta_{\text{fs}}$)

$$\Delta\left(\frac{\Gamma_a}{2}\right) = \frac{a\Gamma_a^4}{8C} + \frac{b\Gamma_a^2}{4C}, \quad (18)$$

$$\Delta(0) = \frac{a\Gamma_a^4}{32C} + \frac{b\Gamma_a^2}{8C} \quad (19)$$

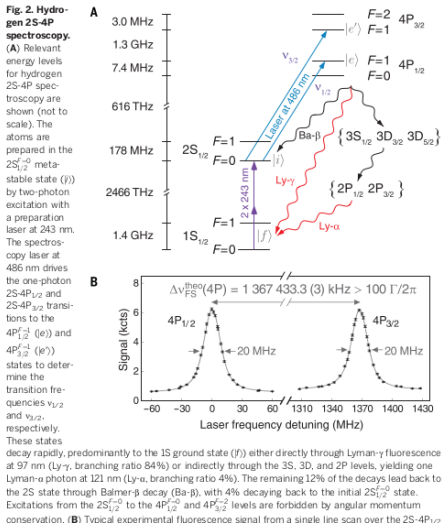
The result was used in the experiment Science 358, 79 (2017): "line center" determination.

$$\delta_{\text{NR}} = \frac{f_{\text{fi}}^{(1\gamma)}(a, a')}{f_{\text{fi}}^{(1\gamma)}(a, a)} \frac{\Gamma_a^2}{4\Delta_{\text{fs}}} - \frac{\left(f_{\text{fi}}^{(1\gamma)}(a, a')\right)^2 \left(2f_{\text{fi}}^{(1\gamma)}(a, a) + f_{\text{fi}}^{(1\gamma)}(a, a')\right)}{f_{\text{fi}}^{(1\gamma)}(a, a)^3} \frac{\Gamma_a^4}{16\Delta_{\text{fs}}^3}. \quad (20)$$

The resonant $f_{\text{fi}}^{(1\gamma)}(a, a)$ and nonresonant $f_{\text{fi}}^{(1\gamma)}(a, a')$ amplitudes determine the angular dependence (polarization and direction vectors, their combination), Δ_{fs} - fine structure interval + HFS

QIE: 2s-4p experiment

Application to hydrogen spectroscopy: 2s — 4p A. Beyer et al, Science 358, 79 (2017)



QIE: 2s-4p experiment

Application to hydrogen spectroscopy: 2s – 4p

If in the process of frequency measurement all radiation is registered (Science 2017):

$$\delta_{\text{NR}} = \frac{\sum_{n_f l_f j_f F_f} f_{\text{nr}}}{\sum_{n_f l_f j_f F_f} f_{\text{res}}} \frac{\Gamma_a^2}{4\Delta_{\text{fs}}} \sim (1 + 3 \cos 2\vartheta) \frac{\Gamma_a^2}{4\Delta_{\text{fs}}}. \quad (21)$$

Using the Fano profile, the asymmetric part was subtracted when processing the experimental data: "line center" = transition frequency $\Rightarrow 10^{-13}$ accuracy: $\nu_{1/2} = 616520152555.1(3.0)$ kHz, $\nu_{3/2} = 616521519990.8(3.0)$ kHz.

The weighted average hyperfine centroid ν_{2s-4p} corrected for hyperfine shift (Δ_{HFS} Science 2017):

$$\nu_{2s-4p} = \frac{1}{3}\nu_{1/2} + \frac{2}{3}\nu_{3/2} - \Delta_{\text{HFS}} = 616\,520\,931\,626.8 \text{ kHz}, \quad (22)$$
$$\Delta_{\text{HFS}} = 132\,552.092(75) \text{ kHz}.$$

$\Rightarrow R_\infty = 10973731.568076(96) \text{ m}^{-1}$, $r_p = 0.8335(95) \text{ fm}$ Still some questions:

- Subtraction procedure - extraction of symmetrical part at magic angle
- The absorption profile was obtained by registering the radiation
- Theory basics: the process should be considered from stable (metastable) to stable (metastable) states

QIE: 2s-4p experiment

If in the process of frequency measurement radiation to certain final state is detected:

Final state, f	$\delta_{NR}^{(2)}$ to $\nu_{1/2}$, kHz	$\delta_{NR}^{(2)}$ to $\nu_{3/2}$, kHz
$1s_{f=0}^{j=0}$	60.7127	-15.1782
$1s_{1/2}^{j=1}$	-30.3563	30.3563
$2s_{f=0}^{j=0}$	60.7127	-15.1782
$2s_{1/2}^{j=1}$	-30.3563	30.3563
$3s_{f=0}^{j=0}$	60.7127	-15.1782
$3s_{1/2}^{j=1}$	-30.3563	30.3563
$3d_{3/2}^{j=2}$	30.3563	30.3563
$3d_{5/2}^{j=2}$	6.0713	-151.7819

At fixed total atomic moment F of the final state, NR does not depend on angles \Rightarrow typical frequency shift.

The "line maximum" for $\nu_{1/2}$:

$$F_f = 0 \quad \omega_{\text{res}} = 616520152619.2 \text{ kHz}, \quad (23)$$

$$F_f = 1 \quad \omega_{\text{res}} = 616520152528.1 \text{ kHz},$$

$$F_f = 2 \quad \omega_{\text{res}} = 616520152564.6 \text{ kHz}.$$

Minus NR correction $\Rightarrow \omega_0$ can differ on few kHz (within experimental error)

- "line maximum" and "line center" can be related by the averaging procedure (ambiguity)
- measurements can be made for each specific transition (photons with a certain frequency)
- Participation of the emission process in determining the frequency of the absorption transition?

QIE in cascade emission

Participation of the emission process in determining the frequency of the absorption transition
Scattering process should be considered from (meta-)stable to (meta-)stable states
More than two photons means a more complex line profile

It can be found that the absorption frequency, determined from the extremum condition, is equal to

$$\omega_{\max} = \omega_0 + \delta\omega_r + \delta\omega_a + \delta\omega_b, \quad (24)$$

where $\delta\omega_i$ is defined by the expression:

$$\delta\omega_i = \frac{f_{nr}^{(c)}}{f_{res}^{(c)}} \frac{\Gamma_r^2}{4\Delta_i} \Upsilon, \quad \Upsilon = \frac{(\Gamma_r + \Gamma_a)^2 (\Gamma_a + \Gamma_b)^2}{(\Gamma_r + \Gamma_a)^2 (\Gamma_a + \Gamma_b)^2 + (\Gamma_r + \Gamma_a)^2 \Gamma_r^2 + (\Gamma_a + \Gamma_b)^2 \Gamma_r^2}. \quad (25)$$

Here i is one of the states labelled r, a, b (resonant, upper cascade, lower cascade).

Assuming that all outgoing photons are directed to the same detector, the NR (type 2) corrections are

$$\delta\omega_r = -\frac{1}{2} (1 - 3 \cos 2\theta) \frac{\Gamma_r^2}{4\Delta_r} \Upsilon, \quad \delta\omega_a = 0, \quad \delta\omega_b = 2 \frac{\Gamma_r^2}{4\Delta_b} \Upsilon. \quad (26)$$

Corrections reach hundreds of kHz, and, with branching ratios for cascade radiation, $W_{ra}^{(1\gamma)}/\Gamma_r$, several kHz.

Decay to the ground state is preferable!

Two-photon spectroscopy of hydrogen

Two types of experiments:

- i) the radiation corresponding to the upper cascade link is detected,
- ii) the population change of the $2s$ states is determined.

i) Cross section of two-photon absorption with subsequent one-photon emission

The cross section has the form:

$$\frac{d\sigma_{f_i}}{dn_{k_3}} = \frac{e^6}{2F_i + 1} \left[\frac{f_{f_i}^{(2\gamma)}(a, a)}{(\omega_0 - 2\omega)^2 + \frac{\Gamma_a^2}{4}} + \frac{2f_{f_i}^{(2\gamma)}(a, a')(\omega_0 - 2\omega)}{((\omega_0 - 2\omega)^2 + \frac{\Gamma_a^2}{4})(\omega_0 - 2\omega + \Delta)} \right]. \quad (27)$$

From the extremum condition:

$$\omega_{\max} = (\omega_0 - \delta_{\text{NR}})/2, \quad \delta_{\text{NR}} = \frac{\sum_f f_{f_i}^{(2\gamma)}(a, a') \Gamma_a^2}{\sum_f f_{f_i}^{(2\gamma)}(a, a) 4\Delta}. \quad (28)$$

Two-photon spectroscopy of hydrogen: $2s - ns$ frequency

$2s - ns$ ($n = 4, 6, 8, 12$) and $1s - 3s$ transition frequencies are shifted at the level of a few kHz, the shift can be nullified at a "magic angle".

Two-photon spectroscopy of hydrogen: $2s - nd$ frequency

$2s - nd$ ($n = 4, 6, 8, 12$) transition frequencies are shifted at kHz level. NR shifts consist of constant and angular dependent parts \Rightarrow asymmetry should be taken into account (cascade QIE - PRA 109, 022806 (2024) - kHz level).

Two-photon spectroscopy of hydrogen

ii) Experiments registering a decrease in the population density of the 2s state

The emission amplitude can be discarded. Then the absorption profile can be written as follows:

$$\frac{d\sigma_{ai}^{(\text{abs})}}{d\omega d\Omega_1 d\Omega_2} \sim \frac{C_a}{(2\omega - \omega_0)^2 + \frac{1}{4}\Gamma_a^2} + \frac{C_{aa'}}{(2\omega - \omega_0)^2 + \frac{1}{4}\Gamma_a^2} \frac{2(2\omega - \omega_0)}{2\omega - \omega_0 - \Delta_{\text{fs}}}. \quad (29)$$

Considering the interfering $2s_{1/2}^{F_i=1} \rightarrow nd_{3/2}^{F_a=2}$, $2s_{1/2}^{F_i=1} \rightarrow nd_{5/2}^{F_{a'}=2}$ transitions for $n = 4, 6, 8, 12$, $\Delta_{\text{fs}} = E_{nd_{3/2}^{F_a=2}} - E_{nd_{5/2}^{F_{a'}=2}}$ and denoting the level width as Γ_{nd} , the results of the calculated NR corrections are shown in Table.

State	Δ_{fs} , Hz	Γ_{nd} , Hz	δ_{NR} , Hz	Unc., Hz
4d	4.557026×10^8	4.40503×10^6	-8691.82	$24. \times 10^3$
6d	1.350231×10^8	1.33682×10^6	-2701.67	$10. \times 10^3$
8d	5.69628×10^7	5.72382×10^5	-1174.02	6.4×10^3
12d	1.68779×10^7	1.72261×10^5	-358.88	7.0×10^3

Two-photon spectroscopy of hydrogen

Rev. Mod. Phys., Vol. 93, No. 2, (2021)

TABLE X. Summary of measured transition energies $\Delta E_{i,f}(r)$ between states i and f for electronic hydrogen ($X = H$) and electronic deuterium ($X = D$) considered in input data for the determination of the Rydberg constant R_∞ . The labels for the first column are as in Table IX, to list correlation coefficients among these data and in Table XXIII for observational equations. Columns two and three give the reference and an abbreviation of the name of the laboratory in which the experiment has been performed. An overview for all observations is found at the end of this report.

Reference	Lab	Energy intervals	Reported value $\Delta E_{i,f}$ (MHz)	Ref. uncer. $\sigma_{\Delta E}$
A1	Witte et al. (1995)	MPQ $\Delta E_{(2S_{1/2}-4S_{1/2})} - [\Delta E_{(2S_{1/2}-2S_{1/2})}]$	4 7971 36(10)	2.1×10^{-8}
A2		$\Delta E_{(1S_{1/2}-4D_{3/2})} - [\Delta E_{(1S_{1/2}-2S_{1/2})}]$	6 400 144(24)	3.7×10^{-8}
A3		$\Delta E_{(2S_{1/2}-4S_{1/2})} - [\Delta E_{(2S_{1/2}-2S_{1/2})}]$	4 801 405(20)	4.2×10^{-8}
A4		$\Delta E_{(1S_{1/2}-4D_{3/2})} - [\Delta E_{(1S_{1/2}-2S_{1/2})}]$	6 404 844(11)	6.3×10^{-8}
A5	Parthey et al. (2010)	MPQ $\Delta E_{(1S_{1/2}-2S_{1/2})} - \Delta E_{(1S_{1/2}-2S_{1/2})}$	6 709 934 334 606(15)	2.2×10^{-11}
A6	Parthey et al. (2011)	MPQ $\Delta E_{(1S_{1/2}-2S_{1/2})}$	2 466 961 413 187 355(10)	4.2×10^{-11}
A7	Meyers et al. (2012)	MPQ $\Delta E_{(1S_{1/2}-2S_{1/2})}$	2 466 961 413 187 403(10)	1.4×10^{-10}
A8	Yost et al. (2016)	MPQ $\Delta E_{(1S_{1/2}-3S_{1/2})}$	2 022 142 278 656(17)	5.8×10^{-12}
A9	Beys et al. (2017)	LKB $\Delta E_{(1S_{1/2}-4P_{1/2})}$	616 520 919 626 82(3)	3.7×10^{-11}
A10	de Bouma et al. (1997)	LKB $\Delta E_{(1S_{1/2}-8S_{1/2})}$	770 649 390 012 08(4)	1.1×10^{-11}
A11		SYRTE $\Delta E_{(1S_{1/2}-8D_{3/2})}$	770 649 388 450 308(3)	1.1×10^{-11}
A12		$\Delta E_{(1S_{1/2}-8D_{3/2})}$	770 649 381 964 236(4)	8.3×10^{-11}
A13		$\Delta E_{(1S_{1/2}-8S_{1/2})}$	770 639 041 245 76(9)	8.9×10^{-12}
A14		$\Delta E_{(1S_{1/2}-8D_{3/2})}$	770 639 195 701 86(3)	8.2×10^{-12}
A15		$\Delta E_{(1S_{1/2}-8D_{3/2})}$	770 639 232 848 55(9)	7.2×10^{-11}
A16	Schroab et al. (1999)	LKB $\Delta E_{(1S_{1/2}-12D_{3/2})}$	799 150 730 472 339(4)	1.2×10^{-11}
A17		$\Delta E_{(1S_{1/2}-12D_{3/2})}$	799 150 727 403 37(3)	8.7×10^{-11}
A18		$\Delta E_{(1S_{1/2}-12D_{3/2})}$	799 409 188 038 008(4)	1.1×10^{-11}
A19		$\Delta E_{(1S_{1/2}-12D_{3/2})}$	799 409 184 966 80(8)	8.5×10^{-12}
A20	Borowitz et al. (1998)	LKB $\Delta E_{(1S_{1/2}-6S_{1/2})} - [\Delta E_{(1S_{1/2}-3S_{1/2})}]$	4 197 606(21)	4.9×10^{-8}
A21		$\Delta E_{(2S_{1/2}-6D_{3/2})} - [\Delta E_{(1S_{1/2}-3S_{1/2})}]$	4 699 596(10)	2.2×10^{-8}
A22	Arnold et al. (2010)	LKB $\Delta E_{(1S_{1/2}-3S_{1/2})}$	2 022 142 278 679(13)	4.4×10^{-12}
A23	Flueberg et al. (2018)	LKB $\Delta E_{(1S_{1/2}-3S_{1/2})}$	2 022 142 278 617 82(20)	8.9×10^{-11}
A24	Berthelend, Hinds, and Boshier (1993)	Yale $\Delta E_{(2S_{1/2}-4P_{1/2})} - [\Delta E_{(1S_{1/2}-2S_{1/2})}]$	4 064 249(15)	3.2×10^{-8}
A25		$\Delta E_{(1S_{1/2}-2P_{1/2})} - [\Delta E_{(1S_{1/2}-2S_{1/2})}]$	6 035 770(10)	1.7×10^{-8}
A26	Higley and Pipkin (1984)	Harvard $\Delta E_{(1S_{1/2}-2P_{1/2})}$	6 911 206(12)	1.2×10^{-8}
A27	Newton, Andrews, and Ussowich (1978)	Stanis $\Delta E_{(2P_{1/2}-2S_{1/2})}$	1 077 842(20)	1.9×10^{-8}
A28	London and Pipkin (1981)	Harvard $\Delta E_{(2P_{1/2}-2S_{1/2})}$	1 077 845 69(6)	8.5×10^{-8}
A29	Bergman et al. (2019)	York $\Delta E_{(2P_{1/2}-2S_{1/2})}$	1 077 820 803(2)	3.0×10^{-8}

The correlation coefficients $r(x_i; x_j)$ (x_i denotes the measured transition) among the input data for the hydrogen and deuterium energy levels are introduced in CODATA

Recommended values: $r_p = 0.8414(19)$ fm, $R_\infty = 10\,973\,731.568\,160(21)$ m⁻¹

TABLE IX. Correlation coefficients $r(x_i, x_j) > 0.0001$ among the input data for the hydrogen and deuterium energy levels given in Tables X and VIII. Coefficients r are strictly zero between input data An and Bm for positive integers n and m .

$r(A1, A2) = 0.3049$	$r(A1, A3) = 0.2595$	$r(A1, A4) = 0.0404$	$r(A2, A3) = 0.0271$	$r(A2, A4) = 0.0467$
$r(A3, A4) = 0.0110$	$r(A6, A7) = 0.7069$	$r(A10, A11) = 0.3478$	$r(A10, A12) = 0.4532$	$r(A10, A13) = 0.1225$
$r(A10, A14) = 0.1335$	$r(A10, A15) = 0.1419$	$r(A10, A16) = 0.0899$	$r(A10, A17) = 0.1206$	$r(A10, A18) = 0.0980$
$r(A10, A19) = 0.1235$	$r(A10, A20) = 0.0228$	$r(A10, A21) = 0.0448$	$r(A11, A12) = 0.4696$	$r(A11, A13) = 0.1273$
$r(A11, A14) = 0.1387$	$r(A11, A15) = 0.1475$	$r(A11, A16) = 0.0934$	$r(A11, A17) = 0.1253$	$r(A11, A18) = 0.1019$
$r(A11, A19) = 0.1284$	$r(A11, A20) = 0.0234$	$r(A11, A21) = 0.0466$	$r(A12, A13) = 0.1648$	$r(A12, A14) = 0.1795$
$r(A12, A15) = 0.1908$	$r(A12, A16) = 0.1209$	$r(A12, A17) = 0.1622$	$r(A12, A18) = 0.1319$	$r(A12, A19) = 0.1662$
$r(A12, A20) = 0.0303$	$r(A12, A21) = 0.0402$	$r(A13, A14) = 0.5699$	$r(A13, A15) = 0.0170$	$r(A13, A16) = 0.1127$
$r(A13, A17) = 0.1512$	$r(A13, A18) = 0.1229$	$r(A13, A19) = 0.1548$	$r(A13, A20) = 0.0282$	$r(A13, A21) = 0.0561$
$r(A14, A15) = 0.6667$	$r(A14, A16) = 0.1228$	$r(A14, A17) = 0.1647$	$r(A14, A18) = 0.1339$	$r(A14, A19) = 0.1687$
$r(A14, A20) = 0.0307$	$r(A14, A21) = 0.0612$	$r(A15, A16) = 0.1305$	$r(A15, A17) = 0.1750$	$r(A15, A18) = 0.1423$
$r(A15, A19) = 0.1793$	$r(A15, A20) = 0.0327$	$r(A15, A21) = 0.0650$	$r(A16, A17) = 0.4750$	$r(A16, A18) = 0.0901$
$r(A16, A19) = 0.1136$	$r(A16, A20) = 0.0207$	$r(A16, A21) = 0.0412$	$r(A17, A18) = 0.1209$	$r(A17, A19) = 0.1524$
$r(A17, A20) = 0.0278$	$r(A17, A21) = 0.0553$	$r(A18, A19) = 0.5224$	$r(A18, A20) = 0.0126$	$r(A18, A21) = 0.0449$
$r(A19, A20) = 0.0284$	$r(A19, A21) = 0.0566$	$r(A20, A21) = 0.1412$	$r(A24, A25) = 0.0834$	

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