Quantum electrodynamical corrections 
to the hyperfine structure of excited S states

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State-dependent quantum electrodynamical corrections are evaluated for the hyperfine splitting of nS states for arbitrary principal quantum number n. The calculations comprise both the self-energy and the vacuum-polarization correction of order \((2^{-Z}) E_r\) and the recoil correction of order \((2^{-Z}) (n \rightarrow l) E_F\). Higher-order corrections are summarized and partly reevaluated as well. Accurate predictions for hydrogen hyperfine splitting intervals of nS states with \(n = 2; 3; \ldots; 8\) are presented. The results obtained are important due to steady progress in hydrogen spectroscopy for transitions involving highly excited S states.

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I. INTRODUCTION

Investigations of the hyperfine structure in light hydrogen-like atomic systems are interesting for two main reasons. First, accurate measurements of the hyperfine splitting (hfs), combined with high-precision \textit{ab initio} calculations, can yield fundamental tests of bound-state QED theory. Second, the components of transitions in hydrogen can be accurately resolved at the current level of spectroscopic accuracy, and the knowledge of the hfs of excited states is therefore necessary for the interpretation of the experimental data.

The ground-state hfs in hydrogen is known with an outstanding accuracy (a part in \(10^{12}\)) for over 3 decades, and the value of

\[ E_{1S} = 1420405751.768 \text{ (1) Hz} \] (1)

has been obtained in Ref. [1] as a conservative average of various experimental investigations of comparable accuracy, the first of which was reported in Ref. [2]. Unfortunately, our theoretical understanding of the ground-state hfs is limited by the insufficient knowledge of the nuclear charge and magnetization distributions, whose contribution of about \(50 \text{ kHz} \) (30 ppm) cannot be accurately calculated at present.

One of the possibilities to overcome this difficulty [3] is to study the normalized difference of the nS and 1S hfs intervals,

\[ n = n^3 E_{nS} \quad E_{1S} : \] (2)

In this combination of energy intervals, the hfs energy shifts due to the nuclear charge and magnetization distributions are largely eliminated. Indeed, the lowest-order nuclear corrections to \(E_{1S}\) and \(E_{nS}\) scale with the nonrelativistic electron density at the position of the nucleus \(j_n (\ell = 0)\) which is strictly proportional to \(n^3\). The nuclear effects thus do not contribute to the difference \(n\) to leading order. Theoretical investigations show that the specific difference \(n\) provides an opportunity to test the QED theory of bound states on a level of about two orders of magnitude better than for the ground-state hyperfine interval \(E_{1S}\) alone [1]. According to widely accepted terminology, the corrections that depend on \(n\) through \(j_n (\ell = 0)\) only are called “state independent”. Thus, only state dependent correction should be considered in theoretical investigations of the difference \(n\).

Accurate experimental results for the difference \(2\) are presently available for the hydrogen, deuterium, and the \(^3\)He ion. Notably, recent progress has been achieved for hydrogen [4] and deuterium [5] via optical spectroscopy, by comparing the 1S and 2S hyperfine splittings via a phase-coherent optical measurements of the 1S \((\ell = 0)\), 2S \((\ell = 0)\) vs. the 1S \((\ell = 1)\), 2S \((\ell = 1)\) transition. The best absolute accuracy for the difference \(2\) is, however, still obtained for the \(^3\)He ion in a combination of two relatively old measurements \([6, 7]\).

\[ 2(3 \text{ He}^+) = 1189.979 (71) \text{ kHz} \quad z : \] (3)

While the specific difference of the 2S and 1S hfs intervals has been a subject of experimental and theoretical \([8, 9]\) investigations for a long time, the difference \(n\) for \(n > 2\) has attracted much less attention up to now. The case \(n > 2\) is, however, becoming of significant interest nowadays, due to steady progress in hydrogen spectroscopy for transitions involving highly excited S states. Two ongoing experiments could be mentioned in this connection, which concern the hydrogen 1S 3S transition \([3, 10]\) and are expected to reach a sub-kHz level of accuracy.

In the present work, we perform a calculation of the leading state-dependent self-energy and vacuum-polarization corrections for an arbitrary nS state. For the case \(n = 2\), we reproduce the well-known results by Zwanziger [8]. We also generalize the derivation of the leading state-dependent recoil correction given by Sternheim [3] for \(n = 2\) to general \(n\). Next, we summarize and partly reevaluate the state-dependent higher-order correction and present numerical results for the difference \(n\) with \(n = 2; 3; \ldots; 8\) for hydrogen.
This paper is organized as follows: Basic quantities are introduced in Sec. III. Third-order state-dependent corrections are analyzed and summarized in Sec. III. Among these, self-energy corrections are treated in Sec. III A. Vacuum-polarization corrections in Sec. III B and recoil corrections in Sec. III C. The current status of higher-order state-dependent corrections is discussed in Sec. IV. Finally, the total theoretical predictions for the normalized difference of the hf intervals \( n \) in hydrogen are presented in Sec. V for \( n = 2, 3, \ldots, 8 \).

II. GENERAL FORMULAS AND NOTATIONS

We are using natural units with \( \hbar = c = \epsilon = 0 = 1 \). The electron charge is denoted by \( e = |e| \) and \( \hbar = \hbar c = (\hbar/4\pi) \). The magnetic dipole moment of the nucleus is

\[
\gamma = g_N I; \quad (4)
\]

where \( g \) denotes the nuclear \( g \) factor, \( N = |e|/(2m_p) \) is the nuclear magneton, and \( m_p \) is the proton mass. The vector potential generated by the nuclear dipole moment is

\[
A = -\frac{4}{r^3} \gamma; \quad (5)
\]

The interaction of the bound electron with the dipole nuclear magnetic field is given by the Fermi-Breit operator,

\[
V_{hf} = e \gamma \cdot A = \frac{3}{4} \gamma \cdot \hat{r}; \quad (6)
\]

The expectation value of the Fermi-Breit operator on Dirac point-nucleus wave functions is well-known. We write it as

\[
E_{hf} = \left( \frac{3}{2} \right)^3 \gamma \left( \frac{n^2}{m_p} \right)^2 \frac{1}{2} \left( \frac{1}{2} \right) + 1 \left( \frac{1}{4} \right) \ \frac{N}{n \times \left( \frac{1}{2} \right)}; \quad (7)
\]

where \( A \left( \frac{3}{2} \right) \) is a relativistic factor \( A \left( \frac{3}{2} \right) = 1 + O \left( \frac{3}{2} \right) \).

\[
A \left( \frac{3}{2} \right) = n^3 \gamma \left( \frac{3}{2} \right) + 1 \left( \frac{1}{2} \right) \frac{N}{n \times \left( \frac{1}{2} \right)}; \quad (8)
\]

Here, \( N = \frac{3}{2} \), \( n \) is the nuclear principal quantum number of the electron, \( n = n + \frac{1}{2} \), \( n \) is its Dirac angular quantum number, \( s = n, j = j + \frac{1}{2} \), \( 1 \) is the total momentum of the electron, and \( m \) is the electron mass.

For future reference, we also give the magnetic field corresponding to the vector potential \( B \).

\[
B = \frac{3}{2} \gamma \cdot \hat{r} = \frac{3}{4} \gamma \cdot \hat{r} + \frac{3}{4} \gamma \cdot \hat{r}; \quad (9)
\]

In the nonrelativistic limit, the hyperfine Hamiltonian \( H_{hf} \) is given by the sum of two terms, the first of which is proportional to \( B \) and is denoted here as \( H_S + H_D \), whereas the second one (labeled \( H_L \)) corresponds to the interaction of the nuclear moment with the magnetic field of the moving electron, which in turn is proportional to the orbital angular momentum \( \Sigma \). We have

\[
H_{hf} = H_S + H_D + H_L; \quad (10a)
\]

\[
H_S = \frac{3}{4m} \gamma \cdot \hat{r} - \frac{1}{8m} \gamma \cdot \hat{r} \times \hat{r}; \quad (10b)
\]

\[
H_D = \frac{3}{8m} \gamma \cdot \hat{r} \times \hat{r}; \quad (10c)
\]

\[
H_L = \frac{3}{4m} \gamma \cdot \hat{r} \times \hat{r}; \quad (10d)
\]

Here, \( \gamma \) is the unit vector in the direction of \( \hat{r} \). For the Schrödinger wave function \( n \) of an \( nS \) state, the expectation value of the nonrelativistic Hamiltonian is

\[
\langle H_{hf} \rangle = \langle H_S \rangle = \frac{3}{4m} \gamma \cdot \hat{r} \times \hat{r}; \quad (11)
\]

and the splitting between the ground-state levels with \( F = I + \frac{1}{2} \) and \( F = I - \frac{1}{2} \) gives us the Fermi energy

\[
E_F = \frac{3}{8m} \gamma \cdot \hat{r} \times \hat{r}; \quad (12)
\]

where \( n = 1 \) \( \left( \frac{1}{2} \right) \) is in the non-recoil limit.

III. THIRD-ORDER CORRECTIONS

A. Self-energy

The leading state-dependent self-energy correction to the hyperfine splitting can be conveniently expressed as

\[
S_n = \frac{1}{2} E_F \left( a_{21}^{(n)} + a_{21}^{(n)} \right) \ln \left( \frac{3}{2} \right) + a_{21}^{(n)} \ln \left( \frac{3}{2} \right); \quad (13)
\]

Here, \( a_{21}^{(n)} \) is the contribution to the normalized difference \( n \) due to self-energy effects, where \( n \) is defined according to Eq. (2). In general, we will denote various contributions to \( n \) by the symbol \( n \) with appropriate superscripts. The coefficients \( a_{21}^{(n)} \) are understood as originating from the difference \( a_{21}^{(n)} = a_{21}^{(n)}(nS) - a_{21}^{(n)}(nS) \), with \( a_{21}^{(n)} \) being the corresponding coefficient for the \( nS \) state. As usual, the first index of \( a_{21}^{(n)} \) counts the power of \( \frac{1}{2} \), and the second one indicates the power of the logarithm \( \ln \left( \frac{3}{2} \right) \).

The self-energy correction \( a_{21}^{(n)} \) consists of two parts induced by the low-energy and the high-energy virtual photons \( n \). The low-energy part can be immediately obtained by generalizing formulas given in Refs. \( 11, 13, 14 \). The corresponding contribution expressed in units of \( \left( \frac{3}{2} \right)^2 \) reads:

\[
C_{\Sigma} = \frac{8}{3} \frac{3}{4} \frac{1}{n} \frac{1}{4n^2} + \frac{1}{n} \ln \left( \frac{3}{2} \right) \ln \left( \frac{3}{2} \right); \quad (14)
\]
Here, \( N (\hbar S) \) is a delta correction to the Bethe logarithm, whose numerical values are given in Table I.

We now turn to the contribution due to high-energy virtual photons. Up to relative order \( (Z)^2 \), we can use the modified Dirac Hamiltonian \( H_{\text{rad}} \) (for a derivation see, e.g., Chap. 7 of [14]), which reads

\[
H_{\text{rad}} = \hbar \epsilon F_1 (\epsilon^2) \mathcal{A} + m + F_1 (\epsilon^2) \mathcal{V} + F_2 (\epsilon^2) \frac{\epsilon}{2m} i\mathcal{E};
\]

This Hamiltonian leads to various self-energy corrections. The first of these is an \( F_2 (\epsilon) \) correction to the effective potential, evaluated on the relativistic wave functions. It is generated by the following term in Eq. (15),

\[
H = F_2 (\epsilon) \frac{\epsilon}{2m} i\mathcal{E} = \frac{\epsilon}{2} (H_S + H_D);
\]

where the Schwinger result \( F_2 (\epsilon) \) has been used, \( H_S \) and \( H_D \) are given in Eqs. (10b) and (10c), respectively, and \( \mathcal{E} \) is the Dirac matrix in the Dirac representation. The corresponding relative correction to the Fermi energy is

\[
\frac{\hbar j}{2} (H_S + H_D) \frac{\hbar j}{1} = \frac{\hbar j}{2} H_S \frac{\hbar j}{1};
\]

The numerator of Eq. (17) diverges in relative order \( (Z)^2 \) when evaluated on an \( nS \) state. A finite result is obtained, however, when the weighted (or normalized) difference of matrix elements is considered. We define the normalized difference for the general operator \( \mathcal{A} \) as

\[
\mathcal{R} = \frac{n S \mathcal{A} \mathcal{R}}{n S \mathcal{R}} = \frac{\hbar j}{2} (H_S + H_D) \frac{\hbar j}{1};
\]

The correction \( C_1 \) leads to the following contribution to the normalized difference \( \mathcal{R} \) of hfs intervals,

\[
C_1 = \frac{\mathcal{R} \mathcal{R}_n}{E_F} = \frac{\hbar j}{2} (H_S + H_D) \frac{\hbar j}{1};
\]

The second correction \( C_2 \) is an \( F_2 (\epsilon) \) correction to the effective potential, i.e.

\[
F_2 (\epsilon) \frac{\epsilon}{2m} i\mathcal{E} = \frac{\epsilon^2}{m} i\mathcal{E};
\]

to be evaluated on the nonrelativistic wave functions. For the third correction \( C_3 \), we have to evaluate an \( F_2 (\epsilon) \) correction to the effective potential; the relevant Hamiltonian can be expressed as \( F_2 (\epsilon) \frac{\epsilon^2}{m} \mathcal{V} \) when the weighted (or normalized) difference of hfs intervals, \( \mathcal{E} \), is used.

\[
V = \frac{\epsilon}{2} (Z) \frac{\epsilon}{2} \frac{\epsilon^2}{m} \mathcal{V} - \frac{\epsilon}{2} \frac{\epsilon^2}{m} \mathcal{V}:
\]

For the fourth correction \( C_4 \), we have to evaluate an \( F_2 (\epsilon) \) correction to the effective potential, which can be expressed as

\[
F_2 (\epsilon) \frac{\epsilon}{2m} i\mathcal{E} = \frac{\epsilon^2}{m} i\mathcal{E};
\]

for the third correction \( C_3 \), we have to evaluate an \( F_2 (\epsilon) \) correction to the effective potential; the relevant Hamiltonian can be expressed as \( F_2 (\epsilon) \frac{\epsilon^2}{m} \mathcal{V} \).

The results for the normalized \( S \)-state difference, expressed in terms of the nonrelativistic wave function, are given in Eq. (6) and the term

\[
F_2 (\epsilon) \frac{\epsilon}{2m} i\mathcal{E} = \frac{\epsilon^2}{m} i\mathcal{E};
\]

from the modified Dirac Hamiltonian \( H_S \), where \( \mathcal{E} \) is the electric field generated by the Coulomb potential. From the \( \epsilon \)-scaling of the two involved Hamiltonians, it is clear that the resulting operator has to be proportional to \( 1=\epsilon^4 \). The prefactor can be obtained using Dirac algebra and considering the fact that the main contribution comes from negative-energy states with an energy \( m \).

The high-energy corrections discussed so far are explicitly given by

\[
C_1 = \frac{\hbar j}{2} (H_S + H_D) \frac{\hbar j}{1};
\]
\[
C_2 = \frac{\hbar j}{2} (H_S + H_D) \frac{\hbar j}{1};
\]
\[
C_3 = \frac{\hbar j}{2} (H_S + H_D) \frac{\hbar j}{1};
\]
\[
C_4 = \frac{\hbar j}{2} (H_S + H_D) \frac{\hbar j}{1};
\]

Here, \( n \) is the nonrelativistic wave function, \( j \) is the relativistic wave function, and all matrix elements \( \mathcal{R} \) by default, are understood in terms of the nonrelativistic wave function.

The results for the normalized \( S \)-state difference, expressed

\[
C_1 = \frac{\hbar j}{2} (H_S + H_D) \frac{\hbar j}{1};
\]
\[
C_2 = \frac{\hbar j}{2} (H_S + H_D) \frac{\hbar j}{1};
\]
\[
C_3 = \frac{\hbar j}{2} (H_S + H_D) \frac{\hbar j}{1};
\]
\[
C_4 = \frac{\hbar j}{2} (H_S + H_D) \frac{\hbar j}{1};
\]

Here, \( \mathcal{E} \) is the nonrelativistic wave function, and all matrix elements \( \mathcal{R} \) are understood in terms of the nonrelativistic wave function.
TABLE II: Numerical values of the nonlogarithmic self-energy coefficients for the normalized difference \( a_{20}^{SE}(\eta;1) \) and for the single \( nS \) states \( a_{20}^{SE}(nS) \) in the range \( n = 1; \cdots; 8 \).

| \( n \) | \( a_{20}^{SE}(\eta;1) \) | \( a_{20}^{SE}(nS) \) |
|---|---|---|
| 1 | — | 17.122 338 75(1) |
| 2 | 5.221 233 33(1) | 11.901 105 41(1) |
| 3 | 6.705 291(1) | 10.417 048(1) |
| 4 | 7.402 951(1) | 9.719 388(1) |
| 5 | 7.809 635(1) | 9.312 703(1) |
| 6 | 8.076 773(1) | 9.045 565(1) |
| 7 | 8.266 081(1) | 8.856 258(1) |
| 8 | 8.407 461(1) | 8.714 878(1) |

In units of \( \zeta^2 \), are:

\[
\frac{C_1}{\zeta^2} = \frac{19}{48} + \frac{5}{8} \frac{49}{48} \frac{1}{4} [ + \langle \eta \rangle \ln \langle \eta \rangle ]; \tag{24a}
\]

\[
\frac{C_2}{\zeta^2} = \frac{1}{6} \frac{1}{n^2} 1; \tag{24b}
\]

\[
\frac{C_3}{\zeta^2} = \frac{1}{6} \frac{1}{n^2} \frac{1}{2} \ln \frac{m}{2} + \frac{11}{36}; \tag{24c}
\]

\[
\frac{C_4}{\zeta^2} = \frac{8}{3} \frac{\ln m}{2} + \frac{5}{6} \frac{1}{n} + \langle \eta \rangle \ln \langle \eta \rangle ; \tag{24d}
\]

\[
\frac{C_5}{\zeta^2} = \frac{2}{3} + \frac{1}{2} \frac{1}{2n} + \frac{1}{6n^2} + \langle \eta \rangle \ln \langle \eta \rangle ; \tag{24e}
\]

Adding all the contributions together, we obtain the following result for the self-energy correction \( a_{20}^{SE}(\eta;1) \):

\[
a_{21}^{SE}(\eta;1) \ln \langle \zeta \rangle + a_{20}^{SE}(\eta;1) = \frac{C_1 + \frac{P}{3} \frac{5}{n^3} C_1}{\zeta^2}; \tag{25}
\]

Of course, the dependence on the noncovariant photon energy cutoff disappears in the final answer. The result for the logarithmic term is \( a_{20}^{SE}(\eta;1) \):

\[
a_{20}^{SE}(\eta;1) = \frac{8}{3} \frac{3}{4} \frac{1}{n} + \frac{1}{4n^2} + \langle \eta \rangle \ln \langle \eta \rangle ; \tag{26}
\]

For the nonlogarithmic term \( a_{20}^{SE}(\eta;1) \), we obtain the general result

\[
a_{20}^{SE}(\eta;1) = N(\eta;S) N(1S) + \frac{71}{48} \frac{79}{72n} \frac{55}{144n^2} + \frac{107}{36} [ + \langle \eta \rangle \ln \langle \eta \rangle ]
\]

\[
+ \frac{8}{3} \ln \langle \zeta \rangle \frac{3}{4} \frac{1}{n} + \frac{1}{4n^2} + \langle \eta \rangle \ln \langle \eta \rangle ; \tag{27}
\]

In the particular case \( n = 2 \), we reproduce the known value for this coefficient \( a_{20}^{SE}(\eta;1) \). Explicit numerical results for \( a_{20}^{SE}(\eta;1) \) are given in Table II for \( n = 1; \cdots; 8 \). In the table, we also list the values of \( a_{20}^{SE}(nS) \) obtained with the help of an improved \( 1S \) numerical value, which we give here for reference purposes,

\[
a_{20}^{SE}(1S) = 17.122 338 75(1); \tag{28}
\]

This result can be immediately obtained according to the improved numerical evaluation of the low-energy part as described in Ref. \( [13] \), which contains a correction to the Bethe logarithm induced by a Dirac-delta local potential \( [9] \), see also the entries in the forth column of Table II of Ref. \( [13] \).

**B. Vacuum polarization**

The leading state-dependent vacuum-polarization correction to the hyperfine splitting can be conveniently expressed as

\[
V_{\nu P} = - \langle \zeta \rangle^2 E_F a_{20}^{V P}(\eta;1); \tag{29}
\]

The correction \( V_{\nu P} \) consists of two parts \( [9] \), with the first one given by a matrix element of the radiatively corrected external magnetic field and the other by a matrix element of the vacuum-polarization operator between the wave functions corrected by the presence of the external magnetic field.

We start with the first part. To the leading order, the radiatively corrected magnetic interaction (magnetic loop) is well-known to be

\[
V_{\nu P} = \frac{Z_1}{3} \frac{P}{1} \frac{e^{t^2}}{t^2} 1 + \frac{1}{2e^2} (1 + 2m \tau t) e^{2m \tau t}; \tag{30}
\]

We recall that the matrix element of \( V_{\nu P} \) between the Dirac wave functions is, for \( nS \) states,

\[
\ln \langle \eta \rangle \frac{Z_1}{3} \frac{P}{1} \frac{e^{t^2}}{t^2} \frac{1 + \frac{1}{2e^2}}{t^2} \tau t + (1 + 2m \tau t) e^{2m \tau t}; \tag{31}
\]

where \( g_n \) and \( f_n \) are the upper and the lower radial component of the Dirac wave function, respectively. We thus immediately have that

\[
E_n^{V P} = \ln \langle \eta \rangle \frac{Z_1}{3} \frac{P}{1} \frac{e^{t^2}}{t^2} \frac{1 + \frac{1}{2e^2}}{t^2} \tau t + (1 + 2m \tau t) e^{2m \tau t}; \tag{32}
\]

To the leading order in \( \zeta \) for an \( nS \) state,

\[
g_n \tau t = \frac{2}{n} \frac{3m^2}{r} e^{\frac{r_m}{n} \frac{1}{r_n} \frac{2}{r_n}}; \tag{33}
\]
where \( n_m \) and \( L^n_{m-1} \) are generalized Laguerre polynomials. Performing the integration over \( \xi \) in Eq. (32) with help of entry (2.19.14.6) in Vol. 2 of Ref. [18], expanding the result in \( Z \), and integrating over \( \tau \), we obtain

\[
E^{\text{VP}}_{n\mu} = \frac{E_F}{n^3} \left( Z \right) \frac{3}{8} \frac{2}{15} 5 + \frac{1}{n^2} \left( Z \right) ;
\]

The corresponding contribution to \( n \) is

\[
E^{\text{VP}}_{n\mu} = \left( Z \right)^2 E_F \frac{2}{15} \frac{1}{n^2} ;
\]

The second vacuum-polarization contribution is given by the second-order correction,

\[
E^{\text{VP}}_{n\mu \xi} = 2 \left( Z \right) E_F \frac{1}{(E + H)^5} V_{\text{VP}} n ;
\]

where \( V_{\text{VP}} \) is the vacuum-polarization potential. Due to spherical symmetry of \( V_{\text{VP}} \), only the \( nS \) intermediate states contribute in the above expression. To the leading order, we have

\[
V_{\text{VP}}(\xi) = \frac{4}{15} \frac{Z}{m} \left( Z \right) \left( \frac{1}{(E + H)^5} \right) \left( \frac{1}{(E + H)^5} \right);
\]

and we can replace \( V_{\text{VP}} \) with \( H_S \) being given in Eq. (10b). The second-order matrix element \( (37) \) diverges for \( nS \) states. It is, however, finite for the normalized difference, with the result

\[
V^{\text{VP}}_{n\mu \xi} = \frac{8}{15} \frac{E_F}{m^5} \left( Z \right)^2 \left( \frac{1}{(E + H)^5} \right) \left( \frac{1}{(E + H)^5} \right);
\]

Using the formulas from Ref. [17] for the matrix element, we arrive at

\[
V^{\text{VP}}_{n\mu \xi} = \left( Z \right)^2 E_F \frac{8}{15} \frac{1}{n^2} + n \ln(n) ;
\]

Finally, the total result for the vacuum-polarization correction [Eq. (39)] reads

\[
a^{\text{VP}}_{20}(n;1) = \frac{8}{15} \frac{3}{4} \frac{1}{n^2} + n \ln(n) ;
\]

in agreement with Ref. [16].

C. Recoil corrections

The leading-order state-dependent recoil correction can be parameterized as

\[
a^{\text{REC}}_{20}(n;1) = \left( Z \right)^2 \frac{m}{M} E_F a^{\text{REC}}_{20}(n;1);
\]

where \( M \) is the mass of the nucleus. The general expression for this correction was derived by Sternheim [3]. It reads

\[
a^{\text{REC}}_{20}(n;1) = \frac{E_F}{n^3} \left( Z \right) \frac{3}{8} \frac{2}{15} 5 + \frac{1}{n^2} \left( Z \right) ;
\]

where

\[
H^{(1)}_M = \frac{e}{8m^2} (E + H) \frac{p^2}{4m^2} \frac{e}{m} \left( \frac{1}{r} \right) \left( \frac{1}{r} \right);
\]

Here, \( A \) is given in Eq. (5). \( E \) is the electric field induced by the scalar potential of a moving magnetic dipole \( V \),

\[
V = \frac{e}{4} \left( \frac{Z}{m} \right) \left( \frac{p}{m} \right) \frac{1}{r} ;
\]

and \( \mu \) is the vector potential of the moving nucleus,

\[
e \mu = \frac{1}{8} \left( \frac{Z}{m} \right) \left( \frac{p}{m} \right) \frac{1}{r} ;
\]

The matrix elements in Eq. (43) diverge for \( nS \) states, but they yield a finite result for the normalized difference \( \langle n \rangle \), which reads

\[
a^{\text{REC}}_{20}(n;1) = \frac{3}{2} \frac{1}{n^2} + \frac{7}{8} \frac{17}{28} \left( \frac{9}{14n} + \frac{1}{28n^2} \right) + \frac{1}{2} \left( \frac{11}{12} + \frac{1}{2n} + \frac{5}{12n^2} \right) + n \ln(n) ;
\]

where \( q = \frac{Z m_p}{n p} \) and \( m_p \) is the proton mass. For the particular case \( n = 2 \), our result is in agreement with the one originally obtained by Sternheim [3].

D. Summary of the theory up to third order

To the leading order in the parameters \( Z \), \( Z \), and \( m = \mu \), the normalized difference of the hyperfine-structure \( nS \) intervals \( \Delta_n \) is given by the sum of the relativistic (Breit), self-energy, vacuum-polarization, and recoil corrections:

\[
\Delta_n = \left( Z \right)^2 \frac{m}{M} a^{\text{SE}}_{20}(n;1) + \frac{h}{M} a^{\text{REC}}_{20}(n;1) + \frac{m}{M} a^{\text{VP}}_{20}(n;1) + a^{\text{REC}}_{20}(n;1) + \frac{m}{M} a^{\text{REC}}_{20}(n;1) ;
\]
where the Fermi energy $E_F$ is defined as the splitting between the ground-state levels with the atomic angular momentum $F' = I + 1 = 2$ and $F' = I = 1 = 2$ calculated within the non-relativistic approximation and is given by

$$E_F = \frac{4}{3} (Z)^3 \frac{m^2}{M} \frac{21 + 1}{21} \frac{1 + \frac{m}{M}}{2} ; (49)$$

with the nuclear magnetic moment $g = n I$. Notice that this expression follows from Eq. (12) after restoring the correct reduced-mass dependence.

For the particular (and the most important) case $n = 2$, the coefficients in Eq. (48) were obtained long ago [18, 19]. The full $n$ dependence of the coefficients $\alpha_{21}^F$ and $\alpha_{20}^F$ was reported in Ref. [16]. In the present investigation, we have derived the results for all coefficients in Eq. (48) for general $n$. The self-energy, vacuum-polarization, and recoil corrections are given by Eqs. (27), (31), and (47), respectively. The remaining second-order Breit contribution to $\mathrm{Br}_{20}^n$ on $n$ is given by

$$\alpha_{20}^F (n; 1) = \frac{1}{3} + \frac{3}{2n} \frac{11}{6n^2} ; (50)$$

IV. HIGHER-ORDER CORRECTIONS

Higher-order QED and nuclear corrections to the difference were extensively investigated during the last years [16, 20, 21, 22, 23, 24, 25]. The general $n$ dependence of the difference $\alpha_{20}^F$ received significantly less attention up to now. In this section, we would like to summarize the results for higher-order corrections and reevaluate some of them.

The higher-order relativistic (Breit) corrections are immediately obtained by expanding the general formula (3):

$$\frac{B_r(n)}{E_F} = (Z)^4 \frac{25}{36} + \frac{25}{8n} \frac{36}{36n^2} \frac{67}{12n^3} + \frac{21}{8n^4}$$

$$+ (Z)^6 \frac{245}{216} + \frac{245}{48n} \frac{721}{432n^2} + \frac{1195}{144n^3}$$

$$+ \frac{33}{16n^4} \frac{147}{16n^5} \frac{163}{48n^6} ; (51)$$

where the sixth-order contribution is included for completeness.

The state-dependent two-loop correction to order $(Z)^2$ was found in Ref. [16] in the logarithmic approximation. This result can be easily derived if we observe that the leading one-loop correction for the ground-state hfs is generated by an effective magnetic form-factor correction [Eq. (10a)] to the Hamiltonian $H_{\mathrm{F}}$. We thus employ (10b) as an input for a Dirac-delta correction to the Bethe logarithm and obtain the result

$$\frac{B_r(n)}{E_F} = - (Z)^2 \frac{4}{3} \frac{3}{4} \frac{1}{n} + \frac{1}{4n^2} + \ln (n) \ln (n) ; (52)$$

in agreement with Ref. [16].

According to Ref. [16], analogous considerations are valid also for the radiative-recoil correction, and hence

$$\frac{\mathrm{rad-rec}}{n} = - (Z)^2 \frac{m}{M} E_F \ln (Z) + \left( \frac{15}{3} + \frac{1}{4n^2} + \ln (n) \ln (n) ; (53)\right.$$}

We now turn our attention to the state-dependent recoil correction to order $(Z)^3 E_F$, which we evaluate in the logarithmic approximation. We have identified two such contributions. The first one can be obtained as a second-order perturbation correction induced by two effective local potentials, the first one being $H_{\mathrm{S}}$ [Eq. (10b)] and the second one corresponding to the logarithmic recoil correction to the Lamb shift to order $(Z)^5 m^2 + M^2$. The result is

$$\frac{H_{\mathrm{REC}}}{n} = (Z)^3 \frac{m}{M} E_F \ln (Z)$$

$$+ \frac{4}{3} + \frac{1}{n} + \ln (n) \ln (n) ; (54)$$

This expression generalizes the result for the difference $(Z)^2$ reported in Ref. [23]. The second contributions (absent in Ref. [23]) is obtained as a second-order perturbation induced by the operator $H_{\mathrm{S}}$ and by the operator responsible for the nonlogarithmic recoil correction to the Lamb shift to order $(Z)^3 m^2 + M^2$. The logarithm of $Z$ then arises from the second term of the $Z$ expansion of the electron propagator after an integration over the logarithmic region [26]. The result reads

$$\frac{H_{\mathrm{REC}}}{n} = (Z)^3 \frac{m}{M} E_F \ln (Z)$$

$$+ \frac{28}{3} + \frac{1}{2n} + \ln (n) \ln (n) ; (55)$$

We note that this contribution, unlike Eq. (54), is finite for single $nS$ states. For $1S$ state, the constant in Eq. (54) turns into $(124 + 9 + 28 = 3 \ln 2)$, which coincides with a part of the complete $1S$ result obtained by Kinoshita [27] ($Z_{\mathrm{S}}$ in his notation). Our result for the logarithmic part of the fourth-order recoil correction is the sum of Eqs. (54) and (55).

$$\frac{H_{\mathrm{REC}}}{n} = (Z)^3 \frac{m}{M} E_F \ln (Z)$$

$$+ \frac{8}{3} + \frac{3}{4n} + \ln (n) \ln (n) ; (56)$$

We do not have a proof that this result is complete.

Some incomplete results for the fourth-order one-loop self-energy and vacuum-polarization corrections were obtained in Ref. [16]. With misprints being corrected in [22], these cor-
able to the normalized difference of theoretical values of in the first five rows of this Table. Forth-order QED correction and third-order corrections summarized by Eq. (48) are given in Table III agree with those from Table 8 of Ref. [1]. Parameters of the proton used for calculating numerical data for principal quantum numbers \( n \) radii, respectively, and the ground-state hfs.

It should be noted that the one-loop self-energy correction yields the largest contribution among all fourth-order corrections mentioned so far and the incompleteness of the result (57a) provides the dominant theoretical uncertainty for \( n \). For the particular case \( n = 2 \), this correction was evaluated numerically to all orders in \( Z \) in Refs. [21, 25]. The deviation of the contribution (57a) from the all-order result was found to be on the level of 20%. The evaluation of the complete result for the fourth-order vacuum-polarization correction is a much simpler task than for the self-energy. It can be solved either analytically, as was done for \( n = 2 \) in Ref. [22, 28], or (which is much easier) numerically, as was done for \( n = 2 \) in Ref. [25]. However, in view of the absence of complete results for the self-energy correction, we do not pursue the matter any further in the current investigation.

The nuclear-structure correction was evaluated in Refs. [16, 20] to be

\[
\begin{align*}
\frac{H_{\text{Nucl}}}{n} &= (2Z)^2 \frac{E_{1S}}{4} + \frac{1}{n} + \frac{9}{4n^2} + (\frac{1}{n}) \ln(\frac{1}{n}) + \frac{4}{3} (2Z)^2 + (\frac{1}{n}) \ln(\frac{1}{n}) \\
&\quad + \frac{n}{R_E} \left( \frac{n^2}{4} + \frac{1}{4n^2} \right) \ln(\frac{R_E}{R_E})^2 \frac{E_F}{\text{Hz}};
\end{align*}
\]

where \( R_E \) and \( R_M \) are the electric and the magnetic charge radii, respectively, and \( E_{1S}^{\text{Nucl}} \) is the nuclear correction for the ground-state hfs.

V. THEORETICAL RESULTS FOR \( n \)

In this section, we collect all theoretical contributions available to the normalized difference of \( nS \) states \( n \) [Eq. (2)]. Numerical results for individual contributions and the total theoretical values of \( n \) in hydrogen are listed in Table III for principal quantum numbers \( n = 1; \ldots; 8 \). The second- and third-order corrections summarized by Eq. (48) are given in the first five rows of this Table. Forth-order QED corrections discussed in Sec. X are tabulated in the next seven rows, and the nuclear-structure correction completes the analysis. Parameters of the proton used for calculating numerical data in Table III agree with those from Table 8 of Ref. [1]. The nuclear-structure correction for the ground-state hfs that enters Eq. (58) was taken from Ref. [22], where it was obtained by subtracting all known QED corrections from the experimental result for the ground-state hfs [1]. Its numerical value is \( 46 \text{ kHz} \).

We already mentioned above that in the particular case \( n = 2 \), there are complete all-order results available for the \( H_{\text{SE}} \) and \( H_{\text{VP}} \) corrections. We thus employ the numerical values for the self-energy and vacuum-polarization remainder functions for the difference \( \Delta \) as given in Ref. [25], as well as the uncertainty estimates given in the cited reference. The corresponding entries in the table are marked with the asterisk. For \( n > 2 \), we use the formulas (57a) and (57b) and ascribe the 50% uncertainty to them. The error estimates for the other forth-order corrections are as follows: for the two-loop and the radiative recoil corrections, we assume the uncertainty to be a half the numerical value of the logarithmic terms, while for the recoil correction we use 100% of the correction given by Eq. (56).

The two last rows of Table III are reserved for the total theoretical predictions for the normalized difference \( n \) and for the complete values of the hfs frequency of excited hydrogenic \( nS \) states. The latter are obtained by combining the highly accurate experimental value of the ground-state hfs interval [1] and the theoretical prediction for \( n \) given in the previous row of the table.

For the case \( n = 2 \), our evaluation differs from the previous investigation of the difference \( \Delta \) presented in Ref. [22] in two ways: (i) we employ the latest numerical results for the self-energy remainder from Ref. [25] and the error estimate from this reference and (ii) we also have found an additional (numerically small) higher-order logarithmic recoil contribution [55]. Despite the small change of the theoretical prediction, our final result for the hfs frequency of the \( 2S \) state still deviates by 14 Hz from the experimental result \( \Delta E_{2S} = 177566860(16) \text{ Hz} \). We mention also a similar (18 Hz) deviation of the theoretical value of \( \Delta \) for the \( ^3\text{He} \) ion from the experimental result [3] observed in Ref. [25].

VI. CONCLUSION

The normalized difference of the hfs intervals \( \Delta = 8 \text{ Hz} \) has been a subject for both theoretical and experimental investigations since a long time. In this paper, we have presented calculations that generalize the previous studies of \( n = n^3 \) to general \( n \). Our results are complete through third order in the parameters \( Z \), \( \alpha \), and \( m = n \); an estimation of the fourth-order corrections is also supplied.

The dominant source of the present theoretical uncertainty for the difference \( \Delta \) is the higher-order one-loop self-energy correction. Further improvement of the theory can be achieved by a numerical all-order (in \( Z \) ) evaluation of this correction. Such a calculation has been carried out for the difference \( \Delta \) in Refs. [21, 25] based on a method developed by a number of authors [29, 30, 31] and seems feasible for higher values of \( n \) as well. It should be noted that the results
for hydrogen reported in Refs. [21, 25] involved an extrapolation of numerical data obtained for \(Z = 5\) towards \(Z = 1\). It would clearly be preferable to perform a direct numerical calculation of the higher-order self-energy correction for \(Z = 1\), as it was done for the Lamb shift in Refs. [32, 33]. This project is underway.

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TABLE III: Individual contributions to the normalized difference \(n\) of hfs frequencies, and absolute values of the hyperfine splitting frequencies of excited \(S\) states in hydrogen. For the entries marked with an asterisk (*), we employ the numerical results for the self-energy and vacuum-polarization remainder functions as reported in Ref. [25] instead of the analytic expressions given in Eqs. (57a) and (57b) used in other cases. The absolute values for the hfs frequencies of excited states are obtained with the help of 1S experimental result in Eq. (1) as a reference. Units are Hz.

| Effect | 2S | 3S | 4S | 5S | 6S | 7S | 8S |
|--------|----|----|----|----|----|----|----|
| \((Z^2)\) | 47 222.0 | 47 571.8 | 44 860.9 | 42 310.9 | 40 226.1 | 38 548.6 | 37 187.3 |
| \((Z^2)\) (SE) | 1 936.0 | 2 718.6 | 3 134.2 | 3 390.9 | 3 564.9 | 3 690.4 | 3 785.3 |
| \((Z^2)\) (VP) | 58.0 | 79.2 | 90.1 | 96.8 | 101.3 | 104.5 | 106.9 |
| \((Z^2)\) in \(\hbar\) | 162.9 | 210.3 | 232.6 | 245.6 | 254.0 | 260.0 | 264.4 |

Sum of 3rd order | 48 937.1 | 50 000.9 | 47 672.4 | 45 359.4 | 43 435.7 | 41 874.5 | 40 601.3 |

| Effect | 3S | 4S | 5S | 6S | 7S | 8S |
|--------|----|----|----|----|----|----|
| \((Z^4)\) | 5.6 | 5.6 | 5.2 | 4.9 | 4.6 | 4.4 |
| \((Z^4)\) (SE) | 3.3(1.7) | 4.5(2.3) | 5.1(2.6) | 5.5(2.8) | 5.8(2.9) | 6.0(3.0) |
| \((Z^4)\) (VP) | 3.1(1.6) | 4.2(2.1) | 4.8(2.4) | 5.2(2.6) | 5.4(2.7) | 5.6(2.8) |
| \((Z^4)\) in \(\hbar\) | 15.8(7.9) | 19.1(9.6) | 21.2(10.6) | 22.7(11.3) | 23.7(11.9) | 24.5(12.3) |
| \((Z^4)\) (SE) | 3.0 | 3.7(1.9) | 3.8(1.9) | 3.7(1.9) | 3.7(1.9) | 3.7(1.9) |
| \((Z^4)\) (VP) | 0.3(3) | 0.4(4) | 0.4(4) | 0.5(5) | 0.5(5) | 0.5(5) |

Sum of 4th order | 18.7(2.3) | 25.8(8.7) | 28.8(10.4) | 30.6(11.4) | 31.8(12.2) | 32.7(12.7) |

Total \(n\) | 48 954.0(2.3) | 50 024.9(8.7) | 47 699.5(10.4) | 45 388.4(11.4) | 43 466.0(12.2) | 41 905.7(12.7) |

HFS freq. | 177 556 838.2(3) | 52 609 473.2(3) | 22 194 585.2(2) | 11 363 609.1(1) | 6 576 153.79(6) | 4 141 246.81(4) |

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For the first time, the coefficient $a_{20}^{20}$ was evaluated by Zwanziger [8] to be $a_{20}^{20} = 5.37(6)$. A more accurate value for this coefficient was later obtained by P. J. Mohr by recalculating the integrals listed in Eq. (B.5) of Ref. [8] (private communication). According to P. J. Mohr, the expression $(1/s)^2$ in Eq. (B.5) of the cited reference should be replaced by $(1/s)$. After the elimination of this typographical error, the formulas of Ref. [8] may be used for an accurate evaluation of the difference $a_{20}^{20}$ and $a_{20}^{20}$. The private communication by P. J. Mohr is also quoted as reference number [18] of Ref. [7], and the value of 5.5515 given in Eq. (37) of Ref. [7] is the sum of $a_{20}^{20} + a_{20}^{20}$, which implies a value of 5.2212 for $a_{20}^{20}$. According to S. G. Karshenboim (private communication), the value of 5.221233(3) for $a_{20}^{20}$ has been obtained independently by J. R. Sapirstein and S. G. Karshenboim in an unpublished investigation, as cited in Ref. [16].

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