Nuclear magnetic shielding in the hydrogen molecule*

Roderick V. Reid, Jr.
Department of Physics, University of California, Davis, California 95616
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Working within the adiabatic approximation in the gauge where the vector potential is zero at the nucleus, Ramsey's diamagnetic part of the shielding constant was calculated using an 87-term James-Coolidge–type wave function. The paramagnetic part of the shielding was determined by means of spin-rotation interaction and isotope-shift data. Results for the shielding constant in isotopes of the hydrogen molecule are reported for a range of temperatures between 0 and 500 K. For H_2 at 295 K and zero pressure, $\sigma = 26.366 \pm 0.070$ ppm was obtained, with the error meant to take at least partly into account presently uncalculated nonadiabatic and relativistic effects. This value is in agreement with $\sigma = 26.23 \pm 0.18$ ppm from experiment.

I. INTRODUCTION

In a weak[1] external magnetic field H, a nucleus within a molecule experiences, on the average, a field $(1-\sigma)H$, which makes its effective g factor $(1-\sigma)g(\text{free})$. While shifts in the value of the nuclear shielding constant σ, for a nucleus in different molecules or upon substitution of a different isotope, have often been observed and indeed their study has developed into a tool used for the investigation of molecular structure, the absolute value of any shielding constant whatsoever, is relatively a much more illusive object. The first reasonably direct observation of a molecular shielding constant was reported by Myint *et al.*[2] in 1966 and the best-known value at present, which is due to combining the work of Winkler *et al.*,[3] Lambe,[4] and Grotch and Hegstrom,[5] is $\sigma = 25.64 \pm 0.07$ ppm for a proton in liquid H_2O at approximately room temperature. For other molecules one starts with H_2O and uses observed chemical shifts. As will be discussed in Sec. III E, the connection with H_2 is presently less than ideal. This is unfortunate because H_2, being the ideal meeting point for experiment and theory, is a candidate for an absolute proton shielding-constant standard.

The theory of nuclear magnetic shielding in molecules was developed by Ramsey[6-8] who, working within the adiabatic approximation, expressed σ in terms of diamagnetic (or Lamb) and paramagnetic (or high-frequency) parts, $\sigma = \sigma^d + \sigma^p$. The complexity of paramagnetic shielding is apparently sufficiently deterring that, for highly accurate calculations, molecules other than hydrogen tend to lose their appeal. Even with the hydrogen molecule all previous work[7,9-17] has been done with relatively simple wave functions; some of the work of others is briefly discussed in Sec. III C.

On the other hand, the paramagnetic term is related[6,7] to the spin-rotation interaction in the molecule and it is possible to use observed spin-rotation interaction constants to avoid direct calculation of the term. By this means σ^p was first obtained by Ramsey[7], and later by Saika and Narumi[14] and Code and Ramsey.[18]

Recently, Reid and Chu[19] have, in effect, removed an old approximation in the theory of the spin-rotation interaction, thereby eliminating a long-standing discrepancy between theory and experiment, and found that for the hydrogen molecule the dependence of σ^p on the internuclear distance, and thus σ^p itself, was not uniquely determined by available spin-rotation data alone.

In the present work σ^d is calculated directly from an 87-term wave function used earlier[20] and σ^p determined from spin-rotation data, the calculated σ^d, and the isotope shift $\sigma(\text{HD}) - \sigma(H_2)$ observed by Evans.[21]

In Sec. II we give the underlying theory, in Sec. III we present the results and discuss them and we conclude in Sec. IV.

II. BACKGROUND THEORY

From the theory of Ramsey,[6-8] in the adiabatic approximation and with the origin of the vector potential at nucleus "a," the shielding in a state characterized by vibrational and rotational quantum numbers ν, J is

$$\sigma_{\nu J} = \sigma^d_{\nu J} + \sigma^p_{\nu J}\,, \tag{1}$$

$$\sigma^d_{\nu J} = \tfrac{1}{3}\alpha^2 \langle 1/r_{1a} + 1/r_{2a} \rangle_{\nu J}\,, \tag{2}$$

$$\sigma^p_{\nu J} = -\frac{4\mu_B^2}{3}\left\langle \sum_n{}' (E_n - E_0)^{-1} \times \left(\langle 0|L_x^a|n\rangle\langle n|L_x^a/r^3|0\rangle + \text{c.c.}\right)\right\rangle_{\nu J}, \tag{3}$$

where α is the fine-structure constant, final expectation values are taken with respect to the ν, Jth vibrational-rotational wave function, r_{1a} and r_{2a}

are distances of the two electrons in the hydrogen molecule from nucleus "a," μ_B is the Bohr magneton, $\hbar L_x^a$ is a component of the electronic angular momentum about nucleus "a" perpendicular to the internuclear line, and

$$\frac{\hbar L_x^a}{r^3} = \sum_{i=1}^{2} r_{ia}^{-3}(\vec{r}_{ia} \times \vec{p}_{ia})_x . \tag{4}$$

If the dependence of the paramagnetic shielding upon the internuclear distance R is denoted by $\tilde{\sigma}^p(R)$ and expressed using the expansion

$$\tilde{\sigma}^p(R) = \sum_{m=0}^{\infty} s_m \xi^m , \tag{5}$$

where $\xi = (R - R_e)/R_e$, with R_e being the equilibrium value of R, then

$$\sigma_{vJ}^p = \langle \tilde{\sigma}^p \rangle_{vJ} \tag{6a}$$

$$= \sum_{m=0}^{\infty} s_m \langle \xi^m \rangle_{vJ} \tag{6b}$$

and $\tilde{\sigma}^p$ is related[6,7] to the electronic part[19] of the spin-rotation interaction constant C_{avJ}^{el}, for nucleus "a" within a given molecule, through

$$C_{avJ}^{el} = (3\mu_N g_a \hbar / 4\pi\mu_B m_r) \langle \tilde{\sigma}^p / R^2 \rangle_{vJ} , \tag{7}$$

where μ_N is the nuclear magneton; m_r is the reduced nuclear mass; and $g_a = \mu_a / I_a \mu_N$, with I_a being the spin of "a," is the nuclear g factor.

At a temperature T, the shielding observed by NMR methods will be a Boltzmann average

$$\sigma = \sum_{vJ} (2J+1)\sigma_{vJ} e^{-E_{vJ}/kT} \Big/ \sum_{vJ} (2J+1) e^{-E_{vJ}/kT} , \tag{8}$$

where E_{vJ} is the vJth vibrational-rotational energy of the molecule. In Eq. (8) only odd J values are included for o-H_2 (ortho-H_2, which is the case observed in NMR work), p-D_2 (para-D_2) and o-T_2, only even J for p-H_2, o-D_2, and p-T_2, while for the heteronuclear molecules the Boltzmann sums are, of course, unrestricted. Intermolecular effects are ignored here; zero pressure is assumed.

TABLE I. Values of $\langle 1/r_{1a} + 1/r_{2a} \rangle$ calculated with an 87-term James-Coolidge-type wave function at various R.

R (a.u.)	α [a]	$\langle 1/r_{1a} + 1/r_{2a} \rangle$ (a.u.)
0.90	0.752	2.217 240 9
1.00	0.820	2.122 926 0
1.10	0.884	2.037 513 4
1.15	0.914	1.997 840 1
1.20	0.944	1.960 039 8
1.25	0.975	1.924 008 5
1.30	1.005	1.889 647 5
1.35	1.034	1.856 865 5
1.40	1.063	1.825 577 7
1.45	1.091	1.795 704 1
1.50	1.119	1.767 171 2
1.55	1.146	1.739 909 4
1.60	1.173	1.713 855 0
1.65	1.199	1.688 947 7
1.70	1.225	1.665 132 0
1.75	1.251	1.642 355 1
1.80	1.277	1.620 570 9
1.85	1.302	1.599 731 5
1.90	1.326	1.579 795 6
2.00	1.374	1.542 479 1
2.10	1.420	1.508 334 9
2.20	1.466	1.477 111 0

[a] Nonlinear parameter in the electronic wave function of Ref. 20.

III. RESULTS AND DISCUSSION

A. Diamagnetic shielding

From the 87-term James-and-Coolidge-type electronic wave functions used in an earlier field gradient calculation,[20] the expectation values given in Table I were obtained. Since $1/r_{1a} + 1/r_{2a}$ is part of the molecular Hamiltonian, one expects the expectation values to be insensitive to small errors in the wave function. Kolos and Wolniewicz[22] have obtained $\langle 1/r_{1a} + 1/r_{2a} \rangle$ at some of the values

TABLE II. Values of the diamagnetic part of the shielding constant in several states of isotopes of the hydrogen molecule.

v	J	σ_{vJ}^d (ppm) H_2	HD	D_2	HT	DT	T_2
0	0	32.0219	32.0718	32.1310	32.0903	32.1539	32.1791
0	1	31.9991	32.0547	32.1196	32.0750	32.1443	32.1715
0	3	31.8868	31.9700	32.0627	31.9995	32.0968	32.1333
0	5	31.6898	31.8204	31.9616	31.8659	32.0121	32.0652
1	0	31.3114	31.4534	31.6231	31.5061	31.6890	31.7620

TABLE III. Values of the electronic part of spin-rotation interaction constants obtained from various paramagnetic expressions of the form of Eq. (6), constrained by the isotope shift $\sigma(\mathrm{HD}) - \sigma(o\text{-}\mathrm{H}_2)$. All molecules are in their ground vibrational state.

	Parameters in σ^p			C^{el} (kHz)				
Case	$10^6 s_0$	$10^6 s_1$	$10^6 s_2$	$H_2(J=1)$	$HD_p(J=1)$	$HD_d(J=1)$	$D_2(J=1)$	$D_2(J=2)$
A	−5.7051	0.0	0.0	−92.336	−69.564	−10.678	−7.157	−7.135
B	−5.7675	0.0	5.02	−92.191	−69.574	−10.680	−7.172	−7.150
C	−5.7233	2.963	0.0	−92.283	−69.568	−10.679	−7.162	−7.135
D	−5.7260	2.810	0.29	−92.277	−69.569	−10.679	−7.163	−7.135
		Experiment[a]		−92.261(30)	−69.583(18)	−10.679(11)	−7.161(3)	−7.140(20)

[a]Reference 29.

of R in Table I using their 54-term basis, which is largely contained within ours. The agreement is good; the maximum difference between their values and ours is 1.5×10^{-6} a.u., except at $R=2.2$ where the difference is 5.7×10^{-6} a.u. The 87-term wave function gives a dissociation energy $D_e=0.1744721$ a.u. which, for comparison, is 2.9×10^{-6} a.u. smaller than the best value of Kolos and Wolniewicz[23] and is in agreement[20] with experiment.

The averaging of $\langle 1/r_{1a}+1/r_{2a}\rangle$, as well as ξ^m and ξ^m/R^2,[24] over vibrational motion was done using wave functions obtained numerically from the adiabatic potential of Kolos and Wolniewicz.[23,25] For the reduced nuclear masses, 918.076, 1223.898, 1835.240, 1376.391, 2200.878, and 2748.459 a.u. were used for H_2, HD, D_2, HT, DT, and T_2, respectively. A few sample values of σ^d_{vJ} are given in Table II; the conversion factor from Eq. (2) that is used is $\alpha^2/3=17.75044$ ppm.[26] As expected, the shielding increases when the molecule settles down into the adiabatic potential well because of increased reduced mass and decreases as the molecule stretches as a result of tumbling motion or, thanks to the anharmonicity of the potential, as a result of being in a higher vibrational state.

B. Paramagnetic shielding

With the diamagnetic shielding now known, it is straightforward to determine the first few parameters in the expansion of $\bar{\sigma}^p$ given in Eq. (5) by using Eq. (7) to fit experimental spin-rotation constants and Eqs. (1), (6), and (8) to fit the isotope shift $\sigma(\mathrm{HD})-\sigma(o\text{-}\mathrm{H}_2)=0.036\pm0.002$ ppm reported by Evans at 295 K.[27] R_e was taken to be 1.4015 a.u.[28]

The results of this are shown in Table III. As is evident from Eq. (3) and shown by case A in Table III, the paramagnetic shielding is, to a first approximation, independent of R in the equilibrium region; terms linear and quadratic in ξ are small corrections. The constant-plus-quadratic term, case B, was earlier[19] found to be in agreement with spin-rotation constants. Here we see that it fails when required to also agree with Evan's HD-H_2 isotope shift.

Case C, which involves a constant plus a linear term, is not only in agreement with the data but the parameters s_0 and s_1 are little changed from those predicted by spin-rotation interaction constants alone, $s_0=-5.725$ and $s_1=3.163$ ppm.[19] The addition of a quadratic term, as in case D, makes few changes.

For case D and the four states in Table III, σ^p is −5.622, −5.637, −5.654, and −5.650 ppm, for $H_2(J=1)$, HD$(J=1)$, $D_2(J=1)$, and $D_2(J=2)$, respectively.

C. Total shielding at 295 K

Shielding constants at 295 K corresponding to the paramagnetic shielding functions of Table III, as well as results of others, are given in Table IV. Ishiguro and Koide[11] and Mangeot *et al.*[13] used relatively simple wave functions and apparently made no attempt at high accuracy. Saika and Narumi[14] used an approach somewhat similar to the one here with the diamagnetic shielding taken from the work of Newell.[9] Among other problems they found that their results depended strikingly on the way Newell's value of σ^d at $R=1.2$, 1.3, 1.4, and 1.5 a.u. were extrapolated and interpolated. Ramsey's[10] work along these lines gave $\sigma(H_2)=26.2\pm0.3$ ppm, a value which has survived two decades rather well.

The work of Raynes *et al.*[15,16] was the first complete calculation. Their unperturbed wave function was a slightly simplified version of the single-determinant model of Fraga and Ransil,[33] with a dissociation energy $D_e=0.132$ a.u., and they allowed the perturbing magnetic field to introduce two perpendicular molecular orbitals of π symmetry. Their results given in Table IV are apparently better than their modest dissociation energy and

TABLE IV. Shielding constants and isotope shifts at 295 K compared with experiment.

Source (Ref.)	σ (ppm) $\sigma(o\text{-}H_2)$	$\sigma(HD)-\sigma(o\text{-}H_2)$	$\sigma(D_2)-\sigma(HD)$	$\sigma(D_2)-\sigma(o\text{-}H_2)$
Ishiguro and Koide (11)[a]	27.56	...	...	0.07
Mangeot *et al.* (13)[a]	26.734	0.042	0.050	0.091
Saika and Narumi (14)	26.51 ± 0.30	0.047	0.053	0.100
Raynes *et al.* (16)	26.297	0.042	0.036	0.078
This work: case A[b]	26.280	0.050	0.058	0.108
case B[b]	26.297	0.038	0.045	0.083
case C[b]	26.369	0.036	0.042	0.078
case D[b]	26.366 ± 0.070[c]	0.036	0.042	0.078
Experiment	26.23 ± 0.18[d]	0.036 ± 0.002[e] 0.038 ± 0.008[g] 0.040 ± 0.010[h]	0.048 ± 0.032[f]	0.065 ± 0.059[f]

[a] Not temperature averaged.
[b] The notation is that of Table III.
[c] See text regarding the error assignment.
[d] See text and Table VII.
[e] Evans (Ref. 21).
[f] Wimett (Ref. 32).
[g] Anders *et al.* (Ref. 30).
[h] Dayan *et al.* (Ref. 31).

relatively simple wave functions might lead one to believe.

Turning now to our work, case A where $\bar{\sigma}^p(R)$ = const, is again of interest because the isotope shifts in Table IV are solely due to the diamagnetic shielding which we have presumably accurately calculated. Furthermore, it seems to give a lower bound to the shielding constant; when $\bar{\sigma}^p$ is allowed to have any R dependence the total shielding is observed to rise.

Case B, which is case A with the addition of a ξ^2 term, was ruled out earlier. Note that even with the relatively large coefficient of ξ^2 given in Table III the net effect on (H_2) is only 0.017 ppm. Addition of terms of order ξ^3 and ξ^4, corresponding roughly to the shape of the $\bar{\sigma}^p(R)$ obtained by Cook *et al.*,[15] produced changes in σ of less than 0.003 ppm and did not reduce $\sigma(HD) - \sigma(o\text{-}H_2)$.

Of all the work in Table IV, only our cases C and D are in good agreement with experiment. We defer discussion of the experimental value for $\sigma(H_2)$ until part E of this section. Case D, which represents only a small improvement over "C," is taken as our final result. Formally, one standard-deviation error in $\sigma(o\text{-}H_2)$ at 295 K is found to be 0.014 ppm. This assumes that the R dependence of $\bar{\sigma}^p$ is no more complicated than quadratic and that both relativistic and nonadiabatic corrections are negligible. We take five times 0.014 for the error giving $\sigma(o\text{-}H_2) = 26.366 \pm 0.070$ ppm at 295 K and zero pressure, which may be compared with the experimental value of 26.23 ± 0.18 ppm.

D. Temperature dependence

From Eq. (8) the shielding constant for isotopes of the hydrogen molecule were calculated and are given in Table V. The gross features of the temperature dependence are similar to those obtained by Raynes *et al.*[16] who discuss NMR aspects.

For a given molecule the shielding decreases as the temperature rises due to increased population of states where the molecule undergoes greater stretching and the shielding is less. The magnitude of the temperature dependence is relatively small. At 295 K, for $o\text{-}H_2$, $d\sigma/dT = -1.0 \times 10^{-4}$ ppm/K, which is one-hundredth that of liquid H_2O.[34]

In Table VI our results are compared with those of Raynes *et al.*; the temperature dependence has not yet been observed. This is unfortunate because from Table VI it clearly gives new information about the shielding. An accurate measurement would distinguish between our case B of Table III, which for $o\text{-}H_2$ gives $\sigma(200\text{ K}) - \sigma(500\text{ K}) = 0.036$ ppm, and the 0.030 ppm for case D, which is strongly preferred by the isotope shift of Evans.

TABLE V. Shielding constants for isotopic forms of the hydrogen molecule at various temperatures. The paramagnetic shielding is that of case D of Table III. Shielding constants are in ppm, and dots indicate that the para version is the same as the ortho.

	Temperature (K) 0	100	200	300	400	500
$\sigma(o\text{-}H_2)$	26.377	26.377	26.374	26.365	26.355	26.344
$\sigma(p\text{-}H_2)$	26.395	26.393	26.379	26.366	...	...
$\sigma(HD)$	26.431	26.423	26.412	26.401	26.390	26.380
$\sigma(o\text{-}D_2)$	26.474	26.467	26.454	26.444	26.433	26.422
$\sigma(p\text{-}D_2)$	26.465	26.464	...	...	...	...
$\sigma(HT)$	26.445	26.436	26.425	26.414	26.404	26.393
$\sigma(DT)$	26.491	26.482	26.471	26.460	26.449	26.438
$\sigma(o\text{-}T_2)$	26.503	26.500	26.489	26.478	26.467	26.456
$\sigma(p\text{-}T_2)$	26.509	...	...	...	...	...

TABLE VI. Comparison of temperature shifts from Table V with those obtained by Raynes *et al*.

	σ(200 K) − σ(500 K) (ppm) This work	Raynes *et al.*[a]
o-H_2	0.030	0.038
HD	0.032	0.037
D_2	0.032	0.044
HT	0.032	0.036
DT	0.033	0.037
T_2	0.033	0.044

[a]Reference 16.

TABLE VII. Some experimental values for $\sigma(H_2)$ at about 295 K starting from $\sigma(H_20) = 25.64 \pm 0.09$ ppm.

Source (Ref.)	$\sigma(H_2)$ (ppm)
Thomas (35)	26.24 ± 0.31
Gutowsky and McClure (36)	25.94 ± 0.46
Hardy (37)	26.24 ± 0.19
H_2O, gas, 22 °C series[a]	26.25 ± 0.18
Benzene, 30 °C series[a]	26.24 ± 0.18
Weighted average	26.23 ± 0.18[a]

[a]See text.

E. Experimental value for $\sigma(H_2)$ at 295 K

The starting point is $\sigma(H_2O) = 25.64 \pm 0.07$ ppm.[3-5] Since the shielding of a proton in liquid H_2O varies by about 0.01 ppm/° C (Ref. 34) and the temperature of Lambe's[4] H_2O sample was not observed, we first fold in an error of 0.05 ppm, giving $\sigma(H_2O$, liquid$) = 25.64 \pm 0.09$ ppm, to possibly partly allow for this. We now give three approaches to $\sigma(H_2)$ and summarize in Table VII.

$\sigma(H_2) - (H_2O)$ was found by Thomas[35] to be 0.6 $\pm$ 0.3 ppm at an H_2 pressure of 40 atm, by Gutowsky and McClure[36] to be 0.3 ± 0.45 ppm at an H_2 pressure of 30 atm, and by Hardy[37] to be 0.6 ± 0.15 ppm, which we alter to 0.6 ± 0.19 ppm to make some allowance for uncertainty in both temperature and pressure. Raynes *et al.*[16] pointed out two less-direct approaches. Assuming 22 °C for H_2O (Lambe), then one can use $\sigma(H_2$, 1 atm, 34 °C) $- \sigma(CH_4$, 9 atm, 34 °C) $= -4.35 \pm 0.15$ ppm,[38] $\sigma(CH_4) - \sigma(H_2O$, gas) $= 0.56 \pm 0.02$ ppm,[34] and $\sigma(H_2O$, gas, 22 °C) $- \sigma(H_2O$, liq., 22 °C) $= 4.400$ ppm,[34] to obtain $\sigma(H_2) = 26.25 \pm 0.18$ ppm. Finally, assuming 30 °C for H_2O (Lambe), one can use the series[39] at 30 °C $\sigma(CH_4$, gas) $- \sigma(C_6H_6$, liq. cylindrical) $= 8.15 \pm 0.01$ ppm,[40] $\sigma(C_6H_6$, liq. cyl.) $- \sigma(H_2O$, liq. cyl.) $= -1.70 \pm 0.02$ ppm,[41] and $\sigma(H_2O$, liq. cyl.) $- \sigma(H_2O$, liq. spherical) $= -1.50 \pm 0.01$ ppm,[39] plus $\sigma(H_2) - \sigma(CH_4)$ above to obtain $\sigma(H_2) = 26.24 \pm 0.18$ ppm.

The error 0.18 ppm assigned to the weighted average in Table VII is merely the least of those in the table. Given the situation, we are reluctant to reduce the error. An accurate determination of $\sigma(H_2) - \sigma(H_2O)$ would be of interest, but the final accuracy for $\sigma(H_2)$ will at present be limited by $\sigma(H_2O)$.

IV. CONCLUSIONS

By calculating the diamagnetic shielding and determining to some extent the R dependence of paramagnetic shielding in the equilibrium region from spin-rotation and isotope-shift data, we have obtained the shielding constant for the hydrogen molecule to an accuracy of 0.07 ppm, which is about the same as the uncertainty in the best known shielding constant, $\sigma(H_2O)$. Our results are in good agreement with experiment. A value for $\sigma(H_2)$ slightly larger than experiment presently indicates, is definitely preferred by our analysis.

For a further advance with the approach used here, nonadiabatic and relativistic corrections should be calculated. While it can hardly be expected that in magnitude they would amount to a sizable fraction of 0.07 ppm, they might in effect change isotope shifts which we observed influence the determination of $\bar{\sigma}^p(R)$, and thus σ itself. Indeed, concern that this might occur is the principal reason for the size of our error assignment. On the experimental side, interesting new results would include spin-rotation interaction constants in higher rotational states and in other isotopic forms of the hydrogen molecule, the hydrogen-water chemical shift, isotope shifts, and the temperature dependence of the shielding.

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