



The magnetizability anisotropy and rotational g factor of deuterium hydride and the deuterium molecule

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Abstract

We present accurate ab initio results for the rotational g factor and the magnetizability anisotropy of the HD and D₂ molecules, comparing with molecular-beam experiments and other theoretical results. We have also calculated other data available from molecular-beam experiments such as the electronic contribution to the quadrupole moment and the expectation value of R^{-3} . All calculated data are in good agreement with experiment.

1. Introduction

In recent years, there has been a marked improvement in the methods for obtaining accurate ab initio data of molecular magnetic properties, related to the development of efficient implementations of response theory [1,2] and to the improved basis-set convergence obtained by using London orbitals [3] and rotational London orbitals [4,5]. This development is especially important for rotational g factors and magnetizability anisotropies, where molecular-beam experiments provide accurate measurements [6]. The experimental error bars are for example less than 0.1% for the rotational g factor of the hydrogen molecule [7–11].

For obtaining theoretical results within the experimental error bars, rovibrational effects on a molecular property must be accounted for. By far the most

important contribution arises from zero-point vibrational effects in an anharmonic potential, which means that the effective geometry is not the same as the geometry of the lowest potential energy. A simple method that includes the major part of the anharmonicity of the potential has been developed [12] by extending the approach by Buckingham [13,14] and applied to the calculation of molecular properties [15,16].

The properties of the hydrogen molecule have been studied extensively with various theoretical methods, see for example Refs. [17–24]. In a previous paper, we presented accurate calculations of the rotational g factor and the magnetizability tensor for H₂ by employing a full configuration interaction (FCI) wavefunction and a large atomic natural-orbital (ANO) basis set [16]. The comparison with experiments was, however, made difficult by the fact that (the neglected) corrections to the Born–Oppenheimer approximation are substantial for the hy-

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drogen molecule [25]. It would therefore be interesting to study HD and D₂, where such effects are smaller and for which accurate experimental data are also available [9–11].

The property of an individual rovibrational state may be calculated as [16]

$$\langle \Omega \rangle_{v,J} = \Omega_{\text{eff}} + \frac{B_{\text{eff}} \Omega_{\text{eff}}''}{\omega_{\text{eff}}} \left(\frac{1}{2} + v \right) + 4J(J+1) \left(\frac{B_{\text{eff}}}{\omega_{\text{eff}}} \right)^2 \Omega_{\text{eff}}', \quad (1)$$

where B is the rotational constant and ω the harmonic frequency. The subscript eff here indicates that the properties have been calculated at a variationally determined geometry, representing the effective geometry of the molecule. The derivatives are defined as $(\Delta \Omega)/(\Delta r/r_{\text{eff}})$. The property derivatives have been calculated numerically, with the second derivatives obtained from a five-point formula.

The accuracy of this approach has been demonstrated by comparison with the Morse potential, [12]

and with numerical integration for the nuclear shieldings of the hydrogen fluoride molecule [15]. Numerical integration gives the exact solution of the vibrational problem and is routinely used for diatomic molecules, see for example the recent paper by Sundholm et al. [26]. For hydrogen fluoride, the approximate method adopted by us gives results that only differ in the fifth digit in comparison with numerical integration [15]. Furthermore, since it describes the nuclear part of the wavefunction by only two parameters, it may straightforwardly be generalized to polyatomic systems and to reaction dynamics. The purpose of this work is to demonstrate the accuracy of methods (perturbation-dependent basis sets and our extension of the perturbation approach for rovibrational averaging) that are also applicable to large molecules.

2. Results

We have calculated the rotational g factor and anisotropy of the magnetizability for HD (Table 1)

Table 1
Calculated properties of HD

	This work			Exptl. ^a	Calc. ^b
	Ω_{eff}	$\Omega_{0,0}$	$\Omega_{0,1}$	$\Omega_{0,1}$	$\Omega_{0,1}$
g	0.66368	0.66342	0.66323	0.663211(14)	0.662893
$\Delta \xi$ (cgs)	-0.5265	-0.5321	-0.5333	-0.535(20)	-0.5302
Q_{el} (au)	0.5627	0.5746	0.5761	0.578(18)	
$\langle R^{-3} \rangle^{-1/3}$ (Å)	0.7635	0.7458	0.7467	0.74604(10)	

$$B_{\text{eff}} = 43.0524 \text{ cm}^{-1}, \quad \omega_{\text{eff}} = 3553.68 \text{ cm}^{-1}.$$

^a See Refs. [11,16]. ^b See Ref. [21].

Table 2
Calculated properties of D₂

	This work			Exptl. ^a	Calc. ^b
	Ω_{eff}	$\Omega_{0,0}$	$\Omega_{0,1}$	$\Omega_{0,1}$	$\Omega_{0,1}$
g	0.44329	0.44263	0.44254	0.44288(5)	0.442823
$\Delta \xi$ (cgs)	-0.5207	-0.5237	-0.5244	-0.528(40)	0.5235
Q_{el} (au)	0.5553	0.5647	0.5657	0.568(54)	
$\langle R^{-3} \rangle^{-1/3}$ (Å)	0.7592	0.7447	0.7453		

$$B_{\text{eff}} = 29.0492 \text{ cm}^{-1}, \quad \omega_{\text{eff}} = 2943.83 \text{ cm}^{-1}.$$

^a See Refs. [9,6]. ^b See Ref. [21].

and D₂ (Table 2). These quantities are all known experimentally [9,11]. Since the experimental results have been measured for the ground vibrational state and the first rotational state ($v = 0$, $J = 1$), we restrict our investigation to the vibrational ground state. Even though these molecules do not exist or cannot be studied with molecular beams for $J = 0$, we have included these values since the magnitude of the rotational contribution is interesting from a theoretical point of view. In addition, we have calculated the electronic contribution to the quadrupole moment and the expectation value of R^{-3} since these properties are also available from experiment. These two properties are also listed for the H₂ molecule (Table 3) since they were not included in our previous work [16]. In this work, we adopt Buckingham's definition of the quadrupole moment [27],

$$Q_{\alpha\beta} = \frac{1}{2}(3R_{\alpha}R_{\beta} - \delta_{\alpha\beta}R^2). \quad (2)$$

For comparison, we have included the properties calculated at the equilibrium geometry (Table 4) and compared these with experiment [28]. The isotope-dependent properties are given in this table for the D₂ molecule. The same potential and property surfaces are employed as in the previous work [16]. The DALTON quantum-chemistry program [29] was used in all calculations.

For the rotational g factor, it is noted that the difference between our calculated numbers and experiment are much smaller for the HD and D₂ molecules than for H₂, in agreement with the fact that corrections to the Born–Oppenheimer approximation are substantial for the hydrogen molecule [25]. These corrections should be larger for H₂ than for HD and D₂.

The anisotropy of the magnetizability, $\Delta\xi$, is calculated within the experimental error bars for HD

Table 3
Calculated properties of H₂

	This work			Exptl.
	Ω_{eff}	$\Omega_{0,0}$	$\Omega_{0,1}$	$\Omega_{0,1}$
Q_{el} (au)	0.5678	0.5818	0.5839	0.595(34) ^a
$\langle R^{-3} \rangle^{-1/3}$ (Å)	0.7665	0.7461	0.7472	0.74677(10) ^b

$$B_{\text{eff}} = 56.9456 \text{ cm}^{-1}, \quad \omega_{\text{eff}} = 4063.27 \text{ cm}^{-1}.$$

^a See Ref. [9]. ^b See Ref. [8].

Table 4
Properties of D₂ at the equilibrium geometry

	Ω_e	Exptl. ^a
R (Å)	0.7417	0.7416
$\Delta\xi$ (cgs)	−0.4978	
Q_{el} (au)	0.5259	
g	0.4457	
B (cm ^{−1})	30.4332	30.429
ω (cm ^{−1})	3115.71	3118.4

^a See Ref. [28].

and D₂, as was the case for the H₂ molecule. The largest contribution to the rovibrational effects arises from a shift of the most probable equilibrium geometry.

In comparison with the work by Rychlewski and Raynes [21], who used an explicitly correlated wavefunction, it is noted that we obtain results closer to experimental data for both the rotational g factor and the magnetizability anisotropy of the HD molecule (Table 1). As for H₂ [16], our calculated value of the magnetizability anisotropy is within the experimental error bars. For the D₂ molecule, our magnetizability anisotropy is slightly closer to experiment and within the experimental error bars, whereas the calculations of Rychlewski and Raynes present excellent results for the rotational g factor of the D₂ molecule with deviations from experiment only in the fifth digit. Although the use of explicitly correlated wavefunctions ensures an accurate description of dynamical correlation effects, we note that it does not guarantee a proper description of perturbed states, as demonstrated for the B¹Σ_u⁺ state of H₂ [30].

The electronic contribution to the quadrupole moment, Q_{el} , of all species is calculated within the experimental error bars. It is noted that the largest contribution to the rovibrational effect arises from a shift of the geometry, although other contributions are also substantial.

The calculated values of $\langle R^{-3} \rangle^{-1/3}$ are slightly outside the experimental error bars, which are as small as 0.015% [8,11]. The rovibrational contribution is as large as -0.0168 Å for HD and -0.0193 Å for H₂. The close agreement with experiment indicates that our value of r_{eff} is a good estimate of the averaged geometry.

3. Conclusions

By carrying out FCI calculations in a basis of perturbation-dependent atomic orbitals, (rovibrationally averaged) magnetic properties such as the rotational g factor and the magnetizability of the HD and D₂ molecules have been calculated to high accuracy. These and other properties are mostly within the experimental error bars. Deviations with respect to experiment are probably due to the Born–Oppenheimer approximation and the truncation of the one-electron basis set. The vibrational wavefunction has been described with a single Gaussian function, demonstrating the adequacy of such an approach.

Acknowledgements

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