A Critical Compilation of Experimental Data for Spectral Lines and Energy Levels of Hydrogen, Deuterium, and Tritium

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Alexander Kramida

National Institute of Standards and Technology,
Gaithersburg, Maryland, USA

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My background:

Atomic spectroscopy, plasma diagnostics, atomic databases, critical compilations of atomic spectra

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1979 - M.S.: Moscow Institute of Physics & Technology.
Lecturers: *I. Sobel’man, L. Vainshtein, V. Letokhov, L. Presnyakov*

1984 - Ph.D: Moscow Institute of Physics & Technology, P.N. Lebedev Physical Institute, Moscow.
Sci. advisor: *I. Sobel’man*

1981-2000: Institute for Spectroscopy, Troitsk, Russia.
Coworkers: *A. Ryabtsev, K. Koshelev, U. Safronova, L. Ivanov, E. Ivanova (et al.)*

2000-2003: Commercial software development.

2003-2008: NIST, Gaithersburg, MD, USA.
Coworkers: *J. Jeader, W. Martin, G. Nave, C. Sansonetti, Y. Ralchenko, (P. Mohr, S. Kotochigova) (et al.)*

Contributors of information

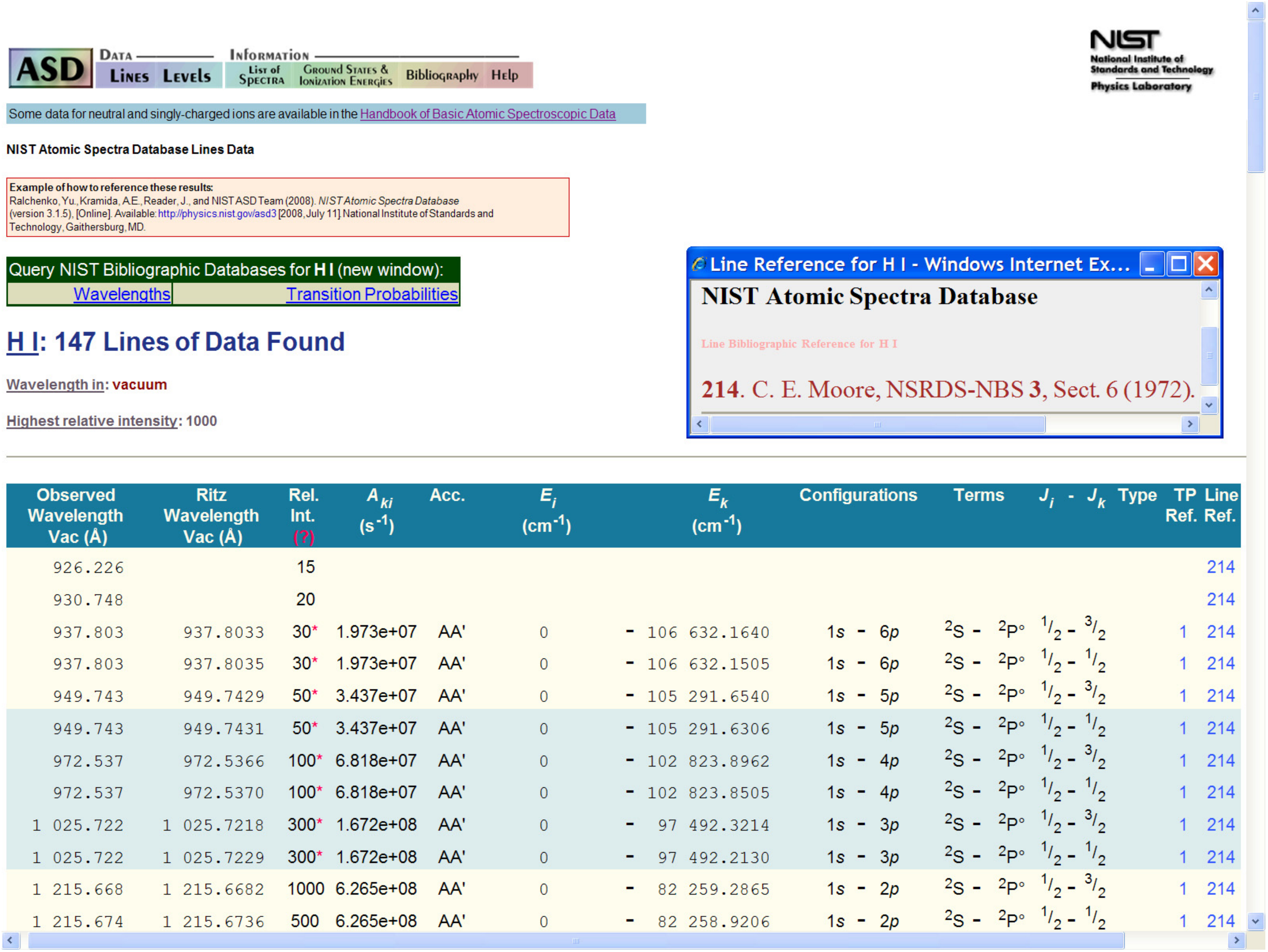
(private communications)

- S.R. Lundeen: Colorado State University, USA
- D.A. Van Baak: Calvin College – Michigan, USA
- F. Biraben, F. Nez: Laboratoire Kastler Brossel, France
- J.C. Bergquist: NIST - Boulder, Colorado, USA
- G.W. Erickson: Univ. of California at Davis, USA

- P.J. Mohr, C.J. Sansonetti, W.C. Martin, J. Reader:
  NIST – Gaithersburg, USA

Motivation

- No existing complete evaluated experimental data on H, D, and T
- Experimental energy levels of H, D, and T do not exist in the literature
- Reference data in Moore 1949-1972 are old theory (last revision is from Garcia and Mack 1965)
- Large amount of high-precision experimental data exist for many transition frequencies
- Large number of energy levels and transition frequencies can be derived with high precision from experimental data w/o sophisticated theory.



Some data for neutral and singly-charged ions are available in the Handbook of Basic Atomic Spectroscopic Data

NIST Atomic Spectra Database Lines Data

Example of how to reference these results:
Ralchenko, Yu., Kramida, A.E., Reader, J., and NIST ASD Team (2008). *NIST Atomic Spectra Database* (version 3.1.5), [Online]. Available: http://physics.nist.gov/asd3 [2008, July 11]. National Institute of Standards and Technology, Gaithersburg, MD.

Query NIST Bibliographic Databases for **H I** (new window):
Wavelengths | Transition Probabilities

H I: 147 Lines of Data Found

Wavelength in: **vacuum**

Highest relative intensity: **1000**

NIST Atomic Spectra Database

Line Bibliographic Reference for H I

214. C. E. Moore, NSRDS-NBS **3**, Sect. 6 (1972).

Observed Wavelength Vac (Å)	Ritz Wavelength Vac (Å)	Rel. Int. (?)	A_{ki} (s^{-1})	Acc.	E_i (cm^{-1})		E_k (cm^{-1})	Configurations	Terms	J_i - J_k	Type	TP Ref.	Line Ref.
926.226		15											214
930.748		20											214
937.803	937.8033	30*	1.973e+07	AA'	0	-	106 632.1640	1s - 6p	^2S - $^2P°$	$^1/_2$ - $^3/_2$		1	214
937.803	937.8035	30*	1.973e+07	AA'	0	-	106 632.1505	1s - 6p	^2S - $^2P°$	$^1/_2$ - $^1/_2$		1	214
949.743	949.7429	50*	3.437e+07	AA'	0	-	105 291.6540	1s - 5p	^2S - $^2P°$	$^1/_2$ - $^3/_2$		1	214
949.743	949.7431	50*	3.437e+07	AA'	0	-	105 291.6306	1s - 5p	^2S - $^2P°$	$^1/_2$ - $^1/_2$		1	214
972.537	972.5366	100*	6.818e+07	AA'	0	-	102 823.8962	1s - 4p	^2S - $^2P°$	$^1/_2$ - $^3/_2$		1	214
972.537	972.5370	100*	6.818e+07	AA'	0	-	102 823.8505	1s - 4p	^2S - $^2P°$	$^1/_2$ - $^1/_2$		1	214
1 025.722	1 025.7218	300*	1.672e+08	AA'	0	-	97 492.3214	1s - 3p	^2S - $^2P°$	$^1/_2$ - $^3/_2$		1	214
1 025.722	1 025.7229	300*	1.672e+08	AA'	0	-	97 492.2130	1s - 3p	^2S - $^2P°$	$^1/_2$ - $^1/_2$		1	214
1 215.668	1 215.6682	1000	6.265e+08	AA'	0	-	82 259.2865	1s - 2p	^2S - $^2P°$	$^1/_2$ - $^3/_2$		1	214
1 215.674	1 215.6736	500	6.265e+08	AA'	0	-	82 258.9206	1s - 2p	^2S - $^2P°$	$^1/_2$ - $^1/_2$		1	214

Goals

- Provide a reference set of essentially experimental values of the energy levels and frequencies for the ***fine structure*** of H, D, and T and compare them with the most precise calculations.
- Provide a reference set of the ***hfs*** data on H, D, and T and outline the problem areas.
- Provide a reference set of experimental wavelengths of ***series lines*** of H and D for astrophysics and laboratory spectral analysis.

Outline

- Brief history
- Selection of data
- Hyperfine structure – measurements and calculations
- Fine structure level optimization
- Comparison with QED calculations
- Line series for practical science
- Conclusions

Brief history: Theory

- Bohr 1913: $E(n) = -RZ^2/n^2$

  Predicted lines observed by Lyman 1914, Brackett 1922, Pfund 1924, Humphreys 1953.

- Reduced-mass adjustment: $R = R_\infty/(1+m_e/M_N)$

- Sommerfeld, Unsöld, Dirac 1926-1928:

$$E_D(n,j) = 2R/\alpha^2[f(n,j) - 1]$$

$$f(n,j) = \left[1 + \left(\frac{Z\alpha}{n-\delta}\right)^2\right]^{-1/2} \qquad \delta = (j+\tfrac{1}{2})\left(1 - \left[1 - \left(\frac{Z\alpha}{j+\frac{1}{2}}\right)^2\right]^{1/2}\right)$$

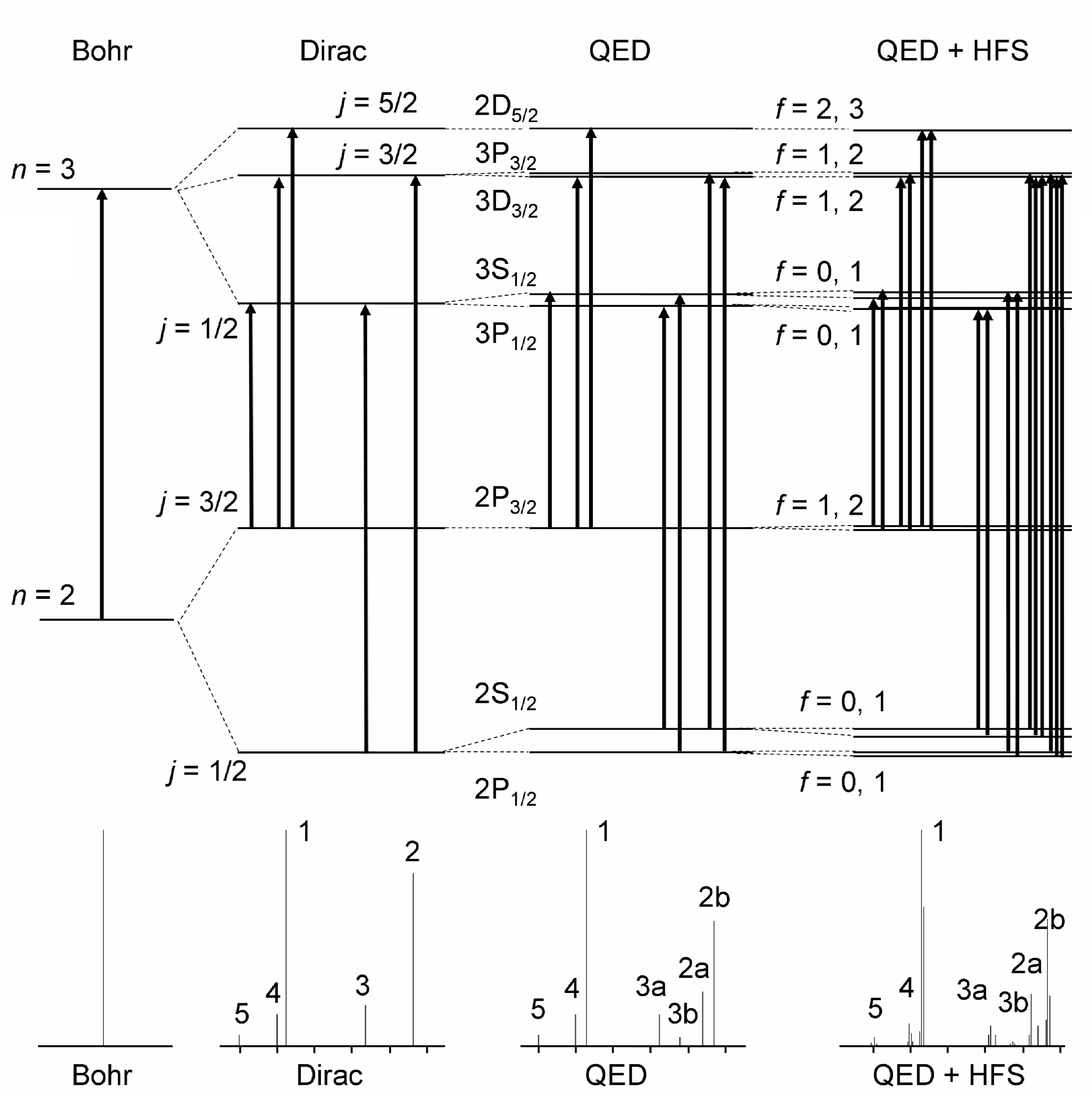
Brief history: Theory

- Barker and Glover 1955, Garcia and Mack 1965, Grotch and Yennie 1967-1969, Sapirstein and Yennie 1990:

$$E_{rel} = E_D \frac{m_r}{m_e} - \frac{R_\infty [f(n,j)-1]^2 m_r^2}{\alpha^2 m_e (m_e + M_N)} + (1-\delta_{l0}) \frac{R_\infty (Z\alpha)^4 m_r^3}{\alpha^2 \kappa (2l+1) n^3 m_e M_N^2} + \ldots$$

$$m_r = m_e/(1+m_e/M_N),\ \kappa = (-1)^{j+l+½}(j+½)$$

- Erickson 1977, Sapirstein and Yennie 1990:
  - Further small corrections related to mass (more complex)



Theoretical structure of Balmer-*α* (not to scale)

Brief history: Experiment and theory

- Houston and Hsieh 1934, Houston 1937:

  Measured doublet separations in Balmer series are consistently smaller than Dirac's theory predictions.
- Pasternack 1938:

  Deviations in Balmer-α doublet separations can be explained by an upward shift of $2S_{1/2}$ by 0.03 cm^{-1}.
- Bethe 1947, 1950: QED theory.
- Lamb *et al*. 1950-1953:

  This shift measured in H and D and proved to be real.
- Garcia and Mack 1965, Erickson 1971-1977, Mohr 1975, Sapirstein 1981, …, Kotochigova *et al*. 2002, …:

  Further development of the QED theory
- Jentschura *et al*. 2005, NIST H&D database

  http://physics.nist.gov/PhysRefData/HDEL/index.html

Brief history: Experiments on FS of H, D, T

- 1806-2008: Line series measured in discharges and Sun with prisms, gratings, and FTS

  (Wollaston), Fraunhofer, Ames, Evershed, Dyson, Paschen, Fowler, Mitchell, Evans, Lyman, Curtis, Paschen, Wood, McLennan, Brackett, Pfund, Poetker, Herzberg, Babcock, Humphreys, Herzberg, Hansen, Rosenberg, Doschek, Feldman, Brault, Noyes, Zirker, Boreiko, T. Clark, Geller, Wallace, Farmer, Chang, Curdt, Parenti, …

- 1887-1973: Optical interferometry of discharges

  Michelson, Morley, Merton, Houstoun, Houston, Hsieh, Kent, Williams, Gibbs, Kopfermann, Spedding, Heyden, Giulotto, Kuhn, Series, Drinkwater *et al*., Kireyev, Csillag, Masui, Kibble, …

- 1950-1998: Microwave and rf measurements with atomic beams

  Lamb *et al*., Lundeen, Pipkin, Hagley, Fabjan, Brown, Baird, B. Clark, Van Baak, Safinya, Glass-Maujean, Robiscoe, Shyn, Newton, Andrews, Cosens, Vorburger, van Wijngaarden, …

Brief history: Laser spectroscopy experiments on FS (H and D)

- 1972-1988: Saturated absorption
  Hänsch *et al*., Nayfeh, Weber, Goldsmith, Petley *et al*., Tate *et al*. …
- 1981-1989: Metastable atomic beam, one-photon
  Amin, Zhao, Lichten, Bergquist, …
- 1975-2000: Two-photon, Doppler-free
  Hänsch *et al*., Biraben, Julien, Garreau, Foot, Beausoleil, Hildum *et al*., Barr *et al*., Boshier, McIntyre, Thompson, Andrae, Nez, Schmidt-Kaler, Weitz, Berkeland, Bourzeix, de Beauvoir, Huber, Schwob, …
- 2000-2008: …, and with frequency combs
  Niering *et al*., Hänsch *et al*., …

Selection of data: Criteria

- Magnitude of applied theoretical corrections or adjustments must be much smaller than the measured value
  - *n*=2 Lamb shift measurement of Pal’chikov and Sokolov (1985) is not included
- The best accuracy of measurement
- The best account for systematic effects
- Only one measurement is included for each measured interval

Selection of data: H (shown 8 out of total 43)

FS interval	Measured value (MHz)	Actually measured interval	Largest theoretical correction	Ref.
$1S_{1/2}$–$2S_{1/2}$	2466061413.187074(34)	$1S_{F=1}$–$2S_{F=1}$	None	Hänsch05
$2P_{1/2}$–$2S_{1/2}$	1057.847(9)	$2P_{1/2,F=1}$–$2S_{F=0}$	(14.7924)(2) =¼ hfs($2P_{1/2}$)	LP86
$2P_{1/2}$–$2P_{3/2}$	10969.13(10)	$2P_{1/2,F=0,1}$–$2P_{3/2,F=1,2}$	hfs($2P_{1/2}$,$2P_{3/2}$)	Baird72
$2S_{1/2}$–$2P_{3/2}$	9911.201(12)	$2S_{F=0}$–$2P_{3/2,F=1}$	(14.7823)(2) =5/8 hfs($2P_{3/2}$)	HP94
$2P_{1/2}$–$3D_{3/2}$	456685852.8(17) + x	$2P_{1/2,F=0,1}$–$3D_{3/2,F=1,2}$	hfs($2P_{1/2}$,$3D_{3/2}$)	Hänsch74
$2S_{1/2}$–$3P_{1/2}$	456681549.9(3) + x	$2S_{F=1}$–$3P_{1/2,F=0,1}$	(1.46098)(2) = 1/12 hfs($3P_{1/2}$)	Zhao86
$2S_{1/2}$–$3P_{3/2}$	456684800.1(3) + x	$2S_{F=1}$–$3P_{3/2,F=1,2}$	(–1.45998)(2) = –5/24 hfs($3P_{3/2}$)	Zhao86
$2P_{3/2}$–$3D_{5/2}$	456675968.3(34) + x	$2P_{3/2,F=1,2}$–$3D_{5/2,F=2,3}$	hfs($2P_{3/2}$,$3D_{5/2}$)	Hänsch74

Selection of data: D (shown 7 out of 36)

FS interval	Measured value (MHz)	Actually measured interval	Largest theoretical correction	Ref.
$1S_{1/2}–2S_{1/2}$	2466732407.52171(15)	$H(1S_{F=1}–2S_{F=1})$ – $D(1S_{F=3/2}–2S_{F=3/2})$	None	Huber98
$2P_{1/2}–2S_{1/2}$	1059.28(6)	$2P_{1/2,F=3/2}–2S_{F=1/2}$ and $2P_{1/2,F=3/2}–2S_{F=3/2}$	(4.54446)(5) $=1/3$ hfs$(2P_{1/2})$	Cosens68, V71
$2S_{1/2}–2P_{3/2}$	9912.61(30)	$2S_{F=3/2}–2P_{3/2,F=5/2}$	(–2.72694)(5) = –1/6 hfs$(2P_{3/2,F=1/2–3/2})$ –1/2 hfs$(2P_{3/2,F=3/2–5/2})$	DTL53, Taylor69
$2P_{1/2}–3D_{3/2}$	456810113.8 (19) + x	$H(2P_{1/2}–3D_{3/2})$ – $D(2P_{1/2}–3D_{3/2})$	None (Assumed Boltzmann in hfs)	Tate88
$2S_{1/2}–3P_{1/2}$	456805811.7(3) + y	$2S_{F=3/2}–3P_{1/2,F=1/2,3/2}$	(0.448839)(6) $= 1/9$ hfs$(3P_{1/2})$	Zhao86
$2S_{1/2}–3P_{3/2}$	456809062.6(3) + y	$2S_{F=3/2}–3P_{3/2,F=1/2,3/2,5/2}$	(–0.448429)(8) = –5/36 hfs$(3P_{3/2,F=1/2–3/2})$ – 1/4 hfs$(3P_{3/2,F=3/2–5/2})$	Zhao86
$2P_{3/2}–3S_{1/2}$	456796251(30)	$D(2P_{3/2}–3S_{1/2})$ – $D(2P_{3/2}–3D_{5/2})$	hfs$(2P_{3/2},3S_{1/2},3D_{5/2})$	Series51

Selection of data: H and D,

some re-calibrated old measurements

Measurements not included in the 1998 CODATA adjustment of the fundamental constants, but included here:

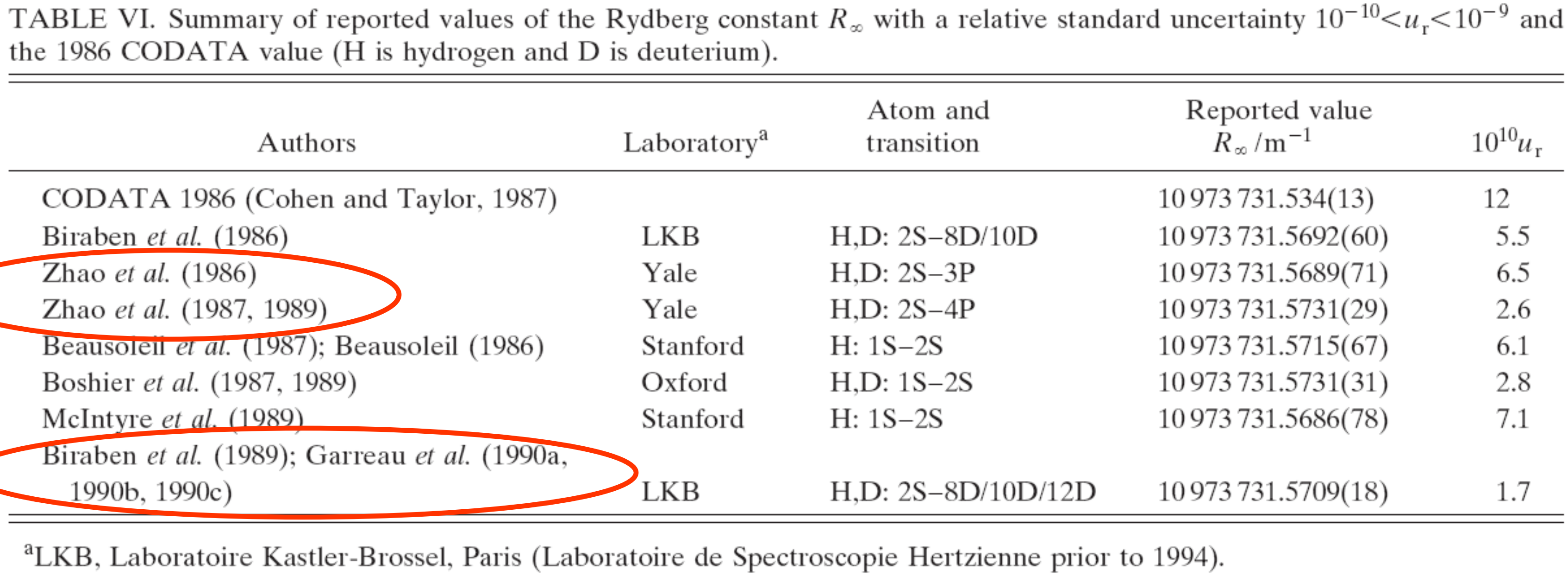


TABLE VI. Summary of reported values of the Rydberg constant R_∞ with a relative standard uncertainty $10^{-10} < u_r < 10^{-9}$ and the 1986 CODATA value (H is hydrogen and D is deuterium).

Authors	Laboratory[a]	Atom and transition	Reported value R_∞ /m^{-1}	$10^{10} u_r$
CODATA 1986 (Cohen and Taylor, 1987)			10 973 731.534(13)	12
Biraben *et al.* (1986)	LKB	H,D: 2S–8D/10D	10 973 731.5692(60)	5.5
Zhao *et al.* (1986)	Yale	H,D: 2S–3P	10 973 731.5689(71)	6.5
Zhao *et al.* (1987, 1989)	Yale	H,D: 2S–4P	10 973 731.5731(29)	2.6
Beausoleil *et al.* (1987); Beausoleil (1986)	Stanford	H: 1S–2S	10 973 731.5715(67)	6.1
Boshier *et al.* (1987, 1989)	Oxford	H,D: 1S–2S	10 973 731.5731(31)	2.8
McIntyre *et al.* (1989)	Stanford	H: 1S–2S	10 973 731.5686(78)	7.1
Biraben *et al.* (1989); Garreau *et al.* (1990a, 1990b, 1990c)	LKB	H,D: 2S–8D/10D/12D	10 973 731.5709(18)	1.7

[a] LKB, Laboratoire Kastler-Brossel, Paris (Laboratoire de Spectroscopie Hertzienne prior to 1994).

Selection of data: T

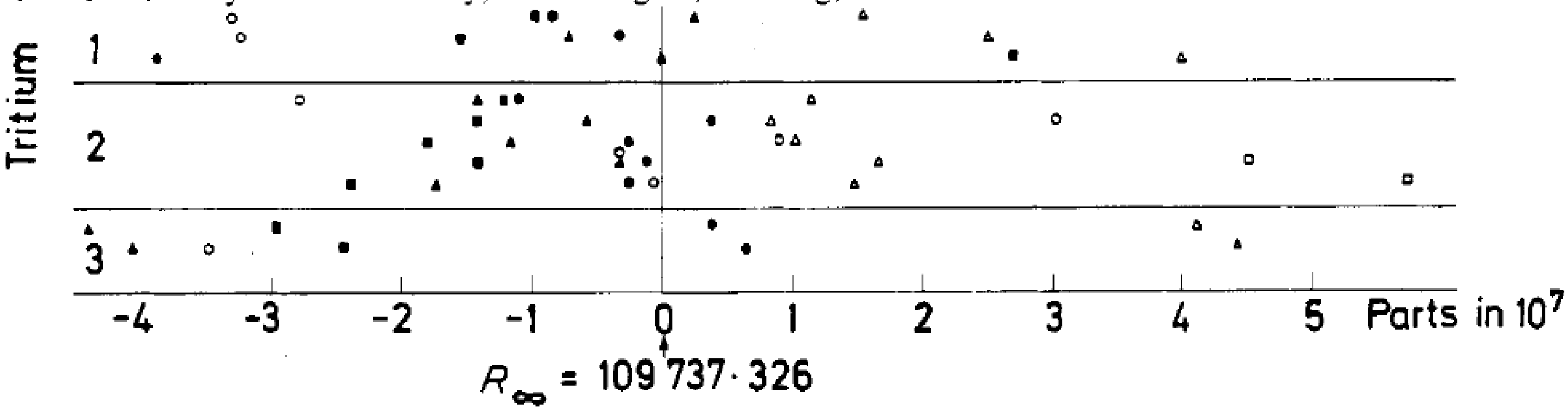
Tritium Balmer-α fine-structure transition frequencies derived from the measurements of Tate *et al*. 1988 (Clarendon Lab., UK).

Transition	Frequency from IS(H-T), MHz	Frequency from IS(H-D), MHz	Frequency from line separation in T, MHz	Mean measured frequency, MHz
$2P_{3/2}$–$3D_{5/2}$	456841568.8(8)(14)	456841568.7(17)(14)	–	456841568.8(16)
$2P_{1/2}$–$3D_{3/2}$	456851457.2(19)(14)	456851457.4(21)(14)	456851457.1(18)	456851457.2(13)
$2S_{1/2}$–$3P_{3/2}$	456850406.2(11)(14)	456850406.2(12)(14)	456850404.9(24)	456850405.8(14)
$2S_{1/2}$–$3P_{1/2}$	456847154.3(18)(14)	456847154.2(18)(14)	456847152.9(29)	456847153.8(16)

B P Kibble,† W R C Rowley,† R E Shawyer† and G W Series‡ J. Phys. B 6, 1079 (1973).

† National Physical Laboratory, Teddington, Middlesex.

‡ J J Thomson Physical Laboratory, Whiteknights, Reading, RG6 2AF.



Hyperfine structure: example for H

Adapted from

S.R. Lundeen and F. M. Pipkin, Metrologia **22**. 9 (1986).

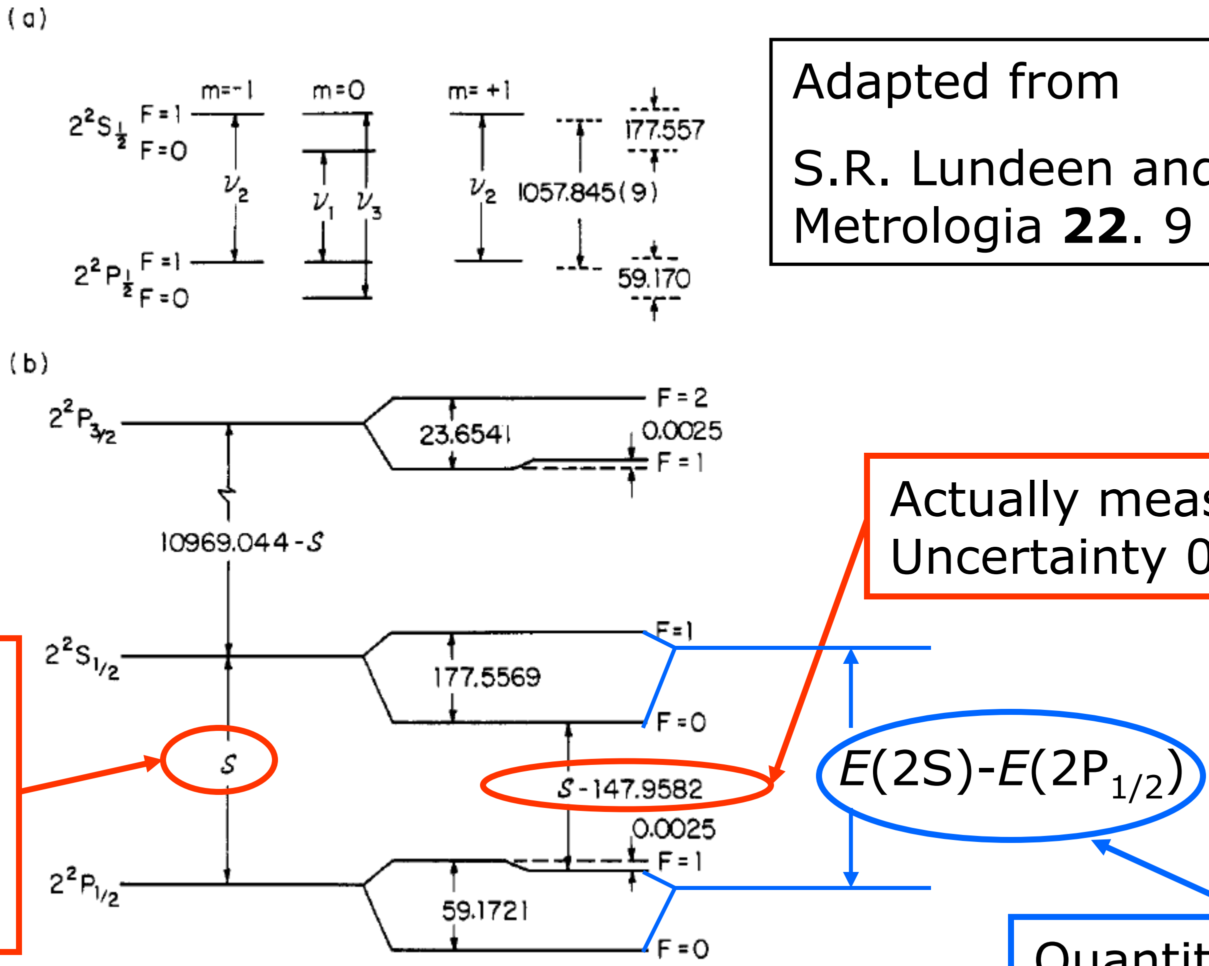


Fig. 11. a Energy levels for the $2^2S_{1/2}$ and $2^2P_{1/2}$ states of hydrogen when one includes the hyperfine splitting. **b** Energy levels for $n = 2$ manifold including both the diagonal and off-diagonal hyperfine interactions

Actually measured quantity. Uncertainty 0.009 MHz

Final reported quantity, ‘Lamb shift’

$E(2S)$-$E(2P_{1/2})$

Quantity reported in this compilation

Hyperfine structure: H, some published data

FS level		HFS splitting (MHz)	Reference
$1S_{1/2}$	Experiment	1420405.751768(1)	Karshenboim05
$2P_{1/2}$	Theory	(59.1501)(1)	LJP75
	Theory	(59.172)	LJP75
	Theory	(59.169)(2)	Andrews76, Safinya80
	Theory	(59.1696)(6)	Newton79, LP86
	Theory	(59.1695)(6)	This work
	Experiment	59.22(14)	LJP75
$2P_{3/2}$	Theory	(23.6521)(8)	Safinya1980, HP94
	Theory	(23.6516)(2)	LP86
	Theory	(23.65157)(24)	This work

Hyperfine structure: D, some published data

Level	Interval		HFS splitting (MHz)	Reference
$1S_{1/2}$	F=1/2-3/2	Exp.	327.3843525222(17)	WR72
$2S_{1/2}$	F=1/2-3/2	Exp.	40.924454(7)	K04
$4S_{1/2}$	F=1/2-3/2	Th.	(5.11554)(3)	Weitz95
		Semi	[5.1155512](12)	This work
$4D_{5/2}$	F=3/2-5/2	Th.	(59.172)	LJP75
		Th.	(59.169)(2)	Andrews76, Safinya80
	F=5/2-7/2	Th.	(0.20464)	Weitz95
		Th.	(0.20452)(21)	This work
$8D_{5/2}$	F=3/2-5/2	Th.	(0.183)	deBeauvoir00
		Th.	(0.18178)(18)	This work
	F=5/2-7/2	Th.	(0.256)	deBeauvoir00
		Th.	(0.2557)(3)	This work

Hyperfine structure: theory

$$\Delta E_{nljIF} = \frac{A_{nlj}}{2}[F(F+1) - I(I+1) - j(j+1)] + \boxed{\Delta E^{off-diag}_{nljIF}}$$

A_{nlj} is a magnetic-dipole hfs constant:

$$A_{nlj} = 2\alpha^2 Z^3 R_\infty c \frac{\mu_e \mu_{nucl}}{\mu_B^2 \left(1 + \frac{m_e}{M_N}\right)^3 n^3 j(j+1)(2l+1)I} \boxed{F^{rel}_{nlj}}$$

Interval between two adjacent hfs levels:

$$\Delta E_{hfs}(F-1, F) = A_{nlj}F + \Delta E^{off-diag}_{nljI}(F-1, F)$$

Hyperfine structure: theory

$$F_{nlj}^{rel} = \frac{1 + \dfrac{1 - N - \dfrac{2\kappa|\kappa|}{n} q}{2\kappa - 1}}{(1-q)N^4 \left[1 - \dfrac{4(\alpha Z)^2}{4\kappa^2 - 1}\right]}$$

Based on

1) I.I. Sobel'man, *Introduction to the Theory of Atomic Spectra* (1972);

2) V.M. Shabaev, J. Phys. B **24**, 4479 (1991).

$\kappa = (-1)^{j + l + ½} (j + ½)$, $q = 1 - [1 - (\alpha Z/\kappa)^2]^{½}$,

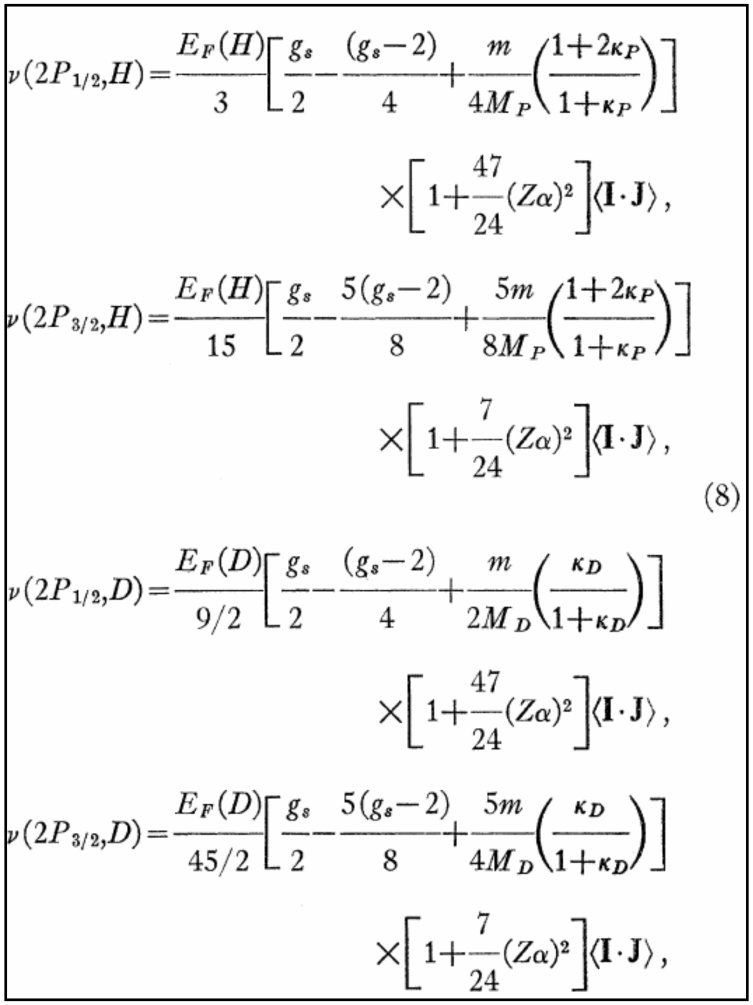
$N = [1 - 2\,|\kappa|\,(n - |\kappa|)\, q\, /\, n^2]^{½}$

With these relations: $\longrightarrow$ $\dfrac{\kappa}{|\kappa|(2\kappa+1)} \equiv \dfrac{1}{|2\kappa+1|} \equiv \dfrac{1}{2l+1}$

the above formula is identical to the one given by U.D. Jentschura and V.A. Yerokhin, Phys. Rev. A **73**, 062503 (2006).

Hyperfine structure: H, D, 2P

S. Brodsky and R.G. Parsons, Phys. Rev. **163**, 134 (1967).

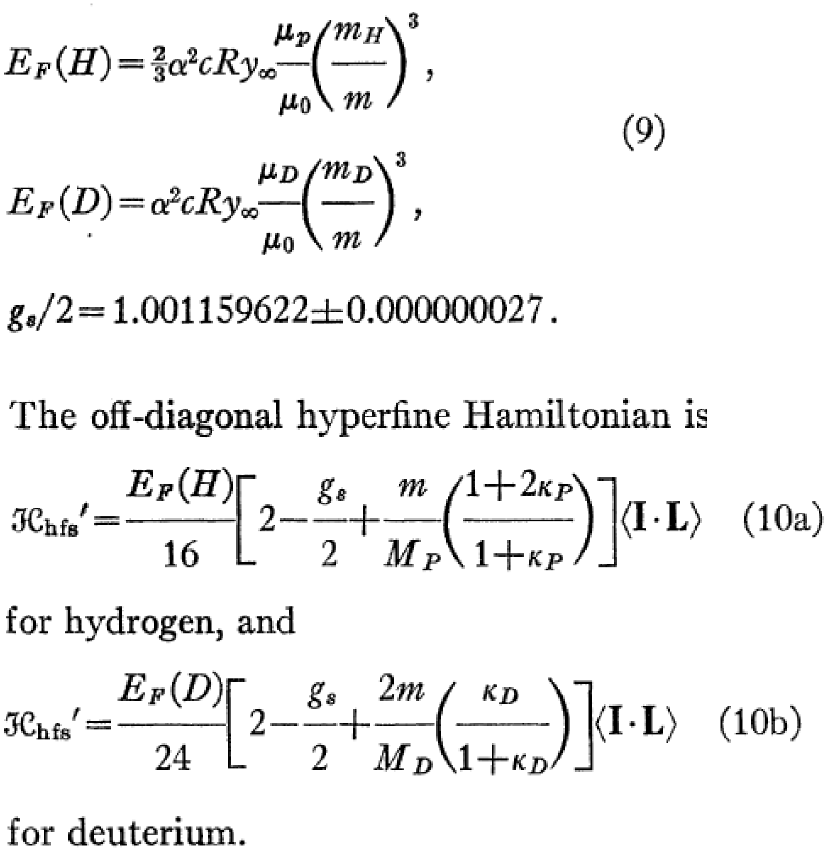


$$\nu(2P_{1/2},H)=\frac{E_F(H)}{3}\left[\frac{g_s}{2}-\frac{(g_s-2)}{4}+\frac{m}{4M_P}\left(\frac{1+2\kappa_P}{1+\kappa_P}\right)\right]\times\left[1+\frac{47}{24}(Z\alpha)^2\right]\langle\mathbf{I}\cdot\mathbf{J}\rangle\,,$$

$$\nu(2P_{3/2},H)=\frac{E_F(H)}{15}\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}+\frac{5m}{8M_P}\left(\frac{1+2\kappa_P}{1+\kappa_P}\right)\right]\times\left[1+\frac{7}{24}(Z\alpha)^2\right]\langle\mathbf{I}\cdot\mathbf{J}\rangle\,,$$

$$\nu(2P_{1/2},D)=\frac{E_F(D)}{9/2}\left[\frac{g_s}{2}-\frac{(g_s-2)}{4}+\frac{m}{2M_D}\left(\frac{\kappa_D}{1+\kappa_D}\right)\right]\times\left[1+\frac{47}{24}(Z\alpha)^2\right]\langle\mathbf{I}\cdot\mathbf{J}\rangle\,,$$

$$\nu(2P_{3/2},D)=\frac{E_F(D)}{45/2}\left[\frac{g_s}{2}-\frac{5(g_s-2)}{8}+\frac{5m}{4M_D}\left(\frac{\kappa_D}{1+\kappa_D}\right)\right]\times\left[1+\frac{7}{24}(Z\alpha)^2\right]\langle\mathbf{I}\cdot\mathbf{J}\rangle\,,\qquad(8)$$



$$E_F(H)=\tfrac{2}{3}\alpha^2 cRy_\infty\frac{\mu_p}{\mu_0}\left(\frac{m_H}{m}\right)^3,$$

$$E_F(D)=\alpha^2 cRy_\infty\frac{\mu_D}{\mu_0}\left(\frac{m_D}{m}\right)^3,\qquad(9)$$

$$g_s/2=1.001159622\pm0.000000027\,.$$

The off-diagonal hyperfine Hamiltonian is

$$\mathcal{H}_{\mathrm{hfs}}'=\frac{E_F(H)}{16}\left[2-\frac{g_s}{2}+\frac{m}{M_P}\left(\frac{1+2\kappa_P}{1+\kappa_P}\right)\right]\langle\mathbf{I}\cdot\mathbf{L}\rangle\qquad(10a)$$

for hydrogen, and

$$\mathcal{H}_{\mathrm{hfs}}'=\frac{E_F(D)}{24}\left[2-\frac{g_s}{2}+\frac{2m}{M_D}\left(\frac{\kappa_D}{1+\kappa_D}\right)\right]\langle\mathbf{I}\cdot\mathbf{L}\rangle\qquad(10b)$$

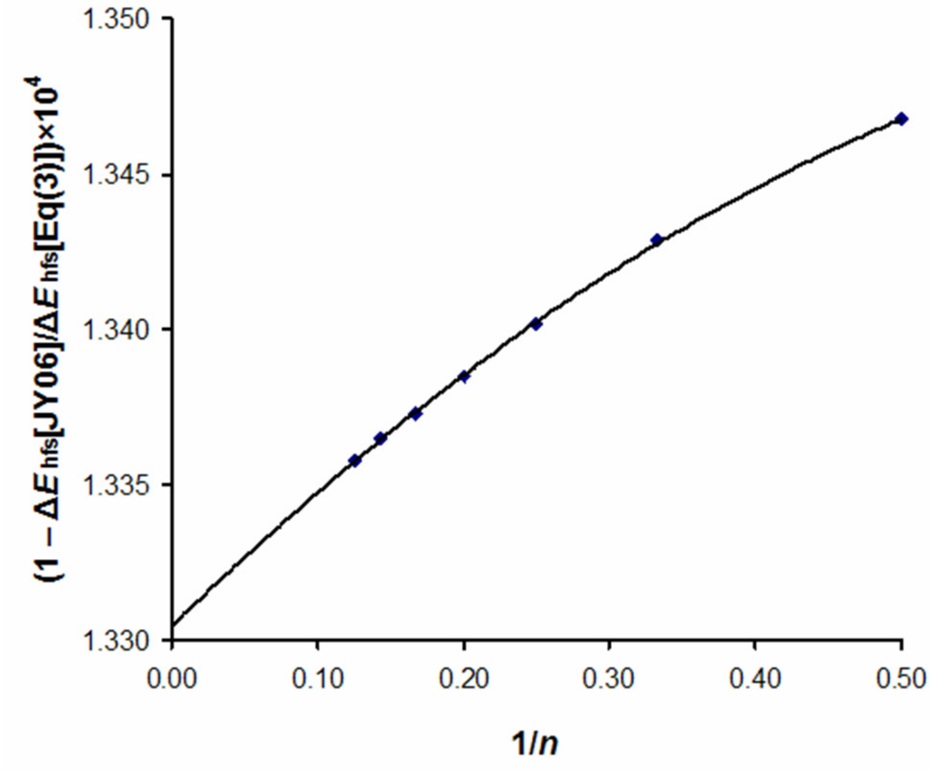
for deuterium.

Hyperfine structure: H, $n\mathrm{S}_{1/2}$

$n = 2\text{-}8$, precise semiempirical calculations of [JY06] =

U.D. Jentschura and V.A. Yerokhin, Phys. Rev. A **73**, 062503 (2006).

$A_{ns}[\mathrm{JY06}] \approx A_{ns}^{\mathrm{approx}}[1 - F_{\mathrm{corr}}(\mathrm{H}, ns)]$



$$F_{\mathrm{corr}}(\mathrm{H}, ns) = 1.33045\times10^{-4} + 4.5583\times10^{-6} / n - 2.5917\times10^{-6} / n^2$$

Fractional uncertainty:

[JY06]:	$\leq 1.1\times10^{-8}$ ($n \leq 8$)
Interpolation:	$\leq 7\times10^{-9}$ ($n \leq 8$)
Extrapolation:	$\approx 10^{-7}$ ($n \geq 9$)

Hyperfine structure: H, D; *n*P, *n*D, *n*F, …

- Use formulas (8, 9, 10, 16) from Brodsky and Parsons 1967
- Replace the relativistic factor in these formulas with ours
- Assume the same dependence on (g_s-2) and κ_P, κ_D for $L > 1$ as for 2P
- For $L > 1$ this introduces uncertainty ~(g_s-2)/2 ≈ 10^{-3}.
- For off-diagonal hfs, use perturbation theory:

$$\Delta E_{nljIF}^{off-diag} = \left\langle H_{hfs,nljj'IF}^{off-diag} \right\rangle^2 / \Delta E_{njj'}$$

Hyperfine structure: Deuterium, electric quadrupole hfs

From Sobel’man 1972:

$$\boxed{\Delta E_{nljF}^{quad} = B_{nlj} C(C+1)}$$

$C = F(F + 1) – j(j + 1) – I(I + 1)$

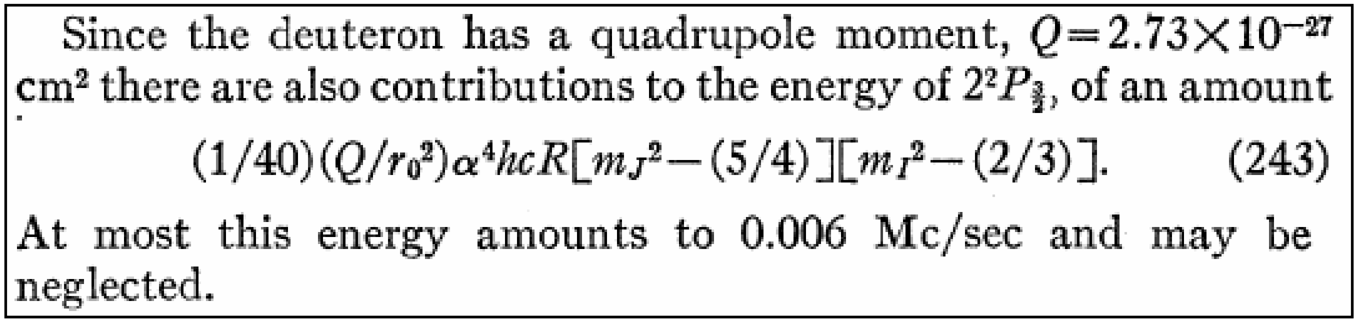
$$B_{nlj} \approx \frac{3(Q_d a_0^{-2}) Z^3 R_\infty c}{8n^3 I(2I-1) j(j+1)(l+1)(l+0.5)l} \approx \frac{126000(700)}{n^3 j(j+1)(l+1)(l+0.5)l} \text{ [Hz]}$$

Quadrupole hfs level shifts in D, 2P

$2P_{1/2}$	F=0.5	14.0 kHz
	F=1.5	14.0 kHz
$2P_{3/2}$	F=0.5	28.0 kHz
	F=1.5	2.8 kHz
	F=2.5	16.8 kHz

Hyperfine structure: D, quadrupole shifts for 2P

W.E. Lamb Jr., Phys. Rev. 85, 259 (1952), Appendix VI:

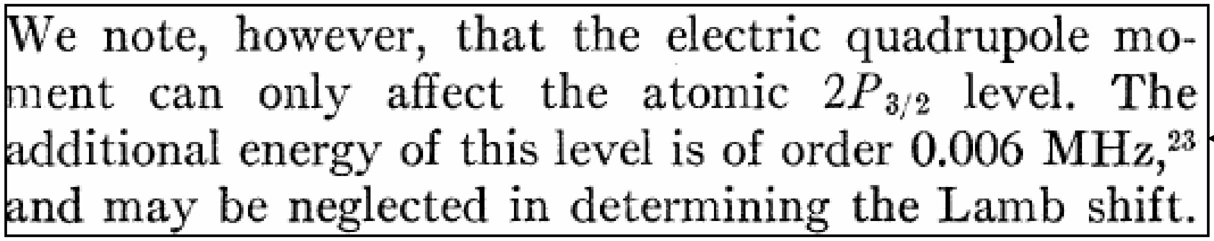


Since the deuteron has a quadrupole moment, $Q=2.73\times10^{-27}$ cm^2 there are also contributions to the energy of $2^2P_{\frac{3}{2}}$, of an amount

$$(1/40)(Q/r_0^2)\alpha^4hcR[m_J^2-(5/4)][m_I^2-(2/3)]. \qquad (243)$$

At most this energy amounts to 0.006 Mc/sec and may be neglected.

S. Brodsky and R.G. Parsons, Phys. Rev. **163**, 134 (1967), Appendix B:



We note, however, that the electric quadrupole moment can only affect the atomic $2P_{3/2}$ level. The additional energy of this level is of order 0.006 MHz,[23] and may be neglected in determining the Lamb shift.

← Lamb 1952

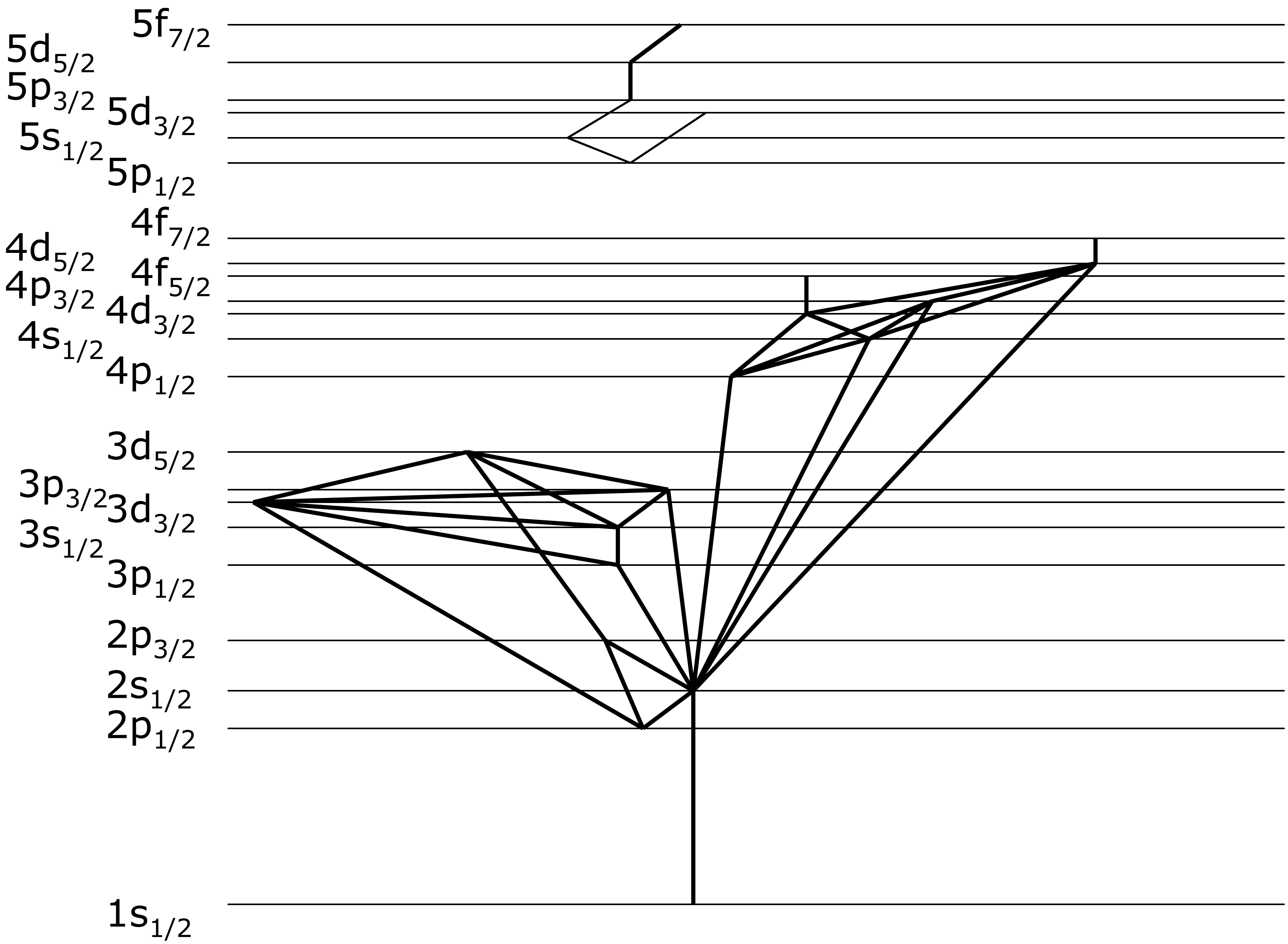
Hfs splittings and off-diagonal shifts in hydrogen (Hz)

n	$\mathbf{S_{1/2}}$	**Ref.**	$\mathbf{P_{1/2}}$	$\Delta E_{\mathrm{c.g.}}$	$\mathbf{P_{3/2}}$	$\Delta E_{\mathrm{c.g.}}$
1	1420405751.768(1)	[K05]				
2	[177556838.2](3)	[JY06]	(59169500)(600)	**(–1870)(19)**	(23651600)(240)	**(935)(9)**
3	[52609473.2](3)	[JY06]	(17531800)(180)	(–554)(6)	(7007920)(70)	(277)(3)
4	[22194585.2](2)	[JY06]	(7396230)(70)	(–234)(2)	(2956470)(30)	(116.9)(12)
6	[6576153.79](6)	[JY06]	(2191470)(22)	(–69.3)(7)	(875992)(9)	(34.6)(3)
8	[2774309.35](3)	[JY06]	(924525)(9)	(–29.2)(3)	(369559)(4)	(14.6)(2)
10	[1420444.48](14)		(473356)(5)	(–15.0)(2)	(189214)(2)	(7.5)(1)
12	[822015.69](8)		(273933)(3)	(–8.7)(1)	(109498.9)(11)	(4.30)(5)
n	$\mathbf{D_{3/2}}$	$\Delta E_{\mathrm{off\text{-}d}}$	$\mathbf{D_{5/2}}$	$\Delta E_{\mathrm{c.g.}}$	$\mathbf{F_{5/2}}$	$\Delta E_{\mathrm{c.g.}}$
3	(4205000)(4000)	**(–1496)(15)**	(2700900)(2700)	**(998)(10)**		
4	(1774000)(1800)	(–631)(6)	(1139400)(1100)	(421)(4)	(813000)(800)	**(–1202)(12)**
6	(525600)(500)	(–187)(2)	(337600)(300)	(124.7)(12)	(240890)(240)	(–356)(4)
8	(221750)(220)	(–78.9)(8)	(142430)(140)	(52.6)(5)	(101620)(100)	(–150)(2)
10	(113540)(110)	(–40.4)(4)	(72920)(70)	(26.9)(3)	(52030)(50)	(–77.0)(8)
12	(65700)(70)	(–23.4)(2)	(42200)(40)	(15.6)(2)	(30110)(30)	(–44.5)(4)

Hfs splittings and shifts in deuterium (Hz)

n	Hfs splitting $F=1/2 – F=3/2$	Hfs splitting $F=1/2 – F=3/2$	$\Delta E_{\text{c.g.}}$	Hfs splitting $F=\lvert j-1\rvert – F=j$	Hfs splitting, $F=j\rvert – F=j+1$	$\Delta E_{\text{c.g.}}$
	$n\mathrm{S}_{1/2}$	$n\mathrm{P}_{1/2}$		$n\mathrm{P}_{3/2}$		
1	327384352.5222(17) **[WR72]**					
2	40924454(7) **[K04]**	(13633390)(140)	**(13530)(70)**	(2699520)(130)	(4554030)(90)	**(14240)(80)**
3	[12125772](3)	(4039550)(40)	**(4009)(21)**	(799860)(40)	(1349350)(30)	**(4218)(22)**
4	[5115551.2](12)	(1704183)(17)	**(1691)(9)**	(337443)(17)	(569259)(11)	**(1779)(9)**
6	[1515714.2](4)	(504942)(5)	(501)(3)	(99983)(5)	(168669)(3)	(527)(3)
8	[639440.63](15)	(213022.1)(21)	(211.4)(11)	(42180.4)(21)	(71157.3)(13)	(222.4)(12)
10	[327393.15](8)	(109067.2)(11)	(108.2)(6)	(21596.4)(11)	(36432.5)(7)	(113.9)(6)
12	[189463.44](5)	(63117.5)(6)	(62.6)(3)	(12497.9)(6)	(21083.6)(4)	(65.9)(3)
n	**Hfs splitting $F=\lvert j-1\rvert – F=j$**	**Hfs splitting $F=j – F=j+1$**	$\Delta E_{\text{c.g.}}$	**Hfs splitting $F=\lvert j-1\rvert – F=j$**	**Hfs splitting $F=j – F=j+1$**	$\Delta E_{\text{c.g.}}$
	$n\mathrm{D}_{3/2}$			$n\mathrm{D}_{5/2}$		
3	(482900)(500)	(808500)(800)	(453.5)(24)	(344700)(400)	(484800)(500)	**(1080)(6)**
4	(203720)(200)	(341100)(300)	(191.3)(10)	(145430)(150)	(204520)(210)	(456)(2)
6	(60360)(60)	(101060)(100)	(56.7)(3)	(43090)(40)	(60600)(60)	(135.1)(7)
8	(25460)(30)	(42640)(40)	(23.92)(13)	(18178)(18)	(25570)(30)	(57.0)(3)
10	(13038)(13)	(21830)(22)	(12.25)(6)	(9307)(9)	(13090)(13)	(29.17)(15)
12	(7545)(8)	(12633)(13)	(7.09)(4)	(5386)(5)	(7575)(8)	(16.88)(9)

Measured fine structure transition frequencies in H



Fine structure level optimization: H, 1st iteration

Number of measured connecting frequencies:
2S: 8; 2P$_{1/2}$: 3; 2P$_{3/2}$: 3
3S: 4; 3P$_{1/2}$: 4; 3P$_{3/2}$: 5; 3D$_{3/2}$: 5; 3D$_{5/2}$: 4
4S: 5; 4P$_{1/2}$: 4; 4P$_{3/2}$: 4; 4D$_{3/2}$: 3; 4D$_{5/2}$: 4; 4F: 1+1
5S: 3; 5P$_{1/2}$: 3; 5P$_{3/2}$: 3; 5D$_{3/2}$: 2; 5D$_{5/2}$: 3; 5F$_{7/2}$: 1
6S: 1; 6D$_{5/2}$: 1
8S: 1; 8D$_{3/2}$: 1; 8D$_{5/2}$: 1
10S: 1; 10D$_{5/2}$: 1
12S: 1; 12D$_{3/2}$: 1; 10D$_{5/2}$: 1

No connection with the ground state for n=5
No measurements at all for n=7, 9, 11
No measurements for 6P, 10P, 12P, 6D$_{3/2}$, 10D$_{3/2}$.

Fine structure level optimization:

H, 2nd iteration, Ritz formula fitting

$\delta_n = c_0 + c_1/(n - \delta_n)^2 + c_2/(n - \delta_n)^4 + \ldots,$

$E_I - E_n = RZ^2/(n - \delta_n)^2,$

where E_I is the ionization energy, δ_n are quantum defects.

(Ritz 1908, Fowler 1912, 1922, Curtis 1914, 1919)

From $n\mathrm{D}_{5/2}$ (n = 3, 4, 6, 8, 10, 12), with a 5-term Ritz formula:

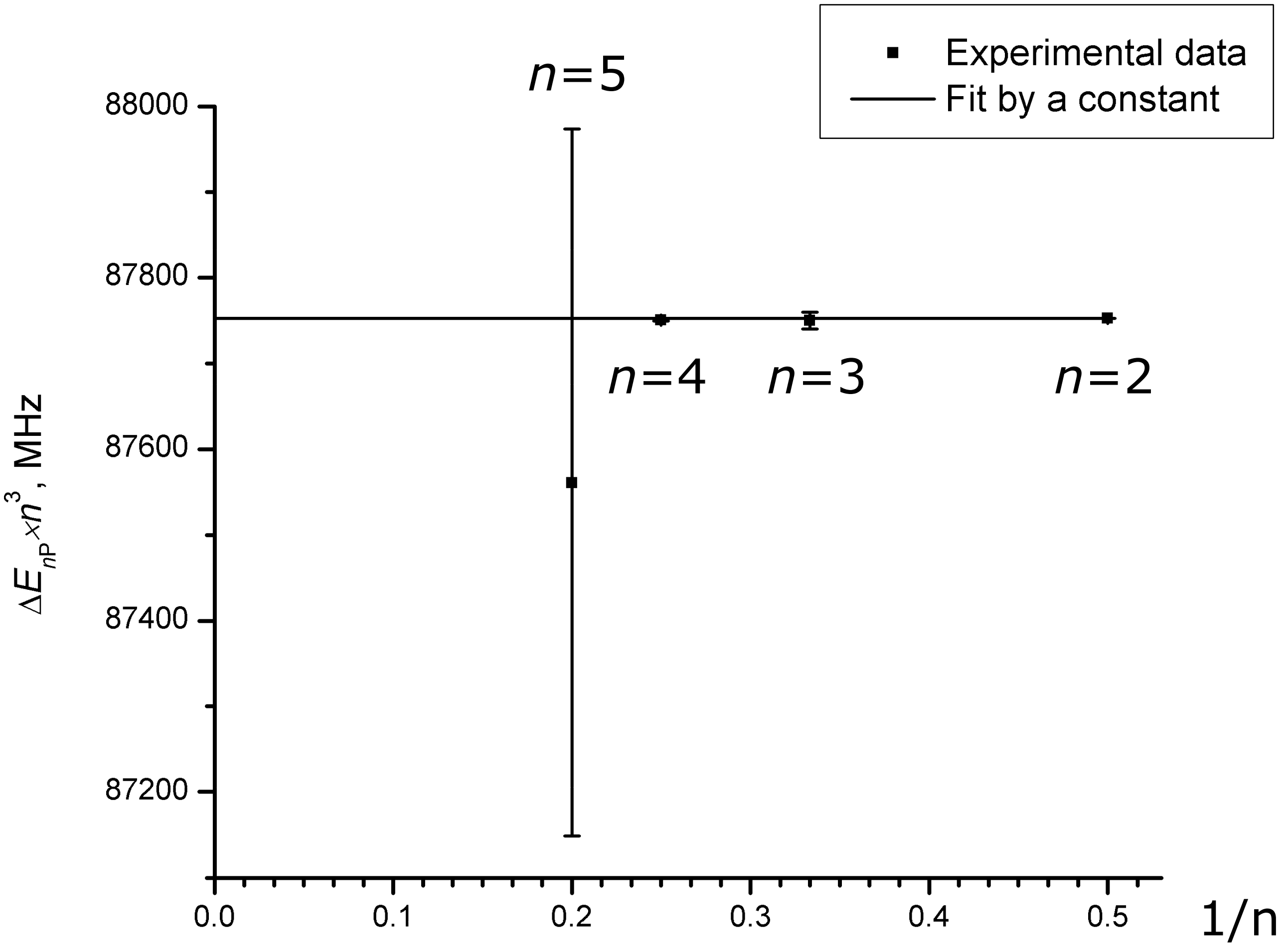
1) E_I = **3288086856.8(7)** MHz
2) $\boldsymbol{n\mathrm{D}_{5/2}}$ **($\boldsymbol{n}$ = 5, 7, 9, 11)** determined to +/- 0.7 MHz

From $n\mathrm{S}_{1/2}$ (n = 1 – 4, 6, 8), with a 6-term Ritz formula:

$\boldsymbol{n\mathrm{S}_{1/2}}$ **($\boldsymbol{n}$ = 5, 7, 9 – 12)** determined to +/- 1.2 MHz

Fine structure level optimization:

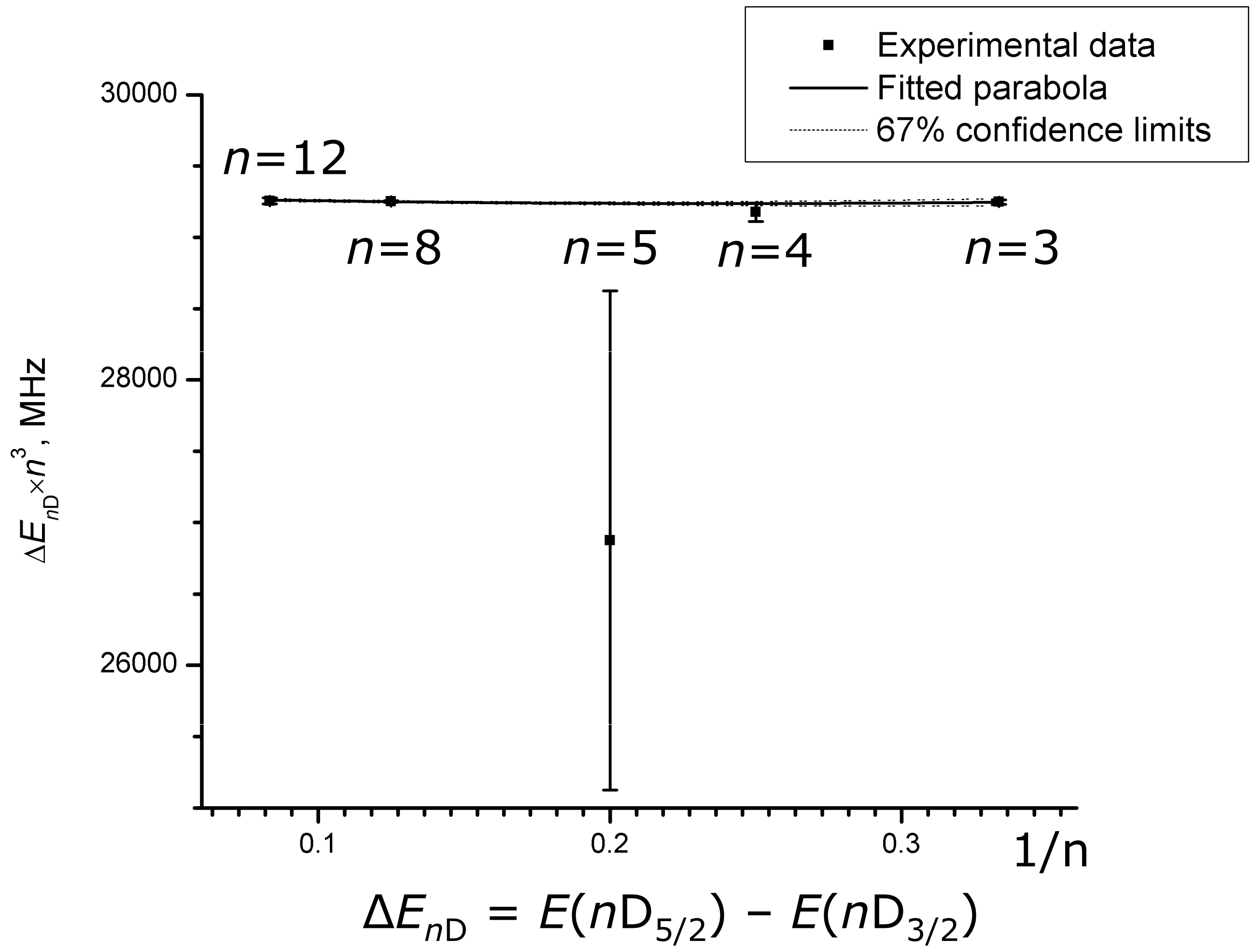
H, 2nd iteration, interpolations & extrapolations



$$\Delta E_{nP} = E(nP_{3/2}) - E(nP_{1/2})$$

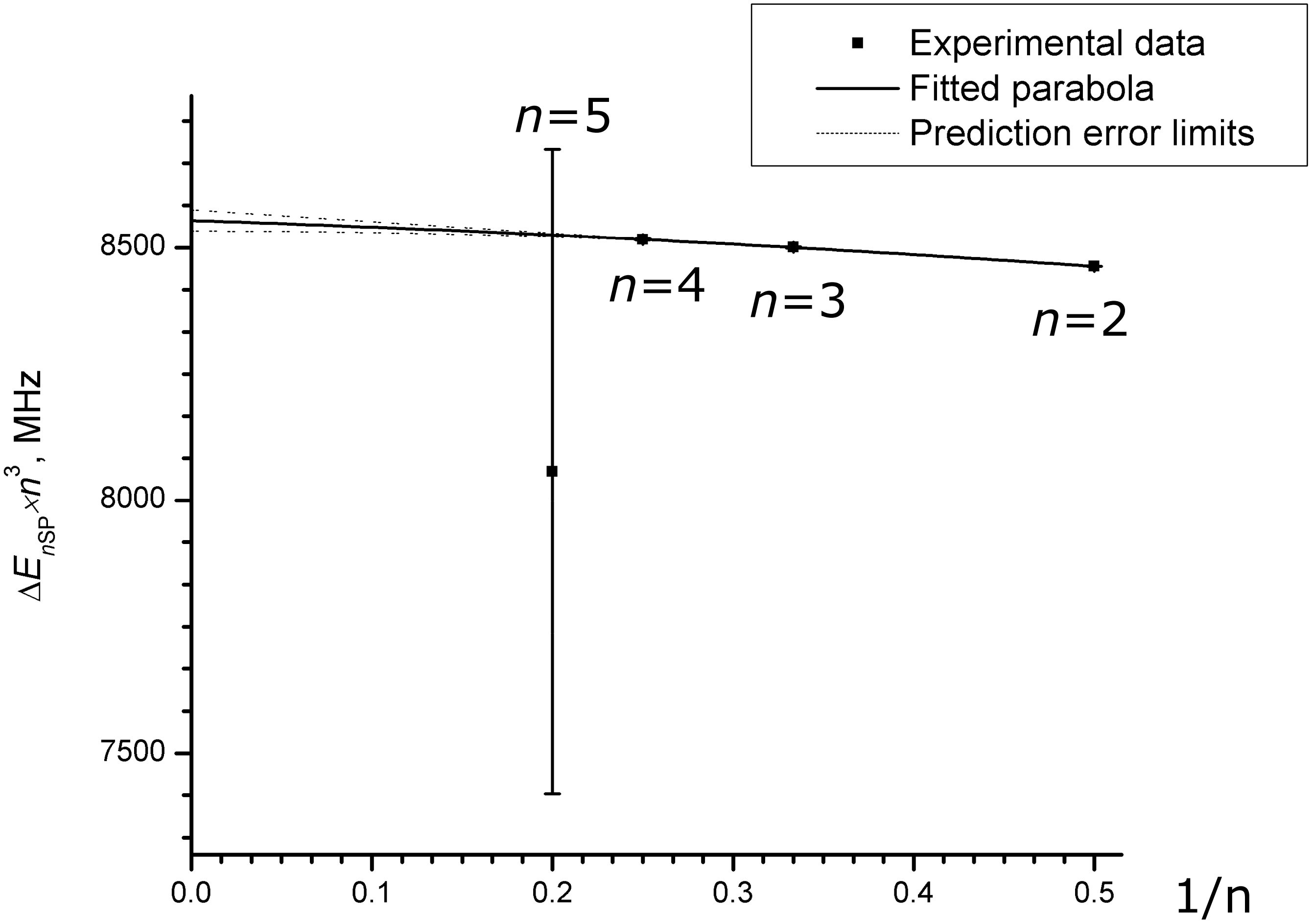
Fine structure level optimization:

H, 2nd iteration, interpolations & extrapolations



Fine structure level optimization:

H, 2nd iteration, interpolations & extrapolations



$$\Delta E_{n\mathrm{SP}} = E(n\mathrm{S}_{1/2}) - E(n\mathrm{P}_{1/2})$$

Fine structure level optimization:

final iteration

- H
  - Input: 40 measured frequencies + 34 interpolated and extrapolated ones
  - Output: 57 energy levels, 174 transition frequencies, $n \leq 12$, l = s, p, d, (f)
  - IP = 3288086856.8(7) MHz
  - Uncertainties vary between 34 Hz (2S) and 1.6 MHz ($4F_{5/2}$, $5F_{7/2}$)
- D
  - Input: 23 measured frequencies + 35 interpolated and extrapolated ones
  - Output: 54 energy levels, 174 transition frequencies, $n \leq 12$, l = s, p, d
  - IP = 3288981521.1(23) MHz
  - Uncertainties vary between 150 Hz (2S) and 6 MHz (nS, nP, n = 5-7, 9-12)
- T
  - Input: 6 measured frequencies + 1 extrapolated ($3D_{3/2}$-$3P_{3/2}$) + 1 calculated ($1S_{1/2}$-$2P_{1/2}$, scaled Erickson 1977)
  - Output: 8 energy levels (n=2, 3) and Balmer-α transitions
  - Uncertainties vary between 1.3 MHz and 240 MHz

Comparison with QED calculations

- QED theory of H and D FS is deeply interrelated with determination of fundamental constants (FC)
- In 2006 CODATA adjustment of FC, there are 25 input data and 3 adjustable parameters related to H and D FS:
  - Rydberg constant R_∞
  - Proton radius R_p
  - Deuteron radius R_d
- Two of the 3 degrees of freedom are exactly determined by two FS measurements: 1S-2S in H and D
- One remaining free parameter is fitted with 23 input measurements, of which 21 are H and D FS.
- Of them, 10 have $|\mathrm{unc}_\mathrm{exp}/\mathrm{unc}_\mathrm{QED}| \leq 3$ – all agree with QED
- QED is confirmed – but …

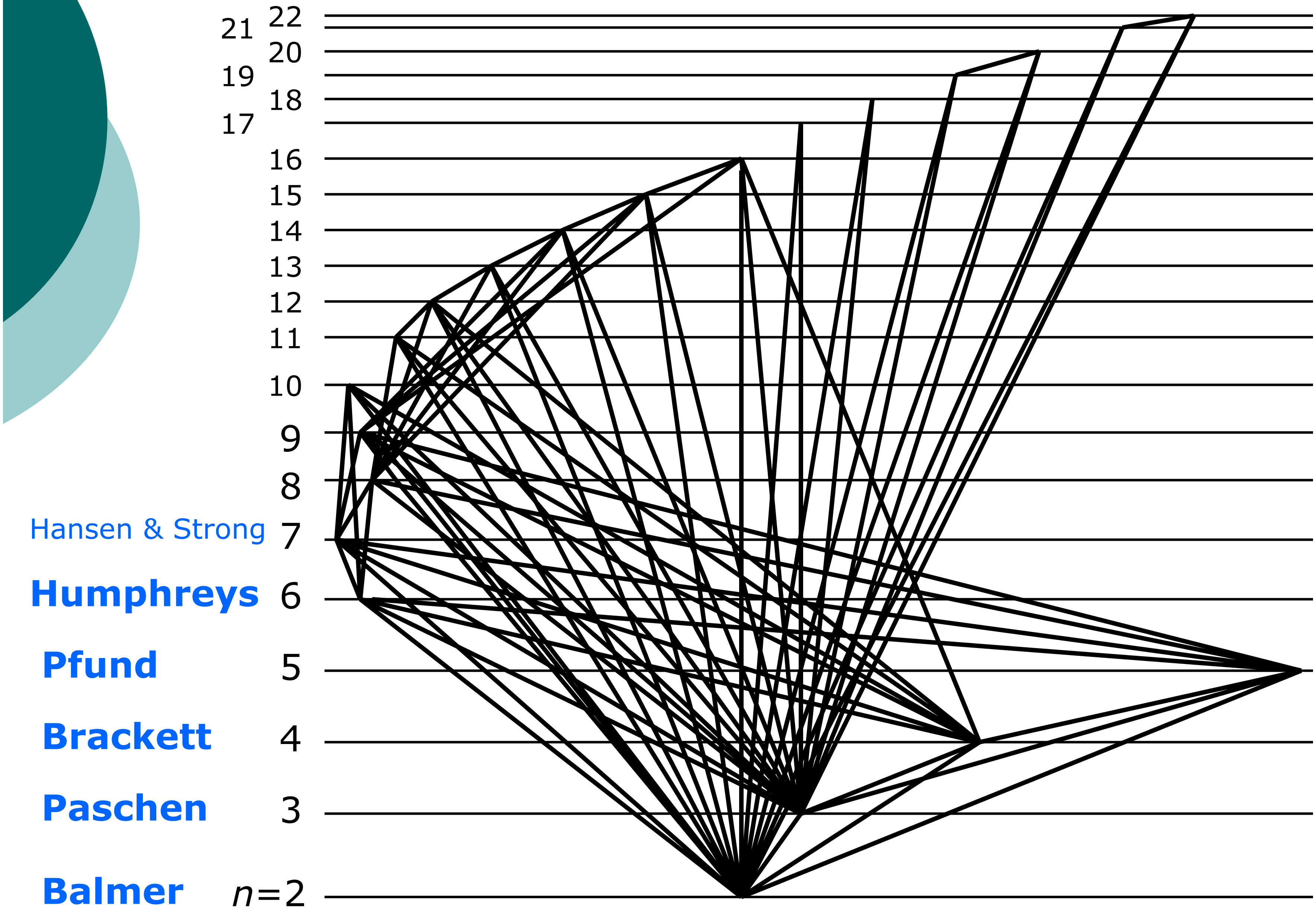
Comparison with QED calculations: disagreements

- Of the 8 FS measurements of Zhao *et al*. 1986-1989 (4 in H, 4 in D), after re-calibration, two **disagree with QED by 4 STD**: 2S-3P$_{1/2,3/2}$. Hence, **all *n*=3 levels in H** disagree by the same amount -0.7 MHz.
- **All *n*=6 in H disagree with QED** by -0.17 MHz = ¼ (-0.7) = **4 STD.**
- **2P$_{3/2}$ in D disagrees with QED by 4 STD** if uncertainty of DTL53 (2S-2P$_{3/2}$, 0.06 MHz) is true. I assumed unc. = 0.3 MHz.

Conclusion:

These measurements must be re-done.

Observed line series in H (some)



Line series in H and D: results

- H, solar atmosphere:

  Predicted (Ritz) wavenumbers for all series, $n \leq 40$, accuracy sufficient for calibration

- H & D, Balmer series in laboratory discharges:

  Experimentally observed variations of relative intensities of FS components limit the accuracy of predicted line center positions to 0.02 cm^{-1} ($n=3$) and 0.006 cm^{-1} ($n \geq 4$).

0.001 $\text{cm}^{-1} \approx$ 30 MHz

Conclusions, for pure science

- Published experimental measurements of FS and HFS of H, D, and T are critically compiled.
- From these data, reference sets of **essentially experimental** energy levels and transition frequencies are derived.
- Overall, these experimental data convincingly confirm the QED theory.
- The only discrepant measurements (**4 STD**) are for n=3 levels in H (Zhao *et al*. 1986) and $2P_{3/2}$ in D (DTL 1953). These measurements need to be redone.
- The main purely theoretical corrections to the measured FS intervals are related to HFS. The accuracy of these corrections **only marginally** exceeds the experimental uncertainties.
- The size of FS level shifts due to off-diagonal M1 HFS (H) and E2 HFS (D) is **much** greater than uncertainties of QED calculations of FS. **More theoretical work on HFS is needed**.

Conclusions, for practical science

- Sets of reference data on H line series are derived for solar spectroscopy.
- The shifts of merged profiles of H and D Balmer series lines due to variations in relative intensities of FS components are evaluated. These shifts limit applicability of these lines to calibration of laboratory spectra.

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