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Spin coupling constants and hyperfine transition frequencies for the hydrogen molecular ion

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We have calculated for the ten lowest vibrational levels of $H_2{}^+$ the first-order hyperfine and spin-rotation constants with the inclusion in perturbation theory of the first-order coupling of the electron and nuclear motion and have determined the hyperfine transition frequencies. The calculated frequencies agree to better than 175 kHz with all the experimentally determined hyperfine frequencies for the $N = 1$ rotational level and to better than 3 kHz for the $N = 2$ rotational level. Relativistic and radiative effects may account for the remaining discrepancy.

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The hyperfine-structure constants of a diatomic molecule are the coupling constants between the electron and nuclear spin and enter, along with the spin-rotation constants, in an effective spin Hamiltonian that couples electron and nuclear spin, orbital, and rotational angular momenta. A reduction of the Dirac equation [1, 2] yields an effective Hamiltonian containing coupling constants that can be expressed as matrix elements of certain spatial operators over nonrelativistic molecular wave functions.

The accuracy of theoretical determinations of these angular momentum coupling constants typically is very much less than the precision with which they can be obtained by experimental measurements. This is similar to the situation for atomic hyperfine constants, except that the best molecular precision is significantly less than that for atoms. For example, while the coupling constants between the nuclear and electronic spin vectors for the 1s hydrogen atom [3] and for the ${}^2\Sigma_g^+$ ground electronic state $N_2{}^+$ molecular ion [4] have been measured about 10^5 times more precisely than the accuracy of the best theoretical determination, the atomic calculations of hyperfine parameters for H are at a level that is testing proton structure (for a review see Ref. [5]) and molecular calculations for $N_2{}^+$ [6] are testing primarily the quality of the nonrelativistic electronic wave function calculated in the Born-Oppenheimer approximation—a test of the Schrödinger-Coulomb equation in the approximation that the nuclei move in the field generated by averaging over the electronic wave function determined at a fixed nuclear geometry.

For the hydrogen molecular ion $H_2{}^+$, the opportunity of testing the molecular hyperfine Hamiltonian, rather than the Coulomb Hamiltonian, appears possible since the electronic wave function in the Born-Oppenheimer approximation can be obtained readily to arbitrary accuracy. There has been a large amount of theoretical activity on the determination of the spin coupling constants for $H_2{}^+$ both within the Born-Oppenheimer [2, 7] and within the adiabatic approximation, in which the accuracy of the Born-Oppenheimer description is improved by addition of the diagonal expectation value of the nuclear kinetic energy [8–12], but discrepancies remain. The accuracy of the wave function may be further improved by allowing for the effect of the motion of the nuclei on the electronic wave function. Such an effect on the wave function is small, depending on the ratio of the electron and nuclear masses, but significant, and it may be treated using perturbation theory [13].

Only a single measurement of the hyperfine transitions has been published [14] and it yielded a set of spin coupling constants for the rotational levels $N = 1$ and 2 of five excited vibrational states $v = 4$–8. In a different analysis of the same data, an alternative set of constants has been determined [15, 16] from the measured radio frequency transitions of the $N = 1$ level. Recently [17], spin coupling constants of the $N = 1$ level of the lowest vibrational state $v = 0$ have been determined experimentally from a study of highly excited Rydberg levels of the hydrogen molecule, and although $H_2{}^+$ was not studied directly the empirically determined constants could be used to determine the hyperfine transition frequencies for the $N = 1$ rotational level.

We have calculated the first-order hyperfine and spin-rotation constants with the inclusion of the first-order coupling of the electron and nuclear motion and determined the hyperfine transition frequencies. The calculated frequencies agree to better than 175 kHz with all experimentally determined hyperfine frequencies for $N = 1$.

In atomic units, let $\mathbf{r}$ be the position vector of the electron measured with respect to the midpoint of the nuclei, $\mathbf{R}$ be the vector joining the nuclei, $\mathbf{r}_a$ be the position vector of the electron measured from one of the nuclei, and the effective electron mass be $\rho = 1 + (1/4m^*)$, where $m^* = \frac{1}{2}M_p$ with M_p the proton mass. The hyperfine constants b and c and the spin-rotation constant d entering the effective spin Hamiltonian [17] may be written in terms of

$$b_{1F} \equiv b + \tfrac{1}{3}c \quad \text{and} \quad d = d_1 + d_2, \tag{1}$$

where d_2 is a second-order term in the electronic wave function [9, 11]. The remaining parameters b_{1F}, c, and d_1 are studied in the present work and may be written symbolically in the Born-Oppenheimer approximation as

$$G = (\tilde{\chi}_{0\beta}|G(R)|\tilde{\chi}_{0\beta}), \tag{2}$$

where G denotes b_{1F}, c, or d_1, $\tilde{\chi}_{0\beta}(\mathbf{R})$ is the vibration-rotation wave function, with 0β denoting the vN level of the $1s\,\sigma_g$ electronic state, and the outer parentheses signify integration over $\mathbf{R}$. Accordingly, $G(R)$ is

$$b_{1F}(R) = \tfrac{8}{3}\pi C\langle\tilde{\phi}_0|\delta(\mathbf{r}_a)|\tilde{\phi}_0\rangle, \tag{3}$$

$$c(R) = -3C\langle\tilde{\phi}_0|K[(x_a^2 - z_a^2)/r_a^5]|\tilde{\phi}_0\rangle, \tag{4}$$

or

$$d_1(R) = 4(C/g_p)\langle\tilde{\phi}_0|K[z_a/(Rr_a^3)]|\tilde{\phi}_0\rangle, \tag{5}$$

where

$$C = g_e g_p \mu_0 \mu_N, \tag{6}$$

$$K = 2\{2 + \alpha^2[\tilde{V}_0(R) - V_{\mathrm{el}}(\mathbf{r},\mathbf{R})]\}^{-1}, \tag{7}$$

and α is the fine-structure constant. The quantities $\tilde{V}_0(R)$ and $\tilde{\phi}_0$ are, respectively, the ground-state electronic eigenenergy and eigenfunction obtained by solution of the nonrelativistic Schrödinger equation

$$\{-\tfrac{1}{2}\nabla^2\rho^{-1} + V_{\mathrm{el}}(\mathbf{r},\mathbf{R}) - \tilde{V}_0(R)\}\tilde{\phi}_0(\mathbf{r},R) = 0, \tag{8}$$

with

$$V_{\mathrm{el}}(\mathbf{r},\mathbf{R}) = -1/|\mathbf{r} - \tfrac{1}{2}\mathbf{R}| - 1/|\mathbf{r} + \tfrac{1}{2}\mathbf{R}|. \tag{9}$$

In Eqs. (3)–(5), g_e and g_p are the free-electron and proton g factors, and μ_0 and μ_N are the Bohr and nuclear magnetons. We have used $g_e = 2.002\,319$ and $g_p = 5.585\,694$ [18], which include the anomalous magnetic moments, in analogy with the theoretical expressions [19] for the hydrogen atom hyperfine splitting. The factor K, Eq. (7), results from the reduction of the Dirac equation [1, 2, 8].

We determined adiabatic expectation values of Eqs. (3)–(5) using the methods of Ref. [13]. Calculation of the electronic matrix element appearing in Eqs. (3) and (5) is straightforward, while for Eq. (4) the integrations were treated in a manner similar to that detailed in Refs. [7, 11]. Averaging over the vibrational wave functions $\tilde{\chi}_{0\beta}$ as in Ref. [13] yields the adiabatic values listed in Table I. We carried out a similar calculation of d_2 using the values tabulated at various values of $\bar{R}$ in Ref. [11], rescaled to $R = \bar{R}/\rho$, since m^* appears in Eq. (8).

We have calculated the first-order corrections to b_{1F}, c, and d_1 arising from the coupling of nuclear and electronic motion using the procedures of Ref. [13]. The corrections are about -600 kHz for b_{1F}, -7 kHz for c, and -2 kHz for d_1. For vibrational level $v = 0$, and $N = 0$, the corrected value of b_{1F} differs by only 1 in the sixth significant figure (about 5 kHz) from the calculation of Babb and Shertzer [20], who included fully the electron-nuclear coupling. In Table I, we give the adiabatic value and the sum of the adiabatic value and first-order correction for b_{1F} and c. For d we give the sum of the adiabatic value and first-order correction for d_1 and the adiabatic value for d_2, as the electron-nuclear coupling correction for d_1 is only a few kHz, and as d_2 is second-order in the electronic wave function the electron-nuclear coupling correction is expected to be insignificant. The values of b_{1F} in Table I are slightly more precise than those given in Ref. [13] (which should be multiplied by the factor [18] $\mu_p/\mu'_p = 1.000\,025\,69$, where μ'_p is the shielded value of the proton magnetic moment).

The differences between the calculated values given in Table I and the values determined by an experimental study of the Rydberg states of H_2 [17] are 50 kHz for b_{1F}, 223 kHz for c, and 73 kHz for d. Because c involves a quadrupole interaction, the larger discrepancy for c may be due in part to a perturbation of the $H_2{}^+$ electron distribution by the effect of the permanent quadrupole moment of the core on the Rydberg electron orbit. However, the value for c obtained from the H_2 Rydberg levels for $v = 0$, $N = 1$ lies on a smooth extrapolation of the

TABLE I. Calculated and measured hyperfine and spin-rotation constants for $H_2{}^+$ for the $N = 1$ rotational level of the ten lowest states with vibrational quantum number v, in MHz. Ad. denotes adiabatic, Expt. denotes experimental, and Cor. denotes the sum of the adiabatic value and first-order electron-nuclear coupling correction.

	b_{1F}			c			d	
v	Ad.	Expt.[a]	Cor.	Ad.	Expt.[a]	Cor.	Expt.[a]	Cor.
0	923.585	922.940(20)	922.990	128.493	128.259(26)	128.482	42.348(29)	42.421
1	899.397		898.805	120.339		120.329		39.816
2	877.038		876.447	112.580		112.571		37.334
3	856.393		855.804	105.169		105.161		34.951
4	837.362	836.727	836.773	98.015	97.930	98.008	32.649	32.658
5	819.857	819.229	819.268	91.151	91.082	91.145	30.432	30.441
6	803.803	803.176	803.214	84.490	84.448	84.485	28.276	28.283
7	789.135	788.509	788.545	78.004	77.985	78.000	26.167	26.173
8	775.799	775.172	775.207	71.647	71.650	71.643	24.090	24.096
9	763.748		763.155	65.487		65.483		22.037

[a] Reference [17] for $v = 0$, Ref. [15] fit to data of Ref. [14] for $v = 4$–8. In addition, for f, the nuclear spin-rotation constant, from [17], $f = -0.003(15)$ for $v = 0$, and from [15] $f = -0.034, -0.033, -0.031, -0.029$, and -0.027, respectively, for $v = 4$–8.

TABLE II. Comparison of calculated spin-rotation constant d for $H_2{}^+$, for the $N = 2$ rotational level of the ten lowest states with vibrational quantum number v, with available measurements [14], in MHz.

v	Experiment	Theory
0		42.168
1		39.576
2		37.103
3		34.733
4	32.448	32.451
5	30.240	30.243
6	28.092	28.095
7	25.991	25.993
8	23.922	23.923
9		21.871

$H_2{}^+$ measurements of Jefferts for v = 4–8, suggesting that the explanation of the discrepancy must be sought elsewhere, presumably in relativistic and radiative corrections.

The agreement between experimental and theoretical transition frequencies is in any case impressive. Using the calculated constants we find transition frequencies for $v = 0$, $N = 1$ of 1412.365, 1404.545, 1392.764, 1315.675, 1296.074, 96.690, 19.601, and 7.821 MHz, which agree in all cases to better than 175 kHz with those obtained by Fu, Hessels, and Lundeen [17]; the previously published adiabatic frequencies of Ref. [11] differ by up to 665 kHz. We also, using our calculated constants, reproduce each of the 25 hyperfine frequencies measured by Jefferts [14] for $N = 1$ to within 150 kHz, in contrast to the previously published adiabatic frequencies of Ref. [11], for which the agreement is to within 750 kHz. Besides the 25 frequencies measured by Jefferts and the spin coupling constants determined from them, which have been the object of much theoretical attention over the years, there is also a measurement of one single transition frequency for $v = 9$, $N = 1$ at 1155.1195 MHz, which is given in footnote 13 of Ref. [14]. Since only one frequency was given for this state, the constants cannot be determined. The constants that we calculated for this state, which are given in Table I, yield a frequency of 1155.173 MHz for the transition $\frac{3}{2}\frac{5}{2} \rightarrow \frac{1}{2}\frac{3}{2}$, labeled by $F_2\,F$, where F_2 is the vector sum of the nuclear and electronic spin momenta, and F is the vector sum of F_2 and N. We also have calculated using the above procedure, the spin-rotation constant d for the $N = 2$ level of the states v = 0–9, for which there is no hyperfine structure, and our results agree to better than 3 kHz with the measured constants [14] as demonstrated in Table II. In contrast, the previously published adiabatic values of d [11] differ by 12–15 kHz from experiment.

Our formulation accounts for reduced-mass effects on the hyperfine constants but not fully for relativistic and radiative effects. For the hydrogen atom, the difference between the theoretical hyperfine transition frequency 1420.486 MHz with only reduced-mass corrections, g_e, and g_p included and the experimental frequency 1420.406 MHz is 80 kHz. There will be presumably a larger analogous difference for $H_2{}^+$ with its two nuclei, and the remaining discrepancies between the measured and predicted hyperfine transition frequencies may arise from relativistic and radiative corrections. There is the further possibility that the representation of the hyperfine interaction for $H_2{}^+$ by an effective Hamiltonian is inadequate at the level of accuracy achieved in the experiment.

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