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Higher-order corrections to spin-spin scalar interactions in HD$^+$ and H$_2^+$

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The largest hyperfine interaction coefficients in the hydrogen molecular ion HD$^+$, i.e., the electron-proton and electron-deuteron spin-spin scalar interactions, are calculated with estimated uncertainties slightly below 1 ppm. The $(Z\alpha)^2 E_F$ relativistic correction for which a detailed derivation is presented, QED corrections up to the order $\alpha^3 \ln^2(\alpha)$ along with an estimate of higher-order terms, and nuclear structure corrections are taken into account. Improved results are also given for the electron-proton interaction coefficient in H$_2^+$, in excellent agreement with rf spectroscopy experiments. In HD$^+$, a 4σ difference is found in the hyperfine splitting of the $(v, L) = (0, 3) \to (9, 3)$ two-photon transition that was recently measured with high precision. The origin of this discrepancy is unknown.

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I. INTRODUCTION

The interest of laser spectroscopy of the HD$^+$ molecular ion for the metrology of fundamental constants was pointed out more than 40 yr ago [1]. This potential was recently realized in two experiments in which a one-photon rotational transition [2] and a two-photon vibrational transition [3] were measured in the Lamb-Dicke regime thereby suppressing the first-order Doppler broadening. In these works, a spin-averaged transition frequency was deduced from the measured hyperfine components with respective accuracies of 13.5 and 2.9 parts per 10^{12}, and compared to theoretical predictions [4], allowing to improve the determination of the proton-electron mass ratio. On the other hand, the experimental data also enable a high-precision investigation of the hyperfine structure of HD$^+$. In the case of the rotational transition [2], six hyperfine components were measured with uncertainties of a few tens of hertz, whereas in the vibrational transition [3], two hyperfine components were measured with uncertainties below 1 kHz.

On the theoretical side, the hyperfine structure of HD$^+$ has been calculated within the Breit-Pauli approximation [5] including the anomalous magnetic moment of the electron, yielding a relative accuracy on the order of α^2. The effective spin Hamiltonian introduced in that work reads

$$\begin{aligned}H_{\rm eff} = {} & E_1(\mathbf{L}\cdot\mathbf{s}_e) + E_2(\mathbf{L}\cdot\mathbf{I}_p) + E_3(\mathbf{L}\cdot\mathbf{I}_d) + E_4(\mathbf{I}_p\cdot\mathbf{s}_e) + E_5(\mathbf{I}_d\cdot\mathbf{s}_e) + E_6\{2\mathbf{L}^2(\mathbf{I}_p\cdot\mathbf{s}_e) - 3[(\mathbf{L}\cdot\mathbf{I}_p)(\mathbf{L}\cdot\mathbf{s}_e) + (\mathbf{L}\cdot\mathbf{s}_e)(\mathbf{L}\cdot\mathbf{I}_p)]\}\\ & + E_7\{2\mathbf{L}^2(\mathbf{I}_d\cdot\mathbf{s}_e) - 3[(\mathbf{L}\cdot\mathbf{I}_d)(\mathbf{L}\cdot\mathbf{s}_e) + (\mathbf{L}\cdot\mathbf{s}_e)(\mathbf{L}\cdot\mathbf{I}_d)]\} + E_8\{2\mathbf{L}^2(\mathbf{I}_p\cdot\mathbf{I}_d) - 3[(\mathbf{L}\cdot\mathbf{I}_p)(\mathbf{L}\cdot\mathbf{I}_d) + (\mathbf{L}\cdot\mathbf{I}_p)(\mathbf{L}\cdot\mathbf{I}_d)]\}\\ & + E_9\left\{2\mathbf{L}^2\mathbf{I}_d^2 - \tfrac{3}{2}(\mathbf{L}\cdot\mathbf{I}_d) - 3(\mathbf{L}\cdot\mathbf{I}_d)^2\right\},\end{aligned} \tag{1}$$

where $\mathbf{s}_e$, $\mathbf{I}_p$, and $\mathbf{I}_d$ are the spins of the electron, proton, and deuteron, respectively, and $\mathbf{L}$ is the total orbital angular momentum. The largest coefficients are the spin-spin scalar interactions, $E_4 \sim 900$ and $E_5 \sim 140$ MHz in the ground vibrational state, followed by the spin-orbit term $E_1 \sim 30$ MHz and the tensor interaction constants E_6, E_7 in the few-megahertz range. Other coefficients range from a few kilohertz to a few tens of kilohertz. In order to improve the theory further, the first priority is to calculate higher-order corrections to the spin-spin coefficients. This has been performed in Refs. [6,7] in the case of H$_2^+$; here, we extend this paper to the HD$^+$ case [2,3,8]. In doing so, we make further improvements in the treatment of nuclear structure corrections and higher-order QED corrections and present extensive numerical results for a range of rovibrational states. This will allow a detailed comparison with recent and future experiments when the theoretical precision of next largest coefficients (E_1, E_6, E_7) is sufficiently improved. Preliminary results for the E_1 coefficient have been obtained in Ref. [9].

The paper is organized as follows. In Sec. II, we briefly review the theory of the ground-state hyperfine splitting in atomic hydrogen and deuterium. The theory of higher-order corrections to E_4 and E_5 in HD$^+$ is described in Sec. III. Two contributions that require new calculations are considered separately in the next sections: the relativistic correction on the order of $(Z\alpha)^2E_F$, and a vibrational contribution at the next order of $\alpha(Z\alpha)^2E_F$. Finally, numerical results are presented in Sec. VI and compared with available experimental data.

II. GROUND-STATE HYPERFINE STRUCTURE IN THE HYDROGEN AND DEUTERIUM ATOMS

The ground-state hyperfine splitting of a hydrogenlike atom is given in the nonrelativistic approximation by the so-called Fermi energy [10], which may be written in (SI) frequency units as

$$E_F = \frac{4}{3}\mu_0\frac{\mu_B}{h}\langle(\mathbf{s}_e\cdot\boldsymbol{\mu}_M)_{F=I+1/2} - (\mathbf{s}_e\cdot\boldsymbol{\mu}_M)_{F=I-1/2}\rangle\langle\delta(\mathbf{r})\rangle$$
$$= \frac{8}{3}Z^3\alpha^2 cR_\infty\mu_M\frac{m}{M_p}\frac{2I+1}{2I}\left(1+\frac{m}{M}\right)^3. \qquad (2)$$

Here, $\boldsymbol{\mu}_M$ is the nuclear magnetic moment, and μ_M is its value in units of the nuclear Bohr magneton: $\boldsymbol{\mu}_M = \mu_M\mu_N\mathbf{I}/I$ with $\mu_N = |e|\hbar/2M_p$. $\mathbf{I}$ is the nuclear spin, F is the total spin quantum number ($\mathbf{F} = \mathbf{I} + \mathbf{s}_e$), and Z is the nuclear charge. Finally, m, M_p, and M are, respectively, the masses of the electron, proton, and nucleus.

QED corrections without recoil terms have been known for some time [11–15] and may be expressed as

$$\Delta E_{\rm hfs}(\text{QED}) = E_F\left\{a_e + \frac{3}{2}(Z\alpha)^2 + \left(\ln 2 - \frac{5}{2}\right)\alpha(Z\alpha) + \frac{\alpha(Z\alpha)^2}{\pi}\left[-\frac{8}{3}\ln^2(Z\alpha) + \frac{8}{3}\ln(Z\alpha)\left(\ln 4 - \frac{281}{480}\right) + 16.903\,772\cdots\right]\right.$$
$$\left. + 0.77099(2)\frac{\alpha^2(Z\alpha)}{\pi} + D^{(4)}(\alpha, Z\alpha) + \cdots\right\}, \qquad (3)$$

where a_e is the electron anomalous magnetic moment. We have kept Z in all expressions in order to identify the origins of different corrections. Corrections on the order of α^4E_F have been partially evaluated [13,15]

$$D^{(4)}(\alpha, Z\alpha) = \frac{17}{8}(Z\alpha)^4 + \alpha(Z\alpha)^3\left[\left(-5\ln 2 + \frac{547}{48}\right)\ln(Z\alpha) - 2.102(3)\right]$$
$$+ \frac{\alpha^2(Z\alpha)^2}{\pi^2}\left[-\frac{4}{3}\ln^2(Z\alpha) + 1.278\,001\cdots\ln(Z\alpha) + 10(2.5)\right] - 1.358(1.0)\frac{\alpha^3(Z\alpha)}{\pi^2}. \qquad (4)$$

Note that the term $[-2.102(3)]$ on the order of $\alpha(Z\alpha)^3$ actually includes corrections of higher order in $Z\alpha$ [16–19].

In addition to QED corrections, there are recoil and nuclear structure corrections. In the hydrogen atom case (see Refs. [11,13,20,21] for a detailed discussion), these corrections are written as

$$\Delta E_S = \Delta E_Z + \Delta E_R^p + \Delta E_{\rm pol}. \qquad (5)$$

The first and largest term is the Zemach correction [22] that reads, including radiative corrections [23],

$$\Delta E_Z = -2(Z\alpha)m\left(1+\delta_Z^{\rm rad}\right)r_ZE_F \sim -40\times10^{-6}E_F, \qquad (6)$$

where $\delta_Z^{\rm rad} = 0.015$, and r_Z is the Zemach radius, a mean radius associated with a convolution of the proton's charge and magnetization distributions,

$$r_Z = \frac{1}{\pi^2}\int\frac{d^3q}{q^4}\left[1 - \frac{G_E(-q^2)G_M(-q^2)}{\mu_p}\right]. \qquad (7)$$

G_E and G_M are the proton's electric and magnetic form factors. The second term of Eq. (5) is the recoil correction where contributions at orders $(Z\alpha)(m/M)E_F$ [21,24–26], $(Z\alpha)^2(m/M)E_F$ [26], and the $\alpha(Z\alpha)(m/M)E_F$ radiative-recoil correction [23] add up to around $5.8\times10^{-6}E_F$ [21,27]. Finally, the last term is the proton polarizability correction, evaluations of which yielded the values of $1.4(6)\times10^{-6}E_F$ [27] and $1.88(64)\times10^{-6}E_F$ [21].

The deuterium atom case is different due to the deuteron being a much more weakly bound system than the proton. Nuclear structure corrections are dominated in this case by the deuteron polarizability contribution which amounts to about $240\times10^{-6}E_F$ [28], whereas the Zemach term contributes at a level of $\sim -100\times10^{-6}E_F$ [29].

In order to get accurate predictions of the HD$^+$ Fermi interaction terms, we will make use of the fact that the total nuclear corrections can be determined phenomenologically with very good accuracy by subtracting the results of the pure QED calculation from the experimental value,

$$\Delta E_{\rm hfs}(\text{nucl}) = E_{\rm hfs}(\text{exp}) - E_{\rm hfs}(\text{QED}), \qquad (8)$$

with $E_{\rm hfs}(\text{QED}) = E_F + \Delta E_{\rm hfs}(\text{QED})$. Being due to short-range interactions, the nuclear correction is mainly determined by the squared value of the electronic wave function at the nucleus $[\psi(0)^2]$ and only very weakly depends on its value at finite distances. This dependence may be neglected without serious loss of accuracy, which allows us to directly plug the nuclear correction as determined phenomenologically from the experimental atomic hyperfine splitting in the theory of hydrogen molecular ions as detailed in the next section.

A summary of QED contributions and the nuclear correction obtained from Eq. (8) are shown in Table I for both the H and the D atoms. For completeness, one should mention additional small corrections not included in $E_{\rm hfs}(\text{QED})$ from muonic and hadronic vacuum polarizations [23] and weak interaction [30]. $E_{\rm hfs}(\text{nucl})$, therefore, corresponds to a sum of nuclear corrections and of these contributions.

TABLE I. Contributions (in kilohertz) to the ground-state hyperfine splitting in the hydrogen and deuterium atoms. The first row is the Fermi energy [Eq. (2)], and rows 2–5 are the QED corrections as written in the first line of Eq. (3). ΔE_{ho} corresponds to the terms appearing in the second line of Eq. (3); uncertainties take into account the theoretical uncertainties indicated in Eq. (4) as well as uncertainties of the nuclear magnetic moment values. The experimental values are, respectively, taken from an adjustment performed in Ref. [31] for the hydrogen atom and from Ref. [32] for deuterium.

	H	D
E_F	1 418 840.093	326 967.681
$a_e E_F$	1 645.361	379.169
$\Delta E_{(Z\alpha)^2}$	113.333	26.117
$\Delta E_{\alpha(Z\alpha)}$	−136.517	−31.460
$\Delta E_{\alpha(Z\alpha)^2 \ln^2(Z\alpha)}$	−11.330	−2.611
ΔE_{ho}	1.089(1)	0.251(1)
E_{hfs}(QED)	1 420 452.028(1)	327 339.147(1)
E_{hfs}(exp)	1 420 405.751 768(1)	327 384.352 522(2)
E_{hfs}(nucl)	−46.276	45.205
$E_{\mathrm{hfs}}(\mathrm{nucl})/E_F$ (ppm)	−32.616	138.256

III. SPIN-SPIN SCALAR INTERACTIONS IN HD$^+$

From here on, we use atomic units. Such as in atoms, the electron-proton and electron-deuteron spin-spin scalar interactions are given at the leading orders ($m\alpha^4$ and $m\alpha^5$) by the Fermi term appearing in the Breit-Pauli Hamiltonian, taking into account the anomalous magnetic moment a_e of the electron [5],

$$H_{ss}^{(0)} = \alpha^2 \frac{8\pi}{3}(1+a_e)\frac{m}{M_p} \times \left[\mu_p \delta(\mathbf{r}_p)(\mathbf{s}_e\cdot\mathbf{I}_p) + \frac{\mu_d}{2}\delta(\mathbf{r}_d)(\mathbf{s}_e\cdot\mathbf{I}_d)\right]. \quad (9)$$

The leading contributions to the E_4 and E_5 hyperfine coefficients [see Eq. (1)] are then

$$E_4^{(\mathrm{lo})} = (1+a_e)E_4^{(F)}, \quad E_4^{(F)} = \alpha^2 \frac{8\pi}{3}\frac{m}{M_p}\mu_p\langle\delta(\mathbf{r}_p)\rangle, \quad (10)$$

$$E_5^{(\mathrm{lo})} = (1+a_e)E_5^{(F)}, \quad E_5^{(F)} = \alpha^2 \frac{4\pi}{3}\frac{m}{M_p}\mu_d\langle\delta(\mathbf{r}_d)\rangle. \quad (11)$$

This corresponds to the leading-order contribution of Eq. (2) with the first term of Eq. (3) included as well and was the only contribution considered in Ref. [5].

In order to improve the theoretical values of E_4 and E_5, one should consider higher-order QED corrections and nuclear structure effects as seen for the atomic case in the previous section. A key point is that the major part of these contributions are state independent, i.e., contact-type interactions only depending on the value of the squared density of the nonrelativistic wave function at the electron-nucleus coalescence point. Such contributions are given by a fixed coefficient taken from the H (respectively, D) atom theory regarding corrections to E_4 (respectively, E_5) multiplied by the expectation values of δ-function operators in HD$^+$, which have been already obtained with very high accuracy from variational three-body wave functions [33]. Thus, they do not require any new calculations. The most important state-dependent contribution is the relativistic correction on the order of $(Z\alpha)^2 E_F$ [the second term of Eq. (3) in the atomic case, also known as the "Breit correction"]. This term requires an independent calculation, which is presented in the next section. All other terms are included in the form of contact interactions,

$$E_{4,5}^{\alpha(Z\alpha)} = \left(\ln 2 - \frac{5}{2}\right)\alpha^2 E_{4,5}^{(F)}, \quad (12)$$

$$E_{4,5}^{\alpha(Z\alpha)^2\ln^2(Z\alpha)} = -\frac{8}{3\pi}\ln^2(\alpha)\alpha^3\, E_{4,5}^{(F)}, \quad (13)$$

$$E_{4,5}^{(\mathrm{ho})} = 0.767 \times 10^{-6} E_{4,5}^{(F)}, \quad (14)$$

$$E_4^{(\mathrm{nucl})} = -32.616 \times 10^{-6} E_4^{(F)}, \quad (15)$$

$$E_5^{(\mathrm{nucl})} = 138.256 \times 10^{-6} E_5^{(F)}. \quad (16)$$

The expressions of the first two terms are exact, whereas the next ones are obtained by neglecting the state dependence of the respective contributions. Among the higher-order nonrecoil QED corrections [Eq. (14)], the largest state-dependent term is that on the order of $\alpha(Z\alpha)^2\ln(Z\alpha)$ [the first term in the second line of Eq. (3)]. Among nuclear corrections [Eqs. (15) and (16)], the only term having a non-negligible state dependence is the recoil correction on the order of $(Z\alpha)^2(m/M)E_F$ [26], whereas for other terms the state dependence is much smaller, e.g., they contribute to the specific difference $D_{21} = 8E_{\mathrm{hfs}}(2S) - E_{\mathrm{hfs}}(1S)$ at the level of a few hertz only [31]. The uncertainty induced by the approximate expressions (14)–(16) can be estimated as equal to the sum of all state-dependent contributions, leading to a theoretical uncertainty,

$$\Delta E_4 \sim 0.93 \times 10^{-6} E_4^{(F)}, \quad \Delta E_5 \sim 0.59 \times 10^{-6} E_5^{(F)}. \quad (17)$$

The difference between the proton and the deuteron cases stems from the different magnitude of the $(Z\alpha)^2(m/M)E_F$ recoil correction [26].

IV. THE $(Z\alpha)^2 E_F$ RELATIVISTIC CORRECTION

We now derive the Breit correction to the spin-spin scalar interaction coefficients (E_4 and E_5) in HD$^+$. In the H$_2^+$ ion, the corresponding contribution was calculated in Refs. [6,7]. The derivation presented here for HD$^+$ is similar in spirit but differs in the details due the existence of two separate interaction constants instead of a global interaction between the electron spin and the total nuclear spin.

We use the adiabatic approximation and calculate the correction to the bound electron. The nonrelativistic electronic Hamiltonian is

$$H_0 = \frac{p^2}{2m} + V, \quad V = -\frac{Z_1}{r_1} - \frac{Z_2}{r_2}, \quad (18)$$

where $\mathbf{p}$ is the electron's impulse operator, Z_1, Z_2 are the nuclear charges, and r_1, r_2 are the distances between the electron and the nuclei. In what follows we will assume that $Z_1 = Z_2 = Z$. We, respectively, denote by E_0 and ψ_0 the nonrelativistic energy and wave function (in our numerical calculations, we will consider only the ground $1s\sigma$ electronic state).

The first step consists in deriving the effective potentials on the order of $m\alpha^6(m/M)$ by the nonrelativistic QED approach.

This was performed in Ref. [6], and these potentials were later rederived in Ref. [9] along with other spin-dependent interactions on the order of $m\alpha^6$. Here, we use the notations of Ref. [6]. The potentials contributing to the spin-spin scalar interactions are the following: (Eq. (42) of Ref. [6], see also Eq. (33) of [9]):

$$\begin{aligned}
\mathcal{V}_4 &= -\alpha^4 \frac{1}{4m^3}\left\{p^2, \left[\frac{8\pi}{3}\mathbf{s}_e\cdot\boldsymbol{\mu}_i\delta(\mathbf{r}_i) - \frac{r_i^2\mathbf{s}_e\cdot\boldsymbol{\mu}_i - 3(\mathbf{s}_e\cdot\mathbf{r}_i)(\boldsymbol{\mu}_i\cdot\mathbf{r}_i)}{r_i^5}\right]\right\},\\
\mathcal{V}_6 &= \alpha^4\frac{Z}{6m^2}\left[\frac{2(\mathbf{r}_1\cdot\mathbf{r}_2)(\mathbf{s}_e\cdot\boldsymbol{\mu}_I)}{r_1^3r_2^3} + \frac{(\mathbf{r}_1\cdot\mathbf{r}_2)(\mathbf{s}_e\cdot\boldsymbol{\mu}_I) - 3(\mathbf{r}_1\cdot\mathbf{s}_e)(\mathbf{r}_2\cdot\boldsymbol{\mu}_2) - 3(\mathbf{r}_2\cdot\mathbf{s}_e)(\mathbf{r}_1\cdot\boldsymbol{\mu}_1)}{r_1^3r_2^3}\right],\\
\mathcal{V}_8 &= \alpha^4\frac{Z}{6m^2}\left[\frac{2(\mathbf{s}_e\cdot\boldsymbol{\mu}_i)}{r_i^4} + \frac{r_i^2(\mathbf{s}_e\cdot\boldsymbol{\mu}_i) - 3(\mathbf{r}_i\cdot\mathbf{s}_e)(\mathbf{r}_i\cdot\boldsymbol{\mu}_i)}{r_i^6}\right].
\end{aligned} \tag{19}$$

Here, $\{X, Y\} = XY + YX$. $\boldsymbol{\mu}_1$, $\boldsymbol{\mu}_2$ are the nuclear magnetic moments ($\boldsymbol{\mu}_1 \equiv \boldsymbol{\mu}_p$, $\boldsymbol{\mu}_2 \equiv \boldsymbol{\mu}_d$), and $\boldsymbol{\mu}_I = \boldsymbol{\mu}_1 + \boldsymbol{\mu}_2$. In each line, the first and second terms contribute to scalar and tensor interactions, respectively. Keeping only the terms contributing to scalar interactions, we arrive at the total effective Hamiltonian,

$$H_s^{(6)} = \alpha^4\left[-\frac{1}{6m^3}\{p^2, 4\pi\delta(\mathbf{r}_1)\} + \frac{Z}{3m^2}\left(\frac{1}{r_1^4} + \frac{\mathbf{r}_1\cdot\mathbf{r}_2}{r_1^3r_2^3}\right)\right]\mathbf{s}_e\cdot\boldsymbol{\mu}_1 + \alpha^4\left[-\frac{1}{6m^3}\{p^2, 4\pi\delta(\mathbf{r}_2)\} + \frac{Z}{3m^2}\left(\frac{1}{r_2^4} + \frac{\mathbf{r}_1\cdot\mathbf{r}_2}{r_1^3r_2^3}\right)\right]\mathbf{s}_e\cdot\boldsymbol{\mu}_2. \tag{20}$$

From now on, we focus on the $\mathbf{s}_e\cdot\boldsymbol{\mu}_1$ interaction term, calculations for the other term being identical. It may be rewritten as

$$H_{s1}^{(6)} = \frac{\alpha^4}{3Zm^2}\left[-\frac{1}{2m}\{p^2, \rho_1\} + \boldsymbol{\mathcal{E}}_1\cdot\boldsymbol{\mathcal{E}}\right]\mathbf{s}_e\cdot\boldsymbol{\mu}_1, \tag{21}$$

with the definitions: $V_i = -Z/r_i$, $4\pi\rho_i = \Delta V_i$, $\boldsymbol{\mathcal{E}}_i = -\boldsymbol{\nabla} V_i$ $(i = 1, 2)$, and $\rho = \rho_1 + \rho_2$, $\boldsymbol{\mathcal{E}} = \boldsymbol{\mathcal{E}}_1 + \boldsymbol{\mathcal{E}}_2$.

According to the nonrelativistic perturbation theory, the total energy correction on theorder of $m\alpha^6(m/M)$ to the $\mathbf{s}_e\cdot\boldsymbol{\mu}_1$ interaction is given by

$$\Delta E_{s1}^{(6)} = \langle H_{s1}^{(6)}\rangle + 2\alpha^4\langle H_B^{(2)}Q(E_0 - H_0)^{-1}QH_{ss1}^{(1)}\rangle. \tag{22}$$

Here, we have omitted a second-order perturbation term induced by the electronic spin-orbit and nuclear spin-orbit interactions (respectively, denoted by $H_{\rm so}$ and $H_{{\rm so}_N}$ in Eq. (28) of Ref. [9]), which is negligibly small for σ electronic states. The brackets denote an expectation value over the nonrelativistic electronic wave function ψ_0, and Q is a projection operator on a subspace orthogonal to ψ_0. $H_{ss1}^{(1)}$ is the leading-order Fermi interaction, and $H_B^{(2)}$ is the spin-independent part of the Breit-Pauli Hamiltonian accounting for leading-order relativistic corrections to the bound electron,

$$\begin{aligned}
H_B^{(2)} &= -\frac{p^4}{8m^3} + \frac{Z}{8m^2}4\pi[\delta(\mathbf{r}_1) + \delta(\mathbf{r}_2)],\\
H_{ss1}^{(1)} &= \frac{2}{3m}H_{B1}^{(1)}\mathbf{s}_e\cdot\boldsymbol{\mu}_1,
\end{aligned} \tag{23}$$

here $H_{B1}^{(1)} = 4\pi Z\delta(\mathbf{r}_1)$. Both terms in Eq. (22) are divergent, but their sum is finite. They need to be transformed in order to separate and cancel divergent terms as was performed in [6] for H_2^+.

The first-order term can be transformed using the relationship $p^2\Psi_0 = 2m(E_0 - V)\Psi_0$, commutation relations, and integration by parts (see the Appendix for details). One gets, using Eq. (A4b),

$$\begin{aligned}
\langle H_{s1}^{(6)}\rangle = \frac{\alpha^4}{3Zm^2}[&-\langle\boldsymbol{\mathcal{E}}_1\cdot\boldsymbol{\mathcal{E}}\rangle + 4m\langle V_1V^2\rangle - 4mE_0\langle V_1V\rangle\\
&+ 2\langle\mathbf{p}V_1V\mathbf{p}\rangle + 4\pi\langle V_2\rho_1 - V_1\rho_2\rangle\\
&- 8\pi E_0\langle\rho_1\rangle]\langle\mathbf{s}_e\cdot\boldsymbol{\mu}_1\rangle.
\end{aligned} \tag{24}$$

Let us now consider the second-order term. We introduce the first-order perturbation wave function $\Psi_{B1}^{(1)}$, solution of the equation,

$$(E_0 - H_0)\Psi_{B1}^{(1)} = QH_{B1}^{(1)}\Psi_0. \tag{25}$$

This wave function behaves, such as $1/r_1$ in the limit $r_1 \to 0$. The $1/r_1$ singularity can be separated by setting

$$\Psi_{B1}^{(1)} = -\frac{2Zm}{r_1}\Psi_0 + \tilde{\Psi}_{B1}^{(1)} = U_1\Psi_0 + \tilde{\Psi}_{B1}^{(1)}, \qquad U_1 = 2mV_1,$$

where $\tilde{\Psi}_{B1}^{(1)}$ is a less singular function, behaving, such as $\ln r_1$ at $r_1 \to 0$ and is a solution of the equation,

$$\begin{aligned}
(E_0 - H_0)\tilde{\Psi}_{B1}^{(1)} &= \left(H_{B1}'^{(1)} - \langle H_{B1}'^{(1)}\rangle\right)\Psi_0,\\
H_{B1}'^{(1)} &= -(E_0 - H_0)U_1 - U_1(E_0 - H_0) + H_{B1}^{(1)}.
\end{aligned}$$

Similarly, for $H_B^{(2)}$, we introduce the first-order wave-function $\Psi_B^{(2)}$,

$$(E_0 - H_0)\Psi_B^{(2)} = QH_B^{(2)}\Psi_0, \tag{26}$$

and separate its $1/r_1$ and $1/r_2$ singularities,

$$\begin{aligned}
\Psi_B^{(2)} &= \frac{Z}{4m}\left[-\frac{1}{r_1} - \frac{1}{r_2}\right]\Psi_0(r) + \tilde{\Psi}_B^{(2)} = U_2\Psi_0 + \tilde{\Psi}_B^{(2)},\\
U_2 &= -\frac{1}{4m}V.
\end{aligned}$$

Here $\tilde{\Psi}_B^{(2)}$ is a solution of the equation,

$$\begin{aligned}
(E_0 - H_0)\tilde{\Psi}_B^{(2)} &= \left(H_B'^{(2)} - \langle H_B'^{(2)}\rangle\right)\Psi_0,\\
H_B'^{(2)} &= -(E_0 - H_0)U_2 - U_2(E_0 - H_0) + H_B^{(2)}.
\end{aligned}$$

Then, the divergent part of the second-order term can be separated as follows:

$$\begin{aligned}\Delta E_{A1} &= \alpha^4 \frac{4}{3m}\langle\Psi_0|H_B^{(2)}Q(E_0-H_0)^{-1}QH_{B1}^{(1)}|\Psi_0\rangle\langle\mathbf{s}_e\cdot\boldsymbol{\mu}_1\rangle\\ &= \alpha^4\frac{4}{3m}(\langle\Psi_0|(H_B^{(2)}-\langle H_B^{(2)}\rangle)U_1|\Psi_0\rangle+\langle\Psi_0|U_2(H_{B1}^{\prime(1)}-\langle H_{B1}^{\prime(1)}\rangle)|\Psi_0\rangle+\langle\Psi_0|H_B^{\prime(2)}Q(E_0-H_0)^{-1}QH_{B1}^{\prime(1)}|\Psi_0\rangle)\langle\mathbf{s}_e\cdot\boldsymbol{\mu}_1\rangle.\end{aligned}$$

In this expression, the last term is finite. The divergences are located in the first two terms, which can be written as the expectation value of an effective Hamiltonian,

$$\begin{aligned}H_{s1}^{\prime(6)} &= \alpha^4\frac{2}{3m}\big\{\big(H_B^{(2)}U_1+U_1H_B^{(2)}\big)+\big(H_{B1}^{(1)}U_2+U_2H_{B1}^{(1)}\big)-2\langle H_B^{(2)}\rangle U_1-2\langle H_{B1}^{(1)}\rangle U_2-U_1(E_0-H_0)U_2-U_2(E_0-H_0)U_1\big\}(\mathbf{s}_e\cdot\boldsymbol{\mu}_1)\\ &= \alpha^4\frac{2}{3Zm}\left[-\frac{p^4V_1+V_1p^4}{4m^2}+\frac{4\pi Z[\rho_2V_1-\rho_1V_2]}{2m}-\frac{(V_1p^2V+Vp^2V_1)}{4m}-V_1V^2+E_0V_1V-4m\langle H_B^{(2)}\rangle V_1+\frac{\langle H_{B1}^{(1)}\rangle V}{2m}\right](\mathbf{s}_e\cdot\boldsymbol{\mu}_1).\end{aligned} \tag{27}$$

Using Eqs. (A3a) and (A4a) (see the Appendix), the expectation value of $H_{s1}^{\prime(6)}$ can be transformed to

$$\begin{aligned}\langle H_{s1}^{\prime(6)}\rangle = \alpha^4\frac{1}{3Zm^2}[&\langle\boldsymbol{\mathcal{E}}_1\cdot\boldsymbol{\mathcal{E}}\rangle-4m\langle V_1V^2\rangle+8mE_0\langle V_1V\rangle\\ &-4\pi\langle V_2\rho_1-V_1\rho_2\rangle-4mE_0^2\langle V_1\rangle-8m^2\langle H_B^{(2)}\rangle\langle V_1\rangle\\ &+\langle H_{B1}^{(1)}\rangle\langle V\rangle]\langle\mathbf{s}_e\cdot\boldsymbol{\mu}_1\rangle.\end{aligned} \tag{28}$$

Finally, the total correction on the order of $m\alpha^6(m/M)$ to the E_4 coefficient is given by

$$\Delta E_4^{(6)} = \Delta E_{A1}^{\prime(6)}+\Delta E_{B1}^{\prime(6)}, \tag{29}$$

$$\Delta E_{A1}^{\prime(6)} = \alpha^4\frac{4}{3}\frac{m}{M_p}\mu_p\langle\Psi_0|H_B^{\prime(2)}Q(E_0-H_0)^{-1}QH_{B1}^{\prime(1)}|\Psi_0\rangle, \tag{29a}$$

$$\begin{aligned}\Delta E_{B1}^{\prime(6)} = \alpha^4\frac{2}{3Z}\frac{m}{M_p}\mu_p\bigg[&\langle\mathbf{p}V_1V\mathbf{p}\rangle+2mE_0\langle V_1V\rangle-2mE_0^2\langle V_1\rangle\\ &-4\pi E_0\langle\rho_1\rangle-4m^2\langle H_B^{(2)}\rangle\langle V_1\rangle+\frac{1}{2}\langle H_{B1}^{(1)}\rangle\langle V\rangle\bigg].\end{aligned} \tag{29b}$$

Both the second-order term and the first-order term in which the divergent terms proportional to $\langle\boldsymbol{\mathcal{E}}_1\cdot\boldsymbol{\mathcal{E}}\rangle$ and to $\langle V_1V^2\rangle$ have been canceled out in the sum $\langle H_{s1}^{(6)}\rangle+\langle H_{s1}^{\prime(6)}\rangle$ are now finite. Expressions for the E_5 coefficient are identical except that the prefactor $(m/M_p)\mu_p$ is replaced by $[m/(2M_p)]\mu_d$.

Comparing our final result (29a) and (29b) with the expression obtained in H_2^+, Eqs. (49) and (50) of Ref. [6], it is easily seen that they are equivalent under the assumption that the electronic wave function is symmetric with respect to the exchange of nuclei, which is the case in the standard adiabatic approximation that we will use here [34]. Indeed, under this assumption the following equalities hold:

$$\langle\mathbf{p}V_1V\mathbf{p}\rangle=\tfrac{1}{2}\langle\mathbf{p}V^2\mathbf{p}\rangle,\quad\langle V_1V\rangle=\tfrac{1}{2}\langle V^2\rangle,$$
$$\langle V_1\rangle=\tfrac{1}{2}\langle V\rangle,\quad\langle\rho_1\rangle=\langle\rho_2\rangle.$$

In the adiabatic framework, corrections to rovibrational energy levels are obtained by averaging the correction curve $\Delta E_{4,5}^{(6)}(R)$ over the adiabatic vibrational wave functions $\chi_{v,L}(R)$. The second-order perturbation term induced by the leading-order Fermi interaction and the spin-independent Breit-Pauli Hamiltonian requires specific attention. The correction written in the second term of Eq. (22) accounts for the perturbation of the electronic part of the wave function only, and one should also take into account the perturbation of the vibrational wave function caused by the shift of the potential-energy curve [7]. The total correction is

$$\Delta E_4^{(Z\alpha)^2}(v,L)=\Delta E_4^{(Z\alpha)^2(\mathrm{el})}(v,L)+\Delta E_4^{(Z\alpha)^2(\mathrm{vb})}(v,L), \tag{30}$$

$$\Delta E_4^{(Z\alpha)^2(\mathrm{el})}(v,L)=\langle\chi_{v,L}|\Delta E_4^{(6)}(R)|\chi_{v,L}\rangle, \tag{30a}$$

$$\begin{aligned}&\Delta E_4^{(Z\alpha)^2(\mathrm{vb})}(v,L)\\ &\quad=2\alpha^4\langle\chi_{v,L}|E_B^{(2)}(R)Q'(E_0-H_{\mathrm{vb}})^{-1}Q'E_{ss1}(R)|\chi_{v,L}\rangle.\end{aligned} \tag{30b}$$

In the last line, $E_{ss1}(R)=\langle H_{ss1}\rangle$, $E_B^{(2)}(R)=\langle H_B^{(2)}\rangle$, Q' is a projection operator onto a subspace orthogonal to $\chi_{v,L}$, and H_{vb} is the nuclear radial Hamiltonian [34],

$$H_{\mathrm{vb}}=-\frac{\Delta_{\mathbf{R}}}{2\mu}+U(R)+\frac{L(L+1)}{2\mu R^2},$$
$$U(R)=E_0(R)+\frac{Z^2}{R}-\frac{\langle\Delta_{\mathbf{r}}\rangle}{8\mu}-\frac{\langle\Delta_{\mathbf{R}}\rangle}{2\mu},$$

where $\mu=m_pm_d/(m_p+m_d)$, and $\mathbf{r}$ denotes the electronic coordinates.

V. VIBRATIONAL CORRECTION ON THE ORDER OF $\alpha(Z\alpha)^2E_F$

There is one last contribution that should be included in our theory. As illustrated in the preceding section, in a molecular system, second-order correction terms consist of an electronic contribution [the second term of Eq. (22)] and a vibrational one [Eq. (30b)]. Our estimate of higher-order corrections in Eq. (14) only includes the electronic part so that the vibrational part must be included separately. One such contribution is significant at the level of the theoretical uncertainties (17), namely, the $\alpha(Z\alpha)^2E_F$-order term induced by the leading-order Fermi interaction and leading-order radiative corrections,

$$\Delta E_4^{\alpha(Z\alpha)^2(\mathrm{vb})}(v,L) = 2\alpha^5 \langle \chi_{v,L} | E_{\mathrm{rad}}(R) Q'(E_0 - H_{\mathrm{vb}})^{-1} Q' E_{ss1}(R) | \chi_{v,L} \rangle, \tag{31}$$

with

$$E_{\mathrm{rad}}(R) = \frac{4}{3}\left[\ln\frac{1}{\alpha^2} - \beta(R) + \frac{5}{6} - \frac{1}{5}\right] Z\langle \delta(\mathbf{r}_1) + \delta(\mathbf{r}_2)\rangle. \tag{32}$$

$\beta(R)$ is the nonrelativistic Bethe logarithm for the bound electron. Its values as a function of R can be found in the Supplemental Material of Ref. [35].

Before discussing numerical results, it is worth summarizing the improvements brought in our present treatment with respect to that presented in Refs. [6,7] in H_2^+ and used in HD$^+$ in Refs. [2,3,8]:

(1) Nuclear corrections are determined phenomenologically from the difference between the experimental ground-state hyperfine splitting in the H and D atoms and the QED prediction [Eq. (8)]. Note that the treatment of Ref. [6] where nuclear correction terms were calculated individually is actually similar in spirit since a value of the proton's Zemach radius deduced from the experimental H-atom ground-state hyperfine splitting was used in that work [20]. The more self-consistent approach used here only leads to small differences in E_4 and E_5 ($\sim$100–200 Hz).

(2) More importantly, we take into account an estimate of higher-order nonrecoil QED corrections [Eq. (14)], which includes as well the vibrational contribution on the order of $\alpha(Z\alpha)^2 E_F$ [Eq. (31)]. In addition, the sum of state-dependent corrections gives an estimate of the theoretical uncertainty.

VI. NUMERICAL RESULTS AND DISCUSSION

We report here the results of calculations of the E_4 and E_5 hyperfine coefficients in HD$^+$ and of the b_F spin-spin coefficient in H_2^+ [6,7], for a range of rovibrational states. For the leading-order contribution [Eqs. (10) and (11)] as well as QED and nuclear corrections [Eqs. (12)–(16)], expectation values of δ-function operators are taken from Ref. [33]. The potential curve corresponding to the $(Z\alpha)^2 E_F$ relativistic correction, $E_{s1}^{(6)}(R)$ [Eqs. (29)–(29b)] has been shown to be identical to that obtained in the H_2^+ case [6] in the adiabatic approximation used here. To calculate corrections to rovibrational levels [Eqs. (30)–(30b) and (31)], adiabatic vibrational wave functions are obtained by solving numerically the radial Schrödinger equation for the nuclear motion.

In H_2^+, the results presented here represent a slight improvement with respect to those of Ref. [7]. As explained above, the main improvement is that (estimated) higher-order QED corrections are taken into account through the term $b_F^{(\mathrm{ho})} = 0.767 \times 10^{-6} b_F^{(F)}$ (where $b_F^{(F)}$ is the Fermi value of b_F), along with the vibrational contribution [Eq. (31)]. As shown in Table II, the excellent agreement with experiments reported in Ref. [7] is not significantly altered by the inclusion of higher-order QED effects. More extensive results for the range ($L = 1, 3, 0 \leqslant v \leqslant 10$) are reported in Table III.

TABLE II. Theoretical and experimental values (in megahertz) of the spin-spin scalar interaction coefficient b_F for a few rovibrational states of H_2^+. The rotational quantum number is $L = 1$.

v	[7]	This paper	Experiment [36]
4	836.7294	836.7287(8)	836.7292(8)
5	819.2272	819.2267(8)	819.2273(8)
6	803.1750	803.1745(7)	803.1751(8)
7	788.5079	788.5075(7)	788.5079(8)
8	775.1714	775.1712(7)	775.1720(8)

In HD$^+$, all contributions to E_4 and E_5 are shown in detail in Table IV for a few rovibrational states probed in high-precision experiments [2,3,37], whereas complete results for a range of states ($0 \leqslant L \leqslant 4, 0 \leqslant v \leqslant 10$) are given in Table V. Inspection of Table IV reveals that our values of $E_4(E_5)$ are smaller than those given in Refs. [2,3] by about 1.7 kHz (0.25 kHz) for $v = 0$ states, whereas differences are much smaller for $v = 9$ ($\sim$0.2 kHz for E_4 and 0.03 kHz for E_5) due to the smaller value of the $\alpha(Z\alpha)^2 E_F$ vibrational correction. This shifts the measured hyperfine components of the $L = 0 \rightarrow 1$ rotational transition [2] by only a few tens of hertz, which does not significantly change the level of agreement between theory and experiment. This is due to a strong cancellation effect as transition frequencies essentially depend on the differences $E_4(v = 0,\ L = 1) - E_4(v = 0,\ L = 0)$ and $E_5(v = 0,\ L = 1) - E_5(v = 0,\ L = 0)$. The rotational transition is, thus, not a stringent test for the theory of spin-spin scalar interactions and is much more sensitive to the spin-orbit and tensor coefficients (E_1, E_6, E_7) in the $L = 1$ state. A more detailed analysis requires calculation of higher-order corrections to these coefficients, which is currently in progress [9].

In the $(L, v) = (3, 0) \rightarrow (3, 9)$ two-photon transition [3], the additional contributions included in the present paper decrease the theoretical value of the separation between the two measured hyperfine components by about 1.5 kHz down to

$$f_{\mathrm{hfs,theo}} = 178.2462(18)\ \mathrm{MHz}, \tag{33}$$

TABLE III. Values (in megahertz) of the spin-spin scalar interaction coefficient b_F for rovibrational states (L, v) of H_2^+.

v	$b_F(L = 1, v)$	$b_F(L = 3, v)$
0	922.9301(9)	917.5297(9)
1	898.7493(8)	893.6950(8)
2	876.3961(8)	871.6699(8)
3	855.7560(8)	851.3422(8)
4	836.7287(8)	832.6136(8)
5	819.2267(8)	815.3988(8)
6	803.1745(7)	799.6241(7)
7	788.5075(7)	785.2269(7)
8	775.1712(7)	772.1546(7)
9	763.1211(7)	760.3644(7)
10	752.3219(7)	749.8233(7)

TABLE IV. Contributions to E_4 and E_5 (in megahertz) for a few rovibrational states (L, v) of HD^+ (columns 3–9). Our final theoretical values are given in column 10. The theoretical values given in Refs. [2,3] are shown in the last column for comparison.

	L	v	lo	$(Z\alpha)^2$	$\alpha(Z\alpha)$	$\alpha(Z\alpha)^2$	ho	$\alpha(Z\alpha)^2$ (vb)	Nucl.	This paper	
E_4	0	0	925.4559	0.0669	−0.0889	−0.0074	0.0007	−0.0029	−0.0301	925.3942(9)	925.39588 [2]
	1	0	924.6295	0.0669	−0.0889	−0.0074	0.0007	−0.0029	−0.0301	924.5677(9)	924.56943 [2]
	3	0	920.5415	0.0665	−0.0885	−0.0073	0.0007	−0.0029	−0.0300	920.4800(9)	920.48165 [3]
	3	9	775.7556	0.0572	−0.0746	−0.0062	0.0006	−0.0012	−0.0253	775.7061(7)	775.70633 [3]
	1	6	816.7692	0.0597	−0.0785	−0.0065	0.0006	−0.0018	−0.0266	816.7161(8)	
E_5	0	0	142.27278	0.01027	−0.01367	−0.00113	0.00011	−0.00045	0.01965	142.28756(8)	142.28781 [2]
	1	0	142.14591	0.01026	−0.01366	−0.00113	0.00011	−0.00045	0.01963	142.16067(8)	142.16092 [2]
	3	0	141.51840	0.01020	−0.01360	−0.00113	0.00011	−0.00044	0.01954	141.53307(8)	141.53332 [3]
	3	9	119.41918	0.00879	−0.01148	−0.00095	0.00009	−0.00019	0.01649	119.43193(7)	119.43196 [3]
	1	6	125.64226	0.00916	−0.01207	−0.00100	0.00010	−0.00027	0.01735	125.65551(7)	

to be compared with the experimental value,

$$f_{\mathrm{hfs,exp}} = 178.2544(9)\ \mathrm{MHz}. \tag{34}$$

The values of the other hyperfine coefficients can be found in the Supplementary Material of Ref. [3] except for E_1 where we used the value of Ref. [9]. To estimate the theoretical uncertainty, we have assumed an uncertainty of 400 Hz for the E_1 coefficient [9] and a relative uncertainty of 10^{-4} for the other (smaller) coefficients. The difference between theory and experiment amounts to 8.2 kHz or 4.1 combined standard deviations, whereas in H_2^+, excellent agreement within the 0.8-kHz experimental error bar is obtained with the same theoretical ingredients.

The origin of this discrepancy is unknown. It is unlikely that it is due to an error in other hyperfine coefficients as they were calculated at the leading order from the well-known Breit-Pauli Hamiltonian [5], and higher-order corrections are on the order of of 1 kHz for E_1 [9] and smaller for other coefficients. In addition, experimental data on the rotational transition [2] has confirmed the theoretical values of these coefficients at the level of a few hundred hertz for the $(L = 1,\ v = 0)$ level. Concerning the theory of the spin-spin

TABLE V. Values (in megahertz) of the spin-spin scalar interaction coefficients E_4 and E_5 for rovibrational states (L, v) of HD^+.

L	v	E_4	E_5	L	v	E_4	E_5
0	0	925.3942(9)	142.28756(8)	2	6	815.5646(8)	125.47914(7)
0	1	904.1471(8)	139.03010(8)	2	7	801.7350(7)	123.37411(7)
0	2	884.2889(8)	135.98714(8)	2	8	788.9278(7)	121.43086(7)
0	3	865.7411(8)	133.14692(8)	2	9	777.1025(7)	119.64475(7)
0	4	848.4337(8)	130.49899(8)	2	10	766.2212(7)	118.01236(7)
0	5	832.3039(8)	128.03411(8)	3	0	920.4800(9)	141.53307(8)
0	6	817.2953(8)	125.74423(7)	3	1	899.5058(8)	138.31764(8)
0	7	803.3575(7)	123.62237(7)	3	2	879.9078(8)	135.31479(8)
0	8	790.4451(7)	121.66266(7)	3	3	861.6089(8)	132.51296(8)
0	9	778.5169(7)	119.86036(7)	3	4	844.5404(8)	129.90192(8)
0	10	767.5349(7)	118.21194(7)	3	5	828.6406(8)	127.47263(8)
1	0	924.5677(9)	142.16067(8)	3	6	813.8543(8)	125.21721(7)
1	1	903.3665(8)	138.91027(8)	3	7	800.1320(7)	123.12888(7)
1	2	883.5519(8)	135.87404(8)	3	8	787.4294(7)	121.20197(7)
1	3	865.0459(8)	133.04026(8)	3	9	775.7061(7)	119.43193(7)
1	4	847.7786(8)	130.39852(8)	3	10	764.9249(7)	117.81546(7)
1	5	831.6874(8)	127.93962(8)	4	0	917.2621(9)	141.03904(8)
1	6	816.7161(8)	125.65551(7)	4	1	896.4674(8)	137.85123(8)
1	7	802.8145(7)	123.53928(7)	4	2	877.0404(8)	134.87475(8)
1	8	789.9372(7)	121.58507(7)	4	3	858.9052(8)	132.09817(8)
1	9	778.0434(7)	119.78818(7)	4	4	841.9938(8)	129.51139(8)
1	10	767.0951(7)	118.14511(7)	4	5	826.2452(8)	127.10551(8)
2	0	922.9238(9)	141.90827(8)	4	6	811.6051(8)	124.87277(7)
2	1	901.8138(8)	138.67192(8)	4	7	798.0247(7)	122.80652(7)
2	2	882.0862(8)	135.64910(8)	4	8	785.4602(7)	120.90121(7)
2	3	863.6634(8)	132.82815(8)	4	9	773.8718(7)	119.15243(7)
2	4	846.4759(8)	130.19874(8)	4	10	763.2228(7)	117.55703(7)
2	5	830.4616(8)	127.75173(8)				

coefficients presented here, the main approximation, apart from neglecting the state dependence of higher-order QED corrections [Eq. (14)], consists in using the adiabatic approximation to calculate the $(Z\alpha)^2 E_F$ relativistic correction. The associated uncertainty can be estimated to be on the relative order (m/M), that is, smaller than 100 Hz. One additional feature of HD$^+$ (as compared to H$_2^+$) that is not taken into account in the adiabatic framework is the g/u symmetry breaking due to the mass asymmetry between proton and deuteron, which strongly affects rovibrational states close to the dissociation limit (see, e.g., Ref. [38]). However, even the $(v = 9,\ L = 3)$ level is quite far from the dissociation limit, and the asymmetry of the wave function is still small (in the 10^{-3} range). In any case, a recalculation of the Breit correction in a full three-body approach would be highly desirable to test the accuracy of our results. Consideration of the state-dependent recoil correction on the order of $(Z\alpha)^2(m/M)E_F$ might also be of interest.

In conclusion, we have presented a theory of higher-order corrections to the spin-spin scalar interaction in hydrogen molecular ions and applied it to obtain improved values of the corresponding hyperfine coefficients for a range of rovibrational states in H$_2^+$ and HD$^+$. Although the agreement with experimental data is excellent in H$_2^+$, a substantial discrepancy is observed in HD$^+$. It is currently unexplained, and will be the object of further investigations.

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APPENDIX: RELATIONS BETWEEN DIVERGENT MATRIX ELEMENTS

In this Appendix, we will assume that the Coulomb potential V is regularized in some way and that the charge distribution ρ $(4\pi\rho = \Delta V)$ is a smooth function of space variables. We recall that the brackets denote an expectation value over the nonrelativistic wave function Ψ_0; the nonrelativistic energy is denoted by E_0. Other relevant definitions are given right after Eq. (21).

The divergent terms that we want to transform are $\langle V_1 p^4\rangle$ and $\langle V_1 p^2 V\rangle$, which appear in the second-order term Eq. (27) and $\langle \rho_1 p^2\rangle$, appearing in the first-order term Eq. (21). Using the relationship $p^2\Psi_0 = 2m(E_0 - V)\Psi_0$, one obtains

$$\langle V_1 p^4\rangle = -2m\langle V_1 p^2 V\rangle - 4m^2 E_0\langle V_1 V\rangle + 4m^2 E_0^2\langle V_1\rangle, \tag{A1a}$$

$$\begin{aligned}\langle \rho_1 p^2\rangle &= 2mE_0\langle\rho_1\rangle - 2m\langle V\rho_1\rangle\\ &= 2mE_0\langle\rho_1\rangle - m(\langle V_1\rho + V\rho_1\rangle + \langle V_2\rho_1 - V_1\rho_2\rangle).\end{aligned} \tag{A1b}$$

Using commutation relations and integration by parts one can obtain the following relationships:

$$\langle V_1 p^2 V\rangle = \langle V_1 V p^2\rangle - 2\pi\langle V_1\rho + V\rho_1\rangle + \langle (V_1\boldsymbol{\mathcal{E}} + V\boldsymbol{\mathcal{E}}_1)\cdot\boldsymbol{\nabla}\rangle, \tag{A2a}$$

$$\langle V_1 p^2 V\rangle = \langle \boldsymbol{\mathcal{E}}_1\cdot\boldsymbol{\mathcal{E}}\rangle - \langle (V_1\boldsymbol{\mathcal{E}} + V\boldsymbol{\mathcal{E}}_1)\cdot\boldsymbol{\nabla}\rangle + \langle \mathbf{p}V_1 V\mathbf{p}\rangle, \tag{A2b}$$

$$2\pi\langle V_1\rho + V\rho_1\rangle = -\langle \boldsymbol{\mathcal{E}}_1\cdot\boldsymbol{\mathcal{E}}\rangle + \langle (V_1\boldsymbol{\mathcal{E}} + V\boldsymbol{\mathcal{E}}_1)\cdot\boldsymbol{\nabla}\rangle. \tag{A2c}$$

Subtracting Eq. (A2c) from Eq. (A2a), and using again $p^2\psi_0 = 2m(E_0 - V)\psi_0$ in the second line, we obtain a suitable expression for the first required expectation value,

$$\langle V_1 p^2 V\rangle = \langle \boldsymbol{\mathcal{E}}_1\cdot\boldsymbol{\mathcal{E}}\rangle + \langle V_1 V p^2\rangle = \langle \boldsymbol{\mathcal{E}}_1\cdot\boldsymbol{\mathcal{E}}\rangle - 2m\langle V_1 V^2\rangle + 2mE_0\langle V_1 V\rangle. \tag{A3a}$$

Adding up (A2b) and (A2c) and taking into account (A3a), we arrive at

$$2\pi\langle V_1\rho + V\rho_1\rangle = -\langle \boldsymbol{\mathcal{E}}_1\boldsymbol{\mathcal{E}}\rangle + 2m\langle V_1 V^2\rangle - 2mE_0\langle V_1 V\rangle + \langle \mathbf{p}V_1 V\mathbf{p}\rangle. \tag{A3b}$$

Finally, using (A1a) and (A1b) we find the following expressions for the other two expectation values:

$$\langle V_1 p^4\rangle = -2m\langle \boldsymbol{\mathcal{E}}_1\boldsymbol{\mathcal{E}}\rangle + 4m^2\langle V_1 V^2\rangle - 8m^2 E_0\langle V_1 V\rangle + 4m^2 E_0^2\langle V_1\rangle, \tag{A4a}$$

$$4\pi\langle \rho_1 p^2\rangle = 2m\langle \boldsymbol{\mathcal{E}}_1\boldsymbol{\mathcal{E}}\rangle - 4m^2\langle V_1 V^2\rangle + 4m^2 E_0\langle V_1 V\rangle - 2m\langle \mathbf{p}V_1 V\mathbf{p}\rangle - 4\pi m\langle V_2\rho_1 - V_1\rho_2\rangle + 8\pi m E_0\langle\rho_1\rangle. \tag{A4b}$$

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