The nuclear magnetic shielding and spin-rotation constants of the hydrogen molecule.

by
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Abstract

The variation-perturbation method, employing an explicitly correlated basis set in the form of gaussian functions with exponential correlation factors, has been used to calculate the paramagnetic component of the nuclear magnetic shielding and electronic contribution to the spin-rotation constant for the hydrogen molecule in its ground state. The diamagnetic components of the shielding tensor have also been computed. The computations have been performed for three internuclear distances in the vicinity of equilibrium. A comparison of the calculated quantities, which are of great accuracy, with the experimental data reveals a small but significant discrepancy between theory and experiment.

1 Introduction

The hydrogen molecule is the simplest molecule to exhibit electron correlation and therefore it has long been a favourite system for testing new theoretical methods. Moreover the hydrogen molecule is easily accessible experimentally. Recently a new and very effective method for variational quantum computations for many-electron systems was introduced [1, 2, 3, 4]. In this method exponentially correlated gaussian functions are employed as basis functions. It has been demonstrated that for the hydrogen molecule this method is able to achieve variational energy at the same level of accuracy as methods which employ generalized James-Coolidge functions. It should be pointed out that the level of accuracy provided by these two methods is better by at least three orders of magnitude than that of any other variational method applied to the ground state of the hydrogen molecule.

In this letter we report the use of exponentially correlated gaussian functions to calculate the components of the nuclear shielding tensor and spin-rotation constant for the ground state of the hydrogen molecule in the vicinity of equilibrium. This paper is a continuation of previous work [5], in which the components of the shielding tensor for the ground state of H_2 at R=1.4011 bohr were calculated. However, in that computation the variation-perturbation method employed an explicitly correlated function with a linear correlation term r_{12} [6]. The method used in this work is the same as that used previously except for the new type of function, involving exponentially correlated gaussians.

2 Method

For a molecule the interaction of the magnetic moment of a nucleus, $\boldsymbol{\mu}_N$, with the applied external uniform magnetic field $\mathbf{B}$, has the form $-\mu_{N\alpha}(\delta_{\alpha\beta} - \sigma_{\alpha\beta})B_\beta$, where $\sigma_{\alpha\beta}$ is a component of the nuclear shielding tensor. $\sigma_{\alpha\beta}$ is a sum of the diamagnetic, $\sigma^d_{\alpha\beta}$, and the paramagnetic, $\sigma^p_{\alpha\beta}$, contributions, which are given by the formulas

$$\sigma^d_{\alpha\beta} = \left(\frac{\mu_o}{4\pi}\right)\frac{e^2}{2m_e}\sum_k\int\Psi^{(00)}\frac{\mathbf{r}_{kN}\cdot\mathbf{r}_{kG}\delta_{\alpha\beta} - r_{kN\alpha}r_{kG\beta}}{r^3_{kN}}\Psi^{(00)}d\tau, \qquad (1)$$

and

$$\sigma^p_{\alpha\beta} = -i\sum_k\left(\frac{e}{2m_e}\int\Psi^{(00)}l_{kG\alpha}\Psi^{(01)}_\beta d\tau + \left(\frac{\mu_o}{4\pi}\right)\frac{e}{m_e}\int\Psi^{(00)}\frac{l_{kN\beta}}{r^3_{kN}}\Psi^{(10)}_\alpha d\tau\right). \qquad (2)$$

where $\Psi^{(00)}$ stands for the zero-order function, which is obtained by solving the standard electronic Schrodinger equation. $\Psi^{(01)}_\beta$ and $\Psi^{(10)}_\alpha$ are the first order functions obtained as variational solutions of the following first order equations

$$(H^{(0)} - E^{(00)})\Psi^{(10)}_\alpha = \frac{ie}{2m_e}\sum_k l_{kG\alpha}\Psi^{(00)}, \qquad (3)$$

and

$$(H^{(0)} - E^{(00)})\Psi^{(01)}_\beta = \left(\frac{\mu_o}{4\pi}\right)\frac{ie}{m_e}\sum_k\frac{l_{kN\beta}}{r^3_{kN}}\Psi^{(00)}. \qquad (4)$$

The Coulomb gauge ($\nabla\cdot\mathbf{A} = 0$) for the vector potential $\mathbf{A}$ has been assumed, G denotes a chosen gauge origin, $\mathbf{r}_{kG}$ and $\mathbf{r}_{kN}$ denote vectors from the gauge origin and from the nucleus of interest to electron k, respectively. $\mathbf{l}$ is the electronic angular momentum operator, $\mathbf{l} = -i\hbar\mathbf{r}\times\nabla$, e is the charge of the proton and m_e—the electron mass.

The spin-rotation interaction for a diatomic molecule can be expressed in the form $-\hbar\mathcal{M}\mathbf{I}_\mathrm{N}\cdot\mathbf{J}$, where $\mathbf{I}_\mathrm{N}$ is the spin of nucleus N, $\mathbf{J}$ is the rotational angular momentum, both dimensionless, and $\mathcal{M}$ is the spin-rotation interaction constant. $\mathcal{M}$ is the sum of three contributions [7]

$$\mathcal{M} = \mathcal{M}^{el} + \mathcal{M}^{nuc} + \mathcal{M}^T \qquad (5)$$

where the electronic contribution $\mathcal{M}^{el}$ is proportional to the perpendicular component of the paramagnetic part of σ, and is given by

$$\mathcal{M}^{el} = \frac{2\beta_N g_N\hbar}{4\pi\beta_e m_r R^2}\sigma^p_{\alpha\alpha}. \qquad (6)$$

The two additional contributions are related to R^{-3} and to $R^{-1}\frac{dU}{dR}$ according to the formulas

$$\mathcal{M}^{nuc} = \left(\frac{\mu_0}{4\pi}\right)\frac{e\beta_N g_N}{2\pi m_r R^3}, \tag{7}$$

and

$$\mathcal{M}^{T} = \frac{\hbar}{4\pi m_N^2 c^2 R}\frac{dU}{dR}. \tag{8}$$

In the above formulas β_N and β_e stand for the nuclear and Bohr magnetons, respectively, g_N is the nuclear g-factor, R is the internuclear distance and U is the potential energy function for the molecule. m_r is the reduced mass of the molecule and m_N is the mass of nucleus N.

For the zero and first-order functions, exponentially correlated gaussian functions were used. The zero-order wavefunction is defined as

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = (1+\hat{\imath})\sum_n c_n[\Phi_n(1,2) + \Phi_n(2,1)], \tag{9}$$

where $\hat{\imath}$ here stands for inversion in the bond midpoint and the basis functions are given by

$$\Phi_n(1,2) = \exp(-\alpha_n r_{a1}^2 - \beta_n r_{b1}^2 - \bar{\alpha}_n r_{a2}^2 - \bar{\beta}_n r_{b2}^2 - \gamma_n r_{12}^2) \tag{10}$$

where $\alpha, \beta, \bar{\alpha}, \bar{\beta}$, and γ are variational parameters, 1 and 2 label electrons, and a and b denote the nuclei.

The first order functions $\Psi_\alpha^{(10)}$ and $\Psi_\beta^{(01)}$ possess $^1\Pi_g$ symmetry. They are defined similarly to $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$ but with $\Phi_n(1,2)$ and $\Phi_n(2,1)$ replaced respectively by $y_1\Phi_n(1,2)$ and $y_2\Phi_n(2,1)$, where y is the coordinate axis perpendicular to the molecular axis. The optimization procedure used for solution of the first order equations (3) and (4) is very time consuming but is essential for achieving the required accuracy. In this work the optimization procedure of Powell has been employed [8].

3 Results and discussion

A 300-term expansion of exponentially correlated gaussian functions has been adopted as the zero-order function. For $R = 1.4$ bohr this function gives an energy of

-1.174475680 hartree which is lower by 0.0022 cm^{-1} than the best energy obtained using the Kołos-Wolniewicz function [9]. For the first-order functions 100-term expansions have been used. Computations have been performed for three internuclear distances, $R = 1.35$, 1.4 and 1.45 bohr, with the x-axis coinciding with the molecular axis. The results are displayed in table 1. It contains expectation values of the relevant operators and of all the shielding components. Particular tensor components are calculated from the following formulas (in atomic units):

$$\sigma^d_{\|}(N) = \frac{2}{c^2}\int \Psi^{(00)}\frac{y^2_{1N}}{r^3_{1N}}\Psi^{(00)}d\tau, \tag{11}$$

$$\sigma^d_{\perp}(N) = \frac{1}{c^2}\int \Psi^{(00)}\frac{x^2_{1N}+y^2_{1N}}{r^3_{1N}}\Psi^{(00)}d\tau, \tag{12}$$

$$\sigma^p_{\perp}(G) = -i\left(\int \Psi^{(00)}l_{1Gz}\Psi^{(01)}_z d\tau + \frac{2}{c^2}\int \Psi^{(00)}\frac{l_{1Nz}}{r^3_{1N}}\Psi^{(10)}_z d\tau\right). \tag{13}$$

These quantities can be combined further according to the following definitions: $\sigma^d = \frac{1}{3}\left(\sigma^d_{\|} + 2\sigma^d_{\perp}\right)$, $\sigma^p = \frac{1}{3}\left(\sigma^p_{\|} + 2\sigma^p_{\perp}\right)$, $\sigma_{\|} = \sigma^d_{\|} + \sigma^p_{\|}$, $\sigma_{\perp} = \sigma^d_{\perp} + \sigma^p_{\perp}$, $\Delta\sigma = \sigma_{\|} - \sigma_{\perp}$, and $\sigma = \frac{1}{3}\left(\sigma_{\|} + 2\sigma_{\perp}\right) = \sigma^d + \sigma^p$. Of course, $\sigma^p_{\|}$ is zero for H_2. The diamagnetic and paramagnetic shielding parts are given for two gauge origins: at the bond midpoint (G) and at the proton position (N) both of which lie on the x-axis. These two quantities are connected via the relation [5, 10]:

$$\sigma^p(G) = \sigma^p(N) + d_x C^p, \tag{14}$$

where d_x is the gauge origin shift along the molecular axis, equal in our case to $R/2$. The paramagnetic part of the gauge constant, C^p, can be determined from

$$C^p = -\frac{2}{3}\int \Psi^{(00)}\frac{\partial}{\partial y_1}\Psi^{(01)}_y d\tau, \tag{15}$$

where $\Psi^{(01)}_y$ is a variational solution of the first-order equation

$$(H^{(00)} - E^{(00)})\Psi^{(01)}_y = -\frac{\partial}{\partial y_1}\Psi^{(00)}. \tag{16}$$

However, it is much easier to calculate the gauge constant for the diamagnetic part of the shielding and then use it to determine C^p. Thus

$$\sigma^d(G) = \sigma^d(N) + d_x C^d, \tag{17}$$

where C^d is the diamagnetic gauge constant which can be calculated from the formula [5, 10]:

$$C^d = -\frac{2}{3c^2}\int \Psi^{(00)}\frac{x_{1N}}{r_{1N}^3}\Psi^{(00)}d\tau. \tag{18}$$

We have calculated the gauge constant from Eq.(18) and equated it to C^p after reversing the sign. This corresponds to the assumption that we are using a complete basis set for which these two gauge constants have the same magnitude and opposite sign. Since we are using very accurate wavefunctions, as can be judged from the ground state energy, this assumption is fully justified. The values of the electronic contribution to the spin-rotation constant, as calculated from Eq.(6) using our σ^p value, are given in table 1.

In order to estimate a vibrationally corrected values of σ and $\sigma^p_\perp$ we fitted a parabola, $P(R)$, to pertinent values from table 1. Next, we calculated

$$< 0|P|0> = \int \chi_0^*(R)\, P(R)\, \chi_0(R)\, dR \tag{19}$$

where $\chi_0(R)$ is a numerical solution of a vibrational Schrödinger equation for the rotationless ground vibrational state of H_2. This procedure yields the following expectation values: $< 0|\sigma^p_\perp(G)|0> = 1.12$ *ppm*, $< 0|\sigma^p_\perp(N)|0> = -8.32$ *ppm*, and $< 0|\,\sigma\,|0> = 26.48$ *ppm*.

In table 2 we compare the presently reported value of $\sigma^p_\perp$ at $R = 1.4$ bohr with other theoretical values of this property. Proton shielding is known to be only slightly affected by electron correlation [11]. This is mainly due to the relatively small value of the paramagnetic component of the shielding. However, there are some exceptions predicted by theory. They are: (*a*) two excited states of H_2[12], *viz.* $B^1\Sigma_u^+$ [13] and $B'\ ^1\Sigma_u^+$[14], and (*b*) BH in its ground state [15, 16, 17, 18, 19]. In these cases the paramagnetic contribution is so large that Van Vleck paramagnetism is exhibited. This effect is due to the strong mixing of the near degenerate excited states which contribute to the paramagnetic components of the magnetizability tensor. Therefore it is to be expected that for these cases electron correlation contributes significantly to the perpendicular component of nuclear shielding [20].

It is not easy to estimate the electron correlation contribution to the nuclear shielding of the ground state of H_2 as values calculated at the SCF level may differ by more than 0.5 ppm from each other and are gauge dependent. The most recent calculations of Bishop and Cybulski [21] and of van Wüllen [22] show a difference of 0.24 ppm. Kutzelnigg *et al.* [11] estimated the electron correlation contribution as being no more than 0.2 ppm increasing the value of the mean shielding. Assuming that Bishop and Cybulski's [21] values of components of the shielding tensor at the SCF level are the closest to the SCF limit, we can estimate this contribution to be 0.32 ppm. The electron correlation contributions to the individual components are, of course, different and are 0.08, 0.21 and 0.23 ppm for $\sigma^d_{||}$, $\sigma^d_{\perp}$ and $\sigma^p_{\perp}$, respectively.

The present $\sigma^p_{\perp}$, calculated at 1.4 bohr, appears to differ from the most accurate value estimated from experimental data for equilibrium geometry (1.40125 bohr) by the small but significant amount of 0.17 ppm [23]. The reason for this discrepancy is not known. However, the present results are believed to be accurate to ±0.01 ppm. A similar discrepancy, of course, occurs between the corresponding values for $\mathcal{M}^{el}$.

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Table 1. Nuclear magnetic shielding, σ, and spin-rotation constant, $\mathcal{M}$, tensor components for the ground state H_2 molecule. Entries related to σ and $\mathcal{M}$ are given in units of *ppm* and *kHz*, respectively. Two different gauge origin locations have been assumed: the bond midpoint (G) and the proton position (N).

R/bohr	1.35	1.40	1.45
$\left\langle \frac{x_N^2}{r_N^3} \right\rangle /\mathrm{bohr}^{-1}$	0.393650	0.388965	0.384436
$\left\langle \frac{y_N^2}{r_N^3} \right\rangle /\mathrm{bohr}^{-1}$	0.267391	0.261912	0.256708
$\left\langle \frac{x_N}{r_N^3} \right\rangle /\mathrm{bohr}^{-2}$	0.264017	0.254901	0.246141
$C^d/\mathrm{ppm} \cdot \mathrm{bohr}^{-1}$	9.3728	9.0492	8.7382
Diamagnetic shielding at N:			
$\sigma^d_\perp(N)$	35.2013	34.6601	34.1418
$\sigma^d_{\|}(N)$	28.4779	27.8943	27.3401
$\sigma^d(N)$	32.9602	32.4048	31.8746
Diamagnetic shielding at G:			
$\sigma^d_\perp(G)$	25.7113	25.1584	24.6390
$\sigma^d(G)$	26.6335	26.0704	25.5393
Paramagnetic shielding at N:			
$\sigma^p_\perp(N)$	-8.4116	-8.3864	-8.3549
$\sigma^p(N)$	-5.6077	-5.5909	-5.5699
Paramagnetic shielding at G:			
$\sigma^p_\perp(G)$	1.0784	1.1153	1.1479
$\sigma^p(G)$	0.7189	0.7435	0.7653
Shielding components:			
$\sigma_\perp$	26.7897	26.2737	25.7869
$\sigma_{\|}$	28.4779	27.8943	27.3401
$\Delta\sigma$	1.6881	1.6206	1.5532
Mean Shielding:			
σ	27.3524	26.8139	26.3046
Spin-rotation constant:			
$\mathcal{M}^{el}(N)$	-100.5699	-93.2342	-86.5891
$\mathcal{M}^{n}(N)$	235.8069	211.4334	190.3066
$\mathcal{M}^{T}(N)$	-0.7951	-0.0149	0.5970
$\mathcal{M}(N)$	134.4418	118.1843	104.3144

Table 2. Comparison of calculated and measured values of perpendicular component of the paramagnetic part of the nuclear magnetic shielding constant, $\sigma_{\perp}^{p}$, at $R = 1.4$ bohr. All entries given in units of *ppm*.

$\sigma_{\perp}^{p}(G)$	$\sigma_{\perp}^{p}(N)$	Reference
	Theoretical	
	-8.565	Kolker and Karplus, 1964 [24]
	-8.55	Hoyland, 1964 [25]
0.518		Cook, Davies and Raynes, 1971 [26]
0.190		Zeroka, 1973 [27]
0.743	-8.296	Sadlej and Raynes, 1978 [28]
	-8.67	Parker, 1982 [29]
0.92	-8.45	Iwai and Saika, 1982 [30], CHF
0.89	-8.05	Iwai and Saika, 1982 [30], MBPT
	-8.615	Cybulski and Bishop, 1993 [31], SCF
	-8.569	Cybulski and Bishop, 1993 [31], MP2
1.0021	-8.4814	Komasa, Cencek and Rychlewski, 1992 [5]
1.1153	-8.3864	present work
	Experimental	
	-8.48	Kolker and Karplus, 1964 [24]
	-8.45 ± 0.12	Code and Ramsey, 1971 [32]
	-8.553 ± 0.005	Raynes and Panteli, 1983 [23]