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Full CI calculations of the magnetizability and rotational g factor of the hydrogen molecule

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Abstract

We present full CI results for the magnetizability and rotational g factor of the hydrogen molecule. Convergence of the results with respect to the size of the one-particle basis has been considered, as well as corrections for rovibrational effects. Our results at $T = 300$ K are: $(-67.13 \pm 0.04) \cdot 10^{-30} \text{ JT}^{-2}$ for the isotropic magnetizability, $(8.91 \pm 0.03) \cdot 10^{-30} \text{ JT}^{-2}$ for the magnetizability anisotropy and 0.8817 ± 0.0002 for the rotational g factor. The results are compared with molecular beam experiments and other theoretical results.

Keywords: Hydrogen molecule; Full CI ; Magnetizability ; Rotational g factor

1. Introduction

In recent years there has been a vigorous activity within the field of ab initio calculation of molecular magnetic properties. The main reason for this renewed interest in magnetic properties is the advent of efficient means of improving the basis set convergence of these properties, in particular through the use of London orbitals [1]. Although London orbitals have been demonstrated to improve the basis set convergence for all properties to which they have been applied [2–9], it is for properties where the basis set depends explicitly on all perturbations applied, that is, magnetizabilities as well as rotational and vibrational g tensors, that the improved convergence has been most pronounced [4,8,9].

Thus, magnetizabilities can now be calculated to within 2% of the Hartree-Fock limit using basis sets of double-zeta (DZ) quality [10]. However, due to the experimental difficulties in detecting the small effects associated with molecular diamagnetism in the gas-phase, the agreement between theory and experiment for the isotropic magnetizability remains an open question [10].

In molecular-beam and microwave-spectroscopy experiments, the rotational g tensor and magnetizability anisotropy can be measured with error bars of less than 1%. However, the magnetizability anisotropies are more difficult to calculate than the isotropic ones, and Hartree-Fock results are in general not as good for anisotropies as for the isotropic values [11]. Furthermore, the calculation of rotational g tensors was until recently hampered by slow basis-set convergence, and it has therefore been difficult to make comparisons between accurate calculations of

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magnetic properties and accurate experimental numbers.

By the introduction of rotational London orbitals [8], the basis-set convergence of the rotational g factor has been significantly improved and Hartree-Fock limit results are now obtained at the augmented DZ/TZ level [8]. It is therefore of interest to investigate the accuracy obtainable from such calculations and compare them with accurate experimental numbers. It is the purpose of this paper to report the rotational g factor and magnetizability of the hydrogen molecule using an exact description of the N -particle basis through the use of a full CI wave function. We employ basis sets that we believe are well converged in the 1-particle basis and furthermore we perform rovibrational corrections. Our investigations thus report one of the most accurate results for these properties to date, and complement the recent paper by Sundholm et al. [12] on FCI calculations of spin-rotation constants and nuclear shieldings of the hydrogen molecule using (rotational) London orbitals.

We shall in this paper not describe the theory underlying our implementation, but refer instead to the original papers on SCF [4] and MCSCF [13] magnetizabilities using London atomic orbitals, as well as a paper describing the principles behind the rotational London orbitals used for the rotational g factor [8]. In all calculations, we have used the DALTON program package [14].

2. Results and discussion

The augmented correlation-consistent basis sets of Dunning and coworkers [15–17] have proved successful for obtaining near-Hartree-Fock limit results for magnetizabilities and rotational g tensors [4,8,9]. However, for the accuracy aimed at in this investigation, the size of the required correlation-consistent basis set is too large. As our MCSCF program cannot handle more than approximately 100 active orbitals on available computers, we have chosen also to investigate the atomic natural orbital (ANO) set of Widmark and coworkers [18].

Our FCI results for the rotational g factor as well as the isotropic and anisotropic magnetizabilities at the experimental geometry of 1.40125 a.u. are reported in

Table 1
Full CI results for the different basis sets investigated

Basis set	ξ	$\Delta\xi$	g
aug-cc-pVTZ	-65.915	8.161	0.8906
aug-cc-pVQZ - f	-65.713	8.225	0.8908
aug-cc-pVQZ	-65.712	8.225	0.8908
ANO decontr.	-65.696	8.252	0.8906
ANO decontr. + $2s/p$	-65.695	8.262	0.8907
ANO decontr. + f	-65.675	8.246	0.8908
ANO decontr. + $2s/p$ at r_{eff}	-67.110	8.810	0.8839
MP2 results at 1.4 a.u., Ref. [19]	-65.882	8.166	0.9013

Magnetizabilities reported in units of 10^{-30} JT^{-2} .

Table 1. We have not listed the aug-cc-pVDZ results as this set is too small for a proper treatment of correlation. Moreover, we have not included in the table any of the results for the contracted ANO sets, as the difference between the results for the contracted and the primitive basis sets is larger than the accuracy aimed at here. Therefore, all extensions to the ANO basis were applied at the uncontracted level only.

From Table 1, we see that there are only small changes when two diffuse s and one diffuse p functions are added to the primitive ANO basis set. The exponents of the diffuse functions are determined from a geometric series. There is a noticeable change on adding to the primitive ANO set the diffuse f function from the cc-pVQZ basis, whereas the second more diffuse f function in the aug-cc-pVQZ set has no effect. The effect of the f functions is entirely a correlation effect — at the Hartree-Fock level these extensions make no difference. As further studies at the FCI level were impossible because of the size of the basis sets, we decided to use for the calculation of rovibrational corrections the decontracted ANO basis set with two s and one p functions added. The effects of basis set incompleteness are incorporated in the error bars of our final results.

The approach for estimating the rovibrational corrections was introduced in Ref. [20] and is based on a method for including the anharmonicity of the potential in the calculation of intermolecular vibrational frequencies [21] and the work by Buckingham [22,23]. The rovibrationally averaged property (Ω) is at the high-temperature limit calculated from the

expression

$$\langle \Omega(T) \rangle = \Omega_{\text{eff}} + \frac{B_{\text{eff}} \Omega'_{\text{eff}}}{\omega_{\text{eff}}} \left(\frac{1}{2} + \frac{e^{-hc\omega_{\text{eff}}/kT}}{1 - e^{-hc\omega_{\text{eff}}/kT}} \right) + \frac{4kT}{\sigma hc B_{\text{eff}}} \left(\frac{B_{\text{eff}}}{\omega_{\text{eff}}} \right)^2 \Omega'_{\text{eff}} \quad (1)$$

in standard notation, where σ is a symmetry factor which is 1 for heteronuclear diatomics and 2 for homonuclear diatomic molecules [24]. The derivatives appearing in Eq. (1) are defined as $\frac{\Delta\Omega}{\Delta r/r_{\text{eff}}}$. Note that the high-temperature limit is not strictly valid for H_2 at 300 K because of its large rotational constant. The property for an individual rovibrational state is analogously given as

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

The subscript “eff” indicates that the properties are calculated at a variationally determined expansion point which may be considered an effective geometry [21]. This effective geometry was found to be 1.4484 a.u. The different parameters appearing in Eq. (1) and Eq. (2) are presented in Table 2.

As seen from Table 1, Table 3 and Table 4, most of the rovibrational corrections arise from the change in the geometry. The changes introduced by the first and second derivatives of the properties, calculated from both three- and five-point formulas with a step of 0.0516 a.u., were found to be small. It turned out to be difficult to obtain a stable second-derivative of the g factor because of its small magnitude. However, the difference between the three- and five-point second derivatives leads to differences only in the fifth digit of the g factor.

Our rovibrationally corrected results at 300 K are reported in Table 3, whereas our results for the state ($v = 0, J = 1$) are reported in Table 4. We believe that the errors in our approach arise mainly from the incompleteness of the one-particle basis. The error bars are thus based on the convergence of the properties with respect to the one-particle basis.

Comparing our results with those of Cybulski and Bishop [19], we note the fairly good agreement for the

Table 2

Values for the different quantities appearing in Eq. (1)

B_{eff} (cm ⁻¹)	56.945590
ω_{eff} (cm ⁻¹)	4063.27
$\xi_{xx,\text{eff}}$ (10 ⁻³⁰ JT ⁻²)	-61.23
$\xi'_{xx,\text{eff}}$ (10 ⁻³⁰ JT ⁻² a.u. ⁻¹)	-22.21
$\xi''_{xx,\text{eff}}$ (10 ⁻³⁰ JT ⁻² a.u. ⁻²)	6.08
$\xi_{zz,\text{eff}}$ (10 ⁻³⁰ JT ⁻²)	-70.04
$\xi'_{zz,\text{eff}}$ (10 ⁻³⁰ JT ⁻² a.u. ⁻¹)	-33.79
$\xi''_{zz,\text{eff}}$ (10 ⁻³⁰ JT ⁻² a.u. ⁻²)	0.53
g_{eff}	0.8839
g'_{eff} (a.u. ⁻¹)	-0.1430
g''_{eff} (a.u. ⁻²)	-0.1324

Note that we here report the derivatives $\frac{\Delta\Omega}{\Delta r}$.

magnetizability, whereas the difference is significantly larger for the rotational g factor. However, recalling that the paramagnetic contribution to the magnetizability is only $1.42 \cdot 10^{-30}$ JT⁻² compared to the total magnetizability of $-65.70 \cdot 10^{-30}$ JT⁻², it is evident that whereas errors in the paramagnetic term will hardly be noticeable in the total magnetizability, it is crucial for a correct description of the rotational g factor. It appears that the paramagnetic contribution of Cybulski and Bishop is too small. Our results are also in good agreement with those of Rychlewski and Raynes [28], obtained using an explicitly correlated wave function.

To our knowledge there are only two experimental results for the isotropic magnetizability of hydrogen, both quoted in Table 3. Neither of these experiments are in good agreement with our result. Walnut [27] has presented a semi-experimental result where the isotropic magnetizability is determined by combining an experimental paramagnetic magnetizability with a

Table 3

Rovibrationally corrected FCI results at $T = 300$ K obtained with the decontracted ANO + 2s/p basis set

	ξ	$\Delta\xi$	g
This work	-67.13 ± 0.04	8.91 ± 0.03	0.8817 ± 0.0002
Experiment	-66.50 ± 0.03^a		
	-65.4^b		
	-67.13 ± 0.03^c	8.77 ± 0.03^c	

Comparisons are made with experiment and other theoretical results. Magnetizabilities reported in units of 10^{-30} JT⁻².

^a Ref. [25].

^b Ref. [26].

^c Walnut, semi-experimental result, Ref. [27].

Table 4

Rovibrationally corrected FCI results for the state ($\nu = 0, J = 1$) obtained with the decontracted ANO + $2s/p$ basis set

	ξ	$\Delta\xi$	g
This work	-67.14 ± 0.04	8.92 ± 0.03	0.8816 ± 0.0002
Cybulski and Bishop, Ref. [19]	-67.357	8.789	0.8955
Rychlewski and Raynes, Ref. [28]	-67.000	8.866	0.88249
Experiment		9.15 ± 0.50^a 8.90^b	0.88291 ± 0.00007^a

Comparisons are made with experiment and other theoretical results. Magnetizabilities reported in units of 10^{-30} JT^{-2} .

^a Ramsey and coworkers [29].

^b Semi-experimental number derived by Buckingham and Cordle, Ref. [30].

theoretical estimate for the diamagnetic part. We note the excellent agreement with our result, as the error bars of the two results overlap.

Our result for the magnetizability anisotropy is in excellent agreement with the experimental result of Ramsey and coworkers [31], where we are within the experimental error bar but we estimate our results to be significantly more accurate. We also note that our result is in good agreement with the semi-experimental estimate of Buckingham and Cordle [30], whereas there is a larger discrepancy with the estimate of Walnut [27]. Neither the results of Cybulski and Bishop [19] nor the results of Rychlewski and Raynes [28] are within our error bars.

For the rotational g factor, there is an apparent difference between our result and experiment. However, this difference is small, less than 0.2%, which may be compared with the difference of more than 3.5% for the magnetizability anisotropy. It is noted that corrections to the Born-Oppenheimer approximation are of the same order of magnitude as the difference between our calculated value and experiment. These corrections to the rotational constant B is about 0.06% for the hydrogen molecule [32], which will directly affect the rotational g factor. It is necessary to analyze these effects in more detail in order to establish a better agreement between theoretical and experimental data of the rotational g factor of the hydrogen molecule.

3. Conclusions

By adopting (rotational) London orbitals and a full CI wave function and by including rovibrational contributions, we have calculated the so far most accurate

values of the rotational g factor and the magnetizability tensor of the hydrogen molecule. For further improvements, higher order terms, such as corrections to the Born-Oppenheimer approximation, must also be considered.

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