

# The effect of correlation on molecular magnetizabilities and rotational $g$ tensors

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Using multiconfigurational self-consistent field (MCSCF) wave functions and perturbation-dependent basis sets, the effect of electron correlation on molecular magnetizabilities and rotational  $g$  tensors is investigated. The eight molecular systems considered ( $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{HF}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{CO}$ ,  $\text{H}_2\text{CO}$ ,  $\text{O}_3$ , and  $\text{LiH}$ ) vary in the importance and relative magnitudes of the static and dynamic correlation contributions. The results for  $\text{O}_3$  are the first correlated calculations of the rotational  $g$  tensor of this system. We confirm previous findings that, except for systems with large static correlation effects, the effect of correlation on molecular magnetizabilities is small. A somewhat larger correlation contribution is usually observed for the rotational  $g$  tensor, although this property is also rather insensitive to the correlation treatment. Agreement with experimental rotational  $g$  tensors is only fair and estimates of rovibrational corrections are needed to assess properly the accuracy of theoretically calculated rotational  $g$  tensors. © 1997 American Institute of Physics. [S0021-9606(97)00448-0]

## I. INTRODUCTION

Recently, Gauss, Ruud, and Helgaker generalized the magnetic-field dependent London atomic orbitals<sup>1</sup> to include a dependence on the molecular rotational magnetic moment.<sup>2</sup> When spin-rotation constants and rotational  $g$  tensors are calculated using these *rotational London atomic orbitals*, superior basis-set convergence is observed compared with calculations carried out with conventional basis sets. For the rotational  $g$  tensor, the results obtained with rotational London orbitals by Gauss *et al.*<sup>2</sup> are within 2% of the Hartree–Fock limit for the basis sets aug-cc-pVXZ with cardinal number  $X \geq 2$ . Conventional basis functions, in contrast, give results that, for CO and  $\text{N}_2$ , are as much as 10% off from the Hartree–Fock limit even at the most expensive aug-cc-pV5Z level. For larger molecules, accurate rotational  $g$  tensors can therefore be obtained only when rotational London atomic orbitals are used. This has been particularly clearly demonstrated for  $\text{PF}_3$ , where the perturbation-independent aug-cc-pVTZ basis set gives the wrong sign for the rotational  $g$ -tensor components and a magnetizability anisotropy that is off by a factor of two from the Hartree–Fock limit.<sup>3</sup>

Using rotational London atomic orbitals, the calculated *ab initio* results should be sufficiently accurate to make a comparison with results from microwave and molecular beam experiments worthwhile. However, such a comparison also requires a knowledge of the effects of electron correlation on the rotational  $g$  tensor. We note that, although it has been demonstrated that, with a few rare exceptions,<sup>4,5</sup> the effects of electron correlation are usually small for

magnetizabilities,<sup>6–9</sup> this may not be the case for the rotational  $g$  tensors. Moreover, for a meaningful comparison with experiment, also the effects due to the nuclear motion at experimental temperatures must be considered. Such studies of the rotational  $g$  tensor were recently presented by Åstrand *et al.* for the hydrogen isotopomers [using full configuration-interaction (FCI) wave function]<sup>10,11</sup> and by Cybulski and Bishop for a number of diatomic molecules.<sup>8</sup> In the present work, we extend our previous study of the rotational  $g$  tensors to multiconfigurational self-consistent field (MCSCF) wave functions so as to investigate the effects of electron correlation for systems larger than the hydrogen molecule.

The remainder of this paper contains four sections. In Sec. II, a short theoretical background is given. In Sec. III we give some computational details, and in Sec. IV we report our results, discussing these in relation to experiment as well as to previous theoretical investigations. Section V contains some concluding remarks.

## II. THEORY

The rotational  $g$  tensor measures the shift of the rotational energy levels in a strong magnetic field,

$$\Delta E = -\frac{\mu_N}{\hbar} \mathbf{B}^T \mathbf{g} \mathbf{J}. \quad (1)$$

Here  $\mu_N$  is the nuclear magneton and  $\mathbf{B}$  and  $\mathbf{J}$  represent the magnetic field and the total rotational angular momentum, respectively. In the above equation we have restricted our attention to singlet states, and therefore do not consider the effects that would otherwise arise from electron spin. For the calculation of the rotational  $g$  tensor, it is convenient to ex-

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press this property as a derivative of the electronic energy with respect to the magnetic field strength and the rotational angular momentum<sup>2</sup>

$$g = - \frac{\hbar}{\mu_N} \left. \frac{\partial^2 \varepsilon(\mathbf{B}, \mathbf{J})}{\partial \mathbf{B} \partial \mathbf{J}} \right|_{\mathbf{B}, \mathbf{J} = \mathbf{0}}, \quad (2)$$

where, in our approach, the molecular energy  $\varepsilon(\mathbf{B}, \mathbf{J})$  is evaluated from a MCSCF wave function. The rotational  $g$  tensor may thus be obtained in the same way as any other time-independent second-order molecular property, once the expression for the molecular electronic energy (including the nuclear contribution) has been written down for a rotating molecular system in the presence of an external magnetic field. We shall not here give the detailed expressions needed for the evaluation of the MCSCF derivative Eq. (2) since, once the Hamiltonian operator and the form of the atomic orbitals have been specified (as done below), these expressions may be derived in the standard manner.

Let us first consider the Hamiltonian operator. Retaining only the terms that are linear and bilinear in  $\mathbf{B}$  and  $\mathbf{J}$ , we obtain the following expression for the Hamiltonian in atomic units:<sup>2</sup>

$$H(\mathbf{B}, \mathbf{J}) = H_0 + \frac{1}{2} \mathbf{L}_O^T \mathbf{B} - \mathbf{L}_{\text{CM}}^T I^{-1} \mathbf{J} + \frac{1}{2} \mathbf{B}^T \sum_i (\mathbf{r}_i^T \mathbf{R}_O \mathcal{T} - \mathbf{r}_i \mathbf{R}_O^T) \\ \times I^{-1} \mathbf{J} - \frac{1}{2} \mathbf{B}^T \sum_K Z_K (\mathbf{R}_K^T \mathbf{R}_K \mathcal{T} - \mathbf{R}_K \mathbf{R}_K^T) I^{-1} \mathbf{J}, \quad (3)$$

where the coordinate system is chosen so that the origin coincides with the center of mass  $\mathbf{R}_{\text{CM}}$  and so that the moment-of-inertia tensor  $I$  is diagonal. The position of the electrons and the nuclei with respect to the center of mass are given by  $\mathbf{r}_i$  and  $\mathbf{R}_K$ , respectively, and  $\mathbf{R}_O$  is the position of the gauge origin for the vector potential representing the magnetic field,

$$\mathbf{A}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times (\mathbf{r} - \mathbf{R}_O). \quad (4)$$

The first term in the Hamiltonian Eq. (3) is the usual nonrelativistic field- and spin-free Hamiltonian operator  $H_0$ . The second and third terms represent the paramagnetic orbital Zeeman interaction of the electrons with the external field  $\mathbf{B}$  and with the field generated by the molecular rotation, respectively. The operators for the angular momentum of the electrons relative to the gauge origin and to the center-of-mass are given by

$$\mathbf{L}_O = \sum_i (\mathbf{r}_i - \mathbf{R}_O) \times \nabla_i, \quad (5)$$

$$\mathbf{L}_{\text{CM}} = \sum_i \mathbf{r}_i \times \nabla_i. \quad (6)$$

The last two terms in the Hamiltonian operator Eq. (3) represent the diamagnetic interaction between the externally applied field and the field generated by the molecular rotation, as mediated by the electrons and by the nuclei. In these ex-

pressions, we have introduced the  $3 \times 3$  unit matrix  $\mathcal{T}$ , the nuclear charges  $Z_K$ , and the proton mass  $M_p$  (in atomic units).

Having specified the form of the Hamiltonian operator, let us now consider the atomic orbitals. The rotational London atomic orbitals are taken as<sup>2</sup>

$$\omega_\mu(\mathbf{B}, \mathbf{J}) = \exp(-i[\mathbf{A}_\mu^{\mathbf{B}} + \mathbf{A}_\mu^{\mathbf{J}}] \cdot \mathbf{r}) \chi_\mu. \quad (7)$$

Here  $\chi_\mu$  is an ordinary Gaussian basis function and the phase factors are given by

$$\mathbf{A}_\mu^{\mathbf{B}} = \frac{1}{2} \mathbf{B} \times (\mathbf{R}_\mu - \mathbf{R}_O), \quad (8)$$

$$\mathbf{A}_\mu^{\mathbf{J}} = -I^{-1} \mathbf{J} \times \mathbf{R}_\mu, \quad (9)$$

where  $\mathbf{R}_\mu$  is the position of the atomic orbital  $\chi_\mu$  relative to the center-of-mass. In effect, these two phase factors transfer the gauge origin and the molecular center of rotation locally to the optimal position for each basis function—that is, to the nucleus to which the basis function is attached. In this way, a rapid convergence with respect to the basis set is ensured as demonstrated elsewhere.<sup>2,3,12</sup>

From the form for the Hamiltonian Eq. (3) and the atomic orbitals Eq. (7), we may derive the expressions for the molecular rotational  $g$  tensor in the same manner as we derive expressions for other second-order properties such as molecular force constants<sup>13</sup> and molecular magnetizabilities.<sup>12</sup> The resulting expression for the rotational  $g$  tensor contains no reference to the gauge origin of the vector potential representing the external magnetic field but depends on the center of mass of the molecular system.<sup>2,5,14</sup> It should also be noted that the expression for the rotational  $g$  tensor is closely related to the expression for the magnetizability tensor

$$\xi = - \left. \frac{\partial^2 \varepsilon(\mathbf{B}, \mathbf{J})}{\partial \mathbf{B}^2} \right|_{\mathbf{B}, \mathbf{J} = \mathbf{0}}. \quad (10)$$

In the center-of-mass coordinate system, the relationship between the magnetizability tensor  $\xi$  and the rotational  $g$  tensor may now be written in the following manner:

$$4\xi + IM_p^{-1} g = \text{Tr}(Q) - Q. \quad (11)$$

We have here introduced the matrix of the second moment of the charge with respect to the center-of-mass,

$$Q = \sum_K Z_K \mathbf{R}_K^T \mathbf{R}_K - \sum_{pq} D_{pq} \langle p | \mathbf{r}^T \mathbf{r} | q \rangle, \quad (12)$$

where the first summation is over all nuclei and the second summation is over all pairs of molecular orbitals, with  $D_{pq}$  representing the one-electron density-matrix elements in the molecular-orbital basis and  $\langle p | \mathbf{r}^T \mathbf{r} | q \rangle$  the corresponding one-electron second-moment integrals. The rotational  $g$  tensor may therefore be programmed and calculated as a simple extension to any code that already calculates the molecular magnetizability tensor.

TABLE I. Experimental geometries used in this investigation.

Molecule	Geometry parameter	Value	Reference
H <sub>2</sub> O	$r_{\text{OH}}$	97.2 pm	39
	$\angle(\text{HOH})$	104.5°	
NH <sub>3</sub>	$r_{\text{NH}}$	102.4 pm	39
	$\angle(\text{HNH})$	107.3°	
HF	$r_{\text{HF}}$	92.6 pm	39
C <sub>2</sub> H <sub>2</sub>	$r_{\text{CC}}$	120.32 pm	39
	$r_{\text{CH}}$	106.06 pm	
CO	$r_{\text{CO}}$	112.8 pm	39
H <sub>2</sub> CO	$r_{\text{CO}}$	120.3 pm	40
	$r_{\text{CH}}$	109.9 pm	
O <sub>3</sub>	$\angle(\text{HCO})$	121.8°	41
	$r_{\text{OO}}$	127.2 pm	
LiH	$\angle(\text{OOO})$	116.58°	41
	$r_{\text{LiH}}$	159.5 pm	

### III. COMPUTATIONAL DETAILS

The calculations presented in this study have all been performed with the DALTON quantum-chemistry program,<sup>15</sup> where we have recently implemented MCSCF rotational  $g$  tensors using rotational London orbitals as described in the previous section.

We have previously shown that, in the aug-cc-pVDZ basis, rotational  $g$  factors are within 2% of the Hartree–Fock limit when rotational London atomic orbitals are used.<sup>2,3</sup> This means that basis-set convergence of the property need not be considered when choosing the basis set, as long as a basis of at least aug-cc-pVDZ quality is used. However, in order to treat correlation effects adequately, a basis set of triple-zeta quality or better is needed. The convergence of the correlated properties were tested on the water molecule, where calculations employing the basis sets aug-cc-pVXZ with  $X \leq 4$  were carried out.

For the remaining calculations (except those on lithium hydride), we used the aug-cc-pVTZ basis set, which is sufficiently flexible to recover adequately the correlation effects at the MCSCF level. For lithium, no correlation-consistent

basis set exists and we have instead used the atomic natural-orbital (ANO) sets of Widmark and co-workers.<sup>16</sup> Test calculations using various contractions of this basis lead to quite large differences compared with the primitive set. The uncontracted primitive basis was therefore used in all the calculations reported here. Additional calculations, with diffuse functions ( $2s2p1d1f$ ) and ( $2s1p1d$ ) added to lithium and hydrogen, respectively, and with exponents derived from a geometric series, gave no changes within the number of digits reported here. No diffuse functions were therefore used in the reported calculations.

All calculations were carried out at the experimental geometries in Table I. In order to compare directly with experiment, rovibrational effects should be taken into account. However, this is beyond the scope of this investigation. We also restrict our attention to transitions between the lowest rotational energy levels, assuming that the dependence of the equilibrium geometry on the rotational energy levels are negligible for these states. The active spaces were selected based on an analysis of the occupation numbers of the second-order Møller–Plesset (MP2) natural orbitals.<sup>17</sup>

### IV. RESULTS

#### A. H<sub>2</sub>O

For the isoelectronic systems H<sub>2</sub>O, NH<sub>3</sub>, and HF, we have previously shown that an active space containing six orbitals of  $A_1$  symmetry, three orbitals of  $B_1$  symmetry, three orbitals of  $B_2$  symmetry, and one orbital of  $A_2$  symmetry gives a good description of the correlation effects.<sup>18</sup> This (6331) active space is used in all calculations on these molecules. To check that our assumptions about the basis-set dependence of the correlated rotational  $g$  tensors are valid, we investigated the basis-set convergence of the rotational  $g$  tensors and magnetizabilities of the water molecule using the aug-cc-pVXZ basis sets with  $X \leq 4$ , see Table II. The convergence of the correlated calculations is good. The results are all within 1.5% of one another, even for the smallest aug-cc-pVDZ basis set.

TABLE II. Rotational  $g$  tensor, magnetizabilities (in units of  $10^{-30} \text{ JT}^{-2}$ ) of water (H<sub>2</sub>O). Convergence with respect to basis set size for an active space of (6331), as well as other theoretical and experimental results.

Ref.	Basis set/method	$g_{xx}$	$g_{yy}$	$g_{zz}$	$\xi$	$\Delta\xi_1^a$	$\Delta\xi_2^a$
	SCF/aug-cc-pVTZ	0.7280	0.6715	0.6576	-232.6	-5.0	8.5
This work	CAS(6331)/aug-cc-pVDZ	0.7316	0.6699	0.6432	-238.0	-6.6	6.3
	CAS(6331)/aug-cc-pVTZ	0.7277	0.6643	0.6511	-236.8	-4.6	7.2
	CAS(6331)/aug-cc-pVQZ	0.7273	0.6634	0.6514	-236.6	-4.4	7.3
8	MP2 (NoLon)	0.7453 <sup>b</sup>	0.6830 <sup>b</sup>	0.6640 <sup>b</sup>	-238.4	-4.4	7.1
9	L-CCD (NoLon)	0.7288	0.6682	0.6507	-234.6		6.9
7,6	MCSCF/IGLO				-230.8		
19	CCPPA				-236.5		
42	Exp. (BM <sup>c</sup> )	0.718(7)	0.657(1)	0.645(6)		-3.3(8)	7.7(4)
43	MW <sup>d</sup>	0.7145(20)	0.6650(20)	0.6465(20)			

<sup>a</sup>The anisotropies are defined as, respectively,  $\Delta\xi_1 = 2\xi_{xx} - \xi_{yy} - \xi_{zz}$  and  $\Delta\xi_2 = -\xi_{xx} + 2\xi_{yy} - \xi_{zz}$ .

<sup>b</sup>Corrected value reported in Ref. 9.

<sup>c</sup>Beam-maser experiment.

<sup>d</sup>Microwave spectroscopy.

TABLE III. Rotational  $g$  tensor, magnetizabilities (in units of  $10^{-30} \text{ J T}^{-2}$ ) for ammonia ( $^{15}\text{NH}_3$ ). All results obtained with the aug-cc-pVTZ and compared with other theoretical estimates and experimental results.

Ref.	Wave function	$g_{\parallel}$	$g_{\perp}$	$\xi$	$\xi_{\perp} - \xi_{\parallel}$
This work	SCF	0.5760	0.5013	-289.4	-17.0
	CASSCF (6331)	0.5755	0.5073	-293.1	-17.0
8	MP2 (NoLon)	0.5920	0.5224	-294.8	-17.04
9	L-CCD (NoLon)	0.5747	0.5044	-290.2	-17.2
6	MCSCF/IGLO (52)			-287.2	-17.8
24	Experiment (MW <sup>a</sup> )	0.5654(7)	0.5024(5)		
25	MW <sup>a</sup>				-16.4(10)
22	DM <sup>b</sup>			-271(13) <sup>c</sup>	

<sup>a</sup>Microwave spectroscopy.

<sup>b</sup>Direct measurement of the magnetizability.

<sup>c</sup>According to the findings of our previous studies on the magnetizability of hydrocarbons (Ref. 23) the results of Barter *et al.* contain a calibration error and should be scaled by 1.07, giving a corrected result of  $-290 \times 10^{30} \text{ J T}^{-2}$ .

For the isotropic magnetizability, the agreement between the various theoretical approaches is good; our MCSCF results are within 1% of the gauge-origin independent CCPA results of Geertsen<sup>19</sup> as well as the MP2 and L-CCD results of Cybulski and Bishop.<sup>8,9</sup> A poorer agreement is observed with the MCSCF-IGLO results of van Wüllen and Kutzelnigg.<sup>6,7</sup> This discrepancy probably arises from their use of a full-valence MCSCF wave function, which has been shown to be unbalanced for the study of magnetic properties.<sup>18</sup> Correlation gives a diamagnetic increase in the magnetizability of 1.8% which, when combined with our semicontinuum result for ice ( $-199.8 \times 10^{-30} \text{ J T}^{-2}$ ),<sup>20</sup> gives an estimated correlated result for ice of  $-203.4 \times 10^{-30} \text{ J T}^{-2}$ —in excellent agreement with the experimental result on solid ice ( $-204 \times 10^{-30} \text{ J T}^{-2}$ ).<sup>21</sup> However, our result is in poor agreement with the experimental result for the gas phase, although we are within the experimental error bars.

Turning our attention to the rotational  $g$  tensors, we note that the agreement with Cybulski and Bishop is now less satisfactory. Our results for the aug-cc-pVQZ basis set are in fairly good agreement with the beam-maser experiments of Verhoeven and Dymanus and are for  $g_{xx}$  and  $g_{zz}$  just outside the experimental error bars. The same applies to the magnetizability anisotropies. In fact, our calculations give more support to the results of Verhoeven and Dymanus than to those of Kukulich, in spite of the much smaller error bars of the latter investigation. However, the effects of rovibrational averaging should be considered before a definite conclusion about the accuracy of these experiments can be reached.

## B. $\text{NH}_3$

The (6331) MCSCF results for  $^{15}\text{NH}_3$  are collected in Table III. The effects of correlation are again quite small. For the rotational  $g$  tensor, the agreement with the results of Cybulski and Bishop is poorer than for the water molecule; for the isotropic magnetizability, the agreement is still very good. As for  $\text{H}_2\text{O}$ , our results deviate somewhat from those

obtained with a full-valence MCSCF wave function and the IGLO approach.<sup>7</sup> This also applies to the anisotropy, where on the other hand our results are identical to the results of Cybulski and Bishop. We also note that our results for the isotropic magnetizability are in excellent agreement with the results of Barter *et al.*<sup>22</sup> when their results are scaled by 1.07, as previously suggested by us in an extensive study of the magnetizability of hydrocarbons.<sup>23</sup> The need for a scaling of these experimental results is probably due to an error in the calibration of the experimental setup. For the magnetizability anisotropy, our results are within the experimental error bars.

The rotational  $g$  tensor of ammonia was reinvestigated by Hüttner *et al.* in 1988, who by and large confirmed older determinations.<sup>24</sup> There are substantial deviations between our results and experiment, although our results are in significantly better agreement with experiment than those of Cybulski and Bishop. Hüttner *et al.* made estimates of the rotational  $g$  tensors for ammonia in different inversion-vibrational states, demonstrating a strong state dependence of the rotational  $g$  tensor.<sup>24</sup> Some of the disagreement may thus be due to the neglect of rovibrational corrections. For the magnetizability anisotropy, our results are within the experimental error bars of Reijnders *et al.*<sup>25</sup>

## C. HF

For hydrogenfluoride, the agreement between the different correlated theoretical approaches is good, with MCSCF-IGLO once again showing a slight deviation for the isotropic magnetizability. To our knowledge, the only experimental measurement of the isotropic magnetizability is for liquid hydrogen fluoride, where the magnetizability of  $-143 \times 10^{-30} \text{ J T}^{-2}$  is quite different from that obtained here for the gas-phase molecule, probably because of molecular association in the liquid phase.

For the rotational  $g$  tensor, for which the agreement with Cybulski and Bishop is very good, there exists a recent experimental determination by Bass *et al.* using molecular-beam electron-resonance spectroscopy and estimating the ro-

TABLE IV. Rotational  $g$  tensor, magnetizabilities (in units of  $10^{-30} \text{ J T}^{-2}$ ) for hydrogen fluoride (HF). All results obtained with the aug-cc-pVTZ and compared with other theoretical estimates and experimental results.

Ref.	Wave function	$g$	$\xi$	$\xi_{\perp} - \xi_{\parallel}$
This work	SCF	0.7583	-173.2	-8.7
	CASSCF(6331)	0.7539	-177.0	-8.5
8	MP2 (NoLon)	0.7535	-178.3	-8.8
9	L-CCD (NoLon)	0.7488	-176.0	-8.5
44	MCSCF/GIAO		-172.0	-8.4
7	MCSCF(3210)/IGLO		-171.7	-8.1
27	Experiment (MB <sup>a</sup> )	0.74105(15)		-8.74
26		0.75449 <sup>b</sup>		-2.8 <sup>c</sup>

<sup>a</sup>Molecular beam experiment.<sup>b</sup>Value extrapolated to rigid, equilibrium geometry. The value observed for the vibrational ground state was 0.741 599.<sup>c</sup>Value observed for the vibrational ground state.

tational  $g$  factor of the rigid molecule.<sup>26</sup> We note the excellent agreement with our results (see Table IV). Their estimate for zero-point rovibrational correction of  $-0.0129$  is larger than Cybulski and Bishop's MP2 estimate of  $-0.0095$ . Apparently, the agreement between theory and experiment is better for the rigid molecule. It is interesting to note that, for this system, the effects of rovibrational corrections are larger than the effects of electron correlation. The excellent agreement for the rotational  $g$  factor indicates that this new measurement is more accurate than the older result of De Leeuw and Dymanus.<sup>27</sup> However, for the magnetizability anisotropy, the situation is reversed. This is accordance with the observations of Bass *et al.*, who noted that their experimental setup was prone to large systematic errors in the determination of the magnetizability anisotropy, as appears to be confirmed by our results.

TABLE V. Rotational  $g$  tensor, magnetizabilities (in units of  $10^{-30} \text{ J T}^{-2}$ ) of acetylene ( $\text{C}_2\text{H}_2$ ). All results obtained with the aug-cc-pVTZ and compared with other theoretical estimates and experimental results.

Ref.	Wave function	$g$	$\xi$	$\xi_{\perp} - \xi_{\parallel}$
This work	SCF	0.0687	-385.4	39.2
	CASSCF			
	(42203110)	0.0604	-378.4	32.3
	(52213110)	0.0610	-376.6	33.7
9	MP2 (NoLon)	0.0612	-378.0	34.3
9	L-CCD (NoLon)	0.0570	-373.4	38.6
28	Experiment(MB <sup>a</sup> )	-0.04903(4)		
31	MVCD <sup>b</sup>	0.0535(33)		
22	DM <sup>c</sup>		-345(13) <sup>d</sup>	

<sup>a</sup>Molecular beam experiments.<sup>b</sup>Magnetic vibrational circular dichroism.<sup>c</sup>Direct measurement of the isotropic magnetizability.<sup>d</sup>According to the findings of our previous studies on the magnetizability of hydrocarbons (Ref. 23) the results of Barter *et al.* contain a calibration error and should be scaled by 1.07, giving a corrected result of  $-370(13) \times 10^{30} \text{ J T}^{-2}$ .TABLE VI. Rotational  $g$  tensor, magnetizabilities (in units of  $10^{-30} \text{ J T}^{-2}$ ) of carbonmonoxide (CO). All results obtained with the aug-cc-pVTZ and compared with other theoretical estimates and experimental results.

Ref.	Wave function	$g$	$\xi$	$\xi_{\perp} - \xi_{\parallel}$
This work	SCF	-0.2801	-206.1	140.4
	CASSCF			
	(8331)	-0.2592	-217.6	126.4
8	MP2 (NoLon)	-0.2583	-217.3	125.9
9	L-CCD (NoLon)	-0.2642	-212.4	133.2
33	SOPPA		-204.7	
6	MCSCF/IGLO (4220)		-215.0	126.0
45	Experiment(MB <sup>a</sup> )	-0.26890(10)		
46	MB <sup>b</sup>	-0.26895(5)		137.2(2)
34	MW <sup>c</sup>			136(13)
21			-163	

<sup>a</sup>Molecular beam experiments.<sup>b</sup>Molecular beam experiments.<sup>c</sup>Microwave spectroscopy.

## D. $\text{C}_2\text{H}_2$

Acetylene has for a long time been of special interest in measurements of the rotational  $g$  factor, as the sign of the  $g$  factor was first determined to be negative.<sup>28</sup> Later measurements using microwave spectroscopy,<sup>29</sup> molecular beam,<sup>30</sup> and very recently magnetic vibrational circular dichroism (MVCD) (Ref. 31) have established the sign to be positive, and this finding is confirmed by our calculations (see Table V). All things considered, *ab initio* calculations probably constitute the simplest and most reliable way of determining the sign of rotational  $g$  factors.<sup>3</sup>

Acetylene is isoelectronic with nitrogen and has a very similar electronic structure. For this reason, we chose to use for acetylene the two largest active spaces of our MCSCF calculations of nuclear shieldings in  $\text{N}_2$  [(42203110) and (52213110)].<sup>18</sup> These active spaces recover the full static correlation, but lack some of the flexibility needed for the description of dynamical correlation—compare the results of Ref. 18 with the recent CCSD(T) results of Gauss and Stanton.<sup>32</sup> This is also apparent when observing the good agreement with the MP2 results of Bishop and Cybulski,<sup>8</sup> whereas there is a greater difference compared with their more recent L-CCD results,<sup>9</sup> which in turn are closer to experiment.

In absolute terms, the correlation contribution to the rotational  $g$  factor in acetylene is about as large as in  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and HF. In relative terms, however, the correlation contribution is much more important for acetylene since the rotational  $g$  factor is an order of magnitude smaller in this system. Our result is in better agreement with the recent MVCD measurements of Tam *et al.*<sup>31</sup> than the older result of Cederberg *et al.*,<sup>28</sup> later corrected for the sign.<sup>30</sup> Tam *et al.* also measured the rotational  $g$  factor of several vibrationally excited states, the difference with respect to the ground state ranging from  $-0.0061$  to  $-0.0080$ . Assuming a change of approximately one-half of this magnitude because of zero-point vibrational effects, our results will come within the error bars of Tam *et al.*

TABLE VII. Rotational  $g$  tensor, magnetizabilities (in units of  $10^{-30} \text{ J T}^{-2}$ ) of formaldehyde ( $\text{CH}_2\text{O}$ ). All results obtained with the aug-cc-pVTZ and compared with other theoretical estimates and experimental results.

Ref.	Wave function	$g_{xx}$	$g_{yy}$	$g_{zz}$	$\xi$	$\Delta\xi_1$	$\Delta\xi_2$
This work	SCF	-2.6997	-0.2210	-0.0684	-139.6	395.3	-9.3
	CASSCF(6420)	-2.5279	-0.2019	-0.0925	-148.2	352.7	-40.8
	$2,0,0,0_{3,2,0,0}$ RASSCF $^{2,0,0,0}_{3,2,0,0}$	-2.5348	-0.2019	-0.0891	-148.3	356.5	-38.9
	$2,0,0,0_{3,2,0,0}$ RASSCF $^{2,0,0,0}_{7,4,3,2}$	-2.7766	-0.2108	-0.0835	-135.7	411.6	-50.3
	$2,0,0,0_{3,2,0,0}$ RASSCF $^{2,0,0,0}_{10,6,5,3}$	-2.7978	-0.2157	-0.0873	-133.4	408.9	-47.4
9	MP2 (NoLon)	-2.8113	-0.2124	-0.0995	-132.5	404.4	
9	L-CCD (NoLon)	-2.8886	-0.2185	-0.0846	-129.9	431.7	
47	Experiment(MW <sup>a</sup> )	-2.899(2)	-0.2256(8)	-0.1004(7)		423(8)	-65(5)
48	MB <sup>b</sup>					422(3)	-68(3)
21					-309		

<sup>a</sup>Microwave spectroscopy.<sup>b</sup>Molecular beam maser experiment.

For the isotropic magnetizability, our results once again confirm the suggested scaling of the results of Barter *et al.*,<sup>23</sup> as previously noted for  $\text{NH}_3$ . Although our result of  $-376.6 \times 10^{-30} \text{ J T}^{-2}$  is not in perfect agreement with the scaled result of  $-370 \times 10^{-30} \text{ J T}^{-2}$ , it is well within the experimental error bars.

## E. CO

Our results for CO are collected in Table VI. The disagreement among experiment and theory is evident for the rotational  $g$  tensor and to some extent also for the magnetizability anisotropy. We note the good agreement among the various theoretical approaches (with the noticeable exception of the SOPPA results of Sauer *et al.*<sup>33</sup>) as well as the good internal consistency of the experimental investigations. Cybulski and Bishop estimated the rovibrational corrections to the various properties, but they are for all properties less than 1% and cannot explain this discrepancy.

For the magnetizability anisotropy, our results are in very good agreement with both MP2 and MCSCF-IGLO,<sup>8,6</sup> whereas a larger difference exist with the recent L-CCD results of Cybulski and Bishop,<sup>9</sup> probably because of a more

complete description of the dynamical correlation in the latter approach. Still, our result is within the experimental error bars of Gustavson and Gordy.<sup>34</sup>

## F. $\text{CH}_2\text{O}$

Because of the large number of valence electrons and the importance of dynamical correlation, formaldehyde is a molecule that is difficult to describe with MCSCF wave functions. All our choices of active spaces in Table VII give corrections away from experiment and also in the opposite direction of the MP2 and L-CCD corrections. Indeed, all the extensions of the active space we have tried, overestimate the effect of electron correlation as compared to the L-CCD results, although the discrepancy is not large for the larger active spaces.

## G. $\text{O}_3$

Ozone is often considered a typical example of a molecule with large static correlation effects, for which multi-configurational wave functions are needed to describe correctly the electronic structure of the molecule [although, for many properties, the single-configuration based CCSD(T)

TABLE VIII. Rotational  $g$  tensor, magnetizabilities (in units of  $10^{-30} \text{ J T}^{-2}$ ) of ozone ( $\text{O}_3$ ). All results obtained with the aug-cc-pVTZ and compared with other theoretical estimates and experimental results.

Ref.	Wave function	$g_{xx}$	$g_{yy}$	$g_{zz}$	$\xi$	$\Delta\xi_1$	$\Delta\xi_2$
This work	SCF	-5.7515	-0.3992	-0.0675	585.4	2647.4	-35.4
	CASSCF						
	(3321)	-2.7101	-0.2132	-0.0704	96.2	1091.3	10.1
	(4421)	-2.6677	-0.2160	-0.0696	90.9	1058.0	42.9
	(5421)	-2.6687	-0.2099	-0.0706	89.0	1072.7	5.1
(6521)	-2.6801	-0.2150	-0.0762	97.8	1050.8	12.8	
7	MCSCF/IGLO				89.7	1085	2.2
37	Experiment(MW <sup>a</sup> )	-2.968(35)	-0.228(7)	-0.081(6)		1627(93)	-288.9(73)
36	MB <sup>b</sup>	-2.9877(9)	-0.2295(3)	-0.0760(3)		1189(5)	20(3)

<sup>a</sup>Microwave spectroscopy.<sup>b</sup>Molecular beam experiments.

TABLE IX. Rotational  $g$  tensor, magnetizabilities (in units of  $10^{-30} \text{ J T}^{-2}$ ) of lithium hydride (LiH). All results obtained with the primitive ANO set and compared with experimental results.

Ref.	Wave function	$g$	$\xi$	$\xi_{\perp} - \xi_{\parallel}$
This work	SCF	-0.6973	-125.2	42.9
	CAS (4110)	-0.6631	-129.3	42.7
	CAS (10 441)	-0.6594	-128.7	43.0
38	Experiment(MB <sup>a</sup> )	-0.654(7)		
21				

<sup>a</sup>Molecular beam experiments, 930 K and  $J=1$ .

<sup>b</sup>Solid lithium hydride crystals.

method appears to yield excellent results for ozone<sup>32,35</sup>]. Our results for this molecule are collected in Table VIII. The Hartree–Fock results are meaningless, differing from experiment by a factor of almost 2 for some of the  $g$ -tensor components. Similarly, the isotropic magnetizability is reduced almost by a factor of 6 when going from Hartree–Fock to even the smallest active space chosen here.

Even a modest active space brings the results into fairly good agreement with experiment. Further extensions of the active space (in order to recover some of the effects of dynamical correlation) lead, as for formaldehyde, only to modest changes in the calculated properties. However, although we are outside the experimental error bars, the agreement must be considered rather satisfactory in view of the complicated electronic structure of this system. Our results also give strong evidence in support of the molecular-beam results of Meerts *et al.*<sup>36</sup> as opposed to the microwave experiments of Pochan *et al.*<sup>37</sup> We also note that our results for the magnetizability is in good agreement with the MCSCF–IGLO results of van Wüllen, obtained using a full-valence CAS wave function.<sup>7</sup>

## H. LiH

Lithium hydride represents another challenge to *ab initio* methods—not so much because of electron correlation effects (there are only four electrons in this system)—but rather because of its diffuse charge distribution as well as the shallowness of the potential energy well. Our results, obtained using the primitive basis of the ANO set, are collected in Table IX. The effects of electron correlation are adequately treated even with the modest (4110) active space, where we have correlated all electrons.

Very few experimental studies of the magnetic properties exist for this molecule. Indeed, only the gas-phase measurements of Lawrence, Anderson, and Ramsey<sup>38</sup> are of interest for comparison with our calculations on the isolated molecule. Our calculated rotational  $g$  factor is in excellent agreement with the experimental measurements of Lawrence *et al.*<sup>38</sup> As their experiment was conducted at a temperature of 930 K, vibrational effects may, however, be important.

## V. CONCLUDING REMARKS

We have presented results for magnetizabilities and rotational  $g$  tensors obtained using large multiconfigurational

SCF wave functions and London atomic orbitals. In particular, we have presented the first correlated calculations of the rotational  $g$  tensor of ozone.

The results have been compared with other theoretical investigations as well as with a large number of experimental results. For the rotational  $g$  tensors, it appears difficult to obtain theoretical results within the experimental error bars, even when rovibrational corrections are taken into account. Nevertheless, the discrepancies among the experimental results are often larger than the discrepancies within the theoretical calculations. The theoretical calculations may therefore be useful when judging the relative quality of the different experimental results.

For the magnetizability anisotropy, we have, for many of the molecules studied, obtained results that are within the experimental error bars. However, this better agreement with experiment arises not only because of the higher accuracy of the calculations but also because of the significantly larger experimental error bars for the magnetizabilities than for the rotational  $g$  tensor. For the isotropic magnetizability, the problems faced by experimental investigations are far greater than those faced by theory. In the few cases where accurate gas-phase measurements of the isotropic magnetizability exist, our results appear to be more accurate.

*Note added in proof.* Upon acceptance of this paper, we became aware of a paper by Ogilvie, Sauer, and Oddershede [Chem. Phys. Lett. **228**, 183 (1994)], in which correlated calculations of the rotational  $g$  factor of LiH are reported. Their best result of  $-0.6351$  (obtained using the CCSDPPA method) is only in fair agreement with our estimate and further away from experiment.

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