

Hyperfine structure in the hydrogen molecular ion

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The hyperfine splitting of energy levels in the H_2^+ molecular ion is calculated within the framework of the spin-dependent part of the Breit-Pauli Hamiltonian. This is the first *ab initio* calculation based on the precise variational solution of the three-body Schrödinger equation. It is shown that inclusion of the nuclear spin-spin tensor interaction, neglected in previous theoretical considerations, brings agreement with the most precise hyperfine transition measurements obtained by Jefferts to about 1 kHz for the lower-frequency intervals in the 5–100 MHz range. Finally, we investigate the hyperfine structure of some transitions, candidates for high-precision two-photon spectroscopy.

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The present study of the hydrogen molecular ion is motivated by recent projects of precise spectroscopy experiments [1,2] aimed at a sub-ppb precision. The accuracy of the non-relativistic energies for the rovibrational states of H_2^+ was constantly increased during recent years [3–8] and achieved a precision of 10^{-15} – 10^{-24} a.u. The leading-order relativistic and radiative corrections required for precise theoretical determination of the optical transition frequencies became available recently [9,10].

The knowledge of the hyperfine splitting is of great importance for accurate comparison between theory and experiment to comply with the aimed goals of sub-ppb spectroscopy. Beyond that, hyperfine structure has a fundamental interest in studies of nuclear properties [11] and in astrophysics [12]. So far, several radio-frequency experiments have provided information on the hyperfine structure of H_2^+ [13,14]; in [13] an uncertainty of ± 1.5 kHz was assigned to the measured hyperfine transition frequencies. Theoretical calculations of the spin Hamiltonian coupling constants were performed in many works by means of the adiabatic approximation (see, for example, Refs. [12,15]). Nonadiabatic corrections were considered in Ref. [16], and shown to be of great importance, in particular for the leading electron-nuclear spin-spin interaction, where they contribute at about the 600 kHz level. The nuclear spin-rotation coupling constant has been calculated in Ref. [17] with a reasonably good accuracy.

The aim of this work is to present extended variational calculation of the hyperfine coupling constants of the rovibrational levels in the H_2^+ molecular ion. We restrict ourselves to the Breit-Pauli interaction only, still taking account of the anomalous magnetic moment of an electron. This allows us to say that our theoretical results for the coupling constants are limited to the relative accuracy of $O(\alpha^2)$. It corresponds to maximal uncertainty of about 50–100 kHz in determination of the hyperfine splitting of a rovibrational level.

The following notations are used throughout this paper. \mathbf{P}_1 , \mathbf{P}_2 , and \mathbf{p}_e are the momenta and \mathbf{R}_1 , \mathbf{R}_2 , \mathbf{r}_e are the coordinates of protons and electron with respect to the center of mass of a molecule, and

$$\mathbf{r}_1 = \mathbf{r}_e - \mathbf{R}_1, \quad \mathbf{r}_2 = \mathbf{r}_e - \mathbf{R}_2, \quad \mathbf{R} = \mathbf{R}_2 - \mathbf{R}_1.$$

$\mu_e = -(1 + \kappa_e)$ is the magnetic moment of an electron in Bohr magnetons, while $\mu_p = 1 + \kappa_p$ is the magnetic moments of proton in nuclear magnetons. \mathbf{I}_1 , \mathbf{I}_2 , and \mathbf{s}_e are the spin operators of nuclei and electron. We use the CODATA02 recommended values of the fundamental constants [18] for our calculations.

The variational bound-state wave functions were obtained by solving the three-body Schrödinger equation with Coulomb interaction using the variational approach, which has been discussed in a variety of works [19,20]. Details and the particular strategy of choice of the variational nonlinear parameters and basis structure that have been adopted in the present work can be found in [4].

Briefly, the wave function for a state with a total orbital angular momentum L and of a total spatial parity $\pi = (-1)^L$ is expanded as follows:

$$\begin{aligned} \Psi_{LM}^\pi(\mathbf{R}, \mathbf{r}_1) &= \sum_{l_1+l_2=L} \mathcal{Y}_{LM}^{l_1 l_2}(\hat{\mathbf{R}}, \hat{\mathbf{r}}_1) G_{l_1 l_2}^{L\pi}(R, r_1, r_2), \\ G_{l_1 l_2}^{L\pi}(R, r_1, r_2) &= \sum_{n=1}^N [C_n \text{Re}(e^{-\alpha_n R - \beta_n r_1 - \gamma_n r_2}) \\ &\quad + D_n \text{Im}(e^{-\alpha_n R - \beta_n r_1 - \gamma_n r_2})], \end{aligned} \quad (1)$$

where the complex exponents α , β , and γ are generated in a pseudorandom way. The use of complex exponents instead of real ones allows us to improve the convergence rate.

For H_2^+ the variational solution with this basis set provides an accuracy of about 10^{-14} – 10^{-15} a.u. for the nonrelativistic energies at basis lengths of $N=4000$ – 5000 .

The leading correction to the nonrelativistic energy is the α^2 -order relativistic correction determined by the Breit-Pauli Hamiltonian. Its derivation can be found in many textbooks; see, for example, Refs. [21,22]. For a composite particle the finite-size electromagnetic structure should be taken into account; the interaction of such a particle with an electromagnetic field in the relativistic formalism is discussed in Ref. [23]. Kinoshita and Nio have shown how the electromagnetic

TABLE I. Coefficients of the effective spin Hamiltonian (3) (in MHz); relative theoretical accuracy is $O(\alpha^2)$. $a[b]=a \times 10^b$.

L	ν	b_F	c_e	c_l	d_1	d_2
1	0	922.992	42.4163	-4.168 [-02]	128.490	-0.2975
1	1	898.809	39.8122	-4.035 [-02]	120.337	-0.2849
1	2	876.454	37.3276	-3.893 [-02]	112.579	-0.2722
1	3	855.812	34.9468	-3.742 [-02]	105.169	-0.2593
1	4	836.784	32.6546	-3.583 [-02]	98.0587	-0.2462
1	5	819.280	30.4372	-3.415 [-02]	91.2043	-0.2330
3	0	917.591	41.7866	-4.076 [-02]	127.013	-0.2917
3	1	893.755	39.2152	-3.944 [-02]	118.940	-0.2791
3	2	871.728	36.7608	-3.803 [-02]	111.255	-0.2665
3	3	851.398	34.4078	-3.654 [-02]	103.910	-0.2538
3	4	832.668	32.1416	-3.496 [-02]	96.8597	-0.2409
L	ν	c_e	L	ν	c_e	
2	0	42.1625	4	0	41.2942	
2	1	39.5716	4	1	38.7483	
2	2	37.0992	4	2	36.3175	
2	3	34.7295	4	3	33.9864	
2	4	32.4479	4	4	31.7404	

structure of nuclei can be incorporated into the Breit-Pauli Hamiltonian using nonrelativistic QED theory [24].

The Breit-Pauli Hamiltonian for a system of three particles is defined by a sum of pairwise interactions. The electron-proton and proton-proton interactions are expressed as

$$\begin{aligned}
V_{ep} = \alpha^2 & \left[\frac{1+2\kappa_e}{2m_e^2} \left(\frac{1}{r_1^3} (\mathbf{r}_1 \times \mathbf{p}_e) + \frac{1}{r_2^3} (\mathbf{r}_2 \times \mathbf{p}_e) \right) \mathbf{s}_e \right. \\
& - \frac{1+\kappa_e}{m_e m_p} \left(\frac{1}{r_1^3} (\mathbf{r}_1 \times \mathbf{P}_1) + \frac{1}{r_2^3} (\mathbf{r}_2 \times \mathbf{P}_2) \right) \mathbf{s}_e \\
& - \frac{1+2\kappa_p}{2m_p^2} \left(\frac{1}{r_1^3} (\mathbf{r}_1 \times \mathbf{P}_1) \mathbf{I}_1 + \frac{1}{r_2^3} (\mathbf{r}_2 \times \mathbf{P}_2) \mathbf{I}_2 \right) \\
& + \frac{1+\kappa_p}{m_e m_p} \left(\frac{1}{r_1^3} (\mathbf{r}_1 \times \mathbf{p}_e) \mathbf{I}_1 + \frac{1}{r_2^3} (\mathbf{r}_2 \times \mathbf{p}_e) \mathbf{I}_2 \right) \\
& - \frac{8\pi \mu_e \mu_p}{3 m_e m_p} [\delta(\mathbf{r}_1) (\mathbf{s}_e \cdot \mathbf{I}_1) + \delta(\mathbf{r}_2) (\mathbf{s}_e \cdot \mathbf{I}_2)] \\
& \left. + \frac{\mu_e \mu_p}{m_e m_p} \left(\frac{r_1^2 (\mathbf{s}_e \cdot \mathbf{I}_1) - 3(\mathbf{r}_1 \cdot \mathbf{s}_e)(\mathbf{r}_1 \cdot \mathbf{I}_1)}{r_1^5} + (1 \leftrightarrow 2) \right) \right]
\end{aligned}$$

TABLE II. Comparison of calculated coefficients of the effective spin Hamiltonian (in MHz).

ν	b_F		c		d		f	
	[16]	This work	[16]	This work	[16]	This work	[17]	This work
0	922.990	922.992	128.482	128.490	42.421	42.416	-0.0417	-0.0417
4	836.773	836.784	98.008	98.059	32.658	32.655	-0.0362	-0.0358
5	819.268	819.280	91.145	91.204	30.441	30.437	-0.0346	-0.0341

$$\begin{aligned}
V_{pp} = \alpha^2 & \left[-\frac{1+2\kappa_p}{2m_p^2} \left(\frac{(-\mathbf{R} \times \mathbf{P}_1) \mathbf{I}_1}{R^3} + \frac{(\mathbf{R} \times \mathbf{P}_2) \mathbf{I}_2}{R^3} \right) \right. \\
& - \frac{\mu_p}{m_p^2} \left(\frac{(-\mathbf{R} \times \mathbf{P}_1) \mathbf{I}_2}{R^3} + \frac{(\mathbf{R} \times \mathbf{P}_2) \mathbf{I}_1}{R^3} \right) - \frac{8\pi \mu_p^2}{3 m_p^2} \delta(\mathbf{R}) \\
& \left. \times (\mathbf{I}_1 \cdot \mathbf{I}_2) + \frac{\mu_p^2}{m_p^2} \left(\frac{R^2 (\mathbf{I}_1 \cdot \mathbf{I}_2) - 3(\mathbf{R} \cdot \mathbf{I}_1)(\mathbf{R} \cdot \mathbf{I}_2)}{R^5} \right) \right]. \quad (2)
\end{aligned}$$

Nuclear spin-spin contact interaction is either negligible, for even L , or vanishes, for odd L , and it will be omitted from further consideration.

After averaging over space variables one can express interaction in terms of an effective spin Hamiltonian:

$$\begin{aligned}
H_{\text{eff}} = & b_F (\mathbf{I} \cdot \mathbf{s}_e) + c_e (\mathbf{L} \cdot \mathbf{s}_e) + c_l (\mathbf{L} \cdot \mathbf{I}) \\
& + \frac{d_1}{(2L-1)(2L+3)} \left(\frac{2}{3} \mathbf{L}^2 (\mathbf{I} \cdot \mathbf{s}_e) - [(\mathbf{L} \cdot \mathbf{I})(\mathbf{L} \cdot \mathbf{s}_e) \right. \\
& \left. + (\mathbf{L} \cdot \mathbf{s}_e)(\mathbf{L} \cdot \mathbf{I}) \right) + \frac{d_2}{(2L-1)(2L+3)} \left(\frac{1}{3} \mathbf{L}^2 \mathbf{I}^2 \right. \\
& \left. - \frac{1}{2} (\mathbf{L} \cdot \mathbf{I}) - (\mathbf{L} \cdot \mathbf{I})^2 \right). \quad (3)
\end{aligned}$$

In our notation for the effective Hamiltonian we tried to follow Ref. [25]. Coefficients are obtained numerically by evaluating vector and tensor operators from (2), which depend on the spatial degrees of freedom. An analytical integration of the matrix elements is then reduced to integrals of the form

$$\Gamma_{lmn}(\alpha, \beta, \gamma) = \int \int r_1^l r_2^m r_{12}^n e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}} dr_1 dr_2 dr_{12},$$

where some of the indices (l, m, n) may acquire negative values up to -4 . The integrals in this case are divergent, but in operators they are encountered in such combinations that the final expression is finite; thus the divergent terms are canceled out. In our calculation we follow the numerical scheme described in [26].

The results of calculation of the coupling constants of Eq. (3) are presented in Table I. The nuclear spin-spin tensor interaction is small, but, as will be seen soon, remains an essential contribution to the hyperfine transition frequencies and its neglect in Eq. (5) is not justified. The major coupling is defined by the spin-spin electron-proton interaction. This interaction determines the principal splitting of the rovibrational levels of H_2^+ . With this consideration in mind, the preferable coupling scheme of angular momentum operators is

TABLE III. Hyperfine splitting (in MHz) of the rovibrational levels in the H_2^+ molecular ion. The states are (F, J) .

L	v	$\left(\frac{1}{2}, L-\frac{1}{2}\right)$	$\left(\frac{1}{2}, L+\frac{1}{2}\right)$	$\left(\frac{3}{2}, L-\frac{3}{2}\right)$	$\left(\frac{3}{2}, L-\frac{1}{2}\right)$	$\left(\frac{3}{2}, L+\frac{1}{2}\right)$	$\left(\frac{3}{2}, L+\frac{3}{2}\right)$	L	v	$\left(\frac{1}{2}, L-\frac{1}{2}\right)$	$\left(\frac{1}{2}, L+\frac{1}{2}\right)$
1	0	-910.7579	-930.4332		385.3985	481.9534	474.1063	2	0	-63.2438	42.1625
1	4	-827.1063	-842.4774		359.8495	433.8744	428.1542	2	4	-48.6718	32.4479
1	5	-810.1969	-824.5781		355.0781	424.0096	418.7520	2	5	-45.3600	30.2400
3	0	-894.6614	-941.1034	341.5540	423.6342	489.5257	507.2568	4	0	-103.236	82.5884
3	1	-872.0486	-915.7408	336.9246	413.6810	475.5771	492.3817	4	1	-96.8707	77.4966
3	2	-851.2013	-892.2611	332.8619	404.5553	462.6345	478.5441	4	2	-90.7937	72.6350

$$\mathbf{F} = \mathbf{I} + \mathbf{s}_e, \quad \mathbf{J} = \mathbf{L} + \mathbf{F}. \quad (4)$$

Note that due to the Pauli symmetrization the total nuclear spin $I=I_1+I_2$ is equal to 0 when L is even, and to 1 when L is odd. As a consequence, the hyperfine structure is much simpler for the states of even L , where only the value $F=1/2$ is allowed.

In early works [13–15] an effective Hamiltonian of a slightly different form has been used:

$$H_{\text{eff}} = b(\mathbf{I} \cdot \mathbf{s}_e) + cI^2s_e^z + d(\mathbf{L} \cdot \mathbf{s}_e) + f(\mathbf{L} \cdot \mathbf{I}), \quad (5)$$

where the coupling constants are related to ours as follows (for $L \neq 0$):

$$b = b_F - c/3, \quad c = d_{11}, \quad d = c_e, \quad f = c_I. \quad (6)$$

Our effective Hamiltonian also takes into account the tensor term of the nuclear spin-spin interaction, which has not been considered in previous work.

Table II contains a comparison with the most accurate calculated values of the coupling constants. As is seen from the table, agreement is almost complete for the ground vibrational state. However, with increase of v the results slightly depart from each other and for $v=5$ the disagreement becomes of about 20–40 kHz. In our case, the numerical accuracy of the calculated matrix elements has been carefully checked, which allows us to claim that the computational uncertainty may be neglected.

The hyperfine splitting of the lower rovibrational levels of H_2^+ is presented in Table III. The results were obtained by diagonalization of the effective spin Hamiltonian (3).

In Table IV the theoretical transition frequencies between hyperfine levels are compared with the most precise experimental measurements by Jefferts [13]. The third line for each v corresponds to theoretical predictions obtained by using the “old” effective spin Hamiltonian of Eq. (5). As can be seen from this comparison, for transitions between substates of the same multiplet F the matching is at the level of 1 kHz, i.e., within experimental accuracy. The similar is for the even L , where only the electron spin-orbit interaction contribute to the splitting. For the spin-flip transitions ($F=3/2$) \rightarrow ($F=1/2$) the discrepancy is approximately 80 kHz. This result is not surprising, since the theoretical limit of the present model of the spin Hamiltonian is $O(\alpha^2) \approx 5 \times 10^{-5}$, and better agreement can only be achieved by inclusion of higher-order corrections. Similar agreement was found for the other levels investigated in [13], i.e., $L=1, 2$ and $v=6-8$.

In order to show the implications of this work for precise spectroscopy of H_2^+ , we now investigate the hyperfine structure of two-photon transitions. $\Delta v=1$ transitions are the most intense, and can be reached by recently developed quantum cascade lasers; among them, $v=0 \rightarrow v=1$ transitions are the most attractive, because detection of excitation by state-selective photodissociation can be easily implemented [27]. Here we calculate the spectrum of two transitions: $(v, L) = (0, 1) \rightarrow (1, 1)$ ($\lambda=9.166 \mu\text{m}$) and $(v, L) = (0, 2) \rightarrow (1, 2)$

TABLE IV. Comparison of transition frequencies (in MHz) with experiment [13]. States are labeled (F, J) , where F is the total spin and J is the total angular momentum of the hydrogen molecular ion.

v		$L=1$				$L=2$	
		$\left(\frac{3}{2}, \frac{3}{2}\right) - \left(\frac{3}{2}, \frac{5}{2}\right)$	$\left(\frac{3}{2}, \frac{3}{2}\right) - \left(\frac{3}{2}, \frac{1}{2}\right)$	$\left(\frac{1}{2}, \frac{3}{2}\right) - \left(\frac{1}{2}, \frac{1}{2}\right)$	$\left(\frac{3}{2}, \frac{5}{2}\right) - \left(\frac{1}{2}, \frac{3}{2}\right)$	$\left(\frac{3}{2}, \frac{3}{2}\right) - \left(\frac{1}{2}, \frac{3}{2}\right)$	$\left(\frac{5}{2}\right) - \left(\frac{3}{2}\right)$
	Experiment	5.721	74.027	15.371	1270.550	1276.271	81.121
4	H_{eff} (3)	5.720	74.025	15.371	1270.632	1276.352	81.120
	H_{eff} (5)	5.762	74.103	15.375	1270.624	1276.386	
	Experiment	5.258	68.933	14.381	1243.251	1248.509	75.601
5	H_{eff} (3)	5.258	68.932	14.381	1243.330	1248.588	75.600
	H_{eff} (5)	5.297	69.005	14.385	1243.323	1248.620	

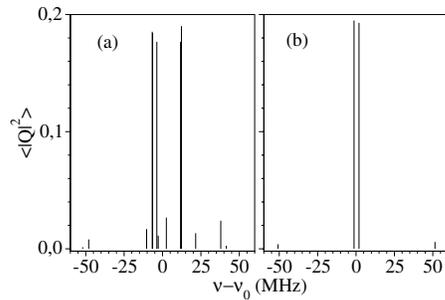


FIG. 1. Intensities of the hyperfine components of the $(\nu, L) = (0, 1) \rightarrow (1, 1)$ (a) and $(0, 2) \rightarrow (1, 2)$ (b) two-photon transitions. The plotted quantity is the two-photon transition squared matrix element $|Q|^2$, averaged over the possible values of the magnetic quantum number M_J , as a function of frequency $\nu - \nu_0$, where ν_0 is the spin-independent frequency.

($\lambda = 9.141 \mu\text{m}$). Assuming a linearly polarized laser field (along Oz), the transition probability is proportional to the squared matrix element of the two-photon transition operator

$$Q(E) = d_z(E - H)^{-1}d_z, \quad (7)$$

where E is the middle energy between initial and final states. Figure 1 shows the intensities of the different hyperfine components for the two selected transitions. A squared matrix element $|Q|^2 = 0.2$ corresponds to a transition probability $\Gamma \approx 70 \text{ s}^{-1}$ assuming a laser power of 50 mW focused on a 1 mm^2 spot in a cavity of finesse 1000, and an instrumental

width $\gamma_e = 10 \text{ kHz}$. Such an excitation rate ensures the feasibility of a two-photon spectroscopy experiment in ion traps, where the ion lifetime is typically of several seconds. Transitions between states of even L [like the $L=2$ transition in Fig. 1(b)] are especially attractive because of their simple hyperfine structure.

In summary, we present the first *ab initio* variational calculation of the hyperfine coupling constants in the rovibrational states of the H_2^+ . The main conclusion is that the nuclear spin-spin tensor interaction is required in the effective spin Hamiltonian in order to get proper interpretation of the experimental results of Jefferts. The obtained numerical values allow theoretical prediction for the hyperfine splitting at the level of 50–100 kHz. We have also shown the hyperfine structure of experimentally relevant two-photon transitions. In order to achieve the aimed sub-ppb level and to get the improved electron-to-proton mass ratio, further calculations are required, which will take into account the $O(m\alpha^6)$ relativistic and radiative corrections as well as finite-size effects like the Zemach electromagnetic radius [28] of the proton. At this stage a consideration of an indirect (via proton-electron spin-spin coupling) nuclear spin-spin interaction [29] is equally desirable.

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- [1] B. Grémaud, D. Delande, and N. Billy, *J. Phys. B* **31**, 383 (1998).
 [2] S. Schiller and C. Lämmerzahl, *Phys. Rev. A* **68**, 053406 (2003).
 [3] L. Hilico *et al.*, *Eur. Phys. J. D* **12**, 449 (2000).
 [4] V. I. Korobov, *Phys. Rev. A* **61**, 064503 (2000).
 [5] D. H. Bailey and A. M. Frolov, *J. Phys. B* **35**, 4287 (2002).
 [6] Z.-C. Yan, J. Y. Zhang, and Y. Li, *Phys. Rev. A* **67**, 062504 (2003).
 [7] M. M. Cassar and G. W. F. Drake, *J. Phys. B* **37**, 2485 (2004).
 [8] J.-Ph. Karr and L. Hilico, *J. Phys. B* **39**, 2095 (2006).
 [9] V. I. Korobov, *Phys. Rev. A* **73**, 024502 (2006).
 [10] V. I. Korobov *Phys. Rev. A* (to be published).
 [11] J. L. Friar, *Can. J. Phys.* **80**, 1337 (2002).
 [12] S. K. Luke, *Astrophys. J.* **156**, 761 (1969).
 [13] K. B. Jefferts, *Phys. Rev. Lett.* **23**, 1476 (1969).
 [14] Z. W. Fu, E. A. Hessels, and S. R. Lundeen, *Phys. Rev. A* **46**, R5313 (1992).
 [15] R. P. McEachran, C. J. Veenstra, and M. Cohen, *Chem. Phys. Lett.* **59**, 275 (1978).
 [16] J. F. Babb and A. Dalgarno, *Phys. Rev. Lett.* **66**, 880 (1992); *Phys. Rev. A* **46**, R5317 (1992).
 [17] J. F. Babb, *Phys. Rev. Lett.* **75**, 4377 (1995).
 [18] P. J. Mohr and B. N. Taylor, *Rev. Mod. Phys.* **77**, 1 (2005).
 [19] J. D. Power and R. L. Somorjai, *Phys. Rev. A* **5**, 2401 (1972).
 [20] A. J. Thakkar and V. H. Smith, Jr., *Phys. Rev. A* **15**, 1 (1977); A. M. Frolov and V. H. Smith, Jr., *J. Phys. B* **28**, L449 (1995).
 [21] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977).
 [22] V. B. Berestetsky, E. M. Lifshitz, and L. P. Pitaevsky, *Relativistic Quantum Theory* (Pergamon, Oxford, 1982).
 [23] A. I. Akhiezer and V. B. Berestetsky, *Quantum Electrodynamics* (Nauka, Moscow, 1969).
 [24] T. Kinoshita and M. Nio, *Phys. Rev. D* **53**, 4909 (1996).
 [25] N. F. Ramsey, *Molecular Beams* (Oxford University Press, New York, 1955).
 [26] V. I. Korobov, *J. Phys. B* **35**, 1959 (2002); F. E. Harris *et al.*, *J. Chem. Phys.* **121**, 6323 (2004).
 [27] L. Hilico *et al.*, *J. Phys. B* **34**, 1 (2001).
 [28] A. C. Zemach, *Phys. Rev.* **104**, 1771 (1956).
 [29] N. F. Ramsey, *Phys. Rev.* **91**, 303 (1953).