

Precise energies of highly excited hydrogen and deuterium

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Abstract: The energy levels of hydrogen and deuterium atoms are calculated to provide frequencies for transitions between highly excited states with principal quantum number n up to 200. All known quantum electrodynamics and relativistic corrections have been included in the calculation. In some cases, contributions originally calculated for a few states have been extrapolated to highly excited states. The fundamental constants necessary for the calculation are taken from the 1998 CODATA least-squares adjustment. Evaluated uncertainties take into account uncertainties in the theoretical calculations, uncertainties in the fundamental constants, and covariances between the various contributions and input parameters.

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Résumé : Nous calculons les niveaux d'énergie de l'hydrogène et du deutérium pour fournir les fréquences de transition entre des niveaux hautement excités dont le nombre quantique principal n peut aller jusqu'à 200. Nous incluons dans les calculs toutes les corrections QED et relativistes connues. Dans certains cas, nous avons extrapolé vers des niveaux hautement excités des contributions initialement calculées pour des niveaux de basse énergie. Les constantes fondamentales nécessaires à ces calculs sont tirées des valeurs de 1998 CODATA obtenues par moindre carré. Notre calcul d'erreur tient compte des incertitudes dans le calcul théorique, des incertitudes dans la valeur des constantes fondamentales et des covariances entre différentes contributions et les paramètres d'entrée.

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1. Introduction

In this article, we describe our calculation of the energy levels of hydrogen and deuterium atoms in a wide range of the principal quantum number n up to 200 and all possible corresponding orbital l and total j angular momenta.

The goal of this research is to provide precise total energies and frequencies for transitions between the metastable 2S and a highly excited state or between any excited states of H and D. Interest in these transitions has been sparked by the possibility of creating ultra-cold samples of 2S hydrogen [1]. Starting from this metastable state, Rydberg levels can be accessed more easily. The use of Rydberg atoms with a large principal quantum number $n \geq 10$ and maximum l in the Rydberg constant experiments offers an opportunity to increase the accuracy of the measurement of this fundamental constant [2]. Moreover,

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from the theoretical point of view, these states are the best candidates for the precise calculation of energy levels. They are least sensitive to nuclear effects, and they have small Lamb-shift and contact-term corrections.

The most accurate measurements of hydrogen transition frequencies do not go beyond excitation to the $n = 12$ level [3]. Precise calculation of energy levels that cover a much higher range of n will provide helpful information for future experiments.

In this paper, we analyze all known contributions to the energy of the ground and excited levels. Together with the main contribution from the Dirac eigenvalues, corrections due to the self energy, vacuum polarization, finite nuclear size, and nuclear-motion effects are considered to obtain precise values. For the energy levels calculated in this work to be consistent with the 1998 CODATA recommended values of the fundamental constants given in ref. 4, we include only the theoretical results that were included in the evaluation of the constants. There has been significant subsequent theoretical work, but its impact on the predicted energy levels is limited by uncertainties in the nuclear size and higher order quantum-electrodynamics (QED) corrections. As a result of this limitation, only theoretical results available on 31 December 1998 are included here as in ref. 4.

The calculation of energy levels is based on many different approaches, including power series in $Z\alpha$, where α is the fine-structure constant, and all-order numerical calculations of the QED contributions. However, in some cases we extend these results to higher n applying extrapolations. To obtain the nuclear mass, we use parameters from the literature, such as the relative atomic mass [5], and the ionization energy [6] rescaled, in this study, to the new recommended value of R_∞ in ref. 4. The fundamental constants used in this calculation are taken from ref. 4.

The calculation of uncertainties is based on the fact that the uncertainties of the different contributions to a given energy level are independent. However, in many cases the uncertainties of contributions of the same type to different energy levels are not independent. Therefore, it is important to also consider the covariances among the theoretical expressions for the energy levels and the fundamental constants. The total energies of hydrogen and deuterium starting for some levels in the range from $n = 16$ to $n = 25$ are presented as an example in Table 1. We provide the total energies of 2S metastable states of H and D as well, to be used to evaluate transition frequencies if necessary. The covariances between the 2S level and the Rydberg levels are not important, because the uncertainty of the 2S level is so much larger.

2. Relativistic corrections

The expression from the Dirac equation that takes into account the finite nuclear mass m_N is given in [7, 8]

$$E_M = Mc^2 + [f(n, j) - 1]m_r c^2 - [f(n, j) - 1]^2 \frac{m_r^2 c^2}{2M} + \frac{1 - \delta_{l0}}{\kappa(2l + 1)} \frac{(Z\alpha)^4 m_r^3 c^2}{2n^3 m_N^2} + \dots \quad (1)$$

where $M = m_e + m_N$, $m_r = m_e m_N / (m_e + m_N)$ is the reduced mass, κ is the angular momentum-parity quantum number, and

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

The eigenvalues of (1) provide the major part of the total energy of an electron in hydrogen.

Higher order relativistic corrections to (1) include the relativistic recoil correction. The numerical calculation of this correction for the 1S, 2S, and 2P_{1/2} levels of order $m_e/m_N(Z\alpha)^5 m_e c^2$ is done in

Table 1. Theoretical total energies of some Rydberg states of hydrogen and deuterium atoms.

<i>nl</i>	<i>j</i>	Hydrogen energy (Hz)	Uncertainty (Hz)	Deuterium energy (Hz)	Uncertainty (Hz)
2S	1/2	-822 025 443 939 668	3522	-822 249 114 536 667	3524
16S	1/2	-12 843 988 804 332	92	-12 847 483 640 810	92
16P	3/2	-12 843 969 464 838	97	-12 847 464 298 187	97
16P	1/2	-12 843 990 888 600	97	-12 847 485 727 796	97
16D	5/2	-12 843 962 360 398	97	-12 847 457 191 834	97
16D	3/2	-12 843 969 501 534	97	-12 847 464 334 919	97
17S	1/2	-11 377 372 248 460	81	-11 380 468 020 174	81
17P	3/2	-11 377 356 125 035	86	-11 380 451 894 140	86
17P	1/2	-11 377 373 986 160	86	-11 380 469 760 141	86
17D	5/2	-11 377 350 202 025	86	-11 380 445 969 536	86
17D	3/2	-11 377 356 155 636	86	-11 380 451 924 771	86
19S	1/2	-9 108 198 444 765	65	-9 110 676 776 710	66
19P	3/2	-9 108 186 895 835	69	-9 110 665 225 912	69
19P	1/2	-9 108 199 689 491	69	-9 110 678 023 060	69
19D	5/2	-9 108 182 653 281	69	-9 110 660 982 215	69
19D	3/2	-9 108 186 917 763	69	-9 110 665 247 861	69
25S	1/2	-5 260 892 299 555	38	-5 262 323 783 438	38
25P	3/2	-5 260 887 229 884	40	-5 262 318 712 947	40
25P	1/2	-5 260 892 845 988	40	-5 262 324 330 584	40
25D	5/2	-5 260 885 367 512	40	-5 262 316 850 073	40
25D	3/2	-5 260 887 239 516	40	-5 262 318 722 589	40

ref. 9 and the result, including additional terms of higher order in m_e/m_N , is given in refs. 6 and 8

$$E_S = \frac{m_r^3}{m_e^2 m_N} \frac{(Z\alpha)^5}{\pi n^3} m_e c^2 \times \left\{ \frac{1}{3} \delta_{l0} \ln(Z\alpha)^{-2} - \frac{8}{3} \ln k_0(n, l) - \frac{1}{9} \delta_{l0} - \frac{7}{3} a_n - \frac{2}{m_N^2 - m_e^2} \delta_{l0} \left[m_N^2 \ln \left(\frac{m_e}{m_r} \right) - m_e^2 \ln \left(\frac{m_N}{m_r} \right) \right] \right\} \quad (3)$$

where

$$a_n = -2 \left[\ln \left(\frac{2}{n} \right) + \sum_{i=1}^n \frac{1}{i} + 1 - \frac{1}{2n} \right] \delta_{l0} + \frac{1 - \delta_{l0}}{l(l+1)(2l+1)} \quad (4)$$

The Bethe logarithms $\ln k_0(n, l)$ are given, for example, in ref. 10.

The contribution of lowest order in m_e/m_N and next order in $Z\alpha$ is

$$E_R = \frac{m_e}{m_N} \frac{(Z\alpha)^6}{n^3} m_e c^2 D_{60} \quad (5)$$

where for S states $D_{60} = 4 \ln 2 - \frac{7}{2}$ [11, 12] and for states with $l \geq 1$, $D_{60} = \left[3 - \frac{l(l+1)}{n^2} \right] \frac{2}{(4l^2-1)(2l+3)}$ [13, 14]. Small additional higher order corrections are included, as described in ref. 4.

The nuclear polarization correction is an effect related to nuclear recoil. This effect has been calculated for the 1S state of hydrogen [15]. The result is

$$E_P(H) = -0.071(13) h \frac{\delta_{l0}}{n^3} \text{ kHz} \quad (6)$$

Table 2. Calculated values of A_{60} .

n	$S_{1/2}$	$P_{1/2}$	$P_{3/2}$
1	-30.924 15(1)		
2	-31.840 47(1)	-0.998 91(1)	-0.503 37(1)
3		-1.147 68(1)	-0.597 56(1)
4		-1.195 68(1)	-0.630 94(1)

We assume that the contribution is proportional to $1/n^3$, since it is mainly proportional to the square of the wave function at the origin. For higher l , we take this contribution to be zero.

For deuterium, the effect is much larger. A recent calculation in ref. 16, which includes corrections that go beyond the unretarded-dipole approximation calculation [17], gives -18.58(7) kHz for the 1S–2S transition. Because of the near $1/n^3$ dependence of this contribution, the value for the 1S state is -21.23(8) [18]. In addition to this deuteron polarizability, the polarizability contributions of the constituent particles, -0.071(13) kHz from the proton and -0.061(12) kHz from the neutron for the 1S state, should be taken into account, although the contribution of the proton polarizability to the H–D isotope shift vanishes [18–20]. See also refs. 21 and 22.

3. QED corrections

The largest QED effect is due to the one-photon electron self-energy. It has the form

$$E_{\text{SE}}^{(2)} = \frac{\alpha}{\pi} \frac{(Z\alpha)^4}{n^3} F(Z\alpha) m_e c^2 \quad (7)$$

where

$$F(Z\alpha) = A_{41} \ln(Z\alpha)^{-2} + A_{40} + A_{50}(Z\alpha) + A_{62}(Z\alpha)^2 \ln^2(Z\alpha)^{-2} + A_{61}(Z\alpha)^2 \ln(Z\alpha)^{-2} + G_{\text{SE}}(Z\alpha)(Z\alpha)^2 \quad (8)$$

with ref. 23

$$A_{41} = \frac{4}{3}\delta_{l0}, \quad A_{40} = -\frac{4}{3}\ln k_0(n, l) + \frac{11}{18}\delta_{l0} - \frac{1}{2\kappa(2l+1)}, \quad A_{50} = \left(\frac{139}{32} - 2\ln 2\right)\pi\delta_{l0} \quad (9)$$

and

$$\begin{aligned} A_{62} = -\delta_{l0}, \quad A_{61} = & \left[4\left(1 + \frac{1}{2} + \dots + \frac{1}{n}\right) + \frac{28}{3}\ln 2 - 4\ln n - \frac{601}{180} - \frac{77}{45n^2} \right]\delta_{l0} \\ & + \left(1 - \frac{1}{n^2}\right)\left(\frac{2}{15} + \frac{1}{3}\delta_{j,\frac{1}{2}}\right)\delta_{l1} + \frac{96n^2 - 32l(l+1)}{3n^2(2l-1)(2l)(2l+1)(2l+2)(2l+3)}(1 - \delta_{l0}) \end{aligned} \quad (10)$$

The low- Z limit of the function $G_{\text{SE}}(Z\alpha) = A_{60}$ has been calculated to high precision in refs. 24, 20, 25, and 26. The results are given in Table 2. The function $F(Z\alpha)$ and the corresponding value for $G_{\text{SE}}(Z\alpha)$ in (8) have been calculated for the 1S state of hydrogen in ref. 27. There have been calculations for other states, but to maintain consistency with ref. 4, we obtain the required information for the $n = 1, 2$ states from values calculated in ref. 28 in the range $10 \leq Z \leq 50$; for the $S_{1/2}, P_{1/2,3/2}$, and $D_{3/2}$ states with $3 \leq n \leq 5$, we use the results given in ref. 29. The function $G_{\text{SE}}(Z\alpha)$ is expected to have an expansion of the form

$$G_{\text{SE}}(Z\alpha) = A_{60} + A_{71}Z\alpha \ln(Z\alpha)^{-2} + A_{70}Z\alpha + \dots \quad (11)$$

Table 3. Values of G_{SE} and the parameters ΔA and B for S states.

$1S_{1/2}$	$2S_{1/2}$	$3S_{1/2}$	$4S_{1/2}$	$5S_{1/2}$	ΔA	B
-30.290 24(2)	-31.17(3)	-31.01(6)	-30.87(5)	-30.83(5)	-0.43	-0.6

Table 4. Values of G_{SE} and the parameters ΔA and B for $P_{1/2}$ states.

$2P_{1/2}$	$3P_{1/2}$	$4P_{1/2}$	ΔA	B
-0.98(1)	-1.13(1)	-1.17(1)	-0.35	0.62

Table 5. Values of G_{SE} and the parameters ΔA and B for $P_{3/2}$ states.

$2P_{3/2}$	$3P_{3/2}$	$4P_{3/2}$	ΔA	B
-0.48(1)	-0.57(1)	-0.61(1)	-0.21	0.36

For higher n , for each value of Z , we fit the values of $G_{\text{SE}}(Z\alpha)$ for $n = 4$ and 5 to a function of the form $G_{\text{SE}}(n, Z\alpha) = A(Z\alpha) + B(Z\alpha)/n$ and use this function to calculate the values for $n > 5$. In fact, we slightly modify the values of $A(Z\alpha)$ and $B(Z\alpha)$ to eliminate fluctuations as a function of Z due to round-off errors in the values of $G_{\text{SE}}(Z\alpha)$. The results are shown in Table 3, where the values of $G_{\text{SE}}(Z\alpha)$ are listed for $n = 1$ to 5, and the values of the parameters $\Delta A(Z\alpha) = A(Z\alpha) - G_{\text{SE}}(1S, Z\alpha)$ and $B(Z\alpha)$ used to obtain values for higher n are also given.

For the $2P_{1/2}$ and $2P_{3/2}$ states, we make similar extrapolations, taking into account the calculated values of A_{60} as given in Table 2. For $nP_{1/2}$ and $nP_{3/2}$ states with $n = 3$ to 5, we extrapolated differences between the calculated values of $G_{\text{SE}}(Z\alpha)$ and the corresponding values for the $2P_{1/2}$ and $2P_{3/2}$ states. In this case, for higher n , the extrapolation parameters A and B given in the above expression for $G_{\text{SE}}(n, Z\alpha)$ are based on the values of $G_{\text{SE}}(Z\alpha)$ for $n = 3$ and $n = 4$, because the values of A_{60} that are available for these states make the extrapolations from higher Z more stable. The results are shown in Tables 4 and 5.

For $D_{3/2}$ states there are calculated values of $F(Z\alpha)$ for $Z \geq 10$ [29] from which values of G_{SE} may be deduced. Extrapolation of these values to $Z \leq 10$ leads to results nearly independent of n that are very small and consistent with zero with an uncertainty of about 0.01.

The effect of the finite mass of the nucleus on the self-energy correction is partially taken into account by multiplying each term of $F(Z\alpha)$ by the reduced-mass factor $(m_r/m_e)^3$, except that the magnetic moment term $-1/[2\kappa(2l+1)]$ in A_{40} is multiplied by the factor $(m_r/m_e)^2$ instead. In addition, the argument $(Z\alpha)^{-2}$ of the logarithms is replaced by $(m_e/m_r)(Z\alpha)^{-2}$ [8]. Other effects of the finite mass of the nucleus are discussed below.

The uncertainty of the self-energy contribution to a given level arises entirely from the uncertainty of $G_{\text{SE}}(Z\alpha)$.

Vacuum polarization is a second-order QED effect corresponding to the creation of a virtual electron-positron pair in the exchange of photons between the electron and the nucleus. The shift of the energy level due to this effect is

$$E_{\text{VP}}^{(2)} = \frac{\alpha}{\pi} \frac{(Z\alpha)^4}{n^3} H(Z\alpha) m_e c^2 \quad (12)$$

where the function $H(Z\alpha)$ is here divided into two parts. The first part $H^{(1)}(Z\alpha)$ is associated with the Uehling potential, and the second part is the higher order remainder $H^{(\text{R})}(Z\alpha) = H^{(3)}(Z\alpha) +$

Table 6. Values of the function $G_{\text{VP}}^{(1)}(Z\alpha)$ for $nS_{1/2}$, $P_{1/2}$, and $P_{3/2}$ states, $n = 1$ to 20 for hydrogen.

n	$S_{1/2}$	$P_{1/2}$	$P_{3/2}$	n	$S_{1/2}$	$P_{1/2}$	$P_{3/2}$
1	-0.618 724			11	-0.771 475	-0.084 635	-0.018 688
2	-0.808 872	-0.064 006	-0.014 132	12	-0.769 151	-0.084 748	-0.018 713
3	-0.814 530	-0.075 859	-0.016 750	13	-0.767 139	-0.084 835	-0.018 732
4	-0.806 579	-0.080 007	-0.017 666	14	-0.765 380	-0.084 905	-0.018 747
5	-0.798 362	-0.081 927	-0.018 090	15	-0.763 831	-0.084 961	-0.018 760
6	-0.791 450	-0.082 970	-0.018 320	16	-0.762 456	-0.085 007	-0.018 770
7	-0.785 811	-0.083 599	-0.018 459	17	-0.761 229	-0.085 045	-0.018 778
8	-0.781 197	-0.084 007	-0.018 549	18	-0.760 125	-0.085 077	-0.018 785
9	-0.777 381	-0.084 287	-0.018 611	19	-0.759 129	-0.085 104	-0.018 791
10	-0.774 184	-0.084 487	-0.018 655	20	-0.758 225	-0.085 127	-0.018 796

$H^{(5)}(Z\alpha) + \dots$, where the superscript denotes the order in powers of the external field. The above terms can be written with the leading powers in $Z\alpha$ given explicitly as

$$H^{(1)}(Z\alpha) = C_{40} + C_{50}(Z\alpha) + C_{61}(Z\alpha)^2 \ln(Z\alpha)^{-2} + G_{\text{VP}}^{(1)}(Z\alpha)(Z\alpha)^2 \quad (13)$$

$$H^{(\text{R})}(Z\alpha) = G_{\text{VP}}^{(\text{R})}(Z\alpha)(Z\alpha)^2 \quad (14)$$

with

$$C_{40} = -\frac{4}{15}\delta_{l0}, \quad C_{50} = \frac{5}{48}\pi\delta_{l0}, \quad C_{61} = -\frac{2}{15}\delta_{l0}$$

The part $G_{\text{VP}}^{(1)}(Z\alpha)$ arises from the Uehling potential, and numerically calculated values based on a formulation in ref. 30 are given in Table 6 for $S_{1/2}$, $P_{1/2}$, and $P_{3/2}$ states. For states with $l \geq 2$, the function $G_{\text{VP}}^{(1)}(Z\alpha)$ is less than 1×10^{-5} for $1 \leq Z \leq 10$, so its contribution to the energy is not included.

The effect of the finite mass of the nucleus is taken into account by multiplying (12) by the factor $(m_r/m_e)^3$ and including a multiplicative factor of (m_e/m_r) in the argument of the logarithm in (13).

The two-photon correction is a QED effect involving two virtual photons, and is of order α^2 . The uncertainty of this correction is the largest intrinsic uncertainty in the theoretical expression for hydrogen energy levels. The shift of energy due to this correction is introduced by a series expansion in powers of $Z\alpha$

$$E^{(4)} = \left(\frac{\alpha}{\pi}\right)^2 \frac{(Z\alpha)^4}{n^3} m_e c^2 F^{(4)}(Z\alpha) \quad (15)$$

where

$$\begin{aligned} F^{(4)}(Z\alpha) &= B_{40} + B_{50}(Z\alpha) + B_{63}(Z\alpha)^2 \ln^3(Z\alpha)^{-2} + B_{62}(Z\alpha)^2 \ln^2(Z\alpha)^{-2} + \dots \\ &= B_{40} + (Z\alpha)G^{(4)}(Z\alpha) \end{aligned} \quad (16)$$

The next and higher order terms $B_{61}(Z\alpha)^2 \ln(Z\alpha)^{-2}$, $B_{60}(Z\alpha)^2$, etc., are not included in (15) because insufficient information existed about them at the time ref. 4 was written, although partial results existed for B_{61} [31–34]. The level shifts of order $(\alpha/\pi)^2(Z\alpha)^4 m_e c^2$ that give rise to B_{40} are well known

$$B_{40} = \left[2\pi^2 \ln 2 - \frac{49}{108}\pi^2 - \frac{6131}{1296} - 3\zeta(3)\right]\delta_{l0} + \left[\frac{1}{2}\pi^2 \ln 2 - \frac{1}{12}\pi^2 - \frac{197}{144} - \frac{3}{4}\zeta(3)\right] \frac{1}{\kappa(2l+1)} \quad (17)$$

where ζ is the Riemann zeta function.

The next two coefficients are $B_{50} = -21.5561(31)$ [35–38] and $B_{63} = -\frac{8}{27}$ [39]. However, to take into account the results of all-order numerical calculations [34, 40], we follow the approach of ref. 4 and evaluate the two-photon contributions of nS states using

$$F^{(4)}(Z\alpha) = B_{40} + (Z\alpha) \left(B_{50} - B_{50}^{\ell\ell} \right) + (Z\alpha) G_{\ell\ell}^{(4)}(Z\alpha) + B_{62}(n)(Z\alpha)^2 \ln^2(Z\alpha)^{-2} + \dots \quad (18)$$

where $B_{50}^{\ell\ell} = 2.29953$ is subtracted to avoid double counting, and where $G_{\ell\ell}^{(4)}(Z\alpha) = -1.3(1.5)$ is taken to be the same for all n . Note that a more recent calculation [41] is in agreement with the result in ref. 34.

The coefficient B_{62} has been calculated in ref. 42 to be

$$B_{62}(n) = \frac{16}{9} \left(C + \psi(n) - \ln n - \frac{1}{n} + \frac{1}{4n^2} \right) \quad (19)$$

where ψ is the psi function [43]. We replace the unknown constant C by zero in the evaluation and include a corresponding component of uncertainty.

For P states we have

$$F^{(4)}(Z\alpha) = B_{40} + B_{62}(n)(Z\alpha)^2 \ln^2(Z\alpha)^{-2} + \dots \quad (20)$$

where in ref. 42

$$B_{62} = \frac{4}{27} \frac{n^2 - 1}{n^2} \quad (21)$$

For D or higher l states, only the contribution of B_{40} is included. More recent calculations of the two-loop corrections are given in refs. 44 and 45.

As in the case of the one-photon self-energy and vacuum polarization contributions, the dominant effect of the finite mass of the nucleus on the two-photon contributions is introduced by multiplying all terms except the magnetic-moment term by the reduced-mass factor $(m_r/m_e)^3$. The magnetic-moment term is multiplied by the factor $(m_r/m_e)^2$. In addition, the argument $(Z\alpha)^{-2}$ of the logarithms is replaced by $(m_e/m_r)(Z\alpha)^{-2}$.

Following ref. 4, we take the correction due to three virtual photons, of order α^3 , to be zero for all states, with a standard uncertainty equal to 1, although the leading three-photon correction has been calculated since then [46].

4. Finite nuclear-size and nuclear-motion effects

At low Z , the leading contribution due to the finite size of the nucleus is $E_{NS} = \mathcal{E}(1 + \eta + \theta')$, where

$$\mathcal{E} = \frac{2}{3} \left(\frac{m_r}{m_e} \right)^3 \frac{(Z\alpha)^2}{n^3} m_e c^2 \left(\frac{Z\alpha R_N}{\lambda_C} \right)^{2s} \quad (22)$$

R_N is the bound-state root-mean-square (rms) charge radius of the nucleus, λ_C is the Compton wavelength of the electron divided by 2π , and $s = \sqrt{1 - (Z\alpha)^2}$. The expressions for η and θ' are

$$\eta = -C_\eta \frac{m_r}{m_e} \frac{Z\alpha R_N}{\lambda_C} \quad (23)$$

and in refs. 47 and 48

$$\theta' = (Z\alpha)^2 C_\theta + (Z\alpha)^2 \left[\ln n - \psi(n) - \gamma + \frac{(5n+9)(n-1)}{4n^2} \right] \quad (24)$$

where γ is the Euler constant. The quantities $C_\eta \approx 1.7$ and $C_\theta = 0.465\,457\dots$, for a Gaussian charge distribution for hydrogen, are numerical constants that contain all of the model dependence.

For deuterium, we take the results obtained in refs. 49 and 18, which can be evaluated to give

$$C_\eta = 2.0, C_\theta = 0.383(3) \quad (25)$$

where the uncertainty of C_θ simply indicates the spread in values resulting from various potential models for the deuteron. For the $P_{1/2}$ states we generalize the expression given in ref. 47 to include the fractional power

$$E_{\text{NS}} = \mathcal{E} \frac{(Z\alpha)^2(n^2 - 1)}{4n^2} \quad (26)$$

For higher j states the nuclear-size contribution is negligible. The uncertainty of the nuclear-size contribution, apart from that due to the rms radius of the nucleus, is negligible.

The nuclear-size correction can effect the self-energy and vacuum-polarization contributions. The additional contribution for the self energy is [50, 51]

$$E_{\text{NSE}} = -1.985(1) \frac{3}{2} \alpha(Z\alpha) \mathcal{E}_{\text{NS}} \delta_{l0} \quad (27)$$

The correction to the vacuum polarization due to nuclear size is calculated in ref. 52

$$E_{\text{NVP}} = \frac{3}{4} \alpha(Z\alpha) \mathcal{E}_{\text{NS}} \delta_{l0} \quad (28)$$

and has been obtained independently in refs. 53 and 50. The additional contribution to the reduced mass that involves both radiative corrections and nuclear motion are known as radiative-recoil effects. For this correction, we use the result of ref. 54, given by

$$E_{\text{RR}} = -1.364\,49(1) \alpha \frac{(Z\alpha)^5}{n^3} \frac{m_e}{m_N} m_e c^2 \delta_{l0} \quad (29)$$

(As indicated by the factor δ_{l0} , this contribution is zero for all states with $l \geq 1$.) For the uncertainty, we take the next term, which is of relative order $Z\alpha$, with numerical coefficient 100. This coefficient corresponds to the higher order uncalculated terms of order $\ln^2(Z\alpha)^{-2}$ and $\ln(Z\alpha)^{-2}$.

5. Nucleus self-energy

The contribution due to the self energy of the nucleus is given in ref. 54

$$E_{\text{NSE}}(n, l) = \frac{4Z^2\alpha(Z\alpha)^4}{3\pi n^3} \frac{m_r^3}{m_N^2} c^2 \times \left[\ln \left(\frac{m_N}{m_r(Z\alpha)^2} \right) \delta_{l0} - \ln k_0(n, l) \right] \quad (30)$$

We take the term itself as its uncertainty.

6. Total energies of Rydberg hydrogen and deuterium atoms

The total energy E_{nLj} of a particular level is just the sum of the various contributions listed above plus an additive correction δ_{nLj} that accounts for the uncertainty in the theoretical expression for E_{nLj} . For hydrogen, best values of the corrections δ_{nLj} , for certain energy levels, have been determined in the least-squares adjustment of the fundamental constants, which included a systematic comparison of theory and experiment in hydrogen and deuterium [4].

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