Hyperfine structure of the ground and first excited states in light hydrogen-like atoms and high-precision tests of QED

S.G. Karshenboim^{1,2,a} and V.G. Ivanov^{1,3}

 $^{1}\,$ D.I. Mendeleev Institute for Metrology, 198005 St. Petersburg, Russia

² Max-Planck-Institut für Quantenoptik, 85748 Garching, Germany

³ Pulkovo Observatory, 196140 St. Petersburg, Russia

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Abstract. We consider hyperfine splitting of 1s and, in part, of 2s levels in light hydrogen-like atoms: hydrogen, deuterium, tritium, helium-3 ion, muonium and positronium. We discuss present status of precision theory and experiment for the hfs intervals. We pay a special attention to a specific difference, $D_{21} = 8E_{\rm hfs}(2s) - E_{\rm hfs}(1s)$, which is known experimentally for hydrogen, deuterium and ³He⁺ ion. The difference is weakly affected by the effects of the nuclear structure and thus may be calculated with a high accuracy. We complete a calculation of the fourth order *QED* contributions to this difference and present here new results on corrections due to the nuclear effects. Our theoretical predictions appear to be in a fair agreement with available experimental data. Comparison of the experimental data with our examination of D_{21} allows to test the state-dependent sector of theory of the hfs separation of the 1s and 2s levels in the light hydrogen-like atoms up to 10^{-8} .

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1 Introduction

The hyperfine structure (hfs) interval in the ground state of a number of simple atoms (hydrogen [1], deuterium [2], tritium [3] and helium-3 ion [4]) has been measured with a high precision. The hfs separation in the 2s metastable state in hydrogen [5,6], deuterium [7] and the ${}^{3}\text{He}^{+}$ ion [8, 9] was also measured accurately. Some experimental results are as old as almost fifty years, but the accuracy of even present-day theoretical calculations for the hfs interval in those light atoms is much lower than that for the experiments (see e.g. Tab. 1). Theory of the hfs interval in simple atoms is essentially based on the bound state Quantum Electrodynamics (QED), however effects due to the nuclear structure are unavoidable and they strongly affect the energy levels. Their uncertainty limits the theoretical accuracy for the hyperfine splitting in hydrogen, deuterium, tritium and helium-3 ion on a level of 10-200 ppm.

One of ways to avoid the problem of the nuclear effects is to study atoms free of any nuclear structure such as muonium and positronium. Hyperfine splitting in these pure leptonic atoms was measured [10-13] with an accuracy appropriate for precision tests of the bound state *QED*. Other possibilities to avoid the problem of lack of accurate knowledge of the corrections induced by the

nuclear effects is related to a fact that those corrections are proportional to the squared value of the wave function at the origin

$$\Delta E(\text{Nucl}) = A(\text{Nucl}) |\Psi_{nl}(\mathbf{r}=0)|^2 , \qquad (1)$$

$$\Psi_{nl}(\mathbf{r}=0) = \frac{(Z\alpha)^3 m_{\rm R}^3}{\pi n^3} \delta_{0l} , \qquad (2)$$

where α is the fine structure constant, Z is the nuclear charge and $m_{\rm R}$ is the reduced mass of the orbiting particle. The relativistic units in which $\hbar = c = 1$ are used here and through the paper. We ignore a difference between energy interval E and a measured frequency $\nu = E/h$: presenting the theoretical expression for the energy splitting E and numerical results for the frequency ν . Here $\Psi_{nl}(\mathbf{r})$ is the Schrödinger-Coulomb wave function and A(Nucl) is a nuclear parameter which does not depend on the atomic state nl. Comparing the hfs for the atoms with a different value of $\Psi_{nl}(0)$ one can reduce influence of the nuclear structure and test the bound state QED with a high accuracy. There are two options to vary $\Psi_{nl}(0)$:

- to compare muonic and electronic atoms (*i.e.* to study atoms with the same nucleus and different values of $m_{\rm R}$);
- to compare hfs intervals for the ns states with different value of n or to study the hyperfine splitting for states $l \neq 0$.

^a e-mail: sek@mpq.mpg.de

Table 1. The ground state hfs interval in hydrogen, deuterium, tritium and helium-3 ion.

Atom	$E_{\rm hfs}^{\rm exp}$ [kHz]	$E_{\rm hfs}^{\rm QED}$ [kHz]	$E_{\rm hfs}^{\rm exp} - E_{\rm hfs}^{\rm QED} [\rm kHz]$	$(E_{\rm hfs}^{\rm exp} - E_{\rm hfs}^{\rm QED})/E_{\rm F} \ [{\rm ppm}]$
hydrogen	1420405.751768(1),[22]	1420452	-46	-33
deuterium	327384.352522(2),[2]	327339	45	138
tritium	1516701.470773(8), [3]	1516760	-58	-38
$^{3}\mathrm{He^{+}}$ ion	-8665649.867(10), [4]	-8667569	1919	221

Presently accurate experimental data are available only for one of these two options: it is possible to take advantage of existence of precision experimental data on the 1s and 2s hyperfine intervals in a few of light twobody atomic systems. A comparison of the data for the 1s and 2s hfs intervals allows to determine value of a specific difference

$$D_{21} = 8E_{\rm hfs}(2s) - E_{\rm hfs}(1s) \tag{3}$$

in hydrogen, deuterium and helium-3 ion. The theory of this specific difference can be developed much more successfully than that for the ground state interval $E_{\rm hfs}(1s)$ because of the essential cancellation of the nuclear effects (see Eqs. (1, 2)).

The most accurate experimental value for D_{21} was obtained for the helium-3 ion

$$D_{21}^{\exp}({}^{3}\text{He}^{+}) = 1\,189.979(71)\,\text{kHz}$$
 (4)

after comparison of results obtained for the 1s state in 1969 [4] and for the 2s state in 1977 [9]. The QED theory was developed by that time up to third order corrections including the $(Z\alpha)^2 E_{\rm F}$, $\alpha(Z\alpha)^2 E_{\rm F}$ and $(Z\alpha)^2 (m/M) E_{\rm F}$ contributions (here $E_{\rm F}$ is the so-called Fermi energy, leading contribution to the 1s hfs separation). The experimental result in equation (4) happened to be in some agreement with theory, however, uncertainty of theory was not properly estimated. Here we present new theoretical results on D_{21} in hydrogen, deuterium and helium-3 ion [14]. In our paper we demonstrate that there are a number of higher-order QED corrections which were not taken into account and which are competitive with the uncertainty of the experiment. We complete calculation of fourth order corrections and present theoretical results with accuracy higher than that for the measurements. The higherorder nuclear-structure effects also contribute to the difference D_{21} and their contribution is important for a comparison with experiment. They are considered in our paper in detail.

The paper is organized as following: in Section 2 we consider the QED theory of 1s hfs interval and determine parameters A(Nucl) for hydrogen, deuterium and ³He⁺ ion. Section 3 is devoted to QED calculations of the difference D_{21} . We study the fourth order QED contributions and, in particular, we find the vacuum polarization contribution in order $\alpha(Z\alpha)^3 E_{\text{F}}$ and the leading logarithmic recoil term in order $(Z\alpha)^3 (m/M) E_{\text{F}}$. The nuclear effects are taken into account in Section 4. We show that study of the difference D_{21} provides an effective test of QED theory of the hfs intervals $E_{\text{hfs}}(1s)$ and $E_{\text{hfs}}(2s)$ on a level of accuracy essentially below 1 ppm and such a test is free of problems of the nuclear structure. That is quite competitive with investigations of the hyperfine splitting in the ground state of muonium and positronium and we present a brief overview of them in Section 5. Section 6 summarized the paper and a comparison of theory and experiment is presented there for the difference D_{21} in hydrogen, deuterium and helium-3 ion and for the ground state *hfs* separation in muonium and positronium.

2 Hyperfine splitting in the ground state in hydrogen, deuterium and helium ion

The hyperfine splitting of an *ns* state in a hydrogen-like atoms is determined in the non-relativistic approximation by the so-called Fermi energy:

$$E_{\rm hfs}(ns) = \frac{E_{\rm F}}{n^3} \,, \tag{5}$$

$$E_{\rm F}/h = \frac{8}{3} Z^3 \alpha^2 c R y \, \frac{\mu}{\mu_{\rm B}} \, \frac{2I+1}{2I} \left(\frac{M}{m+M}\right)^3 \cdot \quad (6)$$

Here Ry is Rydberg constant, c is speed of light, h is the Planck constant, $\mu_{\rm B}$ is the Bohr magneton, m is the electron mass, M is the nuclear mass and I is the nuclear spin. The nuclear magnetic moment μ in our notation can be negative (if its direction is opposite to the nuclear spin) and the Fermi energy $E_{\rm F}$ defined as the splitting between states with atomic angular moments F = I + 1/2 and I - 1/2, calculated within the non-relativistic approximation, can be negative as well.

The result of the *QED* calculations is of the form

$$E_{\rm hfs}^{\rm QED}(1s) = E_{\rm F} \left(1 + Q_{\rm QED}(1s) \right) \,, \tag{7}$$

and

$$Q_{\text{QED}}(1s) = a_e + \left\{ \frac{3}{2} (Z\alpha)^2 + \alpha (Z\alpha) \left(\ln 2 - \frac{5}{2} \right) + \frac{\alpha (Z\alpha)^2}{\pi} \left[-\frac{2}{3} \ln \frac{1}{(Z\alpha)^2} \left(\ln \frac{1}{(Z\alpha)^2} + 4 \ln 2 - \frac{281}{240} \right) + 17.122\,339\dots - \frac{8}{15} \ln 2 + \frac{34}{225} \right] + 0.7718(4) \frac{\alpha^2 (Z\alpha)}{\pi} \right\} .$$
 (8)

The references to all terms can be found in a review in reference [18]. The expression above is a result of the external field approximation. The recoil corrections involve

Table 2. Parameters for calculations of the *hfs* interval in hydrogen, deuterium and helium-3 ion [20,21]. The proton charge radius is taken from reference [24].

Atom	Z	Ι	M/m	$\mu/\mu_{\rm B} \ [10^{-3}]$	$E_{\rm F} [{\rm kHz}]$	η	$R_{\rm E} \ [{\rm fm}]$
hydrogen	1	1/2	1836.153	1.5210322	1418840	5.58569	0.88(3)
deuterium	1	1	3670.483	0.4669755	326968	1.71403	2.13(1)
tritium	1	1/2	5496.922	1.6223936	1515038	17.831	
$^{3}\mathrm{He}^{+}$	2	1/2	5495.885	-1.1587505	-8656598	-6.36836	1.67(1)

integration over high momentum $k \sim M$ and a consideration of a nucleus as a point-like one is not valid in such a case. Actually a theory of a point-like particle with an anomalous magnetic moment is inconsistent and leads to a divergency at high momentum transfer for the nuclear vertex. The muon (and electron) must be treated as either a point-like particle without anomalous moment, or a particle with the anomalous magnetic moment and an internal structure. The magnetic anomaly and "structure" effects come from the same diagrams. As a result one need to be very careful when considering a "point-like" nucleus as an approximation. It is important to mention that the leading recoil corrections [19] and most of non-leading terms involve the nuclear structure effects and proportional to the $|\Psi_{nl}(0)|^2$ (cf. (1)).

To compute any numerical result we use here $\alpha^{-1} = 137.036\,000$, $cRy = 3.289\,841\,960 \times 10^{12}$ kHz, $a_e = 1.159\,652 \times 10^{-3}$ and parameters of nuclei collected in Table 2. The values of the fundamental constants and nuclear parameters are based on data taken from [20,21], but we keep them here only with the accuracy sufficient for our purposes. The results of calculation are summarized in Table 1. Leading recoil corrections depend on nuclear structure. Some pure *QED* corrections of higher order are known but not included being essentially smaller than uncertainty of nuclear effects.

The theoretical calculations above take into account only pure QED terms, while the nuclear effects can be estimated via a comparison of the experiment and the pure QED theory

$$E_{\rm hfs}^{\rm Nucl}(1s) = E_{\rm hfs}^{\rm Exp}(1s) - E_{\rm hfs}^{\rm QED}(1s) , \qquad (9)$$

$$A_{\rm hfs}({\rm Nucl}) = \frac{E^{\rm Exp}(1s) - E^{\rm QED}(1s)}{|\Psi_{1s}(0)^2|}$$
(10)

The nuclear models or study experimental data on nuclei offer another way to find $E^{\text{Nucl}}(1s)$ and A(Nucl) and they are discussed in part in Section 4.

3 QED calculations of D₂₁ in light atoms

The evaluation of the *QED* corrections involves contributions of the second, third and fourth order in unit of the Fermi energy. The second [26] and third [15–17] order corrections were calculated some time ago (see Tab. 3). One of the fourth order corrections, $(Z\alpha)^4 E_{\rm F}$, was also found that time [26]. Other fourth order terms were found only

Table 3. *QED* contributions up to third order to the D_{21} in hydrogen, deuterium and helium-3 ion.

Contribution	Η	D	$^{3}\mathrm{He^{+}}$
	[kHz]	[kHz]	[kHz]
$(Z\alpha)^2 E_{\rm F}$	47.2220	10.8822	-1152.4390
$\alpha(Z\alpha)^2 E_{\rm F}$ (SE)	1.9360	0.4461	-37.4415
$\alpha(Z\alpha)^2 E_{\rm F}$ (VP)	-0.0580	-0.0134	1.4148
$(Z\alpha)^2 \frac{m}{M} E_{\rm F}$	-0.1629	-0.0094	-0.7967
total up to 3rd order	48.9371	11.3056	-1189.2624

recently and the theoretical expression is now of the form

$$D_{21}(QED) = (Z\alpha)^2 E_{\rm F} \times \left\{ \begin{bmatrix} \frac{5}{8} + \frac{177}{128} (Z\alpha)^2 \end{bmatrix} + \frac{\alpha}{\pi} \left[\left(\frac{16}{3} \ln 2 - 7 \right) \ln(Z\alpha) - 5.221 \, 23 \dots \right] + \frac{\alpha}{\pi} \left[\frac{8}{15} \ln 2 - \frac{7}{10} \right] + \frac{m}{M} \left[-\frac{9}{8} + \left(\frac{\ln 2}{2} - \frac{7}{32} \right) \left(1 - \frac{1}{\eta} \right) - \left(\frac{145}{128} - \frac{7}{8} \ln 2 \right) \eta \right] + \frac{\alpha^2}{2\pi^2} \left(\frac{16}{3} \ln 2 - 7 \right) \ln(Z\alpha) - \frac{\alpha}{\pi} \frac{2m}{M} \left(\frac{16}{3} \ln 2 - 7 \right) \ln(Z\alpha) + \frac{Z\alpha}{\pi} \frac{m}{M} \left(\frac{4}{3} \ln 2 - 2 \right) \ln(Z\alpha) + \alpha(Z\alpha) \left(C_{\rm SE} + C_{\rm VP} \right) \right\},$$
(11)

where

$$\eta = \frac{\mu}{\mu_{\rm B}} \frac{M}{m} \frac{1}{ZI} \,. \tag{12}$$

Two corrections in the fourth order, $\alpha(Z\alpha)^2(m/M)E_{\rm F}$ and $\alpha^2(Z\alpha)^2E_{\rm F}$, were found in reference [27] in the leading logarithmic approximation and their uncertainties are estimated by a half-value of the leading logarithmic terms. The coefficients $C_{\rm SE}$ and $C_{\rm VP}$ related to the self-energy and vacuum polarization higher-order radiative corrections were first estimated in reference [27], but with some



Fig. 1. Vacuum polarization contributions to hfs.

misprints. Below we correct that estimation and discuss a recent calculation in reference [28].

The expression takes onto account some recoil effects. As it was demonstrated by Sternheim [16] the *n*-dependent part of the $(Z\alpha)^2(m/M)E_{\rm F}$ contribution into $E_{\rm hfs}(ns)$ does not depend on the nuclear structure. In the case of the $\alpha(Z\alpha)^2(m/M)E_{\rm F}$ and $(Z\alpha)^3(m/M)E_{\rm F}$ that is correct at least for the logarithmic terms. The pure recoil logarithmic correction $(Z\alpha)^3(m/M)\ln(Z\alpha)E_{\rm F}$ is evaluated here. A logarithmic part of the *QED* correction in order $(Z\alpha)^3m/M$ is easy to calculate with help of effective potentials which are responsible for $(Z\alpha)^5m^2/M$ correction to the Lamb shift (*cf.* [31,32]). The result is

$$2\frac{2}{3}\frac{(Z\alpha)^5}{\pi}\frac{m^3}{M}\ln\left(\frac{1}{Z\alpha}\right)\frac{E_{\rm F}}{(Z\alpha m)^2}\left(\frac{3}{2}-\ln 2\right).$$
 (13)

However this result is of a reduced value as far as the effective potential for the Lamb shift in order $(Z\alpha)^5 m^2/M$ has been used. The logarithmic term (with $\ln(Z\alpha)$) in that order is not dominant. That often happens with pure recoil contributions (in contrast the logarithmic terms dominates in the case of most of radiative and radiative-recoil corrections). The other logarithmic contribution in order $(Z\alpha)^5 m^2/M$ (with a recoil logarithm $\ln(mR)$) and a part of the non-logarithmic term are effectively included into the nuclear-structure contributions (see the next section). An essential non-logarithmic part which is not included there is related to two-photon effective potentials with derivatives. The scale of the loop integration momentum is determined by the electron mass and the related contribution does not depend on the nuclear structure (cf. the Sternheim contribution into Eq. (11) in order $(Z\alpha)^2(m/M)E_{\rm F}$). It can be essentially enhanced because of a big value of the nuclear anomalous magnetic moment and we estimate that non-logarithmic contribution as $\pm \eta ((Z\alpha)^3/\pi)(m/M)E_{\rm F}$.

The higher-order vacuum polarization correction related to $C_{\rm VP}$ is found in this paper. The contribution comes from diagrams depicted in Figure 1. They are evaluated with the exact Dirac wave functions and the Green function of an electron in the Coulomb field and the result is expanded in powers of $Z\alpha$. The results for the vacuum polarization contribution to the 2s hfs interval are (cf. Refs. [29,30]):

$$\Delta E(\text{Fig. 1a}) = \frac{\alpha}{\pi} \frac{E_{\text{F}}}{8} \left[\frac{3\pi}{8} Z\alpha - \frac{7}{10} (Z\alpha)^2 + (Z\alpha)^3 \left(\frac{143\pi}{192} - \frac{3\pi}{8} \ln\left(\frac{Z\alpha}{4}\right) \right) + \dots \right],$$

$$\Delta E(\text{Fig. 1b}) = \frac{\alpha}{\pi} \frac{E_{\text{F}}}{8} \left[\frac{3\pi}{8} Z \alpha + (Z\alpha)^2 \left(\frac{34}{225} - \frac{8}{15} \ln(Z\alpha) \right) + (Z\alpha)^3 \left(\frac{1715\pi}{1152} - \frac{\pi}{6} \ln\left(\frac{Z\alpha}{4}\right) \right) + \dots \right]$$

Finally one can obtain

$$\Delta E_{\rm hfs}^{\rm VP}(2s) = \frac{\alpha}{\pi} \frac{E_{\rm F}}{8} \left[\frac{3\pi}{4} Z \alpha + (Z\alpha)^2 \left(-\frac{247}{450} - \frac{8}{15} \ln(Z\alpha) \right) + (Z\alpha)^3 \left(\frac{2573\pi}{1152} - \frac{13\pi}{24} \ln\left(\frac{Z\alpha}{4}\right) \right) + \dots \right].$$
(14)

The derivation is considered in detail in Appendix A. To find a correction to the difference D_{21} one has to compare the result for the vacuum polarization contribution to the 2s hfs obtained above with that for the ground state [29,30]

$$\Delta E_{\rm hfs}^{\rm VP}(1s) = \frac{\alpha}{\pi} E_{\rm F} \left[\frac{3\pi}{4} Z\alpha + (Z\alpha)^2 \left(\frac{34}{225} - \frac{8}{15} \ln(2Z\alpha) \right) + (Z\alpha)^3 \left(\frac{539\pi}{288} - \frac{13\pi}{24} \ln\left(\frac{Z\alpha}{2}\right) \right) + \dots \right].$$
(15)

Finally we find

$$\Delta D_{21}^{\rm VP} = \frac{\alpha}{\pi} E_{\rm F} \left\{ (Z\alpha)^2 \left(-\frac{7}{10} + \frac{8}{15} \ln(2) \right) + (Z\alpha)^3 \left(\frac{139\pi}{384} + \frac{13\pi}{24} \ln(2) \right) + \dots \right\}$$
(16)

and thus

$$C_{\rm VP} = \frac{139}{384} + \frac{13}{24} \ln 2 \simeq 0.74$$
. (17)

As we have mentioned some partial results on $\alpha(Z\alpha)^3 E_{\rm F}$ terms were presented in reference [27] with a misprint. The relative sign in equations (24, 25, 27) of paper [27] is to be corrected and the result is (the corrected sign is marked by *)

$$C_{\rm SE} = \left[\frac{139}{16} - 4\ln 2\right] \left[\frac{3}{2} - \ln 2\right]$$
$$- \left[\frac{13}{4} - \ln 2\right] \left[\ln(2) + \frac{3}{16}\right],$$
$$C_{\rm VP} = \frac{5}{24} \left[\frac{3}{2} - \ln 2\right] + \left[\frac{3}{4} \left[\ln 2 + \frac{3}{16}\right]\right].$$

It was also then expected [27] that the $\alpha(Z\alpha)^3 E_{\rm F}$ results found there are likely incomplete. Recently Yerokhin and Shabaev directly calculated the self-energy contribution [28] after our suggestion

$$C_{\rm SE}(Z=1) = 2.07(25) ,$$

 $C_{\rm SE}(Z=2) = 2.01(19) .$

The self-energy result of reference [28] is affected by the higher order corrections and thus slightly depends on Z.

The complete results (17) and (18) indeed disagree with the corrected above partial results in:

$$C_{\rm SE} = \frac{795}{64} - \frac{7}{4} + 5\ln^2 2 \simeq 2.5 ,$$

$$C_{\rm VP} = \frac{29}{64} + \frac{13}{24}\ln 2 \simeq 0.83 .$$
(18)

and in part it is caused by appearance of effective nonrelativistic operators with derivatives. Those operators do not contribute into logarithmic corrections to ground state hyperfine structure [31,32] and were not considered in reference [27]. The difference for complete and partial results is numerically small for both: the vacuum polarization and self energy. That is related to the fact that only the second derivative of the wave function at origin depends on n

$$\Psi_{ns}(r \to 0) \simeq \frac{(Z\alpha m)^{3/2}}{\pi^{1/2} n^{3/2}} \left\{ 1 - (Z\alpha mr) + \frac{(Z\alpha mr)^2}{2} + \frac{1 - n^2}{n^2} \frac{(Z\alpha mr)^2}{6} + \dots \right\}$$
(19)

and the *n*-dependent coefficient is relatively small. Under these circumstances we consider the partial results in equations (18) as a confirmation of direct calculation of the self-energy [28] and vacuum polarization (see Eq. (17)).

A summary of the contributions of the fourth order terms is presented in Table 4.

4 Nuclear-structure corrections to D₂₁

The leading nuclear-structure corrections to $E_{\rm hfs}^{\rm Nucl}(1s)$ and $E_{\rm hfs}^{\rm Nucl}(2s)$, being proportional to the wave function at origin (see Eq. (2)), cancel each other when calculating the difference D_{21} . However, some higher-order nuclear effects can shift D_{21} and, in fact, they do. The corrections

Table 4. Fourth order *QED* contributions to the D_{21} in hydrogen, deuterium and helium-3 ion.

Contribution	Н	D	$^{3}\mathrm{He}^{+}$
	[kHz]	[kHz]	[kHz]
$(Z\alpha)^4 E_{\rm F}$	0.0056	0.0013	-0.543
$\alpha^2 (Z\alpha)^2 E_{\rm F}$	0.0033(16)	0.0008(4)	-0.069(35)
$\alpha(Z\alpha)^2 \frac{m}{M} E_{\rm F}$	-0.0031(15)	-0.0004(2)	0.022(11)
$\alpha(Z\alpha)^3 E_{\rm F}$ (SE)	0.0083(10)	0.0019(2)	-0.395(37)
$\alpha(Z\alpha)^3 E_{\rm F}$ (VP)	0.0030	0.0007	-0.145
$(Z\alpha)^3 \frac{m}{M} E_{\rm F}$	0.0005(5)	0.0001	-0.007(10)
total: 4th order	0.0178(25)	0.0043(5)	-1.137(53)

related to the nuclear structure effects can be splitted into three terms [23, 27]

$$D_{21}(\text{Nucl}) = D_{21}^A + D_{21}^B + D_{21}^C , \qquad (20)$$

where

$$D_{21}^{A} = \left(\ln 2 + \frac{3}{16}\right) (Z\alpha)^{2} E_{\rm hfs}^{\rm Nucl}(1s) , \qquad (21)$$

$$D_{21}^{B} = \left(\frac{7}{4} - \frac{4}{3}\ln 2\right) (Z\alpha)^{2} (mR_{\rm E})^{2} E_{\rm F} , \qquad (22)$$

$$D_{21}^C = -\frac{\zeta}{4} (Z\alpha)^2 (mR_{\rm E})^2 E_{\rm F} . \qquad (23)$$

Here

$$\zeta = \left(\frac{R_{\rm M}}{R_{\rm E}}\right)^2 - 1 \tag{24}$$

is a ratio of quadratic magnetic and electric charge radii.

Let us discuss origin and accuracy of the nuclear-structure corrections. To find the first term (D_{21}^A) one has to somehow determine a value of the nuclear contribution to the ground state *hfs* separation, $E_{\rm hfs}^{\rm Nucl}(1s)$, which contains three kinds of terms:

- nuclear-finite-size effects of order $(Z\alpha)^3(mR)E_{\rm F}$, where $R \sim R_{\rm E} \sim R_{\rm M}$;
- nuclear polarizability corrections;
- nuclear recoil corrections of order $(Z\alpha)^3(m/M)$ ln(mR).

The correction for the 1s state was studied for hydrogen and deuterium. In the case of the hydrogen the first term is dominant and cannot be calculated with accuracy better than 20% because of lack of knowledge of the proton magnetic form factor at low momentum transfer [23,24]. The proton polarizability cannot be successfully estimated and delivers an essential contribution to the value of $E_{\rm hfs}^{\rm Nucl}(1s)$ in hydrogen. We expect that a theoretical uncertainty of nuclear contribution to the 1s hfs is at least 20% of its value.

Deuteron is a weekly bound nucleus and the dominant nuclear effect for the hyperfine separation in the ground state of deuterium is related to the deuteron polarizability. The nuclear correction was estimated in reference [25] as 43 kHz, however, the uncertainty is not presented there. We expect that the uncertainty lies between 10 and 30 kHz. Our assumption is based on examination of the logarithmic approximation used in reference [25]. Let us concentrate our analysis on two corrections of -19and +11 kHz which were found in the logarithmic approximation. They are proportional to $\ln(m_p/\kappa)$, where $\kappa \simeq 45.7$ MeV is the inverse deuteron size and m_p is the proton mass. The validity of the logarithmic approximation suggests that the logarithm is big enough, but that is not really a case: $\ln(m_p/\kappa) \simeq 3.0$. We expect that the uncertainty of such an approximation lies between 10 and 30 kHz, that depends on possible correlations between these two logarithmic contributions.

To the best of our knowledge there are no results published on the nuclear contributions to the hyperfine separation in the tritium atom and the helium-3 ion. Due to lack of accurate calculations for $E_{\rm hfs}^{\rm Nucl}(1s)$ we estimate the nuclear structure contribution to the 1s hfs interval in all atoms discussed above by a comparison of experimental data with a result of the QED calculations (see Tab. 1 and Eqs. (1, 2, 9, 10)).

All these corrections to $E_{\rm hfs}^{\rm Nucl}(1s)$ are related in the leading order to the two-photon exchange with a hardmomentum exchange loop $(k \gg Z\alpha m)$. Their calculation is similar to that for $\alpha(Z\alpha)^3 E_{\rm F}$ terms. Some of these twophoton contributions can induce additional terms with derivatives but that will involve an additional suppressing factor m/k. The factor m/k is small for the finitesize and polarizability and for a logarithmic part (with $\ln(mR)$) of the nuclear recoil contribution. It is about unity only for a part of the nuclear recoil contribution related to low momentum transfer $k \sim m$ and k < m, however, we have calculated those corrections of order $(Z\alpha)^3(m/M)$ in the leading logarithmic approximation in equation (13). We expect these contributions are relatively small, because the recoil effects are not dominant in the D_{21}^A term and because of small numerical coefficient for state-dependent terms in the hydrogenic wave function at origin (see Eq. (19)). The γ -matrix structure is close to that in the case of the vacuum polarization where the terms with derivatives induce numerically small contributions. We estimate the uncertainty of such an approximation for D_{21}^A as 10%.

To verify the expression for D_{21}^A we also compare value of $E_{\rm hfs}^{\rm Nucl}(1s)$ with that for $E_{\rm hfs}^{\rm Nucl}(2s)/8$ (see Tab. 5). The latter was found via a comparison of a pure *QED* theoretical expression (*cf.* Eqs. (7, 8, 11))

$$E_{\rm hfs}^{\rm QED}(2s) = \frac{E_{\rm F}}{8} \left(1 + Q_{\rm QED}(2s) \right) ,$$

$$Q_{\rm QED}(2s) = a_e + \left\{ \frac{17}{8} (Z\alpha)^2 + \alpha (Z\alpha) \left(\ln 2 - \frac{5}{2} \right) + \frac{\alpha (Z\alpha)^2}{\pi} \left[-\frac{2}{3} \ln \frac{1}{(Z\alpha)^2} \left(\ln \frac{1}{(Z\alpha)^2} + 8 \ln 2 - \frac{1541}{240} \right) + 11.901 \, 106 \dots - \frac{247}{450} \right] + 0.7718(4) \frac{\alpha^2 (Z\alpha)}{\pi} \right\}$$
(25)

Table 5. 2s hyperfine splitting in light atoms. $\Delta E_{\rm hfs} = E_{\rm hfs}^{\rm exp} - E_{\rm hfs}^{\rm QED}$) and measured in ppm in respect to $E_{\rm F}/8$.

Atom,	$E_{ m hfs}^{ m exp}$	$E_{\rm hfs}^{\rm QED}$	$\Delta E_{\rm hfs}$
state	[kHz]	[kHz]	[ppm]
H, $2s$	177556.785(29), [6]	177562.7	-33
H, $2s$	177556.860(50), [5]		-32
D, $2s$	40924.439(20), [7]	40918.81	137
$^{3}\mathrm{He^{+}},2s$	-1083354.981(9), [9]	-1083594.7	221
${}^{3}\text{He}^{+}, 2s$	-1083354.99(20), [8]		221

Table 6. Nuclear-structure contributions to the D_{21} in hydrogen, deuterium and helium-3 ion.

Contribution	Н	D	$^{3}\mathrm{He^{+}}$
	[kHz]	[kHz]	[kHz]
D_{21}^{A}	-0.0022(2)	0.0021(2)	0.360(36)
D_{21}^{B}	0.0003	0.0004	-0.0285
D_{21}^{C}	$-1 \times 10^{-4} \zeta$	$-1.3 \times 10^{-4} \zeta$	$8.6 \times 10^{-3} \zeta$
$D_{21}(\text{Nucl})$	-0.002	0.0026(2)	0.332(36)
	$-1 \times 10^{-4} \zeta$	$-1 \times 10^{-4} \zeta$	$+9 \times 10^{-3} \zeta$

with experimental data. The results for the nuclear contributions to the 1s state in Table 1 and for the 2s state in Table 5 agree with each other.

Two other nuclear contributions, D_{21}^B and D_{21}^C (see Eqs. (22, 23)), are smaller than D_{21}^A and their evaluation is similar to that for the $\alpha(Z\alpha)^2 E_{\rm F}$ contributions and completely understood. They were derived in references [23,27] with help of some effective potentials, and the result does not depend on any nuclear models. The result for the nuclear contribution in equation (20) can be presented in a form slightly different from equations (20–23)

$$\begin{aligned} D_{21}(\text{Nucl}) &= \left(\ln 2 + \frac{3}{16}\right) (Z\alpha)^2 \Delta E_{\text{hfs}}^{\text{Nucl}}(1s) \\ &+ \left(\frac{21}{8} - 2\ln 2\right) \frac{\Delta E_{\text{Lamb}}^{\text{Nucl}}(1s)}{(Z\alpha)^2 m} E_{\text{F}} , \\ &- \frac{3}{8} \zeta \frac{\Delta E_{\text{Lamb}}^{\text{Nucl}}(1s)}{(Z\alpha)^2 m} E_{\text{F}} , \end{aligned}$$

which is more useful for phenomenological applications. We check this expression for the effects caused by a distribution of the nuclear charge and magnetic moment within some models in Appendix B and confirm it. The results on nuclear contributions to the D_{21} in the light hydrogen-like atoms are presented in Table 6.

The final theoretical results

$$D_{21}(\text{theor}) = D_{21}(\text{QED}) + D_{21}(\text{Nucl})$$
 (26)

for hydrogen, deuterium and helium-3 ion are summarized in Table 7. The table contains also the experimental results. The main sources of uncertainty of the theoretical

Table 7. Value of D_{21} in hydrogen, deuterium and helium-3 ion. Results for nuclear correction and theory are for $\zeta = 0$. $\Delta(\exp - \operatorname{th}) = D_{21}(\exp) - D_{21}(\operatorname{theor})$ and σ is a final uncertainty of $\Delta(\exp - \operatorname{th})$. The final nuclear contribution $D_{21}(\operatorname{Nucl})$ here is presented at $\zeta = 0$.

Value	Н	D	$^{3}\mathrm{He^{+}}$
$D_{21}(\exp)$ [kHz]	48.53(23), [6]	11.16(16), [7]	-1189.979(71), [9]
$D_{21}(\text{QED}) [\text{kHz}]$	48.955(3)	11.3099(5)	-1190.400(53)
$D_{21}(\text{Nucl}) [\text{kHz}]$	-0.002	0.0026(2)	0.332(36)
D_{21} (theor) [kHz]	48.953(3)	11.3125(5)	-1190.067(64)
$\Delta(\exp-\text{th})$ [kHz]	-0.42(23)	-0.15(16)	0.09(10)
$\Delta(\exp-\th)/\sigma$	-1.8	-1.0	0.9
$\sigma/E_{\rm F}$ [ppm]	0.16	0.49	0.01

 Table 8. Muonium hyperfine structure.

Term	Fractional	ΔE
	contribution	[kHz]
Fermi energy	$1.000\ 000\ 000$	4.459031.92(51)
a_e	0.001159652	5170.93
2nd order QED	-0.000195815	-873.15
3rd order QED	-0.000005923	-26.41
4th order QED	-0.000000123(49)	-0.55(22)
hadronic effects	0.000000054(1)	0.24
weak int.	-0.000000015	0.06
total	1.000957830(49)	4463302.91(51)(22)

calculations are related to

- the use of logarithmic approximation in evaluation of higher order QED corrections of order $\alpha^2 (Z\alpha)^3 E_{\rm F}$, $\alpha (Z\alpha)^2 (m/M) E_{\rm F}$ and $(Z\alpha)^3 (m/M) E_{\rm F}$;
- calculation of higher-order nuclear effects.

The recoil contributions in order $\alpha(Z\alpha)^2(m/M)E_{\rm F}$ and $(Z\alpha)^3(m/M)E_{\rm F}$ also limit accuracy of the calculations of the hyperfine splitting in the ground state of muonium and positronium and we overview theory of these two quantities in the next section.

5 Hyperfine structure in pure leptonic atoms

The theoretical expression for the hfs interval in the muonium ground state can be presented in the form

$$E_{\rm hfs}(\text{theor}) = E_{\rm F} (1+Q)$$

= $E_{\rm F} (1 + a_e + Q_2 + Q_3 + Q_4 + Q_{\rm h} + Q_{\rm w})$

and the results for the QED contributions of the second (Q_2) , third (Q_3) and fourth order (Q_4) , for the hadronic (Q_h) and weak contributions (Q_w) are reviewed in reference [34] (see also Refs. [18,32,37]) and we follow consideration there. The hadronic contribution is taken from references [34,35]. The results are collected in Table 8.

The dominant QED contribution to the uncertainty (0.22 kHz) comes from unknown non-leading terms in orders $\alpha(Z\alpha)^2 m/M$ and $(Z\alpha)^3 m/M$, which are estimated by a half-value of the leading double logarithmic corrections [31,32], despite some terms beyond the double logarithms are known (see Ref. [34] for discussion).

Table 9. Positronium hyperfine splitting.

Term	q	Q	$\Delta E [\mathrm{MHz}]$
Fermi energy	1	1.0000000	204386.6
1st order QED	-0.67416	-0.0049196	-1005.5
2nd order $Q\!E\!D$	1.084	0.0000577	11.8
3rd order $Q\!E\!D$	-15.6	-0.0000061(22)	-1.2(5)
total		0.9951321(22)	203391.7(5)

To find an absolute value one has to determine the Fermi energy in equation (6) which contains the magnetic moment of the muon. The most accurate value of it can be obtained from study of the ground state hyperfine structure in the magnetic field [10]. The related uncertainty is 0.51 kHz. Opposite to the theory of D_{21} , the Fermi energy has to be calculated very accurately and its value depends on our choice of a value of the fine structure constant. Here we use an original result from study of anomalous magnetic moment of the electron $\alpha^{-1} = 137.035\,999\,58(52)$ [38]. The related uncertainty is only 0.03 kHz, however, scattering of various results for the fine structure constants (see *e.g.* Ref. [20]) corresponds to a much bigger uncertainty.

The positronium hfs interval can be calculated and measured less accurately than that in muonium. However, it provides us with a sensitive test of the same recoil corrections as in the case of muonium and D_{21} . The recoil effects in positronium are essentially bigger than in other atoms, because M = m, and they may be studied in detail. The positronium hyperfine splitting in the ground state can be presented in the form

$$E_{\rm hfs}(\text{theor}) = E_{\rm F} \left(1 + q_1 \,\alpha + q_2 \,\alpha^2 + q_3 \,\alpha^3 \right) \\ = E_{\rm F} \left(1 + Q_1 + Q_2 + Q_3 \right),$$

where coefficients slightly depend on α containing $\ln \alpha$. The Fermi energy is defined in positronium in a different way (comparing with Eq. (6) for hydrogen and muonium)

$$E_{\rm F}({\rm Ps})/h = (7/6)\alpha^2 c \, Ry$$
 (27)

because of annihilation effects and a symmetric treatment of magnetic moments of the electron and the nucleus (positron). The results are summarized in Table 9 (see [18,36,39–42] and references there in). The third order corrections appear to be large because of a double

Atom	Value	Exp. [kHz]	Theor. [kHz]	Δ [kHz]	Δ/σ	$\sigma/E_{\rm F} \ [{\rm ppm}]$
Mu	$E_{\rm hfs}(1s)$	4463302.78(5),[10]	4463302.91(56)			0.12
\mathbf{Ps}	$E_{\rm hfs}(1s)$	$203389.1(7) \times 10^3, [12]$	$203391.9(5) imes 10^3$	-2.8(9)	-3.3	3.4
\mathbf{Ps}	$E_{\rm hfs}(1s)$	$203387.5(16) \times 10^3$, [13]		-4.4(17)	-2.6	7.9
Η	D_{21}	48.53(23), [6]/[22]	48.953(3)	-0.42(23)	-1.8	0.16
Η	D_{21}	49.13(40), [5]/[22]		0.18(40)	0.4	0.28
D	D_{21}	11.16(16), [7]/[2]	11.3125(5)	-0.15(16)	-1.0	0.49
$^{3}\mathrm{He^{+}}$	D_{21}	-1189.979(71), [9]/[4]	-1190.068(64)	0.09(10)	0.9	0.01
$^{3}\mathrm{He}^{+}$	D_{21}	-1190.1(16), [8]/[4]		0.03(160)	-0.02	0.18

Table 10. Hyperfine splitting: precision tests of the bound state *QED*. The final uncertainty σ includes contributions from both: theory and experiment. References for the D_{21} are presented for the both states: 2s and 1s.

logarithmic enhancement [31] ($\ln^2 \alpha \simeq 24$). The value of q_3 is calculated with taking into account recent results on $\alpha^7 m \ln \alpha$ correction [36], however, the uncertainty is estimated by a half-value of the leading $\alpha^7 m \ln^2 \alpha$ [31] (see Ref. [34] for discussion).

6 Summary

The results for the precision calculations of the hyperfine structure in the light hydrogen-like atoms are summarized in Table 10. One can see that investigations of the difference D_{21} provide very accurate tests of the bound state QED calculations. We consider study of D_{21} as a test of a state-dependent sector of theory of the hyperfine splitting of the 1s and 2s states and so the fractional accuracy of such theory is related to the $E_{\rm F}$, the leading contribution to the 1s hfs. The accuracy of comparison of theory and experiment can be characterized by a standard deviation σ which contains contributions to uncertainty from both: theory and experiment. The final uncertainty is found to be for D_{21} as small as few part of 10^7 in the case of hydrogen and deuterium and even better in the case of helium ion: a part of 10^8 . That is competitive with other tests of the bound state QED and in order to clarify advantages and disadvantages of studying D_{21} let us list main problems which theoretical calculations have met by now:

- there are two essential problems of the bound state *QED*:
 - evaluation of higher-order recoil corrections (that is mainly a problem of all QED calculations for the hyperfine structure including D_{21});
 - evaluation of higher-order two-loop corrections (that is rather a problem of the Lamb shift calculation and only one value related to the hyperfine structure, D_{21} , is sensitive to such corrections);
- there are two other problems related to other part of physics:
 - determination of the fundamental constants (like *e.g.* determination of the fine structure constant and magnetic moment of muon needed to calculate the Fermi energy $E_{\rm F}$);

 nuclear structure, which affect energy levels and, in particular, shifts values of the Lamb shift and the hyperfine separation.

The difference D_{21} happens to be an only value that is sensitive to both higher-order corrections: recoil and twoloop and that is not sensitive to problems beyond *QED* (determination of the fundamental constants and nuclear structure). Tests of *QED* are sometimes considered as a search for new physics beyond the standard model. Such exotic contributions are rather expected to be proportional to $1/n^3$ and must vanish for D_{21} in the leading order. The next-to-leading terms could contribute but they effectively would be taken into account in D_{21}^{Nucl} being included into $E_{\text{hfs}}^{\text{Nucl}}(1s)$. That fact makes the difference D_{21} useful for a very specific test of the bound state *QED*, a test which involves no problem beyond *QED*.

Our theoretical predictions appear to be in a fair agreement with four of five accurate measurements (see Tab. 10), while a minor discrepancy of 1.8 σ with the most recent result from reference [6] is observed. Because of agreement with other data and especially with the most accurate result for helium ion [9] we expect that the problem of this minor discrepancy comes from the experimental side. One can see that there have been no improvement in microwave measurements of the 2s hfs for the last few decades. We expect that some progress is still possible and that it is now also possible to perform an optical measurement of this quantity via comparison of different 1s - 2s transitions in hydrogen and deuterium, some of which were measured recently very precisely [43].

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Appendix A: The vacuum polarization contribution to the 2s hyperfine splitting

An exact relativistic expression for the vacuum polarization correction to hfs in the ground state of a hydrogenlike atom with a point-like nucleus was derived in references [29,30]. Using the same method we can calculate the vacuum polarization contribution for the 2s-state. As in the case of the 1s state [29], we study a more general case considering an orbiting particle with the mass m different from the electron mass m_e which is related here to a particle in the vacuum loop (see Fig. 1). That offers an opportunity to perform some additional tests of our results.

The diagrams contributing to the hfs separation are presented in Figure 1. We obtain

$$\begin{aligned} \Delta E_2(\text{VP-TU}) &= \frac{\alpha}{\pi} E_{\text{T}}(2s) \\ \times \frac{1}{2 - 5\epsilon + 2\epsilon^2 - 2\mathcal{E}_{2s}(1 + \mathcal{E}_{2s})(5 - 2\epsilon)} \\ \times \left\{ -4\mathcal{E}_{2s}(1 + \mathcal{E}_{2s})(3 - 2\epsilon)^2(1 - \epsilon) J_{10}(\kappa_2) \\ -(1 + 6\mathcal{E}_{2s} + 6\mathcal{E}_{2s}^2)(3 - 2\epsilon)^2(1 - 2\epsilon) J_{20}(\kappa_2) \\ +2(1 + 2\mathcal{E}_{2s})^2(1 - \epsilon)(5 - 13\epsilon + 6\epsilon^2) J_{30}(\kappa_2) \\ -(1 + 2\mathcal{E}_{2s})^2(1 - \epsilon)(3 - 8\epsilon + 4\epsilon^2) J_{40}(\kappa_2) \right\} \end{aligned}$$

for the single-potential contribution related to Figure 1a and

$$\begin{split} \Delta E_2(\text{VP-UT}) &= -\frac{\alpha}{\pi} E_{\text{T}}(2s) \\ \times \frac{\mathcal{E}_{2s}(Z\alpha)^2 (3-2\epsilon)^2}{\epsilon(1-2\epsilon)^2 (5+4\mathcal{E}_{2s}-2\epsilon)(2-\epsilon)^2} \\ \times \left\{ -\frac{2(1+\epsilon)(2+2\mathcal{E}_{2s}-5\epsilon+2\epsilon^2)}{1-2\epsilon} J_{10}(\tilde{\kappa}_2) \right. \\ &+ \frac{4-9\epsilon^2+4\epsilon^3}{1-\epsilon} J_{20}(\tilde{\kappa}_2) \\ &+ \frac{4-21\epsilon+23\epsilon^2-8\epsilon^3}{(1-\epsilon)^2} \mathcal{E}_{2s} J_{20}(\tilde{\kappa}_2) \\ &- \frac{2(-18+31\epsilon-19\epsilon^2+4\epsilon^3)}{3-2\epsilon} J_{30}(\tilde{\kappa}_2) \\ &- \frac{2(-6+9\epsilon-10\epsilon^2+4\epsilon^3)}{3-2\epsilon} \mathcal{E}_{2s} J_{30}(\tilde{\kappa}_2) \\ &- 2\left[10-9\epsilon+2\epsilon^2+\mathcal{E}_{2s}(13-14\epsilon+4\epsilon^2) \right] J_{40}(\tilde{\kappa}_2) \\ &+ 2(1+2\mathcal{E}_{2s})(2-\epsilon)^2 J_{50}(\tilde{\kappa}_2) \\ &+ \frac{4(2-\epsilon)(1+\mathcal{E}_{2s}-\epsilon)}{1-\epsilon} J_{21}(\tilde{\kappa}_2) \\ &- 8(1+\mathcal{E}_{2s})(2-\epsilon) J_{41}(\tilde{\kappa}_2) \\ &+ 4(1+2\mathcal{E}_{2s})(2-\epsilon) J_{41}(\tilde{\kappa}_2) \\ \end{split}$$

for the double-potential term in Figure 1b. Here we mainly follow notations of references [29,44] and, in particular, we

introduce the relativistic Fermi-Breit energy [26]

$$E_{\rm T}(2s) = E_{\rm F} \frac{\epsilon}{2(Z\alpha)^2} \\ \times \frac{\left[(1 + \mathcal{E}_{2s})(5 - 2\epsilon) - 1 \right]}{(1 + 2\mathcal{E}_{2s})(1 - \epsilon)(2 - \epsilon)(3 - 8\epsilon + 4\epsilon^2)} \\ \approx \frac{E_{\rm F}}{8} \left(1 + \frac{17}{8}(Z\alpha)^2 + \dots \right) \,,$$

where

$$\epsilon = 1 - \sqrt{1 - (Z\alpha)^2} = \frac{(Z\alpha)^2}{2} \left(1 + \frac{(Z\alpha)^2}{4} + \dots \right) ,$$

$$\mathcal{E}_{2s} = \sqrt{\frac{2 - \epsilon}{2}} \simeq 1 - \frac{(Z\alpha)^2}{8} + \dots ,$$

$$\kappa = \frac{Z\alpha m}{m_e} ,$$

$$\tilde{\kappa}_2 = \frac{\kappa}{2\mathcal{E}_{2s}} = \frac{\kappa}{2} \left(1 + \frac{(Z\alpha)^2}{8} + \dots \right) .$$

Basic integrals J_{mn} are defined as

$$J_{mn}(\kappa) = \int_0^1 dv \frac{v^2 (1 - v^2/3)}{1 - v^2} \left(\frac{\kappa \sqrt{1 - v^2}}{1 + \kappa \sqrt{1 - v^2}} \right)^{m-2\epsilon} \\ \times \ln^n \left(\frac{\kappa \sqrt{1 - v^2}}{1 + \kappa \sqrt{1 - v^2}} \right).$$

They can be expressed in terms of the beta-function and the hypergeometric function as follows [29,44]

$$J_{m0} = \frac{1}{2} \kappa^m B(3/2, m/2)$$

$$\times_3 F_2(m/2, m/2 + 1/2, m/2; 1/2, m/2 + 3/2; \kappa^2)$$

$$-\frac{m}{2} \kappa^{m+1} B(3/2, m/2 + 1/2)$$

$$\times_3 F_2(m/2 + 1, m/2 + 1/2, m/2 + 1/2; 3/2, m/2 + 2; \kappa^2)$$

$$-\frac{1}{6} \kappa^m B(5/2, m/2)$$

$$\times_3 F_2(m/2, m/2 + 1/2, m/2; 1/2, m/2 + 5/2; \kappa^2)$$

$$+\frac{m}{6} \kappa^{m+1} B(5/2, m/2 + 1/2)$$

$$\times_3 F_2(m/2 + 1, m/2 + 1/2, m/2 + 1/2; 3/2, m/2 + 3; \kappa^2)$$

and

$$J_{mn} = \frac{\partial^n J_{m0}}{\partial m^n} \cdot$$

In the case of an electronic atom $(m = m_e)$ and small $Z\alpha$ we arrive to a result in equation (14), which reproduces all known terms of the expansion over $Z\alpha$ [15,32,45] and presents a new contribution in order $\alpha(Z\alpha)^3 E_{\rm F}$.

One can also study the vacuum-polarization contribution to the *hfs* in muonic atoms putting $m = m_{\mu}$. In the case of low Z and arbitrary $\kappa = Z \alpha m_{\mu}/m_{\rm e} \simeq 1.5Z$ we reproduce the non-relativistic limits [46]. For the case of small $Z\alpha$ and large κ the result can be presented as an expansion over $Z\alpha$ and κ^{-1} :

$$\Delta E_2(\text{VP}) = \frac{\alpha}{\pi} \frac{E_F}{8} \left\{ \left[\frac{8}{3} \ln(\kappa) + \frac{4\pi^2}{9} - \frac{85}{18} + \frac{49}{\kappa^2} \right] + (Z\alpha)^2 \left[\frac{17}{2} \ln(\kappa) + \frac{3\pi^2}{2} - \frac{37}{3} - \frac{8}{3} \psi''(2) + \frac{303}{4\kappa^2} \right] + \dots \right\}, \quad (A.1)$$

where $\psi(z)$ is the logarithmic derivative of the Γ -function. The logarithmic part of the correction can be easily found within the effective charge approach (*cf.* [29,44]), results agree with (A.1) and that is an additional confirmation of our result.

Appendix B: A model-dependent calculation of the finite-nuclear-size corrections to energy levels

Here we study the contributions to $E_{\text{Lamb}}^{\text{Nucl}}(1s)$, $E_{\text{hfs}}^{\text{Nucl}}(1s)$ and D_{21} related to the distribution of the nuclear charge and the nuclear magnetic moment. The distribution is described by the nuclear electric and magnetic form factors

$$\begin{aligned} G_{\rm E}^{a}(q^{2}) &= 1 + \beta_{\rm E} \left[\left(\frac{\Lambda_{\rm E}^{2}}{q^{2} + \Lambda_{\rm E}^{2}} \right)^{a} - 1 \right] , \\ G_{\rm M}^{a}(q^{2}) &= \mu \left\{ 1 + \beta_{\rm M} \left[\left(\frac{\Lambda_{\rm M}^{2}}{q^{2} + \Lambda_{\rm M}^{2}} \right)^{a} - 1 \right] \right\} . \end{aligned}$$

Parameters Λ and β are free parameters, however, we consider here only linear in β contributions. Since we intend to verify a model independent expression in equation (26), it is not important that the distribution above is not quite a real one.

We perform calculations with the Dirac wave functions and expand the results over $(Z\alpha)$ and m/Λ . In the case of a = 1 the nuclear corrections are

$$\begin{split} E_{\rm Lamb}^{\rm Nucl}(1s) &= 4(Z\alpha)^4 \beta_{\rm E} \left(\frac{m}{\Lambda_{\rm E}}\right)^2 m \;, \\ E_{\rm hfs}^{\rm Nucl}(1s) &= -4Z\alpha \left(\frac{\beta_{\rm E}m}{\Lambda_{\rm E}} + \frac{\beta_{\rm M}m}{\Lambda_{\rm M}}\right) E_{\rm F} \;, \\ D_{21}(\rm Nucl) &= -\left(\frac{3}{4} + 4\ln 2\right) (Z\alpha)^3 \left(\frac{\beta_{\rm E}m}{\Lambda_{\rm E}} + \frac{\beta_{\rm M}m}{\Lambda_{\rm M}}\right) E_{\rm F} \\ &+ (12 - 8\ln 2)(Z\alpha)^2 \beta_{\rm E} \left(\frac{m}{\Lambda_{\rm E}}\right)^2 E_{\rm F} \\ &- \frac{3}{2} (Z\alpha)^2 \beta_{\rm M} \left(\frac{m}{\Lambda_{\rm M}}\right)^2 E_{\rm F} \end{split}$$

and

$$R_{\rm E} = \frac{6\beta_{\rm E}}{\Lambda_{\rm E}^2}, \quad R_{\rm M} = \frac{6\beta_{\rm M}}{\Lambda_{\rm M}^2} \cdot$$

We note that in the case of $\beta_{\rm E} = \beta_{\rm M} = 1$, $\Lambda_{\rm E} = \Lambda_{\rm M}$ we arrive at a = 2 to the so-called dipole model commonly used as an approximation for the proton internal structure. However, since we calculate the linear in β terms the well-known result for the hydrogen *hfs* cannot be reproduced. In the case of a = 2 we find

$$\begin{split} E_{\text{Lamb}}^{\text{Nucl}}(1s) &= 8(Z\alpha)^4 \beta_{\text{E}} \left(\frac{m}{\Lambda_{\text{E}}}\right)^2 m ,\\ E_{\text{hfs}}^{\text{Nucl}}(1s) &= -6Z\alpha \left(\frac{\beta_{\text{E}}m}{\Lambda_{\text{E}}} + \frac{\beta_{\text{M}}m}{\Lambda_{\text{M}}}\right) E_{\text{F}} ,\\ D_{21}(\text{Nucl}) &= -\left(\frac{9}{8} + 6\ln 2\right) (Z\alpha)^3 \left(\frac{\beta_{\text{E}}m}{\Lambda_{\text{E}}} + \frac{\beta_{\text{M}}m}{\Lambda_{\text{M}}}\right) E_{\text{F}} \\ &+ (24 - 16\ln 2)(Z\alpha)^2 \beta_{\text{E}} \left(\frac{m}{\Lambda_{\text{E}}}\right)^2 E_{\text{F}} \\ &- 3(Z\alpha)^2 \beta_{\text{M}} \left(\frac{m}{\Lambda_{\text{M}}}\right)^2 E_{\text{F}} \end{split}$$

and

$$R_{\rm E} = \frac{12\beta_{\rm E}}{\Lambda_{\rm E}^2}, \quad R_{\rm M} = \frac{12\beta_{\rm M}}{\Lambda_{\rm M}^2}$$

The results for a = 1 and a = 2 confirm expression in equation (26). Similar calculations can be performed for any integer value of a. Let us also mention, that in principle any moments of a real distribution $(\langle R^n \rho_N(R) \rangle)$ can be reproduced by a finite sum of $G_{\rm E}^a(q^2)$ and $G_{\rm M}^a(q^2)$ over integer a after adjusting parameters $\Lambda(a)$ and $\beta(a)$.

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