Relativistic corrections of \( m \alpha^6(m/M) \) order to the hyperfine structure of the \( \text{H}_2^+ \) molecular ion

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The \( m \alpha^6(m/M) \)-order corrections to the hyperfine splitting in the \( \text{H}_2^+ \) ion are calculated. That allows a reduction of the uncertainty in the frequency intervals between hyperfine sublevels of a given rovibrational state to about 10 ppm. The results are in good agreement with the high-precision experiment carried out by Jefferts [Phys. Rev. Lett. 23, 1476 (1969)].

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I. INTRODUCTION

In our previous work [1] we calculated the hyperfine structure of the hydrogen molecular ion \( \text{H}_2^+ \) within the Breit-Pauli approximation, taking account of the anomalous magnetic moment of the electron. This approximation includes contributions of order \( m \alpha^2(m/M) \) and \( m \alpha^4(m/M) \) and thus the relative uncertainty in determination of the hyperfine structure intervals is about \( 5 \times 10^{-5} \). That allowed us to confirm the Jefferts measurements [2] to the level of experimental accuracy of 1.5 kHz for transitions within the same multiplet \( F \) (\( F \) is the total spin of a state in the ion). For the spin-flip transitions (\( F=3/2 \) \( \rightarrow \) \( F=1/2 \)) a discrepancy of about 80 kHz still remains.

The main goal of the present work is to consider higher-order corrections to the hyperfine splitting of \( \text{H}_2^+ \) to reduce the discrepancy with the Jefferts experiment for spin-flip lines down to a few ppm. To that end we will calculate the QED contributions of order \( \alpha^2 \gamma_F \) and partially those of order \( \alpha^5 \gamma_F \) along with the proton finite-size corrections such as Zemach and pure recoil contributions, which are essential at this level of accuracy.

The effective Hamiltonian of the spin interaction for the \( \text{H}_2^+ \) ion is (we use the notation of [1])

\[
H_{\text{eff}} = b_F (\mathbf{I} \cdot \mathbf{s}_e) + c_F (\mathbf{L} \cdot \mathbf{s}_e) + c_F (\mathbf{L} \cdot \mathbf{I}) + \frac{d_1}{(2L-1)(2L+3)} \left( \frac{2}{3} \mathbf{L}^2 (\mathbf{I} \cdot \mathbf{s}_e) - [(\mathbf{L} \cdot \mathbf{I}) (\mathbf{L} \cdot \mathbf{s}_e) + (\mathbf{L} \cdot \mathbf{s}_e) (\mathbf{L} \cdot \mathbf{I})] \right)
+ \frac{d_2}{(2L-1)(2L+3)} \left( \frac{1}{3} \mathbf{I}^2 - \frac{1}{2} (\mathbf{L} \cdot \mathbf{I}) - (\mathbf{L} \cdot \mathbf{I})^2 \right).
\]

Here \( \mathbf{I} \) is the total nuclear spin and \( \mathbf{L} \) is the total orbital momentum. The assumed coupling scheme of angular momenta is \( \mathbf{F} = \mathbf{I} + \mathbf{s}_e, \mathbf{J} = \mathbf{L} + \mathbf{F} \).

The major coupling is the spin-spin electron-proton interaction [the first term in (1)], which determines the principal splitting between \( F=1/2 \) and \( 3/2 \) states. So the main contribution to the theoretical uncertainty in the spin-flip transition frequencies is uncertainty in the spin-spin interaction coefficient \( b_F \), and our aim is to calculate an improved value for \( b_F \).

Here it is very useful to make a comparison with the hyperfine splitting (hfs) studies of the hydrogen atom ground state. Indeed, the analytical form of many contributions to the hyperfine splitting of \( \text{H}_2^+ \) can be obtained from these results. Moreover, we will use the known results on the hydrogen atom as a guide and a check for our analytical derivations.

The hyperfine splitting for the ground state of a hydrogen-like atom may be obtained with high accuracy already from nonrelativistic quantum mechanics (see, for example, [3]),

\[
E_F = \frac{16}{3} \alpha^2 c R_e \mu_p \frac{m_e}{M_p} \left( 1 + \frac{m_e}{M_p} \right)^3;
\]

here \( \mu_p \) is the magnetic moment of a proton in nuclear magnets, and \( m_e \) and \( M_p \) are the electron and proton masses, respectively. Quantum electrodynamics corrections without recoil terms have been known for some time [4,5] and may be expressed as...
\[ \Delta E_{\text{hfs,QED}} = E_F \left[ 1 + a_e + \frac{3}{2} (Z \alpha)^2 + \left( \ln 2 - \frac{5}{2} \right) \alpha(Z \alpha) \right. \]
\[ \left. - \frac{8}{3 \pi} (Z \alpha)^2 \ln^2(Z \alpha) + \cdots \right]. \]

where \( a_e \) is the electron anomalous magnetic moment. We keep \( Z \), the nuclear charge number, in all expressions in order to make clear the origins of different corrections.

Beyond pure QED corrections, there are also proton structure effects (see [4,6,7] for a detailed discussion). The leading one is the Zemach correction [8] \([\alpha(Z \alpha)(m/M)E_F] \), which, along with the radiative corrections to the nuclear structure contribution [9], reads

\[ \Delta E_Z = -2 \frac{m_e M_p}{M_p + m_e} (Z \alpha) R_Z (1 + \delta_{Z}^{\text{ad}}) E_F. \] (4)

Here \( R_Z \) is the Zemach radius, a mean radius associated with the proton’s charge-current distribution,

\[ R_Z = \frac{1}{\pi} \int \frac{d^3 q}{q^4} \left( 1 - \frac{G_E(-q^2)G_M(-q^2)}{\mu_p} \right), \]

where \( G_E \) and \( G_M \) are the electric and magnetic form factors of the proton. We take \( R_Z = 1.045(16) \text{ fm} \) [6]. Radiative corrections \( \delta_{Z}^{\text{ad}} \) to the Zemach contribution were obtained in [9], and \( \delta_{Z}^{\text{ad}} = 0.0153 \). The parameter \( \Lambda \) determines the energy scale that corresponds to the mean radius of the proton, and \( \Lambda \approx 0.8M_p \) [9]. Next are the pure recoil proton structure corrections of orders \([Z \alpha]^k (m/M)E_F \) \( (k=1,2) \) [10]

\[ \Delta E_k \approx (5.84 \pm 0.01) \times 10^{-6} E_F. \] (5)

The last remaining effect of order \((Z \alpha)(m/M)E_F \) that has to be included is the proton polarizability [11]

\[ \Delta \rho_{\text{pol}} \approx (1.4 \pm 0.6) \times 10^{-6} E_F. \] (6)

A summary of various contributions to the hfs of the hydrogen ground state is given in Table I. Up to now, in our previous studies for the \( H_2^+ \) ion [1], only the contributions from the first two lines have been taken into consideration. In the present work we intend to extend our research to higher-order QED corrections [up to the \( E_F \alpha(Z \alpha)^2 \ln^2(Z \alpha) \) term] as well as the proton structure effects.

The major part of the contributions mentioned above in Eqs. (4)–(6) may be considered as contact-type interactions, which depend on the value of the squared density of the nonrelativistic wave function at the electron-proton coalescence point. Thus they do not require new extensive calculations; the mean values for the \( \delta \) function operators can be taken from [12]. The main task is calculation of the relativistic correction term of order \( E_F (Z \alpha)^2 \), which may be performed using the nonrecoil limit of the two-center problem. The obtained effective adiabatic potentials are subsequently averaged over the radial wave function as was done for the

\[ m^6 \text{-order relativistic correction to rovibrational energies in} \ [13,14]. \]

The paper is organized as follows. In Secs. II A and II B we use nonrelativistic QED (NRQED) to derive all the spin-dependent interactions of order \( \alpha^k(m/M) \) and the corresponding potentials in the coordinate space. The radiative corrections of orders \( \alpha(Z \alpha)E_F \) and \( \alpha(Z \alpha)^2 \ln^2(Z \alpha)E_F \), as well as proton structure effects, which may be expressed as contact-type interactions in NRQED, are given in Sec. II C. The perturbation formalism used to obtain the energy corrections is described in Sec. II D. In the next two sections, we describe the calculation of the relativistic corrections of order \( (Z \alpha)^2 E_F \). First, for the hfs of the hydrogen ground state (Sec. III), we rederive the well-known Breit correction [15], providing a useful check of our approach. Then in Sec. IV the \( H_2^+ \) ion case is considered. Finally, numerical results are given and discussed in Sec. V.

### II. NRQED Interactions

In this section we use NRQED [17] to describe the interactions which are of relevance to our problem. A nice and illuminative introduction to the NRQED approach may be found in [5]. The units \( c=\hbar=1 \) and \( e^\prime=\alpha \) are used in this section; the elementary charge \( e \) is positive. We consider low-energy scattering, assuming that the momentum of a particle is of order \( Z \alpha \), and we expand the scattering amplitude in terms of \( \alpha \) and \( p^2 \).

#### A. Tree-level interactions of order \( m \alpha^0(m/M) \)

The momentum four-vectors for the scattering of an electron (or proton) by the field of a static external source obey

\[ p_0' = p_0 = E, \quad q = p' - p, \quad q_0 = 0, \quad q^2 = -q'^2. \]

where \( p \) and \( p' \) are the four-momenta of incident and scattered particles, respectively. On-shell Dirac spinors can be
presented via the Schrödinger-Pauli spinors as follows:

\[
\psi(p) = \sqrt{\frac{E_p + m}{2E_p}} \left( \begin{array}{c} X \\ \alpha^p_p \end{array} \right), \quad \psi^*(p)\psi(p) = (X^*X) = 1,
\]

\[
E_p = \sqrt{m^2 + p^2} = m\left(1 + \frac{p^2}{2m^2} - \frac{p^4}{8m^4} + \frac{p^6}{16m^6} + \cdots \right).
\]

Here \(\alpha^p_p\) are the two-component Pauli matrices and \(X\) are the two-component Schrödinger-Pauli wave functions. We assume that Dirac spinors are normalized as \((\psi^*\psi) = 1\). That corresponds to the nonrelativistic normalization: the probability of discovering a particle in a unit of volume is equal to unity. With this normalization Dirac spinors are expanded in the low-energy limit as follows:

\[
\psi(p) \approx \left(1 - \frac{p^2}{8m^2} + \frac{11p^4}{128m^4}\right)X(p),
\]

The nonrelativistic scattering amplitude at tree level for a scalar static field is determined by the following expansion:

\[
\mathcal{A}_Z(p, p') = X^*(p')\mathcal{A}_Z(p)\left(1 - \frac{q^2}{8m^2} + \frac{3q^2(p^2 + p'^2)}{4m^4} + \frac{5(p^2 - p'^2)^2}{128m^6} - \frac{3\alpha^p_p(q \times p)(p^2 + p'^2)}{32m^6} + \cdots \right)X(p),
\]

and for a static vector field one obtains

\[
\mathcal{A}_\gamma(p, p') = X^*(p')\mathcal{A}_Z(p)\left(\frac{p' + p}{2m} - i\frac{\alpha^p_p \times q}{2m} + \frac{p'(3p^2 - p'^2) + p(3p^2 + p'^2)}{16m^3} + \cdots \right)X(p),
\]

where \(Z\) is the charge of a particle \(e, p, \ldots\). For an electron \(Z = -1\).

In what follows an index \(a\) or \(b = 1, 2\) denotes nucleus 1 or 2 in the \(\text{H}_2^+\) ion, and indices \(i, j = 1, 3\) are Cartesian coordinates.

The higher-order vertices of tree level diagrams produce new interactions \((q = p' - p)\): (a) via Coulomb photon exchange,

\[
\mathcal{V}_1 = e^2\left(\frac{3\alpha^p_p(q \times p_z)(p_e^2 + p_z^2)}{32m_e^2}\right)\frac{1}{q^2}(Z_a),
\]

(b) via transverse photon exchange,

\[
\mathcal{V}_2 = e^2\left(\frac{\alpha^p_p(q \times p_z)(3p_e^2 + p_z^2) - \alpha^p_p(q \times p_z)(3p_e^2 + p_z^2)}{16m_e^3}\right)\frac{1}{q^2}\left(\frac{q_j - \frac{q_j q^j}{q^2}}{q^2}\right)\left(-Z_a\frac{P_a + P_a}{2M_a}\right)^j;
\]

\[
\mathcal{V}_3 = e^2\left(\frac{p' q_z(3p_e^2 + p_z^2) + p_z(3p_e^2 + p_z^2)}{16m_e^3}\right)\frac{1}{q^2}\left(\frac{q_j - \frac{q_j q^j}{q^2}}{q^2}\right)\left(-iZ_a\frac{\alpha^p_p(q \times (-q))}{2M_a}\right)^j;
\]

\[
\mathcal{V}_4 = e^2\left(\frac{\alpha^p_p(q \times p_z)(3p_e^2 + p_z^2) - \alpha^p_p(q \times p_z)(3p_e^2 + p_z^2)}{16m_e^3}\right)\frac{1}{q^2}\left(\frac{q_j - \frac{q_j q^j}{q^2}}{q^2}\right)\left(-iZ_a\frac{\alpha^p_p(q \times (-q))}{2M_a}\right)^j.
\]

In parentheses here are the vertex functions of the effective NRQED interaction taken from Eqs. (7) and (8). The approximate transverse photon propagator (see [16], Sec. 83) is placed in the square brackets.

The obtained potentials can be simplified as follows:

\[
\mathcal{V}_2 = e^2\left(\frac{2\alpha^p_p(q \times p_z)(p_e^2 + p_z^2) + [\alpha^p_p(q \times (p' + p_z))(p_e^2 - p_z^2)]}{16m_e^3}\right)\frac{1}{q^2}\left(\frac{q_j - \frac{q_j q^j}{q^2}}{q^2}\right)\left(Z_a\frac{P_a}{M_a}\right)^j.
\]
The last term in the first large parentheses produces a symmetric operator with the property \((\varphi, A\varphi) = 0\) for an arbitrary \(\varphi\). That means that this operator is identical to the zero operator, and \(V_2\) may be rewritten

\[
V_2 = -e^2 \left( \frac{[\sigma^e \times q][p^e_1 + p^e_2]}{8m^3_e} \right) \frac{1}{q^2} \left( \frac{Z_a}{2M_a} \right)^i. \tag{11a}
\]

In a similar way the other operators may be simplified:

\[
V_3 = e^2 \left( \frac{p_e[p_e^2 + p^e_2]}{4m^3_e} \right) \frac{1}{q^2} \left( iZ_a \frac{\sigma^e \times q}{2M_a} \right)^i, \tag{11b}
\]

\[
V_4 = -e^2 \left( \frac{[\sigma^e \times q][p^e_1 + p^e_2]}{8m^3_e} \right) \frac{1}{q^2} \left( \frac{Z_a}{2M_a} \right)^i. \tag{11c}
\]

Transforming the potentials \(V_a\) to the coordinate space \((r_e, R_e, R_a, R_b)\), where \(R_e\) and \(R_a, R_b\) are the coordinates of electron and nuclei with respect to the center of mass, one gets, using the notation \((A, B) = AB + BA,

\[
V_1 = -\frac{3Z_a}{16m^3_e} \left( p_e^2 \frac{1}{r_a} [r_a \times p_e] \right) \mathbf{s}_e,
\]

\[
V_2 = \frac{Z_a}{4m^3_e M_a} \left( p_e^2 \frac{1}{r_a} [r_a \times \mathbf{P}_a] \right) \mathbf{s}_e,
\]

\[
V_3 = -\frac{1}{2m^3_e} \left( p_e^2 \frac{1}{r_a} [r_a \times \mathbf{P}_a] \right) \mathbf{\mu}_a,
\]

\[
V_4 = -\frac{1}{4m^3_e M_b} \left[ p_e^2 \left( \frac{8\pi}{3} s_e \mathbf{\mu}_a \delta(r_a) 
- \frac{r_a^2 s_e \mathbf{\mu}_a - 3(s_e \mathbf{r}_a)(\mathbf{\mu}_a \mathbf{r}_a)}{r_a^3} \right) \right]. \tag{12}
\]

Here \(\mathbf{\mu}_a\) is the magnetic moment operator for nucleus \(a\). Only \(V_4\) involves both electron and nuclear spins and contributes to \(b_F\).

### B. Seagull-type interactions

In Fig. 1, three NRQED seagull diagrams are presented. They may be obtained from the corresponding QED Z diagrams by expanding the scattering amplitude in terms of \(\mathbf{p}^2\). The double Coulomb photon exchange diagram has a leading order \(\alpha^6\); however, it does not involve interactions dependent on spin. The third diagram is the double transverse photon exchange and has a recoil order \((m/M)^2\), and is also out of interest for present consideration.

The potentials that stem from the seagull vertex with one Coulomb and one transverse photon line can be expressed as

\[
V_5 = e^2 \sigma^e \frac{1}{4m^3_e} \left[ \left( \frac{1}{q_6} + \frac{1}{q_4} \right) \mathbf{q}_6 \mathbf{q}_4 \right] \left( \mathbf{P}_a \cdot \mathbf{P}_b \right) \mathbf{s}_e,
\]

\[
V_6 = e^2 \sigma^e \frac{1}{2m^3_e} \left[ \left( \frac{1}{q_6} + \frac{1}{q_2} \right) \mathbf{q}_6 \mathbf{q}_2 \right] \left( \mathbf{P}_a \cdot \mathbf{P}_b \right) \mathbf{s}_e.
\]

The sources \(Z_a\) and \(Z_b\) may belong to the same or two different particles.

In the coordinate space one has, for \(a \neq b\),

\[
V_5 = -\alpha^2 Z_a Z_b \left[ \mathbf{r}_a \times \mathbf{P}_b \right] \left( \mathbf{r}_a \times \mathbf{r}_b \right) \left( \mathbf{r}_a \times \mathbf{r}_b \right) \mathbf{s}_e, \tag{14a}
\]

\[
V_6 = \alpha^2 Z_a Z_b \frac{\mathbf{r}_a \times \mathbf{s}_e \mathbf{r}_b \times \mathbf{s}_e}{2m^3_e M_b r_{a,b}^3} \mathbf{s}_e. \tag{14b}
\]

Using \([a \times b][c \times d] = (ac)(bd) - (cb)(ad)\), one may further simplify \(V_6\).

When the sources coincide \((a=b)\), the interactions are modified as follows:

\[
V_7 = -\alpha^2 Z_a^2 \left( \mathbf{r}_a \times \mathbf{P}_a \right) \mathbf{s}_e. \tag{14c}
\]
among those terms, only $V_6$ and $V_8$ contribute to $b_F$.

C. Contact-type NRQED interactions

Here we introduce corrections already mentioned in the Introduction, which enter into the NRQED Lagrangian as contact-type interactions, since they reproduce effects of the relativistic scale. (1) First, we have radiative interactions of order $\alpha(Z\alpha)E_F$:

$$V^{(6)}_r = \alpha^3 \frac{8\pi Z \mu_e}{3m_e M_p} \ln \left( \frac{2}{\ln 2} - \frac{13}{4} + \frac{3}{4} \right) (s_e \cdot I_a) \delta(r_a),$$  

(15)

and of order $\alpha(Z\alpha)^2\ln^2(Z\alpha)E_F$

$$V^{(7)}_r = \alpha^4 \ln^2(Z\alpha) \frac{8\pi Z^2 \mu_e}{3m_e M_p} \left( -\frac{8}{3\pi} \right) (s_e \cdot I_a) \delta(r_a).$$  

(16)

(2) Next is the Zemach term $[(Z\alpha)(m/\Lambda)E_F]$:

$$V_Z = -2\alpha R_Z (1 + \delta_Z^{ad}) \frac{8\pi Z \mu_e}{3m_e M_p} (s_e \cdot I_a) \delta(r_a),$$

(17)

where $R_Z \approx 1.045(16)$ [6]. (3) There is also a recoil correction of order $Z\alpha(m/M)E_F$ [6,10]:

$$V_{\text{recoil}} = \alpha [5.48(6) \times 10^{-6}] \frac{8\pi Z \mu_e}{3m_e M_p} (s_e \cdot I_a) \delta(r_a).$$

(18)

The correction of order $Z\alpha^2(m/M)E_F$ from Eq. (5) has been omitted since it has to be considered in the context of higher-order corrections, which are out of the scope of the present consideration. (4) Finally, we have the proton polarizability [11]:

$$V_{\text{pol}} = \alpha [1.4(6) \times 10^{-6}] \frac{8\pi Z \mu_e}{3m_e M_p} (s_e \cdot I_a) \delta(r_a).$$

(19)

D. Perturbation formalism

To calculate the bound state problem we use the nonrelativistic Rayleigh-Schrödinger perturbation theory, where the starting point, the zero-order approximation, is the nonrelativistic Schrödinger equation

$$H_0 \Psi_0 = E_0 \Psi_0,$$

(20)

and the perturbation is the effective Hamiltonian $H_{\text{eff}}$ derived from the NRQED Lagrangian and

$$\Delta E = \langle H_{\text{eff}} \rangle + \langle H_{\text{eff}} Q(E_0 - H_0)^{-1} QH_{\text{eff}} \rangle + \langle H_{\text{eff}} \delta E \frac{\partial H_{\text{eff}}}{\partial E} \rangle + \cdots,$$

(21)

where $Q$ is a projector operator on the subspace orthogonal to the zero-order wave function. $H_{\text{eff}}$ has contributions of different orders in $\alpha$:

$$H_{\text{eff}} = H^{(4)} + H^{(5)} + H^{(6)} + \cdots.$$

Then for our case the complete contribution at order $\alpha^6(m/M)$ to the hyperfine structure of the hydrogen atom and ion can be expressed by

$$\Delta E_{\text{hfs}} = \langle H^{(6)} \rangle + \langle H^{(4)} Q(E_0 - H_0)^{-1} QH^{(4)} \rangle,$$

(22)

where $H^{(4)}$ and $H^{(6)}$ are parts of the Breit-Pauli Hamiltonian taken so that the second term in (22) contributes to that particular order. Since the effective Hamiltonian $H^{(6)}$ for the hfs does not depend on $E$ explicitly, the last term of Eq. (21) vanishes. In the following, the second-order contribution and the first-order contribution $\langle H^{(6)} \rangle$ will be denoted $\Delta E_A$ and $\Delta E_B$, respectively.

III. HFS IN THE HYDROGEN GROUND STATE

In the remaining part of this work we will be using the atomic units ($\hbar = 1$ and $\epsilon = \alpha^{-2}$). First, we consider the case of the hfs of the ground state of a hydrogen atom. Our derivation is somewhat similar to the one done by Nio and Kinoshita in [18]. The divergent part is, however, treated in a different way by explicitly separating out and canceling the divergences. We start from the nonrelativistic Schrödinger equation

$$(H_0 - E_0) \Psi_0 = \left( \frac{p^2}{2m_e} + V \right) \Psi_0,$$

(23)

where

$$V = -\frac{Z}{r}.$$  

(24)

A. Separation of divergences in the $ma^6(m/M)$-order effective Hamiltonian

The effective Hamiltonian of order $ma^6(m/M)$ is obtained from Eqs. (12) and (14a)–(14d), interactions $V_4$ and $V_8$, expressed in atomic units. It has the form
\[ H^{(6)} = \alpha^4 \frac{2}{3m_e} \left( -\frac{1}{4m_e^2} p_e^2 + \frac{Z}{2m_e r} \right) s_e \mu_p, \]

where \( \mu_p = (\mu_p, M_p) \mathbf{l}_p \), then using the relation

\[ \langle Z^2(r^2) \rangle = -\langle \mathbf{p}_V \mathbf{V} \rangle^2 \]

\[ = -\left( \frac{p_e^2 V^2}{2} + \frac{V^2 p_e^2}{2} - 4\pi Z V \delta(r) \right) \]

obtained by integration by parts, and the equation \( p_e^2 \Psi_0 = 2(E_0 - V) \Psi_0 \), one gets

\[ \Delta E_B^{(6)} = \langle H^{(6)} \rangle \]

\[ = \alpha^4 \frac{2}{3Z m_e M_p} \left( \frac{2\pi Z V \delta(r)}{m_e} + \langle V^3 \rangle - E_0 \langle V^2 \rangle \right) \]

\[ + \left( \frac{\langle p_e^2 \mathbf{V} \rangle}{2m_e} - 4\pi Z E_0 \delta(r) \right) (s_e \cdot \mathbf{l}_p). \]

In Eq. (27), the divergent contributions are now explicitly collected in the first two terms.

B. Separation of divergences in the second-order contribution

The second-order contribution of order \( m\alpha^6(m/M) \) to the spin-spin interaction can be easily identified from various combinations of terms of the Breit-Pauli Hamiltonian and may be written

\[ \Delta E_A^{(6)} = 2\alpha^4 \left( \frac{\mathbf{p}_e^2}{8m_e} + \frac{Z}{8m_e^2} \right) \Psi_0 \]

\[ - H_0^{-1} Q \left( \frac{8\pi}{3m_e} s_e \mu_p \delta(r) \right). \]

This contribution is divergent due to the presence of the \( \delta \)-function operators on both sides of the second-order iteration.

Let us consider the two operators

\[ H_B^{(1)} = 4\pi \delta(r), \quad H_B^{(2)} = -\frac{p_e^2}{8m_e} + \frac{Z}{8m_e^2} 4\pi \delta(r), \]

and introduce the wave function \( \Psi_B^{(1)} \), solution of the equation

\[ (E_0 - H_0) \Psi_B^{(1)} = Q(4\pi \delta(r)) \Psi_0 = QH_B^{(1)} \Psi_0. \]

\( \Psi_B^{(1)} \) behaves as \( 1/r \) at \( r \to 0 \). We introduce a less singular function \( \tilde{\Psi}_B^{(1)} \) defined by

\[ \tilde{\Psi}_B^{(1)} = -\frac{2m_e \Psi_0}{r} + \Psi_B^{(1)} = U_1 \Psi_0 + \tilde{\Psi}_B^{(1)}, \]

where \( U_1 = -2m_e r = (2m_e / Z) V \). The function \( \tilde{\Psi}_B^{(1)} \) behaves as in \( r \to 0 \). It satisfies the equation

\[ (E_0 - H_0) \tilde{\Psi}_B^{(1)} = (H_B^{(1)} - \langle H_B^{(1)} \rangle) \Psi_0, \]

where

\[ H_B^{(1)} = - (E_0 - H_0) U_1 - U_1 (E_0 - H_0) + H_B^{(1)}. \]

Similar computations can be applied to the scalar part of the Breit-Pauli Hamiltonian \( H_B^{(2)} \):

\[ (E_0 - H_0) \Psi_B^{(2)} = Q \left( -\frac{p_e^2}{8m_e^2} + \frac{Z}{2m_e} \delta(r) \right) \Psi_0 \]

\[ \tilde{\Psi}_B^{(2)} = \frac{Z \Psi_0(r)}{4m_e} + \Psi_B^{(2)} = U_2 \Psi_0 + \tilde{\Psi}_B^{(2)}, \quad U_2 = \frac{Z}{4m_e} = - \frac{1}{4m_e} \Psi_0, \]

and

\[ H_B^{(2)} = - (E_0 - H_0) U_2 - U_2 (E_0 - H_0) + H_B^{(2)}. \]

Using systematically that

\[ \langle \Psi_0 | H_B^{(2)} Q(E_0 - H_0)^{-1} QH_B^{(1)} | \Psi_0 \rangle \]

\[ = \langle \Psi_0 | H_B^{(2)} Q | \tilde{\Psi}_B^{(1)} \rangle \quad \text{or} \quad \langle \Psi_0 | H_B^{(2)} Q | H_B^{(1)} | \Psi_0 \rangle, \]

one may separate the divergent singularities in the following way:
The first two terms of the last expression may be rewritten as the average of a new effective Hamiltonian contributing to the $ma^6(m/M)$ order:

$$H^{(6)} = \alpha^4 \frac{2\mu_p}{3m_e M_p} \left[ (H^{(2)}_B U_1 + U_1 H^{(2)}_B) + (H^{(1)}_B U_2 + U_2 H^{(1)}_B) \right. \\
-2(H^{(2)}_B U_1 - 2H^{(1)}_B U_2) \\
- U_1(E_0 - H_0) U_2 - U_2(E_0 - H_0) U_1 \right] (s_e \cdot I_p). \quad (36)$$

Using regularization and integration by parts in a similar way as in Appendix B of [13], its expectation value may be finally written in the form

$$\langle H^{(6)} \rangle = \alpha^4 \frac{2\mu_p}{3m_e M_p} \left[ -2 \frac{\pi Z(V_0 \delta(r))}{m_e} - \langle V \rangle^2 \right. \\
+ 3E_0(\langle V^2 \rangle - 2E_0^2(\langle V \rangle) - 4m_e \langle H^{(2)}_B \rangle \langle V \rangle + \frac{Z \langle H^{(1)}_B \rangle (\langle V \rangle)}{2m_e} \right]$$

$$\times (s_e \cdot I_p). \quad (37)$$

All the divergent terms of Eq. (35) are collected as the first two terms of Eq. (37). They clearly cancel out those of Eq. (27).

The remaining part of the second-order iteration contribution [the last term in Eq. (35)] is finite,

$$\Delta E^{(6)}_A = \alpha^4 \frac{4\mu_p}{3m_e M_p} \langle \Psi(0)| H^{(2)}_B Q(E_0 - H_0)^{-1} QH^{(1)}_B |\Psi(0)\rangle (s_e \cdot I_p), \quad (38)$$

where $H^{(1)}_B$ and $H^{(2)}_B$ are defined above in Eqs. (32) and (34), respectively. Summing up $\langle H^{(6)} \rangle$ and $\langle H^{(6)} \rangle$ from Eqs. (27) and (37) one gets a finite expression as well:

$$\Delta E^{(6)}_B = \alpha^4 \frac{2\mu_p}{3m_e M_p} \left[ \langle pV^2 p \rangle \frac{1}{m_e} + 2E_0^2 \langle V \rangle - 2E_0 \langle V \rangle \right. \\
- \frac{Z E_0}{m_e} \frac{4 \pi (\delta(r))}{2m_e} - 4m_e \langle H^{(2)}_B \rangle \langle V \rangle + \frac{Z \langle H^{(1)}_B \rangle (\langle V \rangle)}{2m_e} \right] \times (s_e \cdot I_p). \quad (39)$$

C. Calculation of expectation values and final result

We now check that Eq. (39) leads to the usual result in the case of a $1s$ hydrogen atom. Here, $\Psi(0)=2Z^2 e^{-Zr}$ is the ground-state wave function. First we look for a solution of the equation

$$(E_0 - H_0)\tilde{\Psi}^{(1)} = (H^{(1)}_B - \langle H^{(1)}_B \rangle)\Psi(0),$$

$$H^{(2)}_B = -\frac{2}{r} \delta(r) - 2U_1(E_0 - H_0), \quad \langle H^{(2)}_B \rangle = 4Z^2,$$

and get

$$\tilde{\Psi}^{(1)} = 4Z(\ln r - 1 + Zr)\Psi(0).$$

The next step is to calculate the expectation value of

$$\langle \Psi(0)|H^{(2)}_B Q|\tilde{\Psi}^{(1)}\rangle = \langle \Psi(0)|H^{(2)}_B - \langle H^{(2)}_B \rangle|\Psi(0)\rangle,$$

and to get the finite part of the second-order contribution

$$\Delta E^{(6)}_A = \frac{4Zm_e\alpha^4}{3M_p} \langle \Psi(0)|H^{(2)}_B Q(E_0 - H_0)^{-1} QH^{(1)}_B |\Psi(0)\rangle \times (s_e \cdot I_p) = \frac{3(Z\alpha)^2}{2} E_F (s_e \cdot I_p).$$

The expectation values of the operators involved in $\Delta E^{(6)}_A$ are $\langle pV^2 p \rangle = Z^2 \langle V \rangle$, $\langle V \rangle = 2Z^2$, and $\langle V \rangle = -Z$. This contribution is immediately obtained to be 0; indeed,

$$\Delta E^{(6)}_B = \frac{2Zm_e\alpha^4}{3M_p} \left[ 2Z^2 - 2Z^2 + \frac{Z^2}{2} + 2Z^2 - \frac{Z^2}{2} - 2Z^2 \right] \times (s_e \cdot I_p) = 0.$$

Thus, the total contribution is

$$\Delta E^{(6)} = \Delta E^{(6)}_A + \Delta E^{(6)}_B = \frac{3}{2} (Z\alpha)^2 E_F (s_e \cdot I_p),$$

which exactly matches the well-known Breit relativistic correction [15].

IV. HYDROGEN MOLECULAR ION $H_2^+$

Now we are ready to study the hydrogen molecular ion. As in the previous section we start from the nonrelativistic equation with the Hamiltonian

$$H_0 = \frac{p^2}{2m_e} + V, \quad V = -\frac{Z_1}{r_1} - \frac{Z_2}{r_2}. \quad (40)$$

We will assume here that $Z_1 = Z_2 = Z$ and $\mu_1 = \mu_p/\mu_p I_1$, $\mu_2 = \mu_p/\mu_p I_2$, where $I_1$ and $I_2$ are the two proton spin operators.

The second-order correction of the spin-spin interaction of order $ma^6(m/M)$ is expressed by

$$\Delta E_A = \frac{2\alpha^4}{3m_e} \left[ -\frac{p^2}{8m_e} + \frac{Z}{8m_e} \frac{4 \pi (\delta(r_1) + \delta(r_2))}{3m_e} \right] Q(E_0 - H_0)^{-1} Q \left[ \mu_1 \delta(r_1) + \mu_2 \delta(r_2) \right]. \quad (41)$$

The effective Hamiltonian of order $ma^6(m/M)$ is obtained from Eqs. (12) and (14a)–(14d) of Sec. II. Now we have three interactions $V_{1s}$, $V_{e}$, and $V_{\delta}$, because we have as well the seagull interaction $V_{\delta}$ with two different nuclei,

$$V_{\delta} = \frac{1}{4m_e} \left[ \frac{3}{8} \left( \frac{8 \pi}{3} s \mu \delta(r) \right) \right. \right.$$
\[
V_b = \alpha^4 \frac{Z}{6m_e^2} \left( \frac{2(r_1 \cdot r_2)(s_1 \cdot \mu_2)}{r_1^3 r_2^3} + \frac{(r_1 \cdot r_2)(s_1 \cdot \mu_1) - 3(r_1 \cdot s_2)(r_2 \cdot \mu_2) - 3(r_2 \cdot s_1)(r_1 \cdot \mu_1)}{r_1^3 r_2^3} \right),
\]

(42b)

\[
V_{ba} = \alpha^4 \frac{Z}{6m_e^2} \left( \frac{2(s_1 \cdot \mu_2)}{r_1^3} + \frac{r_1^3(s_1 \cdot \mu_2) - 3(r_1 \cdot s_1)(r_1 \cdot \mu_2)}{r_1^5} \right),
\]

(42c)

where \( \mu := \mu_1 + \mu_2 \). It is convenient to separate the effective Hamiltonian into two terms, scalar and tensor,

\[
H_s^{(6)} = \alpha^4 \frac{Z \cdot \mu}{3m_e M_p} \left[ -\frac{1}{4m_e^2} p^2 + 4 \pi [\delta(r_1) + \delta(r_2)] \right]
+ \frac{Z}{2m_e^2} \left( \frac{1}{r_1^3} + \frac{1}{r_2^3} + \frac{2r_1 \cdot r_2}{r_1^3 r_2^3} \right) (s_1 \cdot \mathbf{l}),
\]

\[
H_t^{(6)} = \alpha^4 \frac{Z}{6m_e^2} \left( \frac{r_1^3(s_1 \cdot \mu_2) - 3(r_1 \cdot s_1)(r_1 \cdot \mu_1)}{r_1^5} \right)
+ \frac{r_2^3(s_1 \cdot \mu_2) - 3(r_1 \cdot s_1)(r_2 \cdot \mu_2)}{r_2^5}
+ \frac{(r_1 \cdot r_2)(s_1 \cdot \mu_2) - 3(r_1 \cdot s_1)(r_1 \cdot \mu_1)\cdot 3(r_2 \cdot s_2)(r_1 \cdot \mu_1)}{r_1^5 r_2^5}.
\]

(43)

\[H_t^{(6)} \text{ has a finite expectation value, and since it does not contribute to } b_F, \text{ its consideration will be omitted in what follows. The divergent terms are encountered only in the scalar Hamiltonian.}\]

**A. Separating divergences in the second order contribution**

The operators that appear on the left and on the right of the second order iteration are

\[H_B^{(1)} = 4 \pi [\delta(r_1) + \delta(r_2)],\]

\[H_B^{(2)} = -\frac{p^4}{8m_e^2} + \frac{Z}{8m_e^2} 4 \pi [\delta(r_1) + \delta(r_2)].\]

Now we have to separate the singular part using the method outlined in the hydrogen case. We set

\[(E_0 - H_0)\Psi_B^{(1)} = Q(4 \pi [\delta(r_1) + \delta(r_2)])\Psi_0,\]

\[\Psi_B^{(2)} = 2m_e \left( \frac{1}{r_1} - \frac{1}{r_2} \right) \Psi_0 + \tilde{\Psi}_B^{(1)} = U_1 \Psi_0 + \tilde{\Psi}_B^{(1)},\]

\[U_1 = \frac{2m_e}{Z} V,\]

\[H_B^{(1)} = -(E_0 - H_0)U_1 - U_1(E_0 - H_0) + H_B^{(1)} .\]

(44)

Similarly, one gets for \(H_B^{(2)}\)

\[(E_0 - H_0)\Psi_B^{(2)} = Q \left( -\frac{p^4}{8m_e^2} + \frac{Z}{2m_e^2} \left[ \delta(r_1) + \delta(r_2) \right] \right)\Psi_0,\]

\[\Psi_B^{(2)} = \frac{Z}{4m_e} \left( \frac{1}{r_1} - \frac{1}{r_2} \right) \Psi_0 + \tilde{\Psi}_B^{(2)} = U_2 \Psi_0 + \tilde{\Psi}_B^{(2)},\]

\[U_2 = -\frac{1}{4m_e} V,\]

\[H_B^{(2)} = -(E_0 - H_0)U_2 - U_2(E_0 - H_0) + H_B^{(2)}.\]

(45)

Applying these transformations to the second-order iteration term, we arrive at

\[
\Delta E_A = \alpha^4 \frac{2}{3m_e M_p} [\langle \Psi_0 | (H_B^{(2)} - H_B^{(1)})U_1 | \Psi_0 \rangle + \langle \Psi_0 | U_2(H_B^{(1)}) - (H_B^{(1)}) | \Psi_0 \rangle]
- \langle H_B^{(1)} | \Psi_0 \rangle + \langle \Psi_0 | e_B^{(2)}(E_0 - H_0)^{-1} Q H_B^{(1)} | \Psi_0 \rangle \times (s_1 \cdot \mathbf{l}).
\]

(46)

Again we pick out the first two terms, which can be recast in the form of an effective Hamiltonian:

\[
H_A^{(6)} = \alpha^4 \frac{1}{3Z m_e M_p} \left[ -\frac{p^4 V + V p^4}{4m_e^2} - \frac{(V p^2 V)}{2m_e} - V^3 + E_0 V^2 \right]
- 4m_e \langle H_B^{(2)} | V + \frac{Z (H_B^{(1)})}{2m_e} \rangle (s_1 \cdot \mathbf{l}).
\]

(47)

Its expectation value can be rewritten as follows:

![Graph](image.png)

**FIG. 2.** Adiabatic effective potential for the relativistic correction of order \(m a^4 (m/M)\) to the spin-spin interaction coefficient \(b_F\).

Energy scale for \(\Delta b_F\) is \((\alpha^2 m_p/M) \times (1 \text{ a.u.).}\)
B. Removing divergences and final expressions

The remaining part of the second-order iteration contribution [the last term in Eq. (46)] is now finite:

\[
\Delta E^{(6)}_B = \alpha^4 \frac{1}{3m_e M_p} \left[ \langle \Psi_0 | H_{B(2)}^{(1)} Q(E_0 - H_0) Q | \Psi_0 \rangle (s_x \cdot \mathbf{I}) \right],
\]

where \( H_{B(1)}^{(1)} \) and \( H_{B(2)}^{(2)} \) are defined above. Summing up \( \langle H_S^{(6)} \rangle \) and \( \langle H_B^{(4)} \rangle \) we get a finite expression as well:

\[
\Delta E^{(6)}_B = \alpha^4 \frac{1}{3m_e M_p} \left[ \langle \Psi_0 | H_{B(2)}^{(2)} (E_0 - H_0) | \Psi_0 \rangle \right] (s_x \cdot \mathbf{I}) \quad \text{and} \quad \Delta E^{(6)}_H = \alpha^4 \frac{1}{3m_e M_p} \left[ \langle \Psi_0 | H_{H(2)}^{(2)} (E_0 - H_0) | \Psi_0 \rangle \right] (s_x \cdot \mathbf{I}).
\]

V. RESULTS AND CONCLUSION

Results of numerical calculation as a function of the bond length for the relativistic correction to the Hfs within the framework of the two-center problem are shown in Fig. 2. In our study we use the variational exponential expansion introduced in [19]. In fact, the adiabatic approximations used in [46] already been obtained in the previous work [13] and only the second-order perturbation term [Eq. (49)] with modified operators \( H_{B(1)}^{(1)} \) and \( H_{B(2)}^{(2)} \) requires some additional numerical effort. The potential of the total effective Hamiltonian \( \Delta E^{(6)}_B \) tends to zero when \( R \to 0 \), or \( R \to \infty \), as may be expected from the analysis of the hydrogen atom ground-state hfs.

The relative numerical accuracy of the potential curve plotted in Fig. 2 is estimated to be \(~10^{-5}\); however, the adiabatic approximation itself limits the final uncertainty of the relativistic contribution of \( m_e \alpha^2 (m/M) \) to the spin-spin interaction coefficient \( b_F \) to about 0.1 kHz (3–4 significant digits in \( \Delta b_F \)). The other contributions, which are described by Eqs. (15)–(19), may be obtained using the previously calculated mean values of the \( \delta \)-function operators [12]. The final results for the theoretical value of the coefficient \( b_F \) for the low rovibrational states are presented in Table II.

An experimental value for \( b_F \) can be uniquely calculated by using the mixing parameters [20] of the states \((F,J), (\frac{1}{2}, \frac{1}{2}) \leftrightarrow (\frac{3}{2}, \frac{1}{2}) \) and \((\frac{1}{2}, \frac{3}{2}) \leftrightarrow (\frac{3}{2}, \frac{3}{2}) \), to

\[
\langle h^{(6)} \rangle = \alpha^2 \frac{1}{3m_e M_p} \left[ \langle \Psi_0 | H_{B(2)}^{(2)} Q(E_0 - H_0) Q | \Psi_0 \rangle \right] (s_x \cdot \mathbf{I}),
\]

and the divergent terms, the first two terms, are now written explicitly.

\[
\frac{2\pi Z(V)\{\delta(r_1) + \delta(r_2)\}}{m_e} - \langle V^3 \rangle
\]

\[
+ \frac{1}{2m_e} (3E_0(V^2) - 2E_0^2(V) - 4m_e (H_{B(2)}^{(2)})(V))
\]

\[
+ \frac{Z(H_{B(2)}^{(2)})(V)}{2m_e} (s_x \cdot \mathbf{I}), \quad (48)
\]

TABLE II. Results of numerical calculations for low rovibrational states of the spin-spin interaction coefficient \( b_F \) (in MHz).

<table>
<thead>
<tr>
<th>( L=1 )</th>
<th>( L=3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu=0 )</td>
<td>922.9918</td>
</tr>
<tr>
<td>( \nu=1 )</td>
<td>898.8091</td>
</tr>
<tr>
<td>( \nu=2 )</td>
<td>876.4542</td>
</tr>
<tr>
<td>( \nu=3 )</td>
<td>855.8124</td>
</tr>
<tr>
<td>( \nu=4 )</td>
<td>836.7835</td>
</tr>
</tbody>
</table>

In conclusion, the consideration of \( m_e \alpha^2 (m/M) \) and \( \alpha^2 \) order corrections, as well as proton finite-size effects, has allowed us to improve significantly the agreement with

store the structure of pure \( F=1/2 \) and \( 3/2 \) multiplets and then take the difference between the statistically averaged splittings of these multiplets. In Table III a comparison with experiment is given. As may be seen, the newly obtained results improve the agreement with the experiment by about a factor of 6. The error bars for \( b_F \) from the experimental data are to be about 1 kHz as follows from the claimed accuracy of Ref. [20]. On the other hand, from the comparison with the hydrogen atom case, the theoretical uncertainty should be no more than 2–3 kHz. That indicates substantial discrepancy between theory and experiment of about 6–9 kHz.

In order to try to explain this discrepancy, we have checked several effects which may have impact on the spin-spin interaction. The leading-order retardation effects in the nonrelativistic interaction region [21] as well as the cross terms of the second-order perturbation (when the electron interacts with both protons in \( H_2^+ \)) for the proton-structure-dependent contributions are estimated either equal to zero or negligibly small. We have also analyzed the effect of the \( g-u \) symmetry breaking which is essential for high-\( v \) states; say, for \( v=19 \), it leads to a few megahertz shift in energy [22]. However, for the states below \( v=10 \) this effect is smaller than 1 kHz and, thus, the gap between theory and experiment cannot be accounted for by the \( g-u \) mixing. A possible explanation is that the higher-order corrections \( \alpha^6 (m/M) E_F \) and \( \alpha^2 \) may give a significant contribution.

The contributions to \( b_F \) from various interactions considered in the present work are given in Table IV.

In conclusion, the consideration of \( m_e \alpha^2 (m/M) \) and \( \alpha^2 \) order corrections, as well as proton finite-size effects, has allowed us to improve significantly the agreement with

TABLE III. Comparison of the spin-spin interaction coefficient \( b_F \) (in MHz) with experiment. Reference [1] uses the Breit-Pauli approximation with account of the electron anomalous magnetic moment. \( L=1 \).

<table>
<thead>
<tr>
<th>( \nu )</th>
<th>[1]</th>
<th>This work</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>836.784</td>
<td>836.720</td>
<td>836.729</td>
</tr>
<tr>
<td>5</td>
<td>819.280</td>
<td>819.219</td>
<td>819.227</td>
</tr>
<tr>
<td>6</td>
<td>803.227</td>
<td>803.167</td>
<td>803.175</td>
</tr>
<tr>
<td>7</td>
<td>788.558</td>
<td>788.501</td>
<td>788.508</td>
</tr>
<tr>
<td>8</td>
<td>775.221</td>
<td>775.166</td>
<td>775.172</td>
</tr>
</tbody>
</table>
TABLE IV. A summary of contributions to the spin-spin interaction coefficient $b_F$ (in MHz).

<table>
<thead>
<tr>
<th>Contribution</th>
<th>$v=4$</th>
<th>$v=5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_F$ [1]</td>
<td>836.7835</td>
<td>819.2801</td>
</tr>
<tr>
<td>$(Za)^2$</td>
<td>0.0510</td>
<td>0.0511</td>
</tr>
<tr>
<td>$\alpha(Za)$</td>
<td>-0.0804</td>
<td>-0.0787</td>
</tr>
<tr>
<td>$\alpha(Za)^2 \ln^2(Za)$</td>
<td>-0.0067</td>
<td>-0.0065</td>
</tr>
<tr>
<td>$\Delta E_Z$</td>
<td>-0.0335(5)</td>
<td>-0.0328(5)</td>
</tr>
<tr>
<td>$\Delta E_R$</td>
<td>0.0049(1)</td>
<td>0.0045(1)</td>
</tr>
<tr>
<td>$\Delta E_{pol}$</td>
<td>0.0012(5)</td>
<td>0.0011(5)</td>
</tr>
<tr>
<td>$b_F$ (present work)</td>
<td>836.7197(10)</td>
<td>819.2187(10)</td>
</tr>
</tbody>
</table>

experiment, to about 10 ppm. The remaining discrepancy is somewhat larger than expected from comparison with the hydrogen atom, and further theoretical work to improve the hfs intervals is needed. In any case, a new independent experiment is highly desirable.

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