The hyperfine structure (HFS) intervals of the ground state in a number of neutral atoms and singly charged ions can be measured with a high accuracy. However, theory even in the case of the simplest of them (such as hydrogen isotopes and the helium-3 ion) is essentially affected by nuclear structure effects which contribute from 30 to 200 ppm and cannot be calculated accurately. In contrast the 1s HFS interval in muonium is calculated with an uncertainty of about 0.1 ppm and can be used to accurately test the bound state Quantum Electrodynamics (QED). However, the muonium calculations involve precision values of the fundamental constants ($\alpha$ and $m_\mu/m_e$) and it would be important to test the QED predictions for the HFS interval in muonium up to date. The theory agrees with most of the experimental data.

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$D_{21} = 8E_{\text{HFS}}(2s) - E_{\text{HFS}}(1s)$ (1)

provides us with an opportunity to make a test of the QED theory on a level of accuracy essentially better than 1 ppm. Such a high accuracy is possible because of an essential cancelation of nuclear contributions. We report here new results for the difference in Eq. (1). We complete calculations of the fourth order corrections and find nuclear structure contributions which remain after cancelation of the leading effects. Some of the corrections obtained here are bigger than the experimental uncertainty and must be taken into account.

Our results are found to be in a fair agreement with most experimental data on hydrogen, deuterium and helium-3. We present a significant improvement of the theory for $D_{21}$ and demonstrate that the comparison of theory and experiment for helium tests presently the QED theory of 1s and 2s HFS on the highest level, namely one part in $10^8$. That supercedes the muonium HFS by an order of magnitude.

The hyperfine splitting of an $ns$ state in a hydrogen-like atom with a nuclear mass $M$ and a nuclear spin $I$ can be presented in the form

$E_{\text{HFS}}^{\text{QED}}(ns) = E_F/n^2 \cdot (1 + Q_{\text{QED}}(ns))$, (2)

$E_F/h = \frac{8}{3} Z^3 \alpha^2 c \cdot \frac{\mu}{\mu_B} \frac{2I + 1}{2I} \left( \frac{M}{m + M} \right)^3$. (3)

Here $Ry$ is the Rydberg constant, $c$ is the speed of light, $h$ is the Planck constant, $\mu_B$ is Bohr’s magneton and $m$ is the electron mass. The nuclear magnetic moment $\mu$ in our notation can be negative (if its direction is opposite to the nuclear spin) and the Fermi energy $E_F$, related to an energy splitting between the atomic state with total angular moment $F = I + 1/2$ and $I - 1/2$, can be negative as well. The QED correction for the HFS interval in the ground state is (see Ref. [4] for references)

$Q_{\text{QED}}(1s) = a_e + \left\{ \frac{3}{2} (Z\alpha)^2 + \alpha(Z\alpha) \left( \ln 2 - \frac{5}{2} \right) + \frac{\alpha(Z\alpha)^2}{\pi} \left[ -\frac{2}{3} \ln \frac{1}{(Z\alpha)^2} \left( \frac{1}{(Z\alpha)^2} \right) + 4 \ln 2 - \frac{281}{240} \right] + 17.122339 \ldots \right\}$. (4)

where $a_e$ is the electron’s anomalous magnetic moment. A comparison of the QED calculations with experimental values is summarized in Table 1. To compute theoretical values we use fundamental and auxiliary constants from Refs. [5,6]. The QED expression above does not take into account any recoil effects. Recoil contributions involve high momentum transfer and are essentially affected by the nuclear structure. In Table 1 we also present data for the 2s state, the theoretical expression for which is similar to Eq. (4) but some coefficients are different (see below).

One can see that the 1s hyperfine structure has been measured very accurately but any test of the QED calculations is limited by an essential contribution related to the nuclear structure which cannot be calculated precisely. In fact the uncertainty of the nuclear-structure
contribution is at least 20% in hydrogen [18], and for deuterium the accuracy is not better [19]. In the case of tritium and helium-3 no results on the contribution of the nuclear effects has been obtained to the best of our knowledge. Thus, the pure QED theory is incomplete because of lack of the nuclear-structure contributions and a comparison of the QED theory with the experiment in Table I demonstrates how much it is incomplete. Our final target is a comparison of the QED theory with the experiment in Table I. Namely they are:

• the nuclear charge and magnetic moment distribution (that is the biggest effect in the case of hydrogen);

• a nuclear polarizability contribution (that is the biggest effect in the case of deuterium);

• nuclear recoil contributions of order \((Z\alpha)(m/M)E_F\) and higher.

There is also a correction to the Lamb shift caused by the nuclear structure

\[
\Delta E_{\text{Lamb}}^\text{Nucl}(1s) = \frac{2}{3}(Z\alpha)^4 m^3 R_E^2 ,
\]

where \(R_E\) is the nuclear electric charge radius and relativistic units in which \(\hbar = c = 1\) are used. When the contributions to HFS (3) and the Lamb shift (7) are determined, one can try to obtain a correction for difference \(D_{21}\). That is possible because most of the nuclear-structure corrections do not depend on the details of the atomic structure. Both, the leading contributions to the HFS and the Lamb shift are of a special factorized form

\[
\Delta E(\text{Nucl}) = A(\text{Nucl}) \times |\Psi_n(r = 0)|^2 .
\]

The leading correction to the difference in Eq. (3) must therefore vanish. The non-vanishing contributions can be expressed in terms of some effective \(\delta\)-like potentials

\[
V(\text{Nucl}) = A(\text{Nucl}) \cdot \delta(r) .
\]

The coefficient \(A(\text{Nucl})\) can be for various nuclear contributions calculated (see e.g. Eq. (11)) or determined from a comparison of experimental and a pure QED theory (see e.g. Eq. (3)). The result is of the form (cf. Refs. [18–20])

\[
D_{21}(\text{Nucl}) = \left( \ln 2 + \frac{3}{16} \right) \cdot (Z\alpha)^2 \cdot \Delta E_{\text{HFS}}^\text{Nucl}(1s)
\]

\[
+ \left( \frac{21}{8} - 2 \ln 2 - \frac{3}{8} \zeta \right) \cdot \frac{\Delta E_{\text{HFS}}^\text{Nucl}(1s)}{(Z\alpha)^2 m} E_F ,
\]

where \(1 + \zeta = R_M^2/R_E^2\) is a ratio of quadrupole magnetic and electric nuclear radii. We obtain the nuclear structure contribution to the 1s HFS interval from comparison in Eq. (3) and conservatively estimate the uncertainty as 10%. The Lamb shift contribution is taken from Eq. (3).

The fourth order corrections to \(D_{21}\) have been intensively studied for the last three years. The logarithmic corrections in order \(\alpha^2(Z\alpha)^2\) and \(\alpha(Z\alpha)^2(m/M)\) were calculated in Ref. [18] (cf. [21,22]), the \((Z\alpha)^3(m/M)\) terms are found below (cf. [23]). The only term calculated previously is the relativistic term of the order \((Z\alpha)^3/m\) [24].

Partial results on the \(\alpha(Z\alpha)^3\) contributions were found in Ref. [18]. They are related to effective non-relativistic potentials which lead to logarithmic contributions for the 1s state HFS. The terms in the same order should also appear from potentials which contain some derivatives. A complete result on the self energy contribution was calculated after a suggestion by us in Ref. [27]. We report here the completion of the evaluation of the vacuum polarization effects. We derive an exact result for
HFS of the $2s$ state and a contribution to $D_{21}$ is found via a comparison with the previously obtained result for the $1s$ state [28].

The fourth order contributions are finally found to be

$$D_{21}^{(4)\text{(QED)}} = (Z\alpha)^2 E_F \times \left\{ \frac{\alpha^2}{2\pi} \left( \frac{16}{3} \ln 2 - 7 \right) \ln(Z\alpha) \right. $$

$$- \frac{2m}{\pi M} \left( \frac{16}{3} \ln 2 - 7 \right) \ln(Z\alpha) $$

$$+ \frac{Z\alpha m}{M} \left( \frac{4}{3} \ln 2 - 2 \right) \ln(Z\alpha) $$

$$+ \alpha(Z\alpha) \left( C_{SE} + C_{VP} \right) + \frac{177}{128} (Z\alpha)^2 \left\}, \quad (12) $$

where

$$C_{SE}(Z = 1) = 2.07(25), \quad C_{SE}(Z = 2) = 2.01(19)$$

and

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

The partial results for the constants $C_{SE}$ and $C_{VP}$ that are obtained in Ref. [1] contain some misprints. Being corrected, the partial results ($C_{SE} \simeq 2.5$ and $C_{VP} \simeq 0.83$) are found to be close to the complete results above. That confirms an intuitive assumption that the potentials with derivatives lead to relatively small contributions. Smallness of terms with derivatives is important for our estimation of uncertainties of the nuclear-structure corrections.

Let us discuss the uncertainty of the QED expression. The first two terms in Eq. (12) are found in the logarithmic approximation and we estimate the next-to-leading terms by a half-value of the leading contribution. However, in the case of the third term in Eq. (12) the situation is more complicated. First of all, the $(Z\alpha)(m/M)E_F$ corrections to the $1s$ HFS contain a nuclear-structure dependence presented by $\ln(mR_E)$. Since we have not included them into the QED expression [4], they are effectively taken into account as a part of $\Delta E_{\text{HFS}}^{\text{Nuc}}$. That means that an essential part of the $(Z\alpha)^3(m/M)E_F$ contribution into $D_{31}$ is effectively included into $D_{21}(\text{Nucl})$ via Eq. (11). However, there are some contributions with loop momentum of about one electron mass and below which does not depend on the nuclear structure. They can be enhanced because of a relatively big magnetic moment (compared to the Dirac value) and we estimate the uncertainty of the last term in Eq. (12) as $(\mu/\mu_B)(Z\alpha)^3E_F$ (cf. Eq. (6)).

All contributions to the difference $D_{21}$ in hydrogen, deuterium and helium-3 ion are summarized in Table II. Parameter $\zeta$ is known very badly, but it is not expected to be much larger than unity and hopefully the $\zeta$-term is essentially below the uncertainties related to theory and experiment and thus may be excluded from further considerations.

An essential improvement of the theory is achieved. In previous papers related to third-order QED corrections [29,21] the uncertainty was not spelled out. We found here a number of corrections exceeding the experimental uncertainty. We state that after the examination presented here the theoretical predictions (Table II)

$$D_{21}(\text{theor}) = D_{21}^{(3)\text{(QED)}} + D_{21}^{(4)\text{(QED)}} + D_{21}(\text{Nucl})$$

are more accurate than the experiment. Five accurate measurements performed on three atomic systems are compared with our calculation in Table II. Four experimental results are in fair agreement with our theory, but a recent result for hydrogen [11] shows a 1.8$\sigma$ discrepancy. The most important comparison is related to $^3\text{He}^+$: the $2s$ HFS was measured most accurately [3] and its value is also the most sensitive to higher order corrections (because of larger $Z$ and larger nuclear contributions). Because of a fair agreement of our theory with the helium experiment we expect that in the case of hydrogen the discrepancy is related to a problem on the experimental side.

We consider comparison of theory and experiment for the difference $D_{21}$ as a test of a calculation of a state-dependent part of corrections to $E_{\text{HFS}}^{\text{QED}}(\text{ns})$ and hence we present in the last column in Table II a standard deviation $\sigma$ with respect to the Fermi energy $E_F$, i. e. to a value directly related to the $1s$ HFS. That comparison demonstrates that study of $D_{21}$ in helium ion provides a more accurate test of QED than the study of the muonium HFS ($\sigma/E_F \simeq 0.1$ ppm) and indeed of HFS in hydrogen and other atoms with a structured nucleus. The uncertainty for $D_{21}$ in hydrogen and deuterium is determined experimentally, while in the case of helium a value of $\sigma$ contains an essential contribution from theory as well.

Most of so-called QED tests involve in part some other problems such as

- verification of nuclear models and calculations of nuclear effects and hadronic contributions;
- tests of consistency of data for fundamental constants (such as muon magnetic moment) or effective parameters (such as the proton charge radius) related to completely different experiments.

The $D_{21}$ theory is free of all these problems. No constants are really involved: an effective value of $E_{\text{HFS}}^{\text{Nuc}}(1s)$ related to the nuclear effects arises from HFS theory. Its contribution being relatively small is under control as well as other nuclear contributions.

It is important to mention that presently there are three crucial higher-order QED contributions to hydrogenic energy levels: radiative recoil of the order $\alpha(Z\alpha)^3(m/M)E_F$, pure recoil of the order $(Z\alpha)^3(m/M)E_F$ and two-loop effects of the order $\alpha^3(Z\alpha)^3m$. The difference $D_{21}$ is sensitive to all of them and a progress in its calculation will therefore contribute

3
into progress in theory of the hydrogen Lamb shift, muonium hyperfine structure and positronium energy levels. The most accurate measurement on this difference is related to an 25-years old experiment on helium ions and we can hope that some experimental progress to improve the most precise test of QED theory for the hyperfine structure is possible.

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TABLE I. Fine structure in light atoms. Hydrogen result for 1s is an average value over the most accurate data. The difference between experiment and QED theory is denoted by \(\Delta E\). It is related to the nuclear contribution.

| Atom, state | \(E_{\text{exp}}^\text{HFS} - E_{\text{HFS}}^\text{QED} [\text{kHz}]\) | \(n^3\Delta E/E_F [\text{ppm}]\) |
|---|---|---|
| H, 1s | 1 420 405.751 768(1) | 1 420 452 - 33 |
| D, 1s | 327 384.352 522(2) | 327 339 138 |
| T, 1s | 1 516 701.470 773(8) | 1 516 760 - 38 |
| \(^3\text{He}^+, 1s\) | -8 665 649.867(10) | -8 667 569 222 |
| H, 2s | 1 77 556.785(29) | 1 77 562.7 - 33 |
| H, 2s | 1 77 556.860(50) | 1 77 539.4 32 |
| D, 2s | 4 092 439(20) | 4 091 818.1137 |
| \(^3\text{He}^+, 2s\) | -1 083 354.981(9) | -1 083 594.7 221 |
| \(^3\text{He}^+, 2s\) | -1 083 354.999(24) | -1 083 594.7 221 |

TABLE II. Various contributions to \(D_{21}(\text{theor})\). Theoretical predictions depend on parameter \(\zeta = R_D^2/R_E^2 - 1\).

| Value | H | D | \(^3\text{He}^+\) |
|---|---|---|---|
| \(D_{21}^\text{HFS}^\text{(QED)} [\text{kHz}]\) | 48.937 | 11.305 6 | -1 189 262 |
| \(D_{21}^\text{D}^\text{(QED)} [\text{kHz}]\) | 0.018(3) | 0.004 3(5) | -1 137(53) |
| \(D_{21}(\text{N}ucl) [\text{kHz}]\) | -0.002 | 0.002 6(2) | 0.331(36) |
| | -10\(^{-4}\) \(\zeta\) | -10\(^{-4}\) \(\zeta\) | + 0.009 \(\zeta\) |
| \(D_{21}(\text{theor}) [\text{kHz}]\) | 48.953(3) | 11.312 5(5) | -1 190 067(63) |
| | -10\(^{-4}\) \(\zeta\) | -10\(^{-4}\) \(\zeta\) | + 0.009 \(\zeta\) |

TABLE III. Precision tests of QED theory for \(D_{21}\). The final standard deviation \(\sigma\) includes contributions from both: theory and experiment. \(\Delta D_{21}\) stands for the difference of experiment and theory. References for the \(D_{21}\) are presented for experiment for the 2s HFS. We put here \(\zeta = 0\).

| Atom | \(D_{21}(\text{exp}) [\text{kHz}]\) | \(D_{21}(\text{theor}) [\text{kHz}]\) | \(\Delta D_{21}/\sigma [\text{ppm}]\) |
|---|---|---|---|
| H | 48.53(23) | 48.953(3) | -1.8 0.16 |
| H | 49.13(40) | 0.4 0.28 |
| D | 11.16(16) | 11.312 5(5) | -1.0 0.49 |
| \(^3\text{He}^+\) | -1 189 979(71) | -1 190 067(63) | 0.9 0.01 |
| \(^3\text{He}^+\) | -1 190.1(16) | 0.0 0.18 |