Abstract—We consider the most accurate tests of bound state QED theory of the hyperfine splitting in two-body atoms related to the HFS interval of the 1s state in muonium and positronium and the 2s state in hydrogen, deuterium and the helium-3 ion. We summarize their QED theory and pay special attention to involved effects of strong interactions and to recent optical measurements of the 2s HFS interval in hydrogen and deuterium. We present results for specific ratios of the 1s 2s frequencies in hydrogen and deuterium which happen to be among the most accurately measured and calculated quantities.

I. INTRODUCTION

Recent progress in precision optical measurements provides as new accurate data related to simple atoms. The data are related to such quantities as the Lamb shift and hyperfine intervals. Previously such data were available only from microwave measurements. Precision atomic theory is bound state quantum electrodynamics.

Quantum electrodynamics (QED) by itself is a well established theory. It successfully describe pure leptonic atoms and partly conventional atoms such as hydrogen. Problems with the accuracy of theoretical predictions arise because QED is incomplete in a sense. Even pure leptonic systems are not free of hadronic effects which enter through virtual hadronic intermediate states. In case of hydrogen, deuterium etc we should take into account distribution of the electric charge, magnetic moment and some more complicated effects. Here we consider QED tests involving the hyperfine splitting in light hydrogen-like atoms.

Bound state QED is much more complicated than QED for free particles and deserves serious tests. Some of such tests are significant for the determination of fundamental constants and in particular for the fine structure constant, which may be obtained from the hyperfine structure (HFS) interval in muonium (see reviews [1], [2], [3] for detail).

The HFS interval in hydrogen and some other light atoms has been known for a while with a record experimental accuracy, however, the related theory suffers from uncertainties of the nuclear structure effects at the one-ppm level or higher.

We consider a few possibilities to perform QED tests going far beyond this level of accuracy. Some of them are of metrological interest.

The quantities of interest for the QED tests, such as the Lamb shift and the HFS intervals, lie in the microwave domain and to perform an optical measurement for such a quantity one has to deal with a number of optical quantities and to combine their frequencies to extract a microwave value of interest. Some combinations of this kind can be determined with an extremely high accuracy because in differential measurements some systematic effects can be cancelled.

In particular, we present here results for specific ratios of the 1s 2s transition frequencies in hydrogen and deuterium

\[
R_{\text{HFS}}(1s \rightarrow 2s) = \frac{\lambda_{1s \rightarrow 2s}}{\lambda_{1s \rightarrow 2s}} ; \quad (1)
\]

\[
R_{\text{HFS}}(1s \rightarrow 2s) = \frac{\lambda_{1s \rightarrow 2s}}{\lambda_{1s \rightarrow 2s}} ; \quad (2)
\]

which happen to be among the most accurately measured and calculated quantities.

II. EXPERIMENTAL DETERMINATION OF THE RATIO \( R_{\text{HFS}}(1s \rightarrow 2s) \) IN HYDROGEN AND DEUTERIUM

Some time ago a long-term program was launched at Max-Planck-Institut für Quantenoptik to build a new natural frequency standard locked to the ultraviolet 1s 2s transition [4]. Applying the hydrogen spectrometer developed for this program we performed differential measurements for hyperfine different components of the 1s 2s transition frequency in hydrogen [5] and deuterium [6] (see Fig. 1 for the level scheme in the deuterium atom).

The ratios under question can be present in the form

\[
R_{\text{HFS}}(1s \rightarrow 2s H) = 1 + \frac{\lambda_{1s \rightarrow 2s}}{\lambda_{1s \rightarrow 2s}} ; \quad (3)
\]

\[
R_{\text{HFS}}(1s \rightarrow 2s D) = 1 + \frac{\lambda_{1s \rightarrow 2s}}{\lambda_{1s \rightarrow 2s}} ; \quad (4)
\]

where

\[
\lambda_{1s \rightarrow 2s} = \frac{\lambda_{1s \rightarrow 2s}}{\lambda_{1s \rightarrow 2s}} ; \quad (5)
\]

\[
\lambda_{1s \rightarrow 2s} = \frac{\lambda_{1s \rightarrow 2s}}{\lambda_{1s \rightarrow 2s}} ; \quad (6)
\]

are the subjects of measurements.

The results of our measurements [5], [6], [7]

\[
\lambda_{1s \rightarrow 2s} = 1242848892(16) \, \text{Hz} ; \quad (5)
\]

\[
\lambda_{1s \rightarrow 2s} = 286459899(7) \, \text{Hz} \quad (6)
\]

relate to the following values for the ratio

\[
R_{\text{HFS}}^{\exp}(1s \rightarrow 2s H) = 1 + 503981357(65) \quad 10^{16} ; \quad (10)
\]

\[
R_{\text{HFS}}^{\exp}(1s \rightarrow 2s D) = 1 + 1161293109(28) \quad 10^{16} ; \quad (11)
\]
The hyperfine interval of the deuterium obtained from (5) and (6) are found to be \[5\], \[6\] about three times as precise.

The results for the \(2s\) hyperfine interval in hydrogen and deuterium obtained from [5] and [6] are well with the early microwave data mentioned above and are somewhat improved [10]. Our optical results [5], [6] agree with ordinary hydrogen atoms. To reach a sensitivity to higher-order QED corrections, one has to combine the HFS intervals of the \(1s\) and \(2s\) states in the same atom in the form of \(D_{21}\). That eliminates the leading nuclear contributions.

A substantial cancellation of the nuclear structure contributions takes place because the nuclear contribution in leading approximation is of a specific factorized form of

\[E \langle N \nu c l \rangle = A \langle N \nu c l \rangle \quad n_1(r = 0)^2; \]

In other words, the correction is a product of a certain nuclear-structure parameter \(A \langle N \nu c l \rangle\) and the squared value of the wave function at the origin

\[n_1(r = 0)^2 = \frac{1}{Z} \frac{m_e c^3}{\hbar} \quad \rho \quad \] with \(n_1\) being the principal and orbital quantum numbers, respectively, and \(m_e\) being the reduced mass of the electron.

Still there are higher-order corrections due to the nuclear effects which are of a more complicated form and survive this cancellation. However, they are much smaller and under control [12]. The theory of \(D_{21}\) in light hydrogen-like atoms is presented in Table I [12], [13].

Here we updated results for the one-loop correction by applying the extrapolation procedure developed in [13], [7] to recently obtained numerical data related to hydrogen-like atoms for \(Z = 5\). Our one-loop effective coefficients are found to be \(C_{SE}(Z = 1) = 2.4(4)\) and \(C_{SE}(Z = 2) = 2.23(2)\) in notation of [13].

### TABLE I

| Contribution to HFS in Hydrogen | Deuterium | \(^{3}\)He\(^+\) ion |
|--------------------------------|-----------|----------------------|
| \(D_{21}(QED\ 3)\)            | 48.937    | 11.305 6             |
| \(D_{21}(QED\ 4)\)            | 0.024(3)  | 0.004(6)            |
| \(D_{21}(N u c l)\)            | -0.002(2)| 0.307(35)            |
| \(D_{21}(\text{He}n)\)        | 48.955(3)| 11.312(86)           |

### III. THEORETICAL DETERMINATION OF THE RATIO \(R_{HFS}(1s\ 2s)\) IN HYDROGEN AND DEUTERIUM

For a theoretical determination of the ratio \(R_{HFS}(1s\ 2s)\) it is helpful to re-write the ratios in the form

\[R_{HFS}(1s\ 2s; H) = 1 + \frac{7}{8} \frac{f_{HFS}(1s; H)}{f(1s \ 2sF = 1)} \]
\[\times \frac{1}{f(1s \ 2sF = 1)}; \]
\[R_{HFS}(1s\ 2s; D) = 1 + \frac{7}{8} \frac{f_{HFS}(1s; D)}{f(1s \ 2sF = 3=2)} \]
\[\times \frac{1}{f(1s \ 2sF = 3=2)}; \]

While the frequency of the hyperfine interval of the \(1s\) state, \(f_{HFS}(1s)\), is well-known experimentally

\[f_{HFS}(1s; H) = 1420.405.751.768(1)\ H\ z; \]
\[f_{HFS}(1s; D) = 327.384.352.522(2)\ H\ z; \] and the specific difference

\[D_{21} = 2^3 \ g_{FS}(2s) - f_{HFS}(1s); \]

is a subject of theoretical investigations.

As was shown recently [11], an accurate QED test competitive with other QED tests on the hyperfine theory is possible with ordinary hydrogen atoms. To reach a sensitivity to higher-order QED corrections, one has to combine the HFS intervals of the \(1s\) and \(2s\) states in the same atom in the form of \(D_{21}\).

With the help of the theoretical results for the specific difference \(D_{21}\) in hydrogen and deuterium, described above, we arrive at theoretical predictions for the ratio \(R_{HFS}(1s\ 2s)\) in hydrogen and deuterium

\[R_{HFS}(1s\ 2s; H) = 1 + \frac{5039.813.945(14)}{10^{16}}; \]
\[R_{HFS}(1s\ 2s; D) = 1 + \frac{116.293.091(03)}{10^{16}}; \]
IV. SUMMARY OF THEORETICAL AND EXPERIMENTAL DETERMINATION OF THE RATIO $R_{H\,FS}$ IN HYDROGEN AND DEUTERIUM

Recently there have been a number of discussions on most precisely known quantities from an experimental or a theoretical point of view. It is indeed quite tricky when one discusses a fractional accuracy because in experiment and theory the accurate value can be often achieved when the dominant contribution into a certain quantity is known and a subject of determination is a difference between a real value and a dominant contribution. An example is, e.g., the determination of the Lamb shift in the ground state in the hydrogen atom, where two transitions, with frequencies different by a factor approximately equal to four, were compared

\[ \frac{4f(2s \rightarrow 4s)}{f(1s \rightarrow 2s)} = 1 + 7781376(16) \times 10^{-12}; \quad [15]; \]
\[ \frac{4f(2s \rightarrow 6d_{3/2})}{f(1s \rightarrow 3s)} = 1 + 6431080(14) \times 10^{-12}; \quad [16]; \]
\[ \frac{4f(2s \rightarrow 4p_{3/2})}{f(1s \rightarrow 2s)} = 1 + 9789493(16) \times 10^{-12}; \quad [17]; \]

We consider here a specific ratio of the $1s \rightarrow 2s$ transition frequencies in hydrogen and deuterium which offers one of the most accurate values in both theoretical and experimental lists. The highest accuracy was also achieved by a splitting of the ratio into well-established large contributions and small corrections left to determine experimentally or theoretically.

The results on the determination of $R_{H\,FS}(1s \rightarrow 2s)$ in hydrogen and deuterium are summarized in Table II, which shows that measurements and calculations of the HFS ratio of the $1s \rightarrow 2s$ transition frequencies have record fractional accuracy and the theory is in good agreement with the experiment. Nevertheless, one should not overestimate the importance of such an accuracy. From experimental point of view the most ambitious task is to obtain the highest accuracy for a directly measured value, it is similar for theory. What is more important is which effects could affect the accuracy. In our case, for the experiment those are spin-dependent effects in the absolute $1s \rightarrow 2s$ measurement. Theoretical effects which limit the accuracy of our calculations related to our understanding of so-called state-dependent part of the fourth-order recoil corrections and of the one-loop and two-loop self-energy contributions. Both theoretical and experimental problems mentioned are actual problems to be studied.

| Atom | Method | Value      | $u_r$ |
|------|--------|------------|-------|
| H    | exp    | $1 + 5039813857(65)$ | $16$ | $65$ | $16$ |
| H    | theory | $1 + 50398139453(1.8)$ | $16$ | $1.8$ | $16$ |
| D    | exp    | $1 + 1161293109(28)$ | $16$ | $28$ | $16$ |
| D    | theory | $1 + 11612930919(0.03)$ | $16$ | $0.03$ | $16$ |

V. OTHER TESTS OF BOUND STATE QED RELATED TO THE HYPERFINE EFFECTS

A. The difference $D_{21}$ in atoms other than hydrogen and deuterium

The $1s$ and $2s$ hyperfine intervals are measured much more accurately compared to a theoretical prediction which can be made for each of them separately. However, for the difference $D_{21}$ the experimental and theoretical accuracy become competitive. While for $^3\text{He}^+$ the experimental [18] is already really competitive with the theory [13], in the case of hydrogen and deuterium, the theoretical uncertainty is up-to-date substantially better than the uncertainty related to the measurements of the HFS interval in the $2s$ state. Among other QED tests with $D_{21}$ the case of the helium-3 ion is most sensitive to various higher-order bound state QED effects. That is partly because of a higher fractional accuracy in the determination of the $2s$ hyperfine interval $[18]^1$

\[ f_{H\,FS}^D(2s) = 1083354981(9) \text{ Hz} \quad (14) \]

and partly because various higher-order effects scales with the nuclear charge $Z$ as $Z^5$ or $Z^6$ and thus are enhanced very much for the helium ion ($Z = 2$) in comparison with hydrogen and deuterium ($Z = 1$).

B. The $1s$ hyperfine interval in muonium

An alternative opportunity to verify precision theory for the hyperfine effects is to study pure leptonic atoms. One of them is muonium, a bound system of a positive muon and an electron. In contrast to the hydrogen atom, the nucleus, a muon, is not influenced by the strong interaction. The strong interaction enters only the system through hadronic vacuum polarization, which sets an ultimate limit on any QED tests with muonium. Uncertainties for QED itself and for the hadronic effects are presented in [19], [1]. Muonium has metrological interest due to determination of $\lambda$, $m = m_e$, $p = p$ etc [3].

C. The $1s$ hyperfine interval in positronium

Another atomic system of pure leptonic nature is positronium. The nucleus, a positron, is a very light one. As a result, various recoil effects, which are crucially important in advanced HFS theory, are enhanced and therefore critical QED tests can be performed with a relatively low experimental accuracy (see, e.g., [1] for detail).

VI. SUMMARY OF HFS TESTS OF BOUND STATE QED

Most recent results for precision test of bound state QED involving the hyperfine structure of light hydrogen-like atoms are summarized in Table III. All tests presented are competitive and the theoretical accuracy is limited by our ability to

$^1$The minus sign in the case of helium-3 ion reflects the fact that the direction of the nuclear magnetic moment is opposite to the nuclear spin and that a level with higher total angular momentum ($F = 1$) is below the level with the lower value ($F = 0$). That is different from the atomic hyperfine structure of atoms where the nuclear magnetic moment is directed along the nuclear spin (hydrogen, deuterium, muonium etc.).
calculate higher order radiative, recoil and radiative-recoil effects (see review [1] for detail). Theory and experiment are generally in good agreement, which is important for metrological applications and confirms the reliability of experimental and theoretical methods.

| Atom | Exp. [kHz] | Theor [kHz] | -
|------|------------|-------------|-
| H, D | 49.13(13)  | 48.955(5)   | 1.4 |
| H, D | 48.53(23)  |             | -1.8|
| H, D | 49.13(40)  | 0.4         |    |
| D, D | 11.280(56) | 11.3128(3)  | -0.6|
| D, D | 11.16(16)  | -1.0        |    |
| ^3He, D | -1.18997971 | -1.190146(16) | 1.7 |
| ^3He, D | -1.190146(16) | 0.0        |    |
| Mu, 1s | 4.463(302)78(5) | 4.463(302)88(55) | -0.18 |
| Ps, 1s | 203389100(740) | 203391700(500) | -2.9 |
| Ps, 1s | 203397500(1600) | 2.5        |    |

TABLE III
COMPARISON OF EXPERIMENT AND THEORY OF HYPERFINE STRUCTURE IN LIGHT HYDROGEN-LIKE ATOMS. THE REFERENCE CAN BE FOUND IN REVIEW [1].

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