Excerpted from CODATA Recommended Values of the Fundamental Physical Constants: 2002

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This summary is excerpted from the publication *Reviews of Modern Physics*, **77**, 1-107 (2005). It describes the theory of energy levels in hydrogen and deuterium relevant to the 2002 CODATA adjustment of the fundamental constants.

Contents

I. RYDBERG DATA

The input data for hydrogen and deuterium for the least-squares adjustment are given in Table I and their covariances are given as correlation coefficients in Table II. The δs given in Table I are quantities added to corresponding theoretical expressions to account for the uncertainties of those expressions, as discussed in Appendix A.

APPENDIX A: Theory relevant to the Rydberg constant

This appendix gives a brief summary of the theory of the energy levels of the hydrogen atom relevant to the determination of the Rydberg constant R_∞ based on measurements of transition frequencies. It is an updated version of an earlier review by one of the authors (Mohr, 1996) and a subsequent review in CODATA-98. In this appendix, information to completely determine the theoretical values for the energy levels used in the current adjustment is provided. Results that were included in CODATA-98 are given with minimal discussion, and the emphasis is on results that have become available since then. For brevity, references to most historical works are not included. Eides, Grotch, and Shelyuto (2001b) have recently provided a comprehensive review of the relevant theory.

It should be noted that the theoretical values of the energy levels of different states are highly correlated. For example, for S states, the uncalculated terms are primarily of the form of an unknown common constant divided by n^3. This fact is taken into account by calculating covariances between energy levels in addition to the uncertainties of the individual levels as discussed in detail in Sec. A.12. To provide the information needed to calculate the covariances, where necessary we distinguish between components of uncertainty that are proportional to $1/n^3$, denoted by u_0, and components of uncertainty that are essentially random functions of n, denoted by u_n.

The energy levels of hydrogen-like atoms are determined mainly by the Dirac eigenvalue, QED effects such as self energy and vacuum polarization, and nuclear size and motion effects. We consider each of these contributions in turn.

1. Dirac eigenvalue

The binding energy of an electron in a static Coulomb field (the external electric field of a point nucleus of charge Ze with infinite mass) is determined predominantly by the Dirac eigenvalue

$$E_{\mathrm{D}} = \left[1 + \frac{(Z\alpha)^2}{(n-\delta)^2}\right]^{-1/2} m_{\mathrm{e}}c^2 \ , \tag{A1}$$

where n is the principal quantum number,

$$\delta = |\kappa| - \left[\kappa^2 - (Z\alpha)^2\right]^{1/2} \ , \tag{A2}$$

and κ is the angular momentum-parity quantum number ($\kappa = -1, 1, -2, 2, -3$ for $\mathrm{S}_{1/2}$, $\mathrm{P}_{1/2}$, $\mathrm{P}_{3/2}$, $\mathrm{D}_{3/2}$, and $\mathrm{D}_{5/2}$ states, respectively). States with the same principal quantum number n and angular momentum quantum number $j = |\kappa| - \frac{1}{2}$ have degenerate eigenvalues. The nonrelativistic orbital angular momentum is given by $l = |\kappa + \frac{1}{2}| - \frac{1}{2}$. (Although we are interested only in the case where the nuclear charge is e, we retain the atomic number Z in order to indicate the nature of various terms.)

Corrections to the Dirac eigenvalue that approximately take into account the finite mass of the nucleus m_{N} are

TABLE I Summary of principal input data for the determination of the 2002 recommended value of the Rydberg constant R_∞. [The notation for the additive corrections $\delta_{\mathrm{X}}(n\mathrm{L}_j)$ in this table has the same meaning as the notation $\delta^{\mathrm{X}}_{n\mathrm{L}j}$ in Appendix A, Sec. A.12.]

Item number	Input datum	Value	Relative standard uncertainty[1] u_r	Identification
$A1$	$\nu_\mathrm{H}(1\mathrm{S}_{1/2}-2\mathrm{S}_{1/2})$	2 466 061 413 187.103(46) kHz	1.9×10^{-14}	MPQ-00
$A2$	$\nu_\mathrm{H}(2\mathrm{S}_{1/2}-8\mathrm{S}_{1/2})$	770 649 350 012.0(8.6) kHz	1.1×10^{-11}	LK/SY-97
$A3$	$\nu_\mathrm{H}(2\mathrm{S}_{1/2}-8\mathrm{D}_{3/2})$	770 649 504 450.0(8.3) kHz	1.1×10^{-11}	LK/SY-97
$A4$	$\nu_\mathrm{H}(2\mathrm{S}_{1/2}-8\mathrm{D}_{5/2})$	770 649 561 584.2(6.4) kHz	8.3×10^{-12}	LK/SY-97
$A5$	$\nu_\mathrm{H}(2\mathrm{S}_{1/2}-12\mathrm{D}_{3/2})$	799 191 710 472.7(9.4) kHz	1.2×10^{-11}	LK/SY-98
$A6$	$\nu_\mathrm{H}(2\mathrm{S}_{1/2}-12\mathrm{D}_{5/2})$	799 191 727 403.7(7.0) kHz	8.7×10^{-12}	LK/SY-98
$A7$	$\nu_\mathrm{H}(2\mathrm{S}_{1/2}-4\mathrm{S}_{1/2})-\frac{1}{4}\nu_\mathrm{H}(1\mathrm{S}_{1/2}-2\mathrm{S}_{1/2})$	4 797 338(10) kHz	2.1×10^{-6}	MPQ-95
$A8$	$\nu_\mathrm{H}(2\mathrm{S}_{1/2}-4\mathrm{D}_{5/2})-\frac{1}{4}\nu_\mathrm{H}(1\mathrm{S}_{1/2}-2\mathrm{S}_{1/2})$	6 490 144(24) kHz	3.7×10^{-6}	MPQ-95
$A9$	$\nu_\mathrm{H}(2\mathrm{S}_{1/2}-6\mathrm{S}_{1/2})-\frac{1}{4}\nu_\mathrm{H}(1\mathrm{S}_{1/2}-3\mathrm{S}_{1/2})$	4 197 604(21) kHz	4.9×10^{-6}	LKB-96
$A10$	$\nu_\mathrm{H}(2\mathrm{S}_{1/2}-6\mathrm{D}_{5/2})-\frac{1}{4}\nu_\mathrm{H}(1\mathrm{S}_{1/2}-3\mathrm{S}_{1/2})$	4 699 099(10) kHz	2.2×10^{-6}	LKB-96
$A11$	$\nu_\mathrm{H}(2\mathrm{S}_{1/2}-4\mathrm{P}_{1/2})-\frac{1}{4}\nu_\mathrm{H}(1\mathrm{S}_{1/2}-2\mathrm{S}_{1/2})$	4 664 269(15) kHz	3.2×10^{-6}	Yale-95
$A12$	$\nu_\mathrm{H}(2\mathrm{S}_{1/2}-4\mathrm{P}_{3/2})-\frac{1}{4}\nu_\mathrm{H}(1\mathrm{S}_{1/2}-2\mathrm{S}_{1/2})$	6 035 373(10) kHz	1.7×10^{-6}	Yale-95
$A13$	$\nu_\mathrm{H}(2\mathrm{S}_{1/2}-2\mathrm{P}_{3/2})$	9 911 200(12) kHz	1.2×10^{-6}	Harv-94
$A14.1$	$\nu_\mathrm{H}(2\mathrm{P}_{1/2}-2\mathrm{S}_{1/2})$	1 057 845.0(9.0) kHz	8.5×10^{-6}	Harv-86
$A14.2$	$\nu_\mathrm{H}(2\mathrm{P}_{1/2}-2\mathrm{S}_{1/2})$	1 057 862(20) kHz	1.9×10^{-5}	USus-79
$A15$	R_p	0.895(18) fm	2.0×10^{-2}	Rp-03
$A16$	$\nu_\mathrm{D}(2\mathrm{S}_{1/2}-8\mathrm{S}_{1/2})$	770 859 041 245.7(6.9) kHz	8.9×10^{-12}	LK/SY-97
$A17$	$\nu_\mathrm{D}(2\mathrm{S}_{1/2}-8\mathrm{D}_{3/2})$	770 859 195 701.8(6.3) kHz	8.2×10^{-12}	LK/SY-97
$A18$	$\nu_\mathrm{D}(2\mathrm{S}_{1/2}-8\mathrm{D}_{5/2})$	770 859 252 849.5(5.9) kHz	7.7×10^{-12}	LK/SY-97
$A19$	$\nu_\mathrm{D}(2\mathrm{S}_{1/2}-12\mathrm{D}_{3/2})$	799 409 168 038.0(8.6) kHz	1.1×10^{-11}	LK/SY-98
$A20$	$\nu_\mathrm{D}(2\mathrm{S}_{1/2}-12\mathrm{D}_{5/2})$	799 409 184 966.8(6.8) kHz	8.5×10^{-12}	LK/SY-98
$A21$	$\nu_\mathrm{D}(2\mathrm{S}_{1/2}-4\mathrm{S}_{1/2})-\frac{1}{4}\nu_\mathrm{D}(1\mathrm{S}_{1/2}-2\mathrm{S}_{1/2})$	4 801 693(20) kHz	4.2×10^{-6}	MPQ-95
$A22$	$\nu_\mathrm{D}(2\mathrm{S}_{1/2}-4\mathrm{D}_{5/2})-\frac{1}{4}\nu_\mathrm{D}(1\mathrm{S}_{1/2}-2\mathrm{S}_{1/2})$	6 494 841(41) kHz	6.3×10^{-6}	MPQ-95
$A23$	R_d	2.130(10) fm	4.7×10^{-3}	Rd-98
$A24$	$\nu_\mathrm{D}(1\mathrm{S}_{1/2}-2\mathrm{S}_{1/2})-\nu_\mathrm{H}(1\mathrm{S}_{1/2}-2\mathrm{S}_{1/2})$	670 994 334.64(15) kHz	2.2×10^{-10}	MPQ-98
$A25$	$\delta_\mathrm{H}(1\mathrm{S}_{1/2})$	0.0(1.7) kHz	$[5.3\times10^{-13}]$	theory
$A26$	$\delta_\mathrm{H}(2\mathrm{S}_{1/2})$	0.00(21) kHz	$[2.6\times10^{-13}]$	theory
$A27$	$\delta_\mathrm{H}(3\mathrm{S}_{1/2})$	0.00(12) kHz	$[3.2\times10^{-13}]$	theory
$A28$	$\delta_\mathrm{H}(4\mathrm{S}_{1/2})$	0.000(43) kHz	$[2.1\times10^{-13}]$	theory
$A29$	$\delta_\mathrm{H}(6\mathrm{S}_{1/2})$	0.000(18) kHz	$[2.0\times10^{-13}]$	theory
$A30$	$\delta_\mathrm{H}(8\mathrm{S}_{1/2})$	0.0000(83) kHz	$[1.6\times10^{-13}]$	theory
$A31$	$\delta_\mathrm{H}(2\mathrm{P}_{1/2})$	0.00(63) kHz	$[7.7\times10^{-13}]$	theory
$A32$	$\delta_\mathrm{H}(4\mathrm{P}_{1/2})$	0.000(79) kHz	$[3.9\times10^{-13}]$	theory
$A33$	$\delta_\mathrm{H}(2\mathrm{P}_{3/2})$	0.00(63) kHz	$[7.7\times10^{-13}]$	theory
$A34$	$\delta_\mathrm{H}(4\mathrm{P}_{3/2})$	0.000(79) kHz	$[3.9\times10^{-13}]$	theory
$A35$	$\delta_\mathrm{H}(8\mathrm{D}_{3/2})$	0.0000(25) kHz	$[4.8\times10^{-14}]$	theory
$A36$	$\delta_\mathrm{H}(12\mathrm{D}_{3/2})$	0.000 00(74) kHz	$[3.2\times10^{-14}]$	theory
$A37$	$\delta_\mathrm{H}(4\mathrm{D}_{5/2})$	0.000(20) kHz	$[9.7\times10^{-14}]$	theory
$A38$	$\delta_\mathrm{H}(6\mathrm{D}_{5/2})$	0.0000(59) kHz	$[6.4\times10^{-14}]$	theory
$A39$	$\delta_\mathrm{H}(8\mathrm{D}_{5/2})$	0.0000(25) kHz	$[4.8\times10^{-14}]$	theory
$A40$	$\delta_\mathrm{H}(12\mathrm{D}_{5/2})$	0.000 00(73) kHz	$[3.2\times10^{-14}]$	theory
$A41$	$\delta_\mathrm{D}(1\mathrm{S}_{1/2})$	0.0(1.5) kHz	$[4.5\times10^{-13}]$	theory
$A42$	$\delta_\mathrm{D}(2\mathrm{S}_{1/2})$	0.00(17) kHz	$[2.1\times10^{-13}]$	theory
$A43$	$\delta_\mathrm{D}(4\mathrm{S}_{1/2})$	0.000(41) kHz	$[2.0\times10^{-13}]$	theory
$A44$	$\delta_\mathrm{D}(8\mathrm{S}_{1/2})$	0.0000(81) kHz	$[1.6\times10^{-13}]$	theory
$A45$	$\delta_\mathrm{D}(8\mathrm{D}_{3/2})$	0.0000(21) kHz	$[4.2\times10^{-14}]$	theory
$A46$	$\delta_\mathrm{D}(12\mathrm{D}_{3/2})$	0.000 00(64) kHz	$[2.8\times10^{-14}]$	theory
$A47$	$\delta_\mathrm{D}(4\mathrm{D}_{5/2})$	0.000(17) kHz	$[8.4\times10^{-14}]$	theory
$A48$	$\delta_\mathrm{D}(8\mathrm{D}_{5/2})$	0.0000(21) kHz	$[4.1\times10^{-14}]$	theory
$A49$	$\delta_\mathrm{D}(12\mathrm{D}_{5/2})$	0.000 00(63) kHz	$[2.7\times10^{-14}]$	theory

[1] The values in brackets are relative to the frequency equivalent of the binding energy of the indicated level.

TABLE II Non-negligible correlation coefficients $r(x_i, x_j)$ of the input data related to R_∞ in Table I. For simplicity, the two items of data to which a particular correlation coefficient corresponds are identified by their item numbers in Table I.

$r(A2, A3) = 0.348$	$r(A5, A20) = 0.114$	$r(A25, A27) = 0.544$	$r(A30, A44) = 0.991$
$r(A2, A4) = 0.453$	$r(A6, A9) = 0.028$	$r(A25, A28) = 0.610$	$r(A31, A32) = 0.049$
$r(A2, A5) = 0.090$	$r(A6, A10) = 0.055$	$r(A25, A29) = 0.434$	$r(A33, A34) = 0.049$
$r(A2, A6) = 0.121$	$r(A6, A16) = 0.151$	$r(A25, A30) = 0.393$	$r(A35, A36) = 0.786$
$r(A2, A9) = 0.023$	$r(A6, A17) = 0.165$	$r(A25, A41) = 0.954$	$r(A35, A45) = 0.962$
$r(A2, A10) = 0.045$	$r(A6, A18) = 0.175$	$r(A25, A42) = 0.936$	$r(A35, A46) = 0.716$
$r(A2, A16) = 0.123$	$r(A6, A19) = 0.121$	$r(A25, A43) = 0.517$	$r(A36, A45) = 0.716$
$r(A2, A17) = 0.133$	$r(A6, A20) = 0.152$	$r(A25, A44) = 0.320$	$r(A36, A46) = 0.962$
$r(A2, A18) = 0.142$	$r(A7, A8) = 0.105$	$r(A26, A27) = 0.543$	$r(A37, A38) = 0.812$
$r(A2, A19) = 0.098$	$r(A7, A21) = 0.210$	$r(A26, A28) = 0.609$	$r(A37, A39) = 0.810$
$r(A2, A20) = 0.124$	$r(A7, A22) = 0.040$	$r(A26, A29) = 0.434$	$r(A37, A40) = 0.810$
$r(A3, A4) = 0.470$	$r(A8, A21) = 0.027$	$r(A26, A30) = 0.393$	$r(A37, A47) = 0.962$
$r(A3, A5) = 0.093$	$r(A8, A22) = 0.047$	$r(A26, A41) = 0.921$	$r(A37, A48) = 0.745$
$r(A3, A6) = 0.125$	$r(A9, A10) = 0.141$	$r(A26, A42) = 0.951$	$r(A37, A49) = 0.745$
$r(A3, A9) = 0.023$	$r(A9, A16) = 0.028$	$r(A26, A43) = 0.511$	$r(A38, A39) = 0.807$
$r(A3, A10) = 0.047$	$r(A9, A17) = 0.031$	$r(A26, A44) = 0.317$	$r(A38, A40) = 0.807$
$r(A3, A16) = 0.127$	$r(A9, A18) = 0.033$	$r(A27, A28) = 0.338$	$r(A38, A47) = 0.744$
$r(A3, A17) = 0.139$	$r(A9, A19) = 0.023$	$r(A27, A29) = 0.241$	$r(A38, A48) = 0.740$
$r(A3, A18) = 0.147$	$r(A9, A20) = 0.028$	$r(A27, A30) = 0.218$	$r(A38, A49) = 0.740$
$r(A3, A19) = 0.102$	$r(A10, A16) = 0.056$	$r(A27, A41) = 0.516$	$r(A39, A40) = 0.806$
$r(A3, A20) = 0.128$	$r(A10, A17) = 0.061$	$r(A27, A42) = 0.518$	$r(A39, A47) = 0.741$
$r(A4, A5) = 0.121$	$r(A10, A18) = 0.065$	$r(A27, A43) = 0.286$	$r(A39, A48) = 0.961$
$r(A4, A6) = 0.162$	$r(A10, A19) = 0.045$	$r(A27, A44) = 0.177$	$r(A39, A49) = 0.737$
$r(A4, A9) = 0.030$	$r(A10, A20) = 0.057$	$r(A28, A29) = 0.270$	$r(A40, A47) = 0.741$
$r(A4, A10) = 0.060$	$r(A11, A12) = 0.083$	$r(A28, A30) = 0.244$	$r(A40, A48) = 0.737$
$r(A4, A16) = 0.165$	$r(A16, A17) = 0.570$	$r(A28, A41) = 0.578$	$r(A40, A49) = 0.961$
$r(A4, A17) = 0.180$	$r(A16, A18) = 0.612$	$r(A28, A42) = 0.581$	$r(A41, A42) = 0.972$
$r(A4, A18) = 0.191$	$r(A16, A19) = 0.123$	$r(A28, A43) = 0.980$	$r(A41, A43) = 0.540$
$r(A4, A19) = 0.132$	$r(A16, A20) = 0.155$	$r(A28, A44) = 0.198$	$r(A41, A44) = 0.333$
$r(A4, A20) = 0.166$	$r(A17, A18) = 0.667$	$r(A29, A30) = 0.174$	$r(A42, A43) = 0.538$
$r(A5, A6) = 0.475$	$r(A17, A19) = 0.134$	$r(A29, A41) = 0.410$	$r(A42, A44) = 0.333$
$r(A5, A9) = 0.021$	$r(A17, A20) = 0.169$	$r(A29, A42) = 0.413$	$r(A43, A44) = 0.184$
$r(A5, A10) = 0.041$	$r(A18, A19) = 0.142$	$r(A29, A43) = 0.228$	$r(A45, A46) = 0.717$
$r(A5, A16) = 0.113$	$r(A18, A20) = 0.179$	$r(A29, A44) = 0.141$	$r(A47, A48) = 0.748$
$r(A5, A17) = 0.123$	$r(A19, A20) = 0.522$	$r(A30, A41) = 0.371$	$r(A47, A49) = 0.748$
$r(A5, A18) = 0.130$	$r(A21, A22) = 0.011$	$r(A30, A42) = 0.373$	$r(A48, A49) = 0.741$
$r(A5, A19) = 0.090$	$r(A25, A26) = 0.979$	$r(A30, A43) = 0.206$	

included in the more general expression for atomic energy levels, which replaces Eq. (A1) (Barker and Glover, 1955; Sapirstein and Yennie, 1990):

$$E_M = Mc^2 + [f(n,j) - 1]m_{\rm r}c^2 - [f(n,j) - 1]^2 \frac{m_{\rm r}^2 c^2}{2M} + \frac{1 - \delta_{l0}}{\kappa(2l+1)} \frac{(Z\alpha)^4 m_{\rm r}^3 c^2}{2n^3 m_{\rm N}^2} + \cdots \ , \qquad \text{(A3)}$$

where

$$f(n,j) = \left[1 + \frac{(Z\alpha)^2}{(n-\delta)^2}\right]^{-1/2} \ , \qquad \text{(A4)}$$

$M = m_{\rm e} + m_{\rm N}$, and $m_{\rm r} = m_{\rm e} m_{\rm N}/(m_{\rm e} + m_{\rm N})$ is the reduced mass.

2. Relativistic recoil

Relativistic corrections to Eq. (A3) associated with motion of the nucleus are considered relativistic-recoil corrections. The leading term, to lowest order in $Z\alpha$ and all orders in $m_{\rm e}/m_{\rm N}$, is (Erickson, 1977; Sapirstein and Yennie, 1990)

$$E_{\rm S} = \frac{m_{\rm r}^3}{m_{\rm e}^2 m_{\rm N}} \frac{(Z\alpha)^5}{\pi n^3} m_{\rm e} c^2 \times \left\{ \tfrac{1}{3}\delta_{l0} \ln(Z\alpha)^{-2} - \tfrac{8}{3} \ln k_0(n,l) - \tfrac{1}{9}\delta_{l0} - \tfrac{7}{3} a_n - \frac{2}{m_{\rm N}^2 - m_{\rm e}^2} \delta_{l0} \left[m_{\rm N}^2 \ln\left(\frac{m_{\rm e}}{m_{\rm r}}\right) - m_{\rm e}^2 \ln\left(\frac{m_{\rm N}}{m_{\rm r}}\right) \right] \right\}, \qquad \text{(A5)}$$

where

$$a_n = -2\left[\ln\left(\frac{2}{n}\right) + \sum_{i=1}^{n}\frac{1}{i} + 1 - \frac{1}{2n}\right]\delta_{l0} + \frac{1-\delta_{l0}}{l(l+1)(2l+1)} \,. \tag{A6}$$

To lowest order in the mass ratio, higher-order corrections in $Z\alpha$ have been extensively investigated; the contribution of the next two orders in $Z\alpha$ can be written as

$$E_{\rm R} = \frac{m_{\rm e}}{m_{\rm N}}\frac{(Z\alpha)^6}{n^3}m_{\rm e}c^2 \times\left[D_{60} + D_{72}Z\alpha\ln^2(Z\alpha)^{-2} + \cdots\right] \,, \tag{A7}$$

where for $n{\rm S}_{1/2}$ states (Eides and Grotch, 1997b; Pachucki and Grotch, 1995)

$$D_{60} = 4\ln 2 - \frac{7}{2} \tag{A8}$$

and for states with $l \geq 1$ (Elkhovskiĭ, 1996; Golosov, Elkhovskiĭ, Mil'shteĭn, and Khriplovich, 1995; Jentschura and Pachucki, 1996)

$$D_{60} = \left[3 - \frac{l(l+1)}{n^2}\right]\frac{2}{(4l^2-1)(2l+3)} \,. \tag{A9}$$

[As usual, the first subscript on the coefficient refers to the power of $Z\alpha$ and the second subscript to the power of $\ln(Z\alpha)^{-2}$.] The next coefficient in Eq. (A7) has been calculated recently with the result (Melnikov and Yelkhovsky, 1999; Pachucki and Karshenboim, 1999)

$$D_{72} = -\frac{11}{60\pi}\,\delta_{l0} \,. \tag{A10}$$

The relativistic recoil correction used in the 2002 adjustment is based on Eqs. (A5) to (A10). Numerical values for the complete contribution of Eq. (A7) to all orders in $Z\alpha$ have been obtained by Shabaev, Artemyev, Beier, and Soff (1998). While these results are in general agreement with the values given by the power series expressions, the difference between them for S states is about three times larger than expected [based on the uncertainty quoted by Shabaev *et al.* (1998) and the estimated uncertainty of the truncated power series which is taken to be one-half the contribution of the term proportional to D_{72}, as suggested by Eides *et al.* (2001b)]. This difference is not critical, and we allow for the ambiguity by assigning an uncertainty for S states of 10 % of the contribution given by Eq. (A7). This is sufficiently large that the power series value is consistent with the numerical all-order calculated value. For the states with $l \geq 1$, we assign an uncertainty of 1 % of the contribution in Eq. (A7). The covariances of the theoretical values are calculated by assuming that the uncertainties are predominately due to uncalculated terms proportional to $(m_{\rm e}/m_{\rm N})/n^3$.

3. Nuclear polarization

Another effect involving specific properties of the nucleus, in addition to relativistic recoil, is nuclear polarization. It arises from interactions between the electron and nucleus in which the nucleus is excited from the ground state to virtual higher states.

For hydrogen, the result that we use for the nuclear polarization is (Khriplovich and Sen'kov, 2000)

$$E_{\rm P}({\rm H}) = -0.070(13)h\frac{\delta_{l0}}{n^3}\ {\rm kHz} \,. \tag{A11}$$

Lager values for this correction have been reported by Martynenko and Faustov (2000); Rosenfelder (1999), but apparently they are based on an incorrect formulation of the dispersion relations (Eides *et al.*, 2001b; Khriplovich and Sen'kov, 2000).

For deuterium, to a good approximation, the polarizability of the nucleus is the sum of the proton polarizability, the neutron polarizibility (Khriplovich and Sen'kov, 1998), and the dominant nuclear structure polarizibility (Friar and Payne, 1997a), with the total given by

$$E_{\rm P}({\rm D}) = -21.37(8)h\frac{\delta_{l0}}{n^3}\ {\rm kHz} \,. \tag{A12}$$

We assume that this effect is negligible in states of higher l.

4. Self energy

The second order (in e, first order in α) level shift due to the one-photon electron self energy, the lowest-order radiative correction, is given by

$$E_{\rm SE}^{(2)} = \frac{\alpha}{\pi}\frac{(Z\alpha)^4}{n^3}F(Z\alpha)\,m_{\rm e}c^2 \,, \tag{A13}$$

where

$$F(Z\alpha) = A_{41}\ln(Z\alpha)^{-2} + A_{40} + A_{50}\,(Z\alpha) + A_{62}\,(Z\alpha)^2\ln^2(Z\alpha)^{-2} + A_{61}\,(Z\alpha)^2\ln(Z\alpha)^{-2} + G_{\rm SE}(Z\alpha)\,(Z\alpha)^2 \,, \tag{A14}$$

with (Erickson and Yennie, 1965)

$$\begin{aligned}
A_{41} &= \tfrac{4}{3}\,\delta_{l0} \\
A_{40} &= -\tfrac{4}{3}\ln k_0(n,l) + \tfrac{10}{9}\,\delta_{l0} - \frac{1}{2\kappa(2l+1)}(1-\delta_{l0}) \\
A_{50} &= \left(\tfrac{139}{32} - 2\ln 2\right)\pi\,\delta_{l0} \\
A_{62} &= -\delta_{l0} \\
A_{61} &= \left[4\left(1+\frac{1}{2}+\cdots+\frac{1}{n}\right) + \frac{28}{3}\ln 2 - 4\ln n - \frac{601}{180} - \frac{77}{45n^2}\right]\delta_{l0} + \left(1-\frac{1}{n^2}\right)\left(\frac{2}{15}+\frac{1}{3}\delta_{j\frac{1}{2}}\right)\delta_{l1} \\
&\quad + \frac{96n^2 - 32l(l+1)}{3n^2(2l-1)(2l)(2l+1)(2l+2)(2l+3)}(1-\delta_{l0}) \,.
\end{aligned} \tag{A15}$$

TABLE III Bethe logarithms $\ln k_0(n,l)$ relevant to the determination of R_∞.

n	S	P	D
1	2.984 128 556		
2	2.811 769 893	−0.030 016 709	
3	2.767 663 612		
4	2.749 811 840	−0.041 954 895	−0.006 740 939
6	2.735 664 207		−0.008 147 204
8	2.730 267 261		−0.008 785 043
12			−0.009 342 954

Bethe logarithms $\ln k_0(n,l)$ that appear in Eq. (A15) needed for this work are given in Table III (Drake and Swainson, 1990).

The function $G_{\rm SE}(Z\alpha)$ in Eq. (A14) gives the higher-order contribution (in $Z\alpha$) to the self energy, and the values for $G_{\rm SE}(\alpha)$ that we use here are listed in Table IV. For the states with $n=1$ and $n=2$, the values in the table are based on direct numerical evaluations by Jentschura, Mohr, and Soff (1999, 2001). The values of $G_{\rm SE}(\alpha)$ for higher-n states are based on the low-Z limit of this function, $G_{\rm SE}(0)=A_{60}$, in the cases where it is known, together with extrapolations of the results of complete numerical calculations of $F(Z\alpha)$ [see Eq. (A14)] at higher Z (Kotochigova, Mohr, and Taylor, 2002; Le Bigot, Jentschura, Mohr, and Indelicato, 2003). There is a long history of calculations of A_{60} (Eides *et al.*, 2001b), leading up to the accurate values of A_{60} for the 1S and 2S states obtained by Pachucki (1992, 1993b, 1999). Values for P and D states subsequently have been reported by Jentschura and Pachucki (1996); Jentschura, Le Bigot, Mohr, Indelicato, and Soff (2003); Jentschura, Soff, and Mohr (1997). Extensive numerical evaluations of $F(Z\alpha)$ at higher Z, which in turn yield values for $G_{\rm SE}(Z\alpha)$, have been done by Indelicato and Mohr (1998); Le Bigot (2001); Mohr (1992); Mohr and Kim (1992).

The dominant effect of the finite mass of the nucleus on the self energy correction is taken into account by multiplying each term of $F(Z\alpha)$ by the reduced-mass factor $(m_{\rm r}/m_{\rm e})^3$, except that the magnetic moment term $-1/[2\kappa(2l+1)]$ in A_{40} is instead multiplied by the factor $(m_{\rm r}/m_{\rm e})^2$. In addition, the argument $(Z\alpha)^{-2}$ of the logarithms is replaced by $(m_{\rm e}/m_{\rm r})(Z\alpha)^{-2}$ (Sapirstein and Yennie, 1990).

The uncertainty of the self energy contribution to a given level arises entirely from the uncertainty of $G_{\rm SE}(\alpha)$ listed in Table IV and is taken to be entirely of type u_n.

5. Vacuum polarization

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

$$E^{(2)}_{\rm VP} = \frac{\alpha}{\pi}\frac{(Z\alpha)^4}{n^3}H(Z\alpha)\,m_{\rm e}c^2\ , \tag{A16}$$

where the function $H(Z\alpha)$ is divided into the part corresponding to the Uehling potential, denoted here by $H^{(1)}(Z\alpha)$, and the higher-order remainder $H^{(\rm R)}(Z\alpha) = H^{(3)}(Z\alpha)+H^{(5)}(Z\alpha)+\cdots$, where the superscript denotes the order in powers of the external field. The individual terms are expanded in a power series in $Z\alpha$ as

$$\begin{aligned} H^{(1)}(Z\alpha) &= V_{40}+V_{50}\,(Z\alpha)+V_{61}\,(Z\alpha)^2\ln(Z\alpha)^{-2} \\ &\quad + G^{(1)}_{\rm VP}(Z\alpha)\,(Z\alpha)^2 \qquad \text{(A17)}\\ H^{(\rm R)}(Z\alpha) &= G^{(\rm R)}_{\rm VP}(Z\alpha)\,(Z\alpha)^2\ , \qquad \text{(A18)}\end{aligned}$$

with

$$\begin{aligned} V_{40} &= -\frac{4}{15}\,\delta_{l0} \\ V_{50} &= \frac{5}{48}\pi\,\delta_{l0} \\ V_{61} &= -\frac{2}{15}\,\delta_{l0}\,. \end{aligned} \tag{A19}$$

The part $G^{(1)}_{\rm VP}(Z\alpha)$ arises from the Uehling potential, and is readily calculated numerically (Kotochigova *et al.*, 2002; Mohr, 1982); values are given in Table V. The higher-order remainder $G^{(\rm R)}_{\rm VP}(Z\alpha)$ has been considered by Wichmann and Kroll, and the leading terms in powers of $Z\alpha$ are (Mohr, 1975, 1983; Wichmann and Kroll, 1956)

$$\begin{aligned} G^{(\rm R)}_{\rm VP}(Z\alpha) &= \left(\frac{19}{45}-\frac{\pi^2}{27}\right)\delta_{l0} \\ &\quad + \left(\frac{1}{16}-\frac{31\pi^2}{2880}\right)\pi(Z\alpha)\delta_{l0}+\cdots\ . \end{aligned} \tag{A20}$$

Higher-order terms omitted from Eq. (A20) are negligible.

In a manner similar to that for the self energy, the leading effect of the finite mass of the nucleus is taken into account by multiplying Eq. (A16) by the factor $(m_{\rm r}/m_{\rm e})^3$ and including a multiplicative factor of $(m_{\rm e}/m_{\rm r})$ in the argument of the logarithm in Eq. (A17).

There is also a second-order vacuum polarization level shift due to the creation of virtual particle pairs other than the e^+e^- pair. The predominant contribution for nS states arises from $\mu^+\mu^-$, with the leading term being (Eides and Shelyuto, 1995; Karshenboim, 1995)

$$E^{(2)}_{\mu\rm VP} = \frac{\alpha}{\pi}\frac{(Z\alpha)^4}{n^3}\left(-\frac{4}{15}\right)\left(\frac{m_{\rm e}}{m_\mu}\right)^2\left(\frac{m_{\rm r}}{m_{\rm e}}\right)^3 m_{\rm e}c^2\ . \tag{A21}$$

The next order term in the contribution of muon vacuum polarization to nS states is of relative order $Z\alpha m_{\rm e}/m_\mu$ and is therefore negligible. The analogous contribution

TABLE IV Values of the function $G_{\mathrm{SE}}(\alpha)$.

n	$\mathrm{S}_{1/2}$	$\mathrm{P}_{1/2}$	$\mathrm{P}_{3/2}$	$\mathrm{D}_{3/2}$	$\mathrm{D}_{5/2}$
1	−30.290 24(2)				
2	−31.185 15(9)	−0.973 5(2)	−0.486 5(2)		
3	−31.01(6)				
4	−30.87(5)	−1.165(2)	−0.611(2)		0.031(1)
6	−30.82(8)				0.034(2)
8	−30.80(9)			0.008(5)	0.034(2)
12				0.009(5)	0.035(2)

TABLE V Values of the function $G^{(1)}_{\mathrm{VP}}(\alpha)$.

n	$\mathrm{S}_{1/2}$	$\mathrm{P}_{1/2}$	$\mathrm{P}_{3/2}$	$\mathrm{D}_{3/2}$	$\mathrm{D}_{5/2}$
1	−0.618 724				
2	−0.808 872	−0.064 006	−0.014 132		
3	−0.814 530				
4	−0.806 579	−0.080 007	−0.017 666		−0.000 000
6	−0.791 450				−0.000 000
8	−0.781 197			−0.000 000	−0.000 000
12				−0.000 000	−0.000 000

$E^{(2)}_{\tau\mathrm{VP}}$ from $\tau^+\tau^-$ (−18 Hz for the 1S state) is also negligible at the level of uncertainty of current interest.

For the hadronic vacuum polarization contribution, we take the result given by Friar, Martorell, and Sprung (1999) that utilizes all available $\mathrm{e}^+\mathrm{e}^-$ scattering data:

$$E^{(2)}_{\mathrm{had\,VP}} = 0.671(15)E^{(2)}_{\mu\mathrm{VP}} \ , \tag{A22}$$

where the uncertainty is of type u_0.

The muonic and hadronic vacuum polarization contributions are negligible for P and D states.

6. Two-photon corrections

Corrections from two virtual photons, of order α^2, have been calculated as a power series in $Z\alpha$:

$$E^{(4)} = \left(\frac{\alpha}{\pi}\right)^2 \frac{(Z\alpha)^4}{n^3} m_{\mathrm{e}}c^2 F^{(4)}(Z\alpha) \ , \tag{A23}$$

where

$$\begin{aligned} F^{(4)}(Z\alpha) &= B_{40} + B_{50}\,(Z\alpha) + B_{63}\,(Z\alpha)^2 \ln^3(Z\alpha)^{-2} \\ &\quad + B_{62}\,(Z\alpha)^2 \ln^2(Z\alpha)^{-2} \\ &\quad + B_{61}\,(Z\alpha)^2 \ln(Z\alpha)^{-2} + B_{60}\,(Z\alpha)^2 \\ &\quad + \cdots \ . \end{aligned} \tag{A24}$$

The leading term B_{40} is well known:

$$\begin{aligned} B_{40} &= \left[\frac{3\pi^2}{2}\ln 2 - \frac{10\pi^2}{27} - \frac{2179}{648} - \frac{9}{4}\zeta(3)\right]\delta_{l0} \\ &\quad + \left[\frac{\pi^2 \ln 2}{2} - \frac{\pi^2}{12} - \frac{197}{144} - \frac{3\zeta(3)}{4}\right]\frac{1-\delta_{l0}}{\kappa(2l+1)} \ . \end{aligned} \tag{A25}$$

The second term has been calculated by Eides, Grotch, and Shelyuto (1997); Eides and Shelyuto (1995); Pachucki (1993a, 1994) with the result

$$B_{50} = -21.5561(31)\delta_{l0} \ . \tag{A26}$$

The next coefficient, as obtained by Karshenboim (1993); Manohar and Stewart (2000); Pachucki (2001); Yerokhin (2000), is

$$B_{63} = -\frac{8}{27}\delta_{l0} \ . \tag{A27}$$

For S states the coefficient B_{62} has been found to be

$$B_{62} = \frac{16}{9}\left[\frac{71}{60} - \ln 2 + \gamma + \psi(n) - \ln n - \frac{1}{n} + \frac{1}{4n^2}\right] \ , \tag{A28}$$

where $\gamma = 0.577...$ is Euler's constant and ψ is the psi function (Abramowitz and Stegun, 1965). The difference $B_{62}(1) - B_{62}(n)$ was calculated by Karshenboim (1996) and confirmed by Pachucki (2001) who also calculated the n-independent additive constant. For P states the calculated value is (Karshenboim, 1996)

$$B_{62} = \frac{4}{27}\frac{n^2-1}{n^2} \ . \tag{A29}$$

This result has been confirmed by Jentschura and Nándori (2002) who also show that for D and higher angular momentum states $B_{62} = 0$.

The single-logarithm coefficient B_{61} for S states is

TABLE VI Values of N used in the 2002 adjustment

n	N
1	17.855 672(1)
2	12.032 209(1)
3	10.449 810(1)
4	9.722 413(1)
6	9.031 832(1)
8	8.697 639(1)

TABLE VII Values of $b_{\rm L}$ and B_{60} used in the 2002 adjustment

n	$b_{\rm L}$	B_{60}
1	−81.4(3)	−61.6(9.2)
2	−66.6(3)	−53.2(8.0)
3	−61.7(5.0)	−50.1(9.0)
4	−59.2(5.0)	−48.4(8.8)
6	−56.7(5.0)	−46.7(8.6)
8	−55.5(5.0)	−45.8(8.5)

given by (Pachucki, 2001)

$$B_{61} = \frac{39\,751}{10\,800} + \frac{4N(n)}{3} + \frac{55\pi^2}{27} - \frac{616\,\ln 2}{135} + \frac{3\pi^2\ln 2}{4} + \frac{40\ln^2 2}{9} - \frac{9\zeta(3)}{8} + \left(\frac{304}{135} - \frac{32\,\ln 2}{9}\right) \times \left[\frac{3}{4} + \gamma + \psi(n) - \ln n - \frac{1}{n} + \frac{1}{4n^2}\right] , \qquad \text{(A30)}$$

where $N(n)$ is a term that was numerically evaluated for the 1S state by Pachucki (2001). Jentschura (2003) has evaluated $N(n)$ for excited S states with $n = 2$ to $n = 8$, has made an improved evaluation for $n = 1$, and has given an approximate fit to the calculated results in order to extend them to higher n. Values of the function $N(n)$ for the states of interest here are given in Table VI. The value at $n = 12$ is based on the extrapolation formula of Jentschura (2003). There are no results yet for P or D states for B_{61}. Based on the relative magnitude of A_{61} for the S, P, and D states, we take as uncertainties $u_n(B_{61}) = 5.0$ for P states and $u_n(B_{61}) = 0.5$ for D states.

The two-loop Bethe logarithm $b_{\rm L}$, which is expected to be the dominant part of the no-log term B_{60}, has been calculated for the 1S and 2S states by Pachucki and Jentschura (2003) who obtained

$$b_{\rm L} = -81.4(3) \quad \text{1S state} \qquad \text{(A31a)}$$
$$b_{\rm L} = -66.6(3) \quad \text{2S state .} \qquad \text{(A31b)}$$

An additional contribution for S states,

$$b_{\rm M} = \frac{10}{9}N , \qquad \text{(A32)}$$

was derived by Pachucki (2001), where N is given in Table VI as a function of the state n. These contributions can be combined to obtain an estimate for the coefficient B_{60} for S states:

$$B_{60} = b_{\rm L} + \frac{10}{9}N + \cdots , \qquad \text{(A33)}$$

where the dots represent uncalculated contributions to B_{60} which are at the relative level of 15 % (Pachucki and Jentschura, 2003). In order to obtain an approximate value for B_{60} for S states with $n \geq 3$, we employ a simple extrapolation formula,

$$b_{\rm L} = a + \frac{b}{n} , \qquad \text{(A34)}$$

with a and b fitted to the 1S and 2S values of $b_{\rm L}$, and we include a component of uncertainty $u_0(b_{\rm L}) = 5.0$. The results for $b_{\rm L}$, along with the total estimated values of B_{60} for S states, is given in Table VII. For P states, there is a calculation of fine-structure differences (Jentschura and Pachucki, 2002), but because of the uncertainty in B_{61} for P states, we do not include this result. We assume that for both the P and D states, the uncertainty attributed to B_{61} is sufficiently large to account for the uncertainty in B_{60} and higher-order terms as well.

As in the case of the order α self-energy and vacuum-polarization contributions, the dominant effect of the finite mass of the nucleus is taken into account by multiplying each term of the two-photon contribution by the reduced-mass factor $(m_{\rm r}/m_{\rm e})^3$, except that the magnetic moment term, the second line of Eq. (A25), is instead multiplied by the factor $(m_{\rm r}/m_{\rm e})^2$. In addition, the argument $(Z\alpha)^{-2}$ of the logarithms is replaced by $(m_{\rm e}/m_{\rm r})(Z\alpha)^{-2}$.

7. Three-photon corrections

The leading contribution from three virtual photons is assumed to have the form

$$E^{(6)} = \left(\frac{\alpha}{\pi}\right)^3 \frac{(Z\alpha)^4}{n^3} m_{\rm e}c^2 \left[C_{40} + C_{50}(Z\alpha) + \cdots\right] , \qquad \text{(A35)}$$

in analogy with Eq. (A23) for two photons. The level shifts of order $(\alpha/\pi)^3(Z\alpha)^4 m_{\rm e}c^2$ that contribute to C_{40} can be characterized as the sum of a self-energy correction, a magnetic-moment correction, and a vacuum polarization correction. The self-energy correction arises from the slope of the Dirac form factor, and it has recently been calculated by Melnikov and Ritbergen (2000) who obtained

$$E^{(6)}_{\rm SE} = \left(\frac{\alpha}{\pi}\right)^3 \frac{(Z\alpha)^4}{n^3} m_{\rm e}c^2 \left[- \frac{868\,{\rm a}_4}{9} + \frac{25\,\zeta(5)}{2} - \frac{17\,\pi^2\,\zeta(3)}{6} - \frac{2929\,\zeta(3)}{72} - \frac{217\,\ln^4 2}{54} - \frac{103\,\pi^2\,\ln^2 2}{270} + \frac{41\,671\,\pi^2\,\ln 2}{540} + \frac{3899\,\pi^4}{6480} - \frac{454\,979\,\pi^2}{9720} - \frac{77\,513}{46\,656}\right] \delta_{l0} , \qquad \text{(A36)}$$

where ζ is the Riemann zeta function and $a_4 = \sum_{n=1}^{\infty} 1/(2^n\, n^4) = 0.517\,479\,061\ldots$. The magnetic-moment correction comes from the known three-loop electron anomalous magnetic moment (Laporta and Remiddi, 1996), and is given by

$$E^{(6)}_{\rm MM} = \left(\frac{\alpha}{\pi}\right)^3 \frac{(Z\alpha)^4}{n^3}\, m_{\rm e}c^2 \left[-\frac{100\,{\rm a}_4}{3} + \frac{215\,\zeta(5)}{24} - \frac{83\,\pi^2\,\zeta(3)}{72} - \frac{139\,\zeta(3)}{18} - \frac{25\,\ln^4 2}{18} + \frac{25\,\pi^2\,\ln^2 2}{18} + \frac{298\,\pi^2\,\ln 2}{9} + \frac{239\,\pi^4}{2160} - \frac{17\,101\,\pi^2}{810} - \frac{28\,259}{5184}\right] \frac{1}{\kappa(2l+1)} , \tag{A37}$$

and the vacuum-polarization correction is (Baikov and Broadhurst, 1995; Eides and Grotch, 1995a)

$$E^{(6)}_{\rm VP} = \left(\frac{\alpha}{\pi}\right)^2 \frac{(Z\alpha)^4}{n^3}\, m_{\rm e}c^2 \left[-\frac{8135\,\zeta(3)}{2304} + \frac{4\,\pi^2\,\ln 2}{15} - \frac{23\,\pi^2}{90} + \frac{325\,805}{93\,312}\right] \delta_{l0} . \tag{A38}$$

The total for C_{40} is

$$C_{40} = \left[-\frac{568\,{\rm a}_4}{9} + \frac{85\,\zeta(5)}{24} - \frac{121\,\pi^2\,\zeta(3)}{72} - \frac{84\,071\,\zeta(3)}{2304} - \frac{71\,\ln^4 2}{27} - \frac{239\,\pi^2\,\ln^2 2}{135} + \frac{4787\,\pi^2\,\ln 2}{108} + \frac{1591\,\pi^4}{3240} - \frac{252\,251\,\pi^2}{9720} + \frac{679\,441}{93\,312}\right]\delta_{l0} + \left[-\frac{100\,{\rm a}_4}{3} + \frac{215\,\zeta(5)}{24} - \frac{83\,\pi^2\,\zeta(3)}{72} - \frac{139\,\zeta(3)}{18} - \frac{25\,\ln^4 2}{18} + \frac{25\,\pi^2\,\ln^2 2}{18} + \frac{298\,\pi^2\,\ln 2}{9} + \frac{239\,\pi^4}{2160} - \frac{17\,101\,\pi^2}{810} - \frac{28\,259}{5184}\right] \frac{1-\delta_{l0}}{\kappa(2l+1)} . \tag{A39}$$

An uncertainty in the three-photon correction is assigned by taking $u_0(C_{50}) = 30\delta_{l0}$ and $u_n(C_{63}) = 1$, where C_{63} is defined by the usual convention.

The dominant effect of the finite mass of the nucleus is taken into account by multiplying C_{40} in Eq. (A39) by the reduced-mass factor $(m_{\rm r}/m_{\rm e})^3$ for $l = 0$ or by the factor $(m_{\rm r}/m_{\rm e})^2$ for $l \neq 0$.

The contribution from four photons is expected to be of order

$$\left(\frac{\alpha}{\pi}\right)^4 \frac{(Z\alpha)^4}{n^3} m_{\rm e}c^2 , \tag{A40}$$

which is about 10 Hz for the 1S state and is negligible at the level of uncertainty of current interest.

8. Finite nuclear size

At low Z, the leading contribution due to the finite size of the nucleus is

$$E^{(0)}_{\rm NS} = \mathcal{E}_{\rm NS}\delta_{l0} , \tag{A41}$$

with

$$\mathcal{E}_{\rm NS} = \frac{2}{3}\left(\frac{m_{\rm r}}{m_{\rm e}}\right)^3 \frac{(Z\alpha)^2}{n^3}\, m_{\rm e}c^2 \left(\frac{Z\alpha R_{\rm N}}{\lambda\!\!\!^{-}_{\rm C}}\right)^2 , \tag{A42}$$

where $R_{\rm N}$ is the bound-state root-mean-square (rms) charge radius of the nucleus and $\lambda\!\!\!^{-}_{\rm C}$ is the Compton wavelength of the electron divided by 2π. The leading higher-order contributions have been examined by Friar (1979b); Friar and Payne (1997b); Karshenboim (1997) [see also Borisoglebsky and Trofimenko (1979); Mohr (1983)]. The expressions that we employ to evaluate the nuclear size correction are the same as those discussed in more detail in CODATA-98.

For S states the leading and next-order corrections are given by

$$E_{\rm NS} = \mathcal{E}_{\rm NS}\left\{1 - C_\eta \frac{m_{\rm r}}{m_{\rm e}}\frac{R_{\rm N}}{\lambda\!\!\!^{-}_{\rm C}} Z\alpha - \left[\ln\left(\frac{m_{\rm r}}{m_{\rm e}}\frac{R_{\rm N}}{\lambda\!\!\!^{-}_{\rm C}}\frac{Z\alpha}{n}\right) + \psi(n) + \gamma - \frac{(5n+9)(n-1)}{4n^2} - C_\theta\right](Z\alpha)^2\right\} , \tag{A43}$$

where C_η and C_θ are constants that depend on the details of the assumed charge distribution in the nucleus. The values used here are $C_\eta = 1.7(1)$ and $C_\theta = 0.47(4)$ for hydrogen or $C_\eta = 2.0(1)$ and $C_\theta = 0.38(4)$ for deuterium.

For the $\mathrm{P}_{1/2}$ states in hydrogen the leading term is

$$E_{\rm NS} = \mathcal{E}_{\rm NS}\frac{(Z\alpha)^2(n^2-1)}{4n^2} . \tag{A44}$$

For $\mathrm{P}_{3/2}$ states and D states the nuclear-size contribution is negligible.

9. 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 must also be considered. This same correction is sometimes called the radiative correction to the nuclear-size effect.

For the self energy, the additional contribution due to the finite size of the nucleus is (Eides and Grotch, 1997a; Milstein, Sushkov, and Terekhov, 2002, 2003a; Pachucki, 1993c)

$$E_{\rm NSE} = \left(4\ln 2 - \frac{23}{4}\right)\alpha(Z\alpha)\mathcal{E}_{\rm NS}\delta_{l0} , \tag{A45}$$

and for the vacuum polarization it is (Eides and Grotch, 1997a; Friar, 1979a; Hylton, 1985)

$$E_{\rm NVP} = \frac{3}{4}\alpha(Z\alpha)\mathcal{E}_{\rm NS}\delta_{l0}\ . \qquad \text{(A46)}$$

For the self-energy term, higher-order size corrections for S states (Milstein *et al.*, 2002) and size corrections for P states have been calculated (Jentschura, 2003; Milstein, Sushkov, and Terekhov, 2003b), but these corrections are negligible for the current work, and are not included. The D-state corrections are assumed to be negligible.

10. Radiative-recoil corrections

The dominant effect of nuclear motion on the self energy and vacuum polarization has been taken into account by including appropriate reduced-mass factors. The additional contributions beyond this prescription are termed radiative-recoil effects with leading terms given by

$$\begin{aligned} E_{\rm RR} &= \frac{m_{\rm r}^3}{m_{\rm e}^2 m_{\rm N}}\frac{\alpha(Z\alpha)^5}{\pi^2\, n^3}m_{\rm e}c^2\delta_{l0} \\ &\quad\times\Bigg[6\,\zeta(3) - 2\,\pi^2\ln 2 + \frac{35\,\pi^2}{36} - \frac{448}{27} \\ &\qquad + \frac{2}{3}\pi(Z\alpha)\,\ln^2(Z\alpha)^{-2} + \cdots\Bigg]\ . \qquad \text{(A47)}\end{aligned}$$

The leading constant term in Eq. (A47) is the sum of the analytic result for the electron-line contribution (Czarnecki and Melnikov, 2001; Eides, Grotch, and Shelyuto, 2001a) and the vacuum-polarization contribution (Eides and Grotch, 1995b; Pachucki, 1995). This term agrees with the numerical value (Pachucki, 1995) used in CODATA-98. The log-squared term has been calculated by Melnikov and Yelkhovsky (1999); Pachucki and Karshenboim (1999).

For the uncertainty, we take a term of order $(Z\alpha)\ln(Z\alpha)^{-2}$ relative to the square brackets in Eq. (A47) with numerical coefficients 10 for u_0 and 1 for u_n. These coefficients are roughly what one would expect for the higher-order uncalculated terms.

11. Nucleus self energy

An additional contribution due to the self energy of the nucleus has been given by Pachucki (1995):

$$\begin{aligned} E_{\rm SEN} &= \frac{4Z^2\alpha(Z\alpha)^4}{3\pi n^3}\frac{m_{\rm r}^3}{m_{\rm N}^2}c^2 \\ &\quad\times\left[\ln\left(\frac{m_{\rm N}}{m_{\rm r}(Z\alpha)^2}\right)\delta_{l0} - \ln k_0(n,l)\right]\ . \qquad \text{(A48)}\end{aligned}$$

This correction has also been examined by Eides *et al.* (2001b), who consider how it is modified by the effect of structure of the proton. The structure effect leads to an additional model-dependent constant in the square brackets in Eq. (A48).

To evaluate the nucleus self-energy correction, we use Eq. (A48) and assign an uncertainty u_0 that corresponds to an additive constant of 0.5 in the square brackets for S states. For P and D states, the correction is small and its uncertainty, compared to other uncertainties, is negligible.

12. Total energy and uncertainty

The total energy $E^{\rm X}_{n{\rm L}j}$ of a particular level (where L = S, P, ... and X = H, D) is the sum of the various contributions listed above plus an additive correction $\delta^{\rm X}_{n{\rm L}j}$ that accounts for the uncertainty in the theoretical expression for $E^{\rm X}_{n{\rm L}j}$. Our theoretical estimate of the value of $\delta^{\rm X}_{n{\rm L}j}$ for a particular level is zero with a standard uncertainty of $u(\delta^{\rm X}_{n{\rm L}j})$ equal to the square root of the sum of the squares (rss) of the individual uncertainties of the contributions, since, as they are defined above, the contributions to the energy of a given level are independent. (Components of uncertainty associated with the fundamental constants are not included here, because they are determined by the least squares adjustment itself.) Thus we have for the square of the uncertainty, or variance, of a particular level

$$u^2(\delta^{\rm X}_{n{\rm L}j}) = \sum_i \frac{u_{0i}^2({\rm XL}j) + u_{ni}^2({\rm XL}j)}{n^6}\ , \qquad \text{(A49)}$$

where the individual values $u_{0i}({\rm XL}j)/n^3$ and $u_{ni}({\rm XL}j)/n^3$ are the components of uncertainty from each of the contributions, labeled by i, discussed above. (The factors of $1/n^3$ are isolated so that $u_{0i}({\rm XL}j)$ is explicitly independent of n.)

The covariance of any two δ's follows from Eq. (F7) of Appendix F of CODATA-98. For a given isotope X, we have

$$u(\delta^{\rm X}_{n_1{\rm L}j}, \delta^{\rm X}_{n_2{\rm L}j}) = \sum_i \frac{u_{0i}^2({\rm XL}j)}{(n_1 n_2)^3}\ , \qquad \text{(A50)}$$

which follows from the fact that $u(u_{0i}, u_{ni}) = 0$ and $u(u_{n_1 i}, u_{n_2 i}) = 0$ for $n_1 \neq n_2$. We also set

$$u(\delta^{\rm X}_{n_1{\rm L}_1 j_1}, \delta^{\rm X}_{n_2{\rm L}_2 j_2}) = 0\ , \qquad \text{(A51)}$$

if $\rm L_1 \neq L_2$ or $j_1 \neq j_2$.

For covariances between δ's for hydrogen and deuterium, we have for states of the same n

$$\begin{aligned} & u(\delta^{\rm H}_{n{\rm L}j}, \delta^{\rm D}_{n{\rm L}j}) \\ &= \sum_{i=i_{\rm c}} \frac{u_{0i}({\rm HL}j)u_{0i}({\rm DL}j) + u_{ni}({\rm HL}j)u_{ni}({\rm DL}j)}{n^6}\ , \qquad \text{(A52)}\end{aligned}$$

and for $n_1 \neq n_2$

$$u(\delta^{\rm H}_{n_1{\rm L}j}, \delta^{\rm D}_{n_2{\rm L}j}) = \sum_{i=i_{\rm c}} \frac{u_{0i}({\rm HL}j)u_{0i}({\rm DL}j)}{(n_1 n_2)^3}\ , \qquad \text{(A53)}$$

where the summation is over the uncertainties common to hydrogen and deuterium. In most cases, the uncertainties can in fact be viewed as common except for a known multiplicative factor that contains all of the mass dependence. We assume

$$u(\delta^{\mathrm{H}}_{n_1\mathrm{L}_1 j_1}, \delta^{\mathrm{D}}_{n_2\mathrm{L}_2 j_2}) = 0 \ , \tag{A54}$$

if $\mathrm{L}_1 \neq \mathrm{L}_2$ or $j_1 \neq j_2$.

The values of $u(\delta^{\mathrm{X}}_{n\mathrm{L}j})$ of interest for the 1998 adjustment are given in Table I of Sec. I, and the nonnegligible covariances of the δ's are given in the form of correlation coefficients in Table II of that section. These coefficients are as large as 0.991.

Since the transitions between levels are measured in frequency units (Hz), in order to apply the above equations for the energy level contributions we divide the theoretical expression for the energy difference ΔE of the transition by the Planck constant h to convert it to a frequency. Further, since we take the Rydberg constant $R_\infty = \alpha^2 m_{\mathrm{e}} c/2h$ (expressed in m^{-1}) rather than the electron mass m_{e} to be an adjusted constant, we replace the group of constants $\alpha^2 m_{\mathrm{e}} c^2/2h$ in $\Delta E/h$ by cR_∞.

13. Transition frequencies between levels with $n = 2$

As an indication of the consistency of the theory summarized above and the experimental data, we list values of the transition frequencies between levels with $n = 2$ in hydrogen. These results are based on values of the constants obtained in a variation of the 2002 least squares adjustment in which the measurements of the directly related transitions (items $A13$, $A14.1$, and $A14.2$ in Table I) are not included. The results are

$$\begin{aligned}
\nu_{\mathrm{H}}(2\mathrm{P}_{1/2} - 2\mathrm{S}_{1/2}) &= 1\,057\,844.5(2.6)\ \mathrm{kHz} \quad [2.4 \times 10^{-6}] \\
\nu_{\mathrm{H}}(2\mathrm{S}_{1/2} - 2\mathrm{P}_{3/2}) &= 9\,911\,197.1(2.6)\ \mathrm{kHz} \quad [2.6 \times 10^{-7}] \\
\nu_{\mathrm{H}}(2\mathrm{P}_{1/2} - 2\mathrm{P}_{3/2}) & \\
&= 10\,969\,041.57(89)\ \mathrm{kHz} \quad [8.1 \times 10^{-8}] \ ,
\end{aligned} \tag{A55}$$

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