Leading-order relativistic corrections to the g-factor of H2+

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Relativistic corrections of order α^2 to the g-factor of H_2^+ are calculated with a high accuracy of 9 significant digits for a wide range of rovibrational states. The precision of previous calculations [R. A. Hegstrom, Phys. Rev. A **19**, 17 (1979)] is improved by about 5 orders of magnitude by performing nonadiabatic variational calculations and by including recoil corrections. These results allow for non-destructive identification of the internal state through measurement of spin-flip transition frequencies, which is a crucial requirement for proposed spectroscopy experiments on H_2^+ and its antimatter counterpart $\bar{H}_2^-$ in Penning traps [E. G. Myers, Phys. Rev. A **98**, 010101(R) (2018)]. Further, they pave the way towards precision calculations of the g-factor through calculation of higher-order QED corrections and hence to an alternative precision route to obtaining the proton-electron mass ratio.

I. INTRODUCTION

Spectroscopic measurements of the antihydrogen molecular ion $\bar{H}_2^-$, compared with its normal matter counterpart, have been recently proposed as a new avenue towards improved tests of the CPT symmetry [1]. This perspective relies on the possibility to store a single $\bar{H}_2^-$ or H_2^+ ion in a Penning trap and identify its ro-vibrational state in a non-destructive way. The envisaged experiments use similar methods to those developed for high-precision measurements of bound-electron g-factors (see e.g. [2]). They would be performed in a double Penning trap consisting of a "precision trap" with a highly uniform magnetic field, where spectroscopic measurements are carried out, and an "analysis trap" with an inhomogeneous magnetic field allowing the positron or electron spin state to be determined via the so-called continuous Stern-Gerlach technique. The ion's internal state can then be determined using the fact that the spin-flip frequencies depend in a resolvable and calculable way on the ro-vibrational and hyperfine state. This detection technique requires knowledge of a large number of Zeeman transition frequencies in a ~ 5 Tesla magnetic field, at a precision level of $\sim 10^{-6} - 10^{-7}$. Since the dominant contribution to the Zeeman shift stems from the interaction of the magnetic field with the positron/electron spin (through the term $g\,\mathbf{s}{\cdot}\mathbf{B}$), this implies that the bound positron/electron g factors should be determined theoretically with similar precision for an extensive range of rovibrational levels.

Beyond its importance for nondestructive internal state detection, the g-factor itself could be measured with high precision from the ratio of the cyclotron and spin-flip frequencies [2]. As discussed in [1], measuring this frequency ratio in $\bar{H}_2^-$ and H_2^+ provides a way to compare $m(e^-)/m(p)$ with $m(e^+)/m(\bar{p})$ at a competitive precision level, under the assumptions that charges and g-factors have opposite signs in matter and antimatter. Further, if the theoretical g-factor of H_2^+ is calculated with sufficiently high accuracy, the comparison between theory and experiment would lead to a stringent test of bound-state QED or to an independent determination of $m(e^-)/m(p)$.

The theoretical g-factors of hydrogen molecular ions have been calculated by Hegstrom [3]. In that work, the author derived an effective Hamiltonian describing leading-order relativistic (α^2) and radiative (α^3) corrections in the nonrecoil limit, and performed numerical calculations of the α^2-order correction in the adiabatic approximation, for 43 rovibrational levels of H_2^+. The theoretical uncertainty of the g-factor was estimated to about 10^{-7} due to uncalculated α^3-order corrections. It is worth noting that the g-factor of H_2^+ has so far been measured in only one experiment [4] for a mixture of three (unresolved) vibrational levels, with a relative uncertainty of 0.9 ppm. The experimental result was found to be in good agreement with the theoretical predictions of [3].

The present work pursues a double aim. Firstly, in order to enable state identification of (anti-)hydrogen molecular ions in Penning trap experiments, it is important to extend g-factor calculations to a wider range of rovibrational states, covering all possible states the ions may be found in. H_2^+ ions are conveniently produced by electron-impact ionization of H_2, which creates ions predominantly in $v = 0 - 12$, $L = 0 - 4$ [5] or may be produced in a selected rovibrational state using resonance-enhanced multi-photon ionization (REMPI) [6, 7]. Formation of $\bar{H}_2^-$ ions through the reaction $\bar{H}^+ + \bar{p} \to \bar{H}_2^- + e^+$, leading to production in $v = 0 - 8$, $L = 0 - 27$, has been proposed in [1]. Assuming these production schemes, and taking into account the possible use of the Stark quenching induced by the ion's motion in the trap's magnetic field to accelerate vibrational decay [8], 201 rovibrational levels (out of 481 bound levels in total [9]) have been identified as the most experimentally relevant. Other mechanisms to produce $\bar{H}_2^-$, using collisions between laser-excited $\bar{H}$ atoms, have been explored in [10], but resulting ro-vibrational distributions were not discussed in that work.

The second aim is to provide complete and accurate calculations of the α^2-order relativistic correction, that may serve as a reliable basis for future high-precision calculations of the g-factor through inclusion of higher-order corrections. To this end, we improve the calculations of Ref. [3] by performing extensive nonadiabatic (three-body) calculations, and by including recoil corrections, which had been neglected in [3]. This allows us to compute the α^2 correction with an (absolute) numerical uncertainty of about 10^{-13}.

II. THEORY

In this section, we write the theoretical expressions of corrections to the g-factor in the general case of a one-electron diatomic molecule. We thus consider a three-body system made of two nuclei, with masses m_1, m_2 and charges $Z_1 e$, $Z_2 e$, and one electron (mass $m_3 \equiv m_e$, charge $-e$). Particle positions are denoted by $\mathbf{R_1}$, $\mathbf{R_2}$, $\mathbf{R_3} \equiv \mathbf{R}_e$, and we use the internal coordinates $\mathbf{r_1} = \mathbf{R}_e - \mathbf{R_1}$, $\mathbf{r_2} = \mathbf{R}_e - \mathbf{R_2}$, and $\mathbf{r_{12}} = \mathbf{R_1} - \mathbf{R_2} = \mathbf{r_2} - \mathbf{r_1}$. The nuclear and electronic momenta are denoted by $\mathbf{P_1}, \mathbf{P_2}$ and $\mathbf{p}_e$, respectively.

The α^2-order relativistic correction to the g-factor including recoil terms can be described in an effective Hamiltonian approach [3, 11–16]. The first contribution at this order to the interaction of the electron spin $\mathbf{s}_e$ with an external magnetic field $\mathbf{B}$ is

$$H_1 = -g_e \frac{e}{2m_e} (\mathbf{s}_e \cdot \mathbf{B}) \frac{\mathbf{p}_e^2}{2m_e^2}, \tag{1}$$

where g_e is the free electron's g-factor. A second term comes from the electronic spin-orbit Hamiltonian H_{so} in the external field, which can be written in the center-of-mass frame as

$$H_{so} = \frac{g_e - 1}{2m_e^2} \left(\frac{Z_1}{r_1^3} (\mathbf{r_1} \times \boldsymbol{\pi}_e) + \frac{Z_2}{r_2^3} (\mathbf{r_2} \times \boldsymbol{\pi}_e) \right) \cdot \mathbf{s}_e - \frac{g_e}{2m_e} \left(\frac{Z_1}{m_1 r_1^3} (\mathbf{r_1} \times \mathbf{\Pi_1}) + \frac{Z_2}{m_2 r_2^3} (\mathbf{r_2} \times \mathbf{\Pi_2}) \right) \cdot \mathbf{s}_e, \tag{2}$$

where [3]

$$\begin{aligned}
\boldsymbol{\pi}_e &= \mathbf{p}_e + e\mathbf{A}(\mathbf{r}_{eC}) - e\frac{m_e}{M} \left(Z_1 \mathbf{A}(\mathbf{r}_{1C}) + Z_2 \mathbf{A}(\mathbf{r}_{2C}) - \mathbf{A}(\mathbf{r}_{eC}) \right), \\
\mathbf{\Pi}_1 &= \mathbf{P_1} - Z_1 e \mathbf{A}(\mathbf{r}_{1C}) - e\frac{m_1}{M} \left(Z_1 \mathbf{A}(\mathbf{r}_{1C}) + Z_2 \mathbf{A}(\mathbf{r}_{2C}) - \mathbf{A}(\mathbf{r}_{eC}) \right), \\
\mathbf{\Pi}_2 &= \mathbf{P_2} - Z_2 e \mathbf{A}(\mathbf{r}_{2C}) - e\frac{m_2}{M} \left(Z_1 \mathbf{A}(\mathbf{r}_{1C}) + Z_2 \mathbf{A}(\mathbf{r}_{2C}) - \mathbf{A}(\mathbf{r}_{eC}) \right), \\
\mathbf{A}(\mathbf{r}) &= \frac{1}{2} \mathbf{B} \times \mathbf{r}.
\end{aligned} \tag{3}$$

Here, $M = m_1 + m_2 + m_e$, and $\mathbf{r}_{eC}, \mathbf{r}_{1C}, \mathbf{r}_{2C}$ are the positions of the electron and nuclei with respect to the center of mass, which are given by

$$\begin{aligned}
\mathbf{r}_{1C} &= \frac{-(m_2 + m_e)\mathbf{r_1} + m_2 \mathbf{r_2}}{M}, \\
\mathbf{r}_{2C} &= \frac{m_1 \mathbf{r_1} - (m_1 + m_e)\mathbf{r_2}}{M}, \\
\mathbf{r}_{eC} &= \frac{m_1 \mathbf{r_1} + m_2 \mathbf{r_2}}{M}.
\end{aligned} \tag{4}$$

As shown in [3], the expressions of the momenta in Eq. (3) result from careful separation of the center-of-mass motion, following a procedure that was first proposed in [11, 12] in atomic systems. The latter results have been confirmed using the NRQED approach [14–16]. In the present work, we improve the treatment of Ref. [3] by keeping all recoil terms in Eqs. (2-4). The full contribution from H_{so} to the g-factor is then given by the following effective Hamiltonian (taking $g_e = 2$ in order to retain only the α^2-order contribution):

$$
\begin{aligned}
H_2 &= \frac{e}{2m_e}\sigma^{ij} s_e^i B^j\,, && (5)\\
\sigma^{ij} &= \frac{1}{2m_e}\left\{ c_1\left(\frac{r_1^2\delta^{ij} - r_1^i r_1^j}{r_1^3}\right) + c_2\left(\frac{r_2^2\delta^{ij} - r_2^i r_2^j}{r_2^3}\right) + c_{12}^{(1)}\left(\frac{\mathbf{r_1}\cdot\mathbf{r_2}\delta^{ij} - r_1^i r_2^j}{r_1^3}\right) + c_{12}^{(2)}\left(\frac{\mathbf{r_1}\cdot\mathbf{r_2}\delta^{ij} - r_1^i r_2^j}{r_2^3}\right)\right\},\\
c_1 &= \frac{1}{M^2}\left((M-m_e)m_1 Z_1 + m_1 m_e Z_1 Z_2 - \frac{(2M+m_1)(m_2+m_e)m_e Z_1^2}{m_1}\right),\\
c_2 &= \frac{1}{M^2}\left((M-m_e)m_2 Z_2 + m_2 m_e Z_1 Z_2 - \frac{(2M+m_2)(m_1+m_e)m_e Z_2^2}{m_2}\right),\\
c_{12}^{(1)} &= \frac{1}{M^2}\left((M-m_e)m_2 Z_1 - (m_1+m_e)m_e Z_1 Z_2 + \frac{(2M+m_1)m_2 m_e Z_1^2}{m_1}\right),\\
c_{12}^{(2)} &= \frac{1}{M^2}\left((M-m_e)m_1 Z_2 - (m_2+m_e)m_e Z_1 Z_2 + \frac{(2M+m_2)m_1 m_e Z_2^2}{m_2}\right).
\end{aligned}
$$

The last contribution comes from the second-order energy shift induced by the orbital Zeeman term H_Z and the spin-orbit coupling term:

$$
\begin{aligned}
\Delta E_{so-Z} &= 2\langle\psi_0|H_{so}Q(E_0-H_0)^{-1}QH_Z|\psi_0\rangle\,, && (6)\\
H_Z &= \left(\frac{e}{2m_e}\mathbf{L}_{eC} - \frac{Z_1 e}{2m_1}\mathbf{L}_{1C} - \frac{Z_2 e}{2m_2}\mathbf{L}_{2C}\right)\cdot\mathbf{B}
\end{aligned}
$$

Here, H_0 is the nonrelativistic (Schrödinger) Hamiltonian of the three-body system, ψ_0 the wave function for the rovibrational state under consideration, E_0 the corresponding nonrelativistic energy level, and Q is a projection operator on a subspace orthogonal to ψ_0. $\mathbf{L}_{eC}, \mathbf{L}_{1C}, \mathbf{L}_{2C}$ are the angular momenta of the electron and nuclei about the center of mass. Again, in our calculations we take into account all the recoil terms in H_{so} and H_Z.

Corrections to the electronic g-factor can be deduced from Eqs. (1), (5) and (6). The H_1 term [Eq. (1)] induces a correction for a rovibrational state (v, L),

$$
\frac{\Delta g_1(v,L)}{g_e} = -\frac{\langle v,L|\mathbf{p}_e^2|v,L\rangle}{2m_e}. \tag{7}
$$

The other terms, H_2 [Eq. (5)] and ΔE_{so-Z} [Eq. (6)] are anisotropic. This is linked to the departure from spherical symmetry in a molecule, which led Hegstrom to introduce a g tensor in Ref. [3]. Alternatively, the results can be expressed in terms of a g-factor similarly to the atomic case, the difference being that in a molecule, the g-factor acquires a dependence on the magnetic quantum number M.

The term H_2 may be decomposed into irreducible tensor components as follows:

$$
\begin{aligned}
H_2 &= \sigma^{(0)}\left(\mathbf{s}_e\cdot\mathbf{B}\right) + \sigma^{(2)}\cdot\left(\mathbf{s}_e\otimes\mathbf{B}\right)^{(2)}\,, && (8)\\
\sigma^{(0)} &= \frac{1}{2m_e}\frac{2}{3}\left(\frac{c_1}{r_1} + \frac{c_2}{r_2} + \frac{c_{12}^{(1)}\mathbf{r_1}\cdot\mathbf{r_2}}{r_1^3} + \frac{c_{12}^{(2)}\mathbf{r_1}\cdot\mathbf{r_2}}{r_2^3}\right), && (9)\\
\sigma^{(2)} &= \frac{1}{2m_e}\frac{1}{3}\left(\frac{c_1 Q_{11}^{(2)}}{r_1^3} + \frac{c_2 Q_{22}^{(2)}}{r_2} + \frac{c_{12}^{(1)}Q_{12}^{(2)}}{r_1^3} + \frac{c_{12}^{(2)}Q_{12}^{(2)}}{r_2^3}\right), && (10)
\end{aligned}
$$

where $Q_{ab}^{(2)}$ $(a,b = 1,2)$ is the tensor having the Cartesian components

$$
Q_{ab}^{(2)ij} = \mathbf{r}_a\cdot\mathbf{r}_b\delta^{ij} - 3r_a^i r_b^j. \tag{11}
$$

The second-order term ΔE_{so-Z} can also be decomposed into irreducible tensor components following the Appendix B of [17]. One obtains

$$
\Delta E_{so-Z} = \frac{\langle vL\|\mathbf{T}^{(0)}\|vL\rangle}{\sqrt{2L+1}}\langle\mathbf{s}_e\cdot\mathbf{B}\rangle + \frac{\langle vL\|\mathbf{T}^{(2)}\|vL\rangle}{\langle L\|\left(\mathbf{L}\otimes\mathbf{L}\right)^{(2)}\|L\rangle}\left\langle\left(\mathbf{L}\otimes\mathbf{L}\right)^{(2)}\cdot\left(\mathbf{s}_e\otimes\mathbf{B}\right)^{(2)}\right\rangle, \tag{12}
$$

where the orbital reduced matrix elements are given by [17]

$$T_s = \frac{\langle vL\|\mathbf{T}^{(0)}\|vL\rangle}{\sqrt{2L+1}} = \frac{1}{3}\left(a_- + a_0 + a_+\right), \tag{13}$$

$$T_t = \frac{\langle vL\|\mathbf{T}^{(2)}\|vL\rangle}{\sqrt{2L+1}} = \frac{\sqrt{L(L+1)(2L-1)(2L+3)}}{3}\left(-\frac{a_-}{L(2L-1)} + \frac{a_0}{L(L+1)} - \frac{a_+}{(L+1)(2L+3)}\right). \tag{14}$$

Here, a_-, a_0, and a_+ are the contributions to the second-order perturbation term from intermediate states of angular momentum $L-1, L$, and $L+1$, respectively:

$$a_- = -\frac{1}{2L+1}\sum_{n\neq 0}\frac{\langle vL\|\mathbf{O}_Z^{(1)}\|v_nL-1\rangle\langle v_nL-1\|\mathbf{O}_{so}^{(1)}\|vL\rangle}{E_0-E_n}, \tag{15}$$

$$a_0 = \frac{1}{2L+1}\sum_{n\neq 0}\frac{\langle vL\|\mathbf{O}_Z^{(1)}\|v_nL\rangle\langle v_nL\|\mathbf{O}_{so}^{(1)}\|vL\rangle}{E_0-E_n}, \tag{16}$$

$$a_+ = -\frac{1}{2L+1}\sum_{n\neq 0}\frac{\langle vL\|\mathbf{O}_Z^{(1)}\|v_nL+1\rangle\langle v_nL+1\|\mathbf{O}_{so}^{(1)}\|vL\rangle}{E_0-E_n}, \tag{17}$$

with

$$\mathbf{O}_Z^{(1)} = \frac{e}{m_e}\mathbf{L}_{eC} - \frac{Z_1e}{m_1}\mathbf{L}_{1C} - \frac{Z_2e}{m_2}\mathbf{L}_{2C}, \tag{18}$$

$$\mathbf{O}_{so}^{(1)} = \frac{1}{2m_e^2}\left(\frac{Z_1}{r_1^3}(\mathbf{r_1}\times\mathbf{p}_e) + \frac{Z_2}{r_2^3}(\mathbf{r_2}\times\mathbf{p}_e)\right) - \frac{1}{m_e}\left(\frac{Z_1}{m_1r_1^3}(\mathbf{r_1}\times\mathbf{P_1}) + \frac{Z_2}{m_2r_2^3}(\mathbf{r_2}\times\mathbf{P_2})\right). \tag{19}$$

Finally, the g-factor including the complete α^2-order relativistic correction is given by

$$g(v,L,M) = g_s(v,L) + \frac{3M^2 - L(L+1)}{\sqrt{L(L+1)(2L-1)(2L+3)}}\,g_t(v,L), \tag{20}$$

where the scalar part of the g-factor is

$$\frac{g_s(v,L)}{g_e} = 1 - \frac{\langle vL|\mathbf{p}_e^2|vL\rangle}{2m_e^2} + \sigma_s + T_s\,, \tag{21}$$

and the tensor part is

$$\frac{g_t(v,L)}{g_e} = \sigma_t + T_t\,, \tag{22}$$

with the definitions:

$$\sigma_s = \frac{\langle vL\|\sigma^{(0)}\|vL\rangle}{\sqrt{2L+1}},\quad \sigma_t = \frac{\langle vL\|\sigma^{(2)}\|vL\rangle}{\sqrt{2L+1}}. \tag{23}$$

The expressions (21-22) are correct to order α^2. The approximation $g_e \simeq 2$ has been used in the last two terms of Eq. (21) (which comes to neglecting terms of order $(\alpha/\pi)(\sigma_s + T_s)$), and in Eq. (22).

Now, we can relate the above expressions to those given in Ref. [3]. In that work, the g tensor is defined by writing the interaction of the electron spin with the magnetic field in the form

$$H_{\text{eff}} = \frac{e}{2m_e}\sum_{i,j} g_{ij}s_e^iB^j\,, \tag{24}$$

and the components $g_\perp = g_{xx} = g_{yy}$ and $g_\parallel = g_{zz}$ are calculated with the z axis taken to be along the internuclear axis (let us recall that all calculations were done in the Born-Oppenheimer approximation). The g-factor of a (v,L,M) state can be obtained from these quantities through the relationship [18]

$$g(v,L,M) = \frac{2}{3}g_\perp + \frac{1}{3}g_\parallel + \frac{2}{3}\frac{3M^2 - L(L+1)}{(2L-1)(2L+3)}\left(g_\perp - g_\parallel\right). \tag{25}$$

Comparing Eqs. (25) and (20) one gets

$$g_s = \frac{2}{3}g_\perp + \frac{1}{3}g_\parallel, \tag{26}$$

$$g_t = \frac{2}{3}\sqrt{\frac{L(L+1)}{(2L-1)(2L+3)}}\left(g_\perp - g_\parallel\right). \tag{27}$$

III. NUMERICAL RESULTS

In order to calculate the scalar [Eq. (21)] and tensor [Eq. (22)] corrections to the g-factor, the three-body Schrödinger equation is solved using a variational expansion of the wavefunction involving exponentials of interparticle distances [8, 9, 19]:

$$\begin{aligned}
&\Psi_0^{(vL)}(\mathbf{R},\mathbf{r}_1) = \sum_{l_1+l_2=L} \mathcal{Y}_{LM}^{l_1l_2}(\hat{\mathbf{R}},\hat{\mathbf{r}}_1)G_{l_1l_2}(R,r_1,r_2),\\
&\mathcal{Y}_{LM}^{l_1l_2}(\hat{\mathbf{R}},\hat{\mathbf{r}}_1) = R^{l_1}r_1^{l_2}\left\{Y_{l_1}(\hat{\mathbf{R}})\otimes Y_{l_2}(\hat{\mathbf{r}}_1)\right\}_{LM},\\
&G_{l_1l_2}(R,r_1,r_2) = \sum_{n=1}^{N/2}\left\{C_n\,\mathrm{Re}\left[e^{-\alpha_nR-\beta_nr_1-\gamma_nr_2}\right] + D_n\,\mathrm{Im}\left[e^{-\alpha_nR-\beta_nr_1-\gamma_nr_2}\right]\right\}.
\end{aligned} \tag{28}$$

where $\mathbf{R}$ is the internuclear vector, and $\mathbf{r}_1, \mathbf{r}_2$ the electron's position with respect to both nuclei. The complex exponents α_n, β_n and γ_n are generated pseudorandomly in several intervals. The interval bounds as well as the number of basis functions N_{i,l_1} in each interval i and angular momentum subset $\{l_1, l_2\}$ (keeping the total basis length N constant), have been optimized for a few tens of rovibrational states. This was sufficient to have good convergence for all the states considered in this work, because the wave functions (and therefore the optimal values of the parameters) evolve only slowly with the rotational quantum number.

The expectation values of $\mathbf{p}_e^2$, $\sigma^{(0)}$, and $\sigma^{(2)}$ [Eqs. (9-10)] are obtained with 9-10 digits of accuracy, using basis lengths N between 2000 and 5600, depending on the operator and on the rovibrational state. The second-order terms T_s and T_t [Eqs. (13-14)] are more challenging to calculate with high accuracy. However, they are still simpler than the singular second-order terms discussed in [17]. The basis set used for intermediate states includes "regular" subsets where the interval bounds for the exponents α_n, β_n, γ_n are the same as those used for to obtain the zero-order wavefunction $\Psi_0^{(vL)}$. In contradistinction with the singular terms evaluated in [17], it is not strictly necessary to add "singular" subsets containing higher exponents, but we found that the inclusion of two additional subsets with exponents β_n, γ_n up to 10 improves the convergence. Overall, a 9-digit accuracy is achieved for all rovibrational states using intermediate basis sets of length $N' \sim 4000 - 12000$.

Detailed numerical results for g_s and g_t are shown in Table I and compared with those of [3] for 38 rovibrational states. Differences with respect to Hegstrom's values amount to a few 10^{-8}, or a few 10^{-3} in relative value, which is consistent with the order of magnitude of nonadiabatic and recoil corrections. Complete results for the 201 states identified as the most experimentally relevant are given in Tables II and III. All digits are converged, so that the uncertainty of the α^2-order relativistic correction to the g-factor is smaller than 10^{-13}.

IV. CONCLUSION

The complete relativistic corrections of order α^2 to the g-factor have been calculated with high accuracy for a wide range of rovibrational states. For the time being, the accuracy gain is not relevant for experiments since the theoretical uncertainty due to uncalculated α^3-order radiative corrections is about 0.1 ppm [3]. However, these results are a first step towards high-precision calculation of the g-factor; in this perspective, it was important to show that the numerically challenging second-order contribution induced by the Zeeman and spin-orbit Hamiltonians can be evaluated with high precision, so that they do not represent a serious limitation regarding the achievable accuracy level.

These results may now be readily used to calculate spin-flip transition frequencies in the magnetic field of a Penning trap. Precise knowledge of these frequencies is required for nondestructive identification of the molecule's internal state in future experiments with H_2^+ and $\bar{\mathrm{H}}_2^-$ [1]. To achieve this, one should diagonalize the Hamiltonian $H_Z + H_{\mathrm{hfs}}$, where H_Z and H_{hfs} are respectively the Zeeman and hyperfine structure Hamiltonians. The Zeeman effect has been studied in [20], and the hyperfine structure has been investigated in detail in [17, 21, 22]. Using the results of those

v	L	$\langle \mathbf{p}_e^2 \rangle$	σ_s	T_s	$1-g_s/g_e$ (this work)	$1-g_s/g_e$ [3]	σ_t	T_t	$-g_t/g_e$ (this work)	$-g_t/g_e$ [3]
0	0	1.188584982	0.197953422	0.014090083	20.3552762	20.359	0.000000000	0.000000000	0.0000000	0.000
0	1	1.187531896	0.197777979	0.014101909	20.3359500	20.340	-0.032682214	0.008941067	0.5286804	0.526
0	2	1.185438336	0.197429194	0.014125424	20.2975286	20.302	-0.035634946	0.007569228	0.4455650	0.444
0	3	1.182329094	0.196911198	0.014160360	20.2404665	20.245	-0.040692364	0.007330723	0.4286492	0.427
0	4	1.178240299	0.196230013	0.014206324	20.1654259	20.169	-0.045474983	0.007258466	0.4206783	0.419
0	6	1.167317949	0.194410381	0.014329191	19.9649660	19.969	-0.053897721	0.007247903	0.4100693	0.408
0	8	1.153136628	0.192047838	0.014488785	19.7046887	19.709	-0.061075213	0.007301354	0.4000008	0.398
0	10	1.136248917	0.189234465	0.014678648	19.3947475	19.399	-0.067289815	0.007384038	0.3887244	0.387
0	12	1.117244006	0.186068437	0.014891527	19.0459880	19.051	-0.072714188	0.007484065	0.3758892	0.374
0	14	1.096705506	0.182647005	0.015119723	18.6691807	18.674	-0.077452803	0.007594643	0.3614692	0.360
0	16	1.075181550	0.179061504	0.015355330	18.2744772	18.280	-0.081569610	0.007710556	0.3455422	0.344
0	18	1.053167409	0.175394464	0.015590341	17.8710960	17.877	-0.085102995	0.007827188	0.3282231	0.327
0	20	1.031098644	0.171718462	0.015816634	17.4672018	17.473	-0.088073738	0.007940156	0.3096381	0.308
0	26	0.968081716	0.161222808	0.016356395	16.3194982	16.326	-0.093621519	0.008212290	0.2474918	0.247
1	0	1.159234438	0.193064762	0.014421001	19.8165041	19.821	0.000000000	0.000000000	0.0000000	0.000
1	1	1.158250614	0.192900862	0.014431537	19.7984759	19.803	-0.031894491	0.009149724	0.4933508	0.491
1	2	1.156294965	0.192575061	0.014452475	19.7626398	19.767	-0.034772716	0.007744201	0.4157136	0.414
1	3	1.153391076	0.192091290	0.014483546	19.7094287	19.714	-0.039702043	0.007497771	0.3998213	0.398
1	4	1.149573307	0.191455274	0.014524357	19.6394735	19.644	-0.044359752	0.007420710	0.3922428	0.390
2	0	1.132170502	0.188557196	0.014689251	19.3216577	19.327	0.000000000	0.000000000	0.0000000	0.000
2	1	1.131253178	0.188404379	0.014698386	19.3048846	19.310	-0.031058959	0.009318676	0.4586657	0.457
2	2	1.129429961	0.188100651	0.014716519	19.2715486	19.276	-0.033858126	0.007885496	0.3864088	0.385
2	3	1.126723309	0.187649753	0.014743382	19.2220626	19.227	-0.038651541	0.007632107	0.3715242	0.370
2	4	1.123165936	0.187057137	0.014778579	19.1570284	19.162	-0.043176666	0.007550435	0.3643344	0.363
3	0	1.107303081	0.184415723	0.014889282	18.8694330	18.875	0.000000000	0.000000000	0.0000000	0.000
3	1	1.106449987	0.184273612	0.014896877	18.8538819	18.859	-0.030170737	0.009444398	0.4246628	0.422
3	2	1.104754698	0.183991205	0.014911929	18.8229807	18.828	-0.032885813	0.007990107	0.3576827	0.356
3	3	1.102238625	0.183572071	0.014934166	18.7771239	18.782	-0.037534640	0.007730789	0.3437892	0.342
3	4	1.098932954	0.183021406	0.014963189	18.7168863	18.722	-0.041918645	0.007644688	0.3369849	0.335
4	0	1.084559830	0.180628298	0.015014469	18.4588976	18.465	0.000000000	0.000000000	0.0000000	0.000
4	1	1.083769176	0.180496594	0.015020357	18.4445458	18.450	-0.029223896	0.009522682	0.3913838	0.389
4	2	1.082198272	0.180234919	0.015031993	18.4160343	18.421	-0.031849229	0.008054448	0.3295705	0.328
4	3	1.079867562	0.179846681	0.015049100	18.3737409	18.379	-0.036343726	0.007790306	0.3166502	0.315
4	4	1.076806815	0.179336839	0.015071268	18.3182157	18.323	-0.040576987	0.007699943	0.3102274	0.309
6	0	1.045243047	0.174081855	0.015007517	17.7610388	17.767	0.000000000	0.000000000	0.0000000	0.000
8	0	1.013989580	0.168879593	0.014587468	17.2282898	17.236	0.000000000	0.000000000	0.0000000	0.000
10	0	0.990865938	0.165032806	0.013643118	16.8677417	16.878	0.000000000	0.000000000	0.0000000	0.000
12	0	0.976285366	0.162610698	0.012022406	16.6948098	16.705	0.000000000	0.000000000	0.0000000	0.000

TABLE I: Relativistic corrections to the g-factor for rovibrational states (v, L) of H_2^+, and comparison with previous calculations. Column 3-5 (resp. 8-9) are the contributions to the scalar (tensor) part of the g-factor (see Eqs. (21) and (22), respectively), in atomic units. The values of $1 - g_s/g_e$ (resp. $-g_t/g_e$) obtained in this work and in Ref. [3] are given in columns 6-7 (resp. 10-11); they should be multiplied by 10^{-6}.

works, the spin-flip transition frequencies can be obtained with a relative uncertainty of 0.1 ppm, limited by the uncertainty of the g-factor, which is expected to be sufficient for unambiguous identification of the internal state.

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L/v	0	1	2	3	4	5	6	7	8	9	10	11	12
0	20.3552762	19.8165041	19.3216577	18.8694330	18.4588976	18.0894923	17.7610388	17.4737565	17.2282898	17.0257451	16.8677417	16.7564767	16.6948098
1	20.3359500	19.7984759	19.3048846	18.8538819	18.4445458	18.0763272	17.7490588	17.4629723	17.2187253	17.0174399	16.8607533	16.7508857	16.6907247
2	20.2975286	19.7626398	19.2715486	18.8229807	18.4160343	18.0501813	17.7252762	17.4415750	17.1997625	17.0009915	16.8469365	16.7398629	16.6827166
3	20.2404665	19.7094287	19.2220626	18.7771239	18.3737409	18.0114167	17.6900395	17.4099013	17.1717278	16.9767191	16.8266059	16.7237234	
4	20.1654259	19.6394735	19.1570284	18.7168863	18.3182157	17.9605617	17.6438568	17.3684420	17.1350982	16.9450894	16.8002231	16.7029297	
5	20.0732560	19.5535825	19.0772169	18.6430043	18.2501637	17.8982925	17.5873794	17.3178273	17.0904867	16.9067036	16.7683843		
6	19.9649660	19.4527165	18.9835440	18.5563529	18.1704225	17.8254135	17.5213827	17.2588078	17.0386253	16.8622818	16.7318065		
7	19.8416965	19.3379607	18.8770441	18.4579200	18.0799385	17.7428343	17.4467442	17.1922353	16.9803466	16.8126464			
8	19.7046887	19.2104957	18.7588427	18.3487813	17.9797424	17.6515461	17.3644222	17.1190422	16.9165655	16.7587058			
9	19.5552544	19.0715693	18.6301291	18.2300736	17.8709248	17.5525999	17.2754351	17.0402223	16.8482622				
10	19.3947475	18.9224690	18.4921312	18.1029717	17.7546143	17.4470851	17.1808417	16.9568141	16.7764672				
11	19.2245376	18.7644980	18.3460929	17.9686672	17.6319573	17.3361123	17.0817256	16.8698863					
12	19.0459880	18.5989543	18.1932540	17.8283498	17.5041025	17.2207971	16.9791819	16.7805270					
13	18.8604366	18.4271127	18.0348350	17.6831936	17.3721865	17.1022504	16.8743077						
14	18.6691807	18.2502117	17.8720236	17.5343453	17.2373250	16.9815686	16.7681961						
15	18.4734657	18.0694430	17.7059667	17.3829164	17.1006059	16.8598302							
16	18.2744772	17.8859442	17.5377637	17.2299789	16.9630866	16.7380940							
17	18.0733360	17.7007953	17.3684638	17.0765631	16.8257931	16.6174014							
18	17.8710960	17.5150169	17.1990654	16.9236587	16.6897234								
19	17.6687439	17.3295713	17.0305181	16.7722177	16.5558524								
20	17.4672018	17.1453645	16.8637261	16.6231601									
21	17.2673297	16.9632512	16.6995538	16.4773816									
22	17.0699309	16.7840401	16.5388337										
23	16.8757577	16.6085010	16.3823749										
24	16.6855183	16.4373730											
25	16.4998839	16.2713749											
26	16.3194982												
27	16.1449866												

TABLE II: Values of $1 - g_s/g_e$ for selected rovibrational states of H_2^+. All values should be multiplied by 10^{-6}.

L/v	0	1	2	3	4	5	6	7	8	9	10	11	12
1	0.5286804	0.4933508	0.4586657	0.4246628	0.3913838	0.3588750	0.3271877	0.2963777	0.2665050	0.2376304	0.2098133	0.1831034	0.1575306
2	0.4455650	0.4157136	0.3864088	0.3576827	0.3295705	0.3021114	0.2753488	0.2493301	0.2241055	0.1997269	0.1762437	0.1536973	0.1321115
3	0.4286492	0.3998213	0.3715242	0.3437892	0.3166502	0.2901453	0.2643165	0.2392095	0.2148732	0.1913570	0.1687085	0.1469666	
4	0.4206783	0.3922428	0.3643344	0.3369849	0.3102274	0.2840996	0.2586433	0.2339035	0.2099286	0.1867673	0.1644649	0.1430589	
5	0.4150504	0.3868176	0.3591138	0.3319683	0.3054166	0.2794952	0.2542461	0.2297144	0.2059474	0.1829939	0.1608970		
6	0.4100693	0.3819643	0.3543914	0.3273812	0.3009670	0.2751856	0.2500811	0.2256979	0.2020812	0.1792812	0.1573383		
7	0.4051363	0.3771253	0.3496511	0.3227443	0.2964386	0.2707701	0.2457841	0.2215249	0.1980380	0.1753692			
8	0.4000008	0.3720682	0.3446783	0.3178614	0.2916517	0.2660872	0.2412098	0.2170644	0.1936976	0.1711542			
9	0.3945480	0.3666876	0.3393763	0.3126447	0.2865271	0.2610618	0.2362908	0.2122591	0.1890127				
10	0.3887244	0.3609349	0.3337016	0.3070552	0.2810305	0.2556658	0.2310035	0.2070884	0.1839655				
11	0.3825070	0.3547903	0.3276373	0.3010791	0.2751506	0.2498907	0.2253419	0.2015482					
12	0.3758892	0.3482490	0.3211806	0.2947153	0.2688882	0.2437388	0.2193092	0.1956433					
13	0.3688738	0.3413154	0.3143371	0.2879704	0.2622509	0.2372185	0.2129148						
14	0.3614692	0.3339987	0.3071167	0.2808551	0.2552503	0.2303416	0.2061709						
15	0.3536873	0.3263113	0.2995324	0.2733831	0.2478997	0.2231220							
16	0.3455422	0.3182675	0.2915987	0.2655686	0.2402141	0.2155743							
17	0.3370488	0.3098826	0.2833311	0.2574275	0.2322085	0.2077131							
18	0.3282231	0.3011725	0.2747452	0.2489747	0.2238980								
19	0.3190809	0.2921527	0.2658563	0.2402257	0.2152970								
20	0.3096381	0.2828389	0.2566800	0.2311950									
21	0.2999100	0.2732463	0.2472305	0.2218961									
22	0.2899119	0.2633891	0.2375216										
23	0.2796579	0.2532811	0.2275659										
24	0.2691617	0.2429350											
25	0.2584359	0.2323621											
26	0.2474918												
27	0.2363399												

TABLE III: Values of $-g_t/g_e$ for selected rovibrational states of H_2^+. All values should be multiplied by 10^{-6}.