# Nuclear Spin-Rotation Interaction in the Hydrogen Molecular Ion

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The nuclear spin-rotation interaction in the hyperfine structure of the hydrogen molecular ion is investigated. The interaction constants are determined and are found to differ in sign and magnitude compared to another theory, but they are in agreement with some values derived from experiment.

Information on molecular structure [1], nuclear forces [2,3], fundamental symmetries [4,5], and even interstellar molecules [6] can be gleaned from experimental and theoretical studies of molecular hyperfine structure. The precision of measurements of diatomic hyperfine transition frequencies is continually improving because of developments such as ion trap–rf spectroscopy [7], ion beam–laser beam [8,9], and laser–radio frequency double-resonance [10] methods. Moreover, a recent proposal [11] for the trapping and cooling of paramagnetic neutral molecules should offer—once spectroscopy has been carried out—the ultimate in precision: natural linewidth resolution of hyperfine frequencies.

For $^1\Sigma$ molecules, which have no net electronic spin, the interaction energy of each nuclear magnetic moment with fields generated by the motion of the other charged particles in the molecule is important. It has been studied in detail both experimentally and theoretically for a number of such molecules (cf. Ramsey [12] and Townes and Schawlow [1]). The primary effect is the nuclear spin-rotation interaction originating with the magnetic fields generated by the rotating nuclei and orbiting electrons. The interaction constant can be related to the magnetic shielding constant [13,14], which describes the effective magnetic field at a nucleus in an external magnetic field and is the basis of chemical shifts in NMR spectroscopy [13,15]. It is also a sensitive test of electronic wave function calculations [14,16,17]. Recently, nuclear spin-rotation interaction has been interpreted as a (Berry- or geometric-phase-like) manifestation of a non-Abelian gauge potential in molecular physics [18].

Nuclear spin-rotation interaction is also present in $^2\Sigma$ molecules, which have a net electronic spin, and although it is of a magnitude comparable with the effect in $^1\Sigma$ molecules, it now causes a much smaller energy in comparison to energies arising from the interactions of the electron spin, and thus it is usually not included in the phenomenological spin Hamiltonians used for fitting measured hfs transition frequencies. Some exceptions are $H_2^+$ [7], $N_2^+$ [19], and alkaline earth monofluorides [5,20], where effective values for nuclear spin-rotation interaction constants have been obtained.

In this Letter, the nuclear spin-rotation interaction for the hydrogen molecular ion $H_2^+$ is studied. It is found that for the ground vibrational state the interaction constant is $-41$ kHz, less than $\frac{1}{2}$ the value for $H_2$, $-113$ kHz [12], but differing from a previous theory in both magnitude and sign. For higher vibrational states there is agreement with some empirical data.

Theories giving nuclear spin-rotation interaction constants for diatomics with other than $^1\Sigma$ states exist, but they are complex. A simplification for $H_2^+$ is obtained by utilizing the theory for $H_2$. The isotropic magnetic shielding constant $\sigma$, where $1 - \sigma$ is the proportionality constant giving the net magnetic field seen at a nucleus in an external uniform applied magnetic field, is related to the nuclear spin-rotation interaction constant. The shielding constant for nucleus $a$ can be written

$$\sigma(R) = \sigma_L(R) + \sigma_{\rm hf}(R), \qquad (1)$$

where, in atomic units, $R$ is the internuclear distance, and

$$\sigma_L(R) = \tfrac{1}{3}\alpha^2 \langle 0|1/r_a|0\rangle \qquad (2)$$

is the "Lamb" [12,21] or diamagnetic part, where $\mathbf{r}_a$ joins the nucleus to the electron and $|0\rangle$ is the $^2\Sigma_g^+$ electronic wave function, and $\sigma_{\rm hf}(R)$ is the high-frequency or paramagnetic part. The designation high frequency [22] arises because the expression for $\sigma_{\rm hf}$ involves highly excited electronic states [12],

$$\sigma_{\rm hf}(R) = \frac{\alpha^2}{6}\sum_{i\neq 0}\left[\frac{\langle 0|\mathbf{L}_a|i\rangle \cdot \langle i|r_a^{-3}\mathbf{L}_a|0\rangle}{E_0(R) - E_i(R)} + {\rm adj}\right], \quad (3)$$

where the symbol $\sum_{i\neq 0}$ represents an infinite summation and integration over the intermediate electronic states with wave functions $|i\rangle$, "adj" indicates the Hermitian adjoint of the preceding term, $E_0(R)$ and $E_i(R)$ are the respective electronic energies, and $\mathbf{L}_a$ is the orbital angular momentum of the electron about the nucleus $a$, for which $\sigma$ is being evaluated.

The separation (1) into a diamagnetic and a paramagnetic part is not unique [13,14]. It is related to the choice of origin for the electron orbital angular momentum and other vectors, which in turn is related to the choice of a gauge constant associated with the magnetic vector potential in the Coulomb gauge (cf. [13,15,23]). Expressions (2) and (3) above adopt the convention of the vectors origin at the nucleus.

       

Let $\mathbf{I}$ and $\mathbf{N}$ be, respectively, the total nuclear spin and rotational angular momenta and define the nuclear spin-rotation interaction constant $f$, a frequency, through the energy $hf\mathbf{I} \cdot \mathbf{N}$ in the hfs Hamiltonian [24,25], where $h$ is Planck's constant. Introducing

$$f(R) = f_1(R) + f_2(R), \qquad (4)$$

the major contributions [12,26] to the energy are from the interaction of each nuclear magnetic moment with the magnetic field generated by the other rotating nucleus,

$$hf_1(R) = -\frac{4g_p\mu_N^2}{R^3}, \qquad (5)$$

and with the magnetic field generated by the orbiting electron [13],

$$hf_2(R) = -\frac{12g_p\mu_N^2}{\alpha^2 R^2}\sigma_{hf}(R), \qquad (6)$$

where $R$ is the internuclear distance, and the dimensionless quantities $\alpha$, $g_p \approx 5.586$, and $\sigma_{hf}$ are, respectively, the fs constant, the proton $g$ factor, and the high-frequency component of the magnetic shielding constant as defined in Eq. (3). Atomic units are used throughout, except for $f$, which is expressed in kHz.

Direct computation of $\sigma_{hf}(R)$ is rather involved and requires evaluation of a term in second-order perturbation theory. It is much easier to use (1) because values of $\sigma$ are available and values of $\sigma_L$ are easily calculable. Moreover, because $\sigma$ is gauge independent the irreducible components of the (symmetric, second rank) shielding tensor calculated with a different gauge origin by Hegstrom [27] could be utilized here to calculate $\sigma$ [28]. Values of $\sigma_L(R)$ were calculated [29] at various internuclear distances $R$ and are given in Table I. Then, $\sigma_{hf}$ was determined using (1) and (2) and values of $f$ were determined using (4). Values of $\sigma$ and $f$ are given in Table I.

Jefferts [7] measured hfs transition frequencies of the vibrational $v = 4$–$8$ states of the $^2\Sigma_g^+$ ground electronic state of $H_2^+$. For the rotational quantum number $N = 1$ for each $v$, he fit the transition frequencies by the

Hamiltonian

$$H_{hfs} = b\mathbf{I} \cdot \mathbf{S} + cI_zS_z + d\mathbf{S} \cdot \mathbf{N} + f\mathbf{I} \cdot \mathbf{N}, \qquad (7)$$

and obtained values for the coupling constants $b$, $c$, $d$, and $f$, where $\mathbf{I}$ and $\mathbf{N}$ have been defined and $\mathbf{S}$ is the electronic spin angular momentum vector, and his results for $f$ are given in Table II, column 2. The measured hfs transition frequencies were refit by the Hamiltonian (7) independently by Kalaghan [30], Menasian [31], and Varshalovich and Sannikov [32], who all obtained mutually consistent results for $f$ that had the opposite sign and somewhat different magnitude than those of Jefferts. The values of [30] are given in Table II, column 3.

McEachran, Veenstra, and Cohen [33] obtained a theoretical expression for a nuclear spin-rotation interaction constant by simply multiplying the first-order *electronic* spin-rotation constant $d_1$ [34] by the ratio of the electron mass and the nuclear reduced mass. Their formula gives a positive interaction constant. Interestingly, it is independent of the proton $g$ factor $g_p$, and thus does not contain the proton magnetic moment. Nevertheless, close agreement was obtained with the empirical values of $f$ obtained by Jefferts. The values for $v = 4$–$8$ of McEachran, Veenstra, and Cohen and the $v = 0$ value calculated using their formula are given in column 5 of Table II.

Fu, Hessels, and Lundeen [35] extracted hfs constants for $H_2^+$ from an analysis of their measured transition energies for highly excited Rydberg states of the hydrogen molecule. Their value for $f$ for the $v = 0$, $N = 1$ state is given in column 4 of Table II. It is consistent with zero.

In order to compare the present results with the above, the values of $f$ in kHz—a partial listing is given in Table I—were averaged over the vibrational-rotational wave functions for various $v$ with $N = 1$ calculated with the Born-Oppenheimer potential using standard methods. The results are given in the last column of Table II.

TABLE I. Electronic expectation values of the shielding constants $\sigma_L(R)$ and $\sigma(R)$, dimensionless, and values of $f(R)$, in kHz.

| $R/a_0$ | $\sigma_L(R) \times 10^6$ | $\sigma(R) \times 10^6$ | $f(R)$ |
|---|---|---|---|
| 1.0 | 21.5183 | 17.6401 | −453.7 |
| 1.25 | 19.3436 | 15.3584 | −213.8 |
| 1.50 | 17.6258 | 13.6704 | −114.5 |
| 1.75 | 16.2484 | 12.3995 | −67.21 |
| 2.0 | 15.1295 | 11.4296 | −42.31 |
| 2.25 | 14.2116 | 10.6825 | −28.16 |
| 2.50 | 13.4530 | 10.1046 | −19.63 |
| 2.75 | 12.8232 | 9.6575 | −14.22 |
| 3.0 | 12.2991 | 9.3133 | −10.65 |
| 4.0 | 10.9538 | 8.6124 | −4.285 |
| 5.0 | 10.3478 | 8.4913 | −2.215 |

TABLE II. Comparison of experimental and theoretical values of the nuclear spin-rotation coupling constant for $H_2^+$ for various vibrational states $v$ with rotational quantum number $N = 1$, in kHz. The column labeled "Refit" gives results obtained by refitting the raw experimental transition frequencies from [7]. Numbers in parentheses are quoted experimental uncertainties.

| | Empirical | | | Theory | |
|---|---|---|---|---|---|
| $v$ | Expt. [7] | Refit[a] | Expt. [35] | [33] | Present[b] |
| 0 | | | −3(15) | 46 | −41.7 |
| 4 | 38(1.5) | −34(1.5) | | 38.8 | −36.2 |
| 5 | 36(1.5) | −33(1.5) | | 36.2 | −34.6 |
| 6 | 34(1.5) | −31(1.5) | | 33.6 | −32.9 |
| 7 | 32(1.5) | −29(1.5) | | 31.1 | −31.0 |
| 8 | 30(1.5) | −27(1.5) | | 28.6 | −29.1 |

[a]Values are from Ref. [30] and are identical with those given in Refs. [31] and [32], except [31] gives −32(1.5) for $v = 5$.
[b]Values for $v = 1$, 2, and 3 are, respectively, −40.8, −39.4, and −38.0.

Good agreement, including the sign, is obtained with the empirical results of [30–32].

The expression (4) can be obtained using more formal arguments. The first term in (4), $f_1$, follows by consideration of the interaction of a nuclear moment with the magnetic field generated by the rotation of the other nucleus [36]. The second term in (4), $f_2$, would be expected to occur in second-order perturbation theory through the electron orbital-rotation interaction

$$H_4 = -\frac{2}{M_p R^2} \mathbf{L} \cdot \mathbf{N}, \tag{8}$$

where $\mathbf{L}$ is the electronic angular momentum about the center of nuclear mass and $M_p$ is the proton mass, and the electron orbital-nuclear spin interaction

$$H_1' = H_{1a}' + H_{1b}', \tag{9}$$

where

$$H_{1a}' = 2g_p \mu_B \mu_N \mathbf{I}_a \cdot r_a^{-3} \mathbf{L}_a \tag{10}$$

and

$$H_{1b}' = 2g_p \mu_B \mu_N \mathbf{I}_b \cdot r_b^{-3} \mathbf{L}_b, \tag{11}$$

where $\mathbf{I}_a$ and $\mathbf{I}_b$ are the nuclear spin angular momenta, and where the terms $H_4$ and $H_1'$ were derived by Dalgarno, Patterson, and Somerville [34] from a nonrelativistic reduction of the Dirac equation for $H_2^+$. Writing

$$H_4 = -\frac{1}{M_p R^2}(\mathbf{L}_a + \mathbf{L}_b) \cdot \mathbf{N} \equiv H_{4a} + H_{4b}, \tag{12}$$

where $\mathbf{L}_a$ is the electronic angular momentum about nucleus $a$, and similarly for $\mathbf{L}_b$, the corresponding energy in perturbation theory is, schematically, $T \equiv T_a + T_b$, where

$$T_a = \sum_{i \neq 0}\left[ \frac{\langle 0|H_{4a}|i\rangle \langle i|H_{1a}'|0\rangle}{E_0(R) - E_i(R)} + \text{adj} \right], \tag{13}$$

and similarly for $T_b$. It follows that

$$T_a = -\frac{4g_p \mu_N^2}{R^2}$$
$$\times \sum_{i \neq 0}\left[ \frac{\langle 0|\mathbf{L}_a|i\rangle \cdot \langle i|r_a^{-3}\mathbf{L}_a|0\rangle}{E_0(R) - E_i(R)} + \text{adj} \right]\mathbf{I}_a \cdot \mathbf{N}, \tag{14}$$

and similarly for $T_b$. Since $\mathbf{I} = \mathbf{I}_a + \mathbf{I}_b$ and $T \equiv hf_2 \mathbf{I} \cdot \mathbf{N}$, the desired result Eq. (6) is obtained by substituting Eq. (3) for $\sigma_{\text{hf}}$ into $T_a$, Eq. (14), and into $T_b$, although a more careful derivation is desirable.

Elaborate treatments of the Hamiltonians for diatomic molecules in other than $^1\Sigma$ states including all angular momenta have yielded nuclear spin-rotation interactions for various electronic states [37–41]. In particular, terms similar to $f_1$ and $f_2$ were given by Mizushima [38] for a $^2\Sigma$ state, although they were not related to Ramsey's theory.

The present approach may be generalizable to other $^2\Sigma$ molecules. Hegstrom [27] has shown for $H_2^+$ that

there is a relation between the second-order *electron* spin-rotation interaction constant $d_2$ and a second-order part of the shielding constant $\sigma$. Equation (6) would thus imply that there is a relation connecting $d_2$ and $f_2$. Physically, such a relation might be anticipated because the nuclear spin and electron spin are both separately coupled to rotation through the excitation of electronic angular momenta. Such a relation would make it possible to estimate $f$, if $d$ were measured, using theoretical values of $f_1$ and $d_1$. Moreover, through the above arguments, the recent findings that electron spin rotation in a paramagnetic molecule and nuclear spin rotation in a diamagnetic molecule are each, separately, describable using a non-Abelian gauge potential method in molecular physics [18,42] can probably be related.

The present paper demonstrates that there is a solid theoretical basis for nuclear spin rotation in a $^2\Sigma$ molecule. A synthesis of the theories for $^1\Sigma$ molecules and $^2\Sigma$ molecules has yielded a simple expression for the interaction constant in $H_2^+$. Using calculated properties of $H_2^+$ numerical values obtained for the interaction constant were found to be in good agreement with empirical results. The sign of the effect is found to be the same as for $H_2$, making $H_2^+$ another rare example of a diatomic with negative nuclear spin-rotation interaction.

[1] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955), pp. 207–247.

[2] R. F. Code and N. F. Ramsey, Phys. Rev. A **4**, 1945 (1971).

[3] R. V. Reid and M. L. Vaida, Phys. Rev. Lett. **34**, 1064 (1975).

[4] M. G. Kozlov and L. N. Labzowsky, J. Phys. B **28**, 1933 (1995).

[5] B. E. Sauer, J. Wang, and E. A. Hinds, Phys. Rev. Lett. **74**, 1554 (1995).

[6] A. H. Saleck, R. Simon, and G. Winnewisser, Astrophys. J. **436**, 176 (1994).

[7] K. B. Jefferts, Phys. Rev. Lett. **23**, 1476 (1969).

[8] W. H. Wing, G. A. Ruff, W. E. Lamb, Jr., and J. J. Spezeski, Phys. Rev. Lett. **36**, 1488 (1976).

[9] A. Carrington, I. R. McNab, and C. A. Montgomerie, J. Phys. B **22**, 3551 (1989).

[10] W. J. Childs, Phys. Rep. **211**, 113 (1992).

[11] J. M. Doyle, B. Friedrich, J. Kim, and D. Patterson, Phys. Rev. A **52**, 2515 (1995).

[12] N. F. Ramsey, *Molecular Beams* (Oxford University Press, Oxford, 1990), pp. 162–166, 208–213.

[13] N. F. Ramsey, Phys. Rev. **78**, 699 (1950).

[14] W. H. Flygare, J. Chem. Phys. **41**, 793 (1964).

[15] N. F. Ramsey, Phys. Rev. **86**, 243 (1952).

[16] K. Kirby Docken and R. R. Freeman, J. Chem. Phys. **61**, 4217 (1974).

[17] J. Komasa, J. Rychlewski, and W. T. Raynes, Chem. Phys. Lett. **236**, 19 (1995).

[18] Y. A. Serebrennikov and U. E. Steiner, Mol. Phys. **84**, 627 (1995).

[19] N. Berrah Mansour, C. Kurtz, T. C. Steimle, G. L. Goodman, L. Young, T. J. Scholl, S. D. Rosner, and R. A. Holt, Phys. Rev. A **44**, 4418 (1991).

[20] W. J. Childs, L. S. Goodman, and I. Renhorn, J. Mol. Spectrosc. **87**, 522 (1981).

[21] W. E. Lamb, Phys. Rev. **60**, 817 (1941).

[22] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford, London, 1932).

[23] W. H. Flygare, *Molecular Structure and Dynamics* (Prentice-Hall, Englewood Cliffs, NJ, 1978), pp. 392–400.

[24] E. Hirota *et al.*, J. Mol. Spectrosc. **168**, 628 (1994).

[25] In Ramsey's notation $hc_W = -hf$ is the analogous coefficient. The IUPAC [24] sign convention is adopted in the present paper.

[26] A much smaller effect due to terms arising from the acceleration of the nuclei is ignored in the application here to $H_2^+$ until experimental precision warrants its inclusion. See N. F. Ramsey, Phys. Rev. **90**, 232 (1953); R. V. Reid, Jr., and A. H.-M. Chu, Phys. Rev. A **9**, 609 (1974).

[27] R. A. Hegstrom, Phys. Rev. A **19**, 17 (1979).

[28] In the notation of [27], $\sigma = \frac{1}{3}[2\sigma_\perp + \sigma_\parallel]$, where $\sigma_\perp = \sigma_\perp^{(1)} + \sigma_\perp^{(2)}$.

[29] The Born-Oppenheimer electronic wave functions of the ground state were calculated using the methods detailed in G. Hunter and H. O. Pritchard, J. Chem. Phys. **46**, 2146 (1967), with 25 terms in the polynomial expansion for each prolate spheroidal coordinate. The energies agreed with standard tabular values to at least 10 decimal places.

[30] P. M. Kalaghan, Ph.D. thesis, Harvard University, 1972.

[31] S. C. Menasian, Ph.D. thesis, University of Washington, 1973.

[32] D. A. Varshalovich and A. V. Sannikov, Astron. Lett. **19**, 290 (1993). This paper also discusses searches and prospects for detection of $H_2^+$ in the interstellar medium.

[33] R. P. McEachran, C. J. Veenstra, and M. Cohen, Chem. Phys. Lett. **59**, 275 (1978).

[34] A. Dalgarno, T. N. L. Patterson, and W. B. Somerville, Proc. R. Soc. London A **259**, 100 (1960).

[35] Z. W. Fu, E. A. Hessels, and S. R. Lundeen, Phys. Rev. A **46**, R5313 (1992).

[36] R. A. Frosch and H. M. Foley, Phys. Rev. **88**, 1337 (1952).

[37] K. F. Freed, J. Chem. Phys. **45**, 4214 (1966).

[38] M. Mizushima, *The Theory of Rotating Diatomic Molecules* (Wiley, New York, 1975), p. 250, Eq. (5-2-2).

[39] J. M. Brown, M. Kaise, C. M. L. Kerr, and D. J. Milton, J. Mol. Spectrosc. **36**, 553 (1978).

[40] M. Broyer, J. Vigué, and J. C. Lehmann, J. Phys. (Paris) **39**, 591 (1978).

[41] A. G. Adam *et al.*, J. Chem. Phys. **100**, 6240 (1994).

[42] U. E. Steiner and Y. A. Serebrennikov, J. Chem. Phys. **100**, 7503 (1994).