

The magnetizability, rotational g tensor and quadrupole moment of the boron trihalides

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We present the results of an *ab initio* study of the molecular Zeeman properties—that is, the magnetizabilities, rotational g tensors, and electric quadrupole moments—for BX_3 ($X = F, Cl, Br, I$) within Hartree–Fock and density-functional theories. Basis-set convergence is ensured by the use of large basis sets of London atomic orbitals. Calculated trends are discussed and comparisons are made with available experimental data.

Keywords: Boron trihalides; Magnetizability; Rotational g tensor; Quadrupole moment

1. Introduction

The electronic charge structure and magnetic properties of the simple D_{3h} molecules BX_3 with X as F, Cl, Br, and I have been the subject of a number of recent experimental and theoretical birefringence studies [1–8]. Such studies enable the determination of molecular properties such as magnetizabilities (ξ), quadrupole moments (Θ), polarizabilities (α) and various mixed electric and magnetic hyperpolarizabilities. Alternatively, molecular beam [9] and microwave (MW) [10, 11] spectroscopy measurements of the molecular Zeeman effect offer another means of measuring accurate magnetic properties—in particular, for rotational g tensors. However, with MW spectroscopy, direct measurement of the isotropic magnetizability is not possible, but rather it is the anisotropy of the magnetizability that is observed. The combination of this property with the rotational g tensor enables experimental quadrupole moments to be derived. Most of these MW measurements were carried out in the 1960s and early 1970s, and the reviews of Flygare [10, 11] still represent the standard compilation of experimental gas-phase rotational g tensors.

A theoretical difficulty encountered in calculating properties involving an external magnetic field is that standard approximate methods do not give results

independent of the gauge origin of the magnetic potential. One approach to solving the gauge-origin problem is to employ London atomic orbitals (also known as gauge-invariant atomic orbitals), with an explicit phase-dependence on the magnetic field [12]. An additional feature of the London approach is an improved basis-set convergence of the calculated magnetic properties [13]. The use of London atomic orbitals with standard *ab initio* methods for improving basis-set convergence has become widespread in the calculation of a range of molecular magnetic properties, including rotational g tensors [13–15], magnetizabilities [16, 17], nuclear magnetic shieldings [16, 18], vibrational and electronic circular dichroism [19–21], Raman optical activity [22], and natural optical activity [23]. Of these properties, the magnetizability, which represents the second-order change of the energy in an external magnetic field, shows the greatest improvement in basis-set convergence with the use of London orbitals [14, 17]. For rotational g tensors, basis-set convergence may be similarly improved by employing rotational London atomic orbitals, which explicitly depend upon both the external magnetic field and the molecular angular momentum [13].

Recently, we have implemented code to enable density functional theory (DFT) calculations of magnetizabilities and rotational g tensors within DALTON [24] employing rotational London atomic orbitals. These methods were utilized in a recent study of molecular properties pertaining to Cotton–Mouton and Buckingham birefringences of BF_3 and BCl_3 [8]

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with local density approximation (LDA) [25], Becke-3-parameter-Lee–Yang–Parr (B3LYP) [26], and Keal–Tozer (KT) [27–29] functionals. With the recent debate in the literature regarding the electric and magnetic properties of these simple yet challenging molecules, it is timely to carry out a theoretical investigation of the molecular Zeeman properties of the entire series of boron trihalides.

In this paper, we report the results of a Hartree–Fock and DFT investigation of the magnetizabilities, rotational g tensors and electric quadrupole moments of the full series of boron trihalides. Previous benchmarking of DFT functionals in the calculation of rotational g tensors has highlighted the applicability and accuracy of the B3LYP [26, 30, 31] and the series of Keal–Tozer (KT1, KT2, KT3) [27–29] functionals for the calculation of this property [15]. In addition, Ref. [15] considered the LDA and Becke–Lee–Yang–Parr (BLYP) [30, 31] functionals. In this work, we use only the B3LYP and KT2 functionals (which perform best for rotational g tensors), with Hartree–Fock calculations also performed for comparison. While also of intrinsic interest, the calculation of the magnetic and electric properties of the series of boron trihalides enables a systematic investigation of the trends predicted by Ritchie and co-workers [2, 3].

2. Theory

The rotational g tensor \mathbf{g} of a molecular system measures the shift of the rotational energy levels in an external magnetic field

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

This shift may be viewed as arising from a first-order Zeeman interaction of the external induction \mathbf{B} with the rotationally induced magnetic dipole moment $\mu_N \mathbf{g} \mathbf{J}$, where \mathbf{J} is the molecular angular momentum and μ_N the nuclear magneton, related to the mass of the proton m_p as $\mu_N = 1/2m_p$. The g tensor may be expressed as a second derivative of the molecular electronic energy $\varepsilon(\mathbf{B}, \mathbf{J})$ with respect to the magnetic induction and the rotational angular momentum at $\mathbf{B} = \mathbf{0}$ and $\mathbf{J} = \mathbf{0}$ in the following manner [13]:

$$\begin{aligned} \mathbf{g} &= -\frac{1}{\mu_N} \left. \frac{d^2 \varepsilon(\mathbf{B}, \mathbf{J})}{d\mathbf{B} d\mathbf{J}} \right|_{\mathbf{B}, \mathbf{J} = \mathbf{0}} \\ &= m_p \sum_K Z_K (\mathbf{R}_K^T \mathbf{R}_K \mathbf{I}_3 - \mathbf{R}_K \mathbf{R}_K^T) \mathbf{I}^{-1} \\ &\quad - 2m_p \sum_{n \neq 0} \frac{\langle 0 | \mathbf{I}_O | n \rangle \langle n | \mathbf{I}_{CM}^T | 0 \rangle}{E_n^{(0)} - E_0^{(0)}} \mathbf{I}^{-1}. \end{aligned} \quad (2)$$

In the summation over nuclei, Z_K denotes the charge and \mathbf{R}_K the position of nucleus K relative to the center of mass, and \mathbf{I}_3 is the three-by-three unit tensor; in the summation over excited electronic states $|n\rangle$ of energy $E_n^{(0)}$, \mathbf{I}_O and \mathbf{I}_{CM} are the operators for the electronic angular momentum about the gauge origin and the center of mass, respectively:

$$\mathbf{I}_O = \sum_i \mathbf{r}_{iO} \times \mathbf{p}_i, \quad (3)$$

$$\mathbf{I}_{CM} = \sum_i \mathbf{r}_{iCM} \times \mathbf{p}_i. \quad (4)$$

Here \mathbf{r}_{iO} is the position of electron i relative to the origin of the vector potential representing the external magnetic field, whereas \mathbf{r}_{iCM} is the position relative to the center of mass. Also, \mathbf{p}_i is the linear-momentum operator of electron i . Finally, the moment-of-inertia tensor \mathbf{I} is given by

$$\mathbf{I} = \sum_K m_K \mathbf{R}_K \mathbf{R}_K^T, \quad (5)$$

where the summation is over all atoms of masses m_K . In the following, we assume that all calculations have been carried out in the center-of-mass system with a diagonal moment-of-inertia tensor.

In the same manner, the molecular magnetizability tensor ξ may be expressed as the second derivative of the molecular energy with respect to the magnetic induction:

$$\begin{aligned} \xi &= - \left. \frac{d^2 \varepsilon(\mathbf{B})}{d\mathbf{B}^2} \right|_{\mathbf{B} = \mathbf{0}} \\ &= -\frac{1}{4} \sum_i \langle 0 | \mathbf{r}_{iO}^T \mathbf{r}_{iO} \mathbf{I}_3 - \mathbf{r}_{iO} \mathbf{r}_{iO}^T | 0 \rangle + \frac{1}{2} \sum_{n \neq 0} \frac{\langle 0 | \mathbf{I}_O | n \rangle \langle n | \mathbf{I}_O^T | 0 \rangle}{E_n^{(0)} - E_0^{(0)}}. \end{aligned} \quad (6)$$

Comparing this expression for the magnetizability with the corresponding expression for the g tensor in equation (2), we note that each consists of two separate contributions. Thus, in the g tensor, there is a trivial nuclear contribution and an electronic sum-over-states contribution, which, for the isotropic component, are positive and negative, respectively. In the magnetizability, there is likewise a diamagnetic expectation-value contribution and a paramagnetic sum-over-states contribution (similar to that for the g tensor). For the isotropic magnetizability, the diamagnetic contribution is negative and the paramagnetic positive. Clearly, the rotational g tensor may be programmed and calculated as a simple extension to any code that already calculates the molecular magnetizability and *vice versa*, using standard theory for time-independent second-order molecular properties.

For the calculation of rotational g tensors and magnetizabilities, the use of rotational London orbitals has been demonstrated not only to ensure rigorous gauge-origin-independent results but also to accelerate the convergence toward the basis-set limit (compared with conventional field-independent orbitals) [13]. For a conventional atomic orbital χ_μ centered at \mathbf{R}_μ and an induction \mathbf{B} with gauge origin at \mathbf{R}_O , the rotational London orbital is given by

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

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

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

In a basis of such orbitals, the expressions for the rotational g tensor and the magnetizability contain no reference to the gauge origin of the external magnetic field (but the g tensor does depend properly on the center of mass) [13]. The implementation of rotational London orbitals within Hartree–Fock theory and DFT has been outlined elsewhere [15, 16].

Comparing equation (2) for the g tensor and equation (6) for the magnetizability calculated with the gauge origin at center of mass (as indicated by subscript CM), we obtain

$$4\xi_{\text{CM}} + m_p^{-1} g_{\text{CM}} \mathbf{I} = \mathbf{I}_3 \text{Tr } \mathbf{Q} - \mathbf{Q}, \quad (10)$$

where \mathbf{Q} is the second electric moment tensor,

$$\mathbf{Q} = \sum_i q_i \langle 0 | \mathbf{r}_{i\text{CM}} \mathbf{r}_{i\text{CM}}^T | 0 \rangle, \quad (11)$$

with contributions from all particles (nuclei as well as electrons) of charge q_i and position $\mathbf{r}_{i\text{CM}}$. For the D_{3h} boron trihalides discussed here, there are only two independent components of the tensors in equation (10): the one parallel to the symmetry axis and the one perpendicular to it. Alternatively, we may work in terms of the isotropic and anisotropic components, which we define here as (in the center-of-mass coordinate system)

$$\xi_{\text{iso}} = \frac{1}{3}(\xi_{\parallel} + 2\xi_{\perp}), \quad \xi_{\text{ani}} = \xi_{\parallel} - \xi_{\perp}, \quad (12)$$

$$g_{\text{iso}} = \frac{1}{3}(g_{\parallel} + 2g_{\perp}), \quad g_{\text{ani}} = g_{\parallel} - \frac{1}{2}g_{\perp}. \quad (13)$$

Noting that $I_{\parallel} = 2I_{\perp}$ for these D_{3h} systems, we then obtain from equation (10) the expression

$$4\xi_{\text{ani}} + m_p^{-1} g_{\text{ani}} I_{\parallel} = -\Theta_{\parallel}, \quad (14)$$

where $\Theta_{\parallel} = Q_{\parallel} - Q_{\perp}$ is the parallel component of the traceless quadrupole moment tensor

$$\Theta = \frac{3}{2} \mathbf{Q} - \frac{1}{2} \text{Tr } \mathbf{Q}. \quad (15)$$

Because of the trace condition $\Theta_{\parallel} + 2\Theta_{\perp} = 0$, the quadrupole moment of the trihalides has only one symmetry-independent component. In microwave Zeeman measurements, only the anisotropic component of the magnetizability is measured, together with the parallel and perpendicular components of the g tensor. Equation (14) relates these observed properties in a simple manner to the permanent molecular quadrupole moment.

Next, we note that, in equation (10), the paramagnetic contribution to the magnetizability is cancelled exactly by the electronic contribution to the g tensor. We may therefore rewrite it in the form

$$\xi_{\text{ani}}^{\text{dia}} = -\frac{1}{4} m_p^{-1} g_{\text{ani}}^{\text{nuc}} I_{\parallel} - \frac{1}{4} \Theta_{\parallel}, \quad (16)$$

which, from the explicit form of the nuclear contribution to the g tensor in equation (6) and the symmetry of the D_{3h} boron trihalides, may be written as

$$\xi_{\text{ani}}^{\text{dia}} = -\frac{3}{8} Z R^2 - \frac{1}{4} \Theta_{\parallel}, \quad (17)$$

where R is the bond distance, allowing us to extract the diamagnetic contribution to the anisotropic component of the magnetizability from the quadrupole moment and knowledge of the molecular structure.

According to equation (17), the diamagnetic contribution to the magnetizability increases linearly with the atomic number of the halide and quadratically with the bond distances. Let us now consider the diamagnetic and paramagnetic contributions to the magnetizability from a more general point of view. Let us assume that a large system consists of a set of non-interacting atoms. The magnetizability is additive and may be calculated separately for each atom, using some global gauge origin such as the center of mass. For atoms far from the gauge origin, we see from equation (6) that the diamagnetic contribution depends linearly on the number of particles and quadratically on their distance from the gauge origin. The total diamagnetic contribution (for all atoms) therefore increases cubically with system size (assuming a uniform distribution of atoms). Moreover, since the magnetizability of each non-interacting atom is independent of the gauge origin, this large diamagnetic contribution must be (nearly) cancelled by an equally large paramagnetic contribution. The total magnetizability therefore arises as the difference of two large terms, both of which depend cubically on system size. For non-interacting atoms, we may proceed by calculating the magnetizability of each

atom separately with the gauge origin at the nucleus (and a zero paramagnetic term) but, for interacting atoms, this is impossible and we must work with one global gauge origin and the resulting cancellation of large diamagnetic and paramagnetic terms. We note that the use of London orbitals does not in itself solve the problem of large cancellations in large systems—it only ensures that the residual, total magnetizability is rigorously independent of the gauge origin.

Let us now consider the rotational g tensor. First, from a comparison of equations (2) and (6), we conclude that the product \mathbf{gI} behaves in the same manner as the magnetizability, with a near cancellation of large nuclear and electronic contributions in a large system. In \mathbf{g} itself, however, the moments of inertia occur inversely, ensuring that the nuclear contribution $\Sigma_K Z_K (\mathbf{R}_K^T \mathbf{R}_K \mathbf{I}_3 - \mathbf{R}_K \mathbf{R}_K^T) / \Sigma_K m_K \mathbf{R}_K \mathbf{R}_K^T$ does not increase with system size (but decreases upon substitution with heavier atoms, which have a smaller Z_K/m_K ratio). Since, from our consideration of \mathbf{gI} , the cancellation between the nuclear and electronic contributions becomes more complete for large systems, we conclude that the g tensor itself decreases with increasing system size.

3. Computational details

Experimental D_{3h} equilibrium geometries were employed in all calculations, with bond lengths $R_{\text{BF}} = 130.70$ pm [32], $R_{\text{BCl}} = 174.21$ pm [33], $R_{\text{BBr}} = 189.30$ pm [34], and $R_{\text{BI}} = 211.20$ pm [35]. All calculations were performed with DALTON [24].

We have carried out DFT calculations for rotational g tensors, magnetizabilities and electric quadrupole moments with the density functionals B3LYP [26] and KT2 [27, 28]. Both functionals have been shown to be accurate in the calculation of molecular magnetic properties [15, 27], with the KT2 functional being better for magnetic properties and B3LYP better for electric properties [29]. For comparison, all molecular properties were computed also with Hartree–Fock theory.

In our calculations, we have used the augmented correlation-consistent polarized valence aug-cc-pVXZ basis sets of Dunning [36]. In addition, some calculations have been carried out in the doubly augmented d-aug-cc-pVXZ basis sets and in the augmented core–valence aug-cc-pCVTZ basis sets. For iodine, no correlation-consistent basis sets exist and we have instead used modified SVPall, TZVPall, and TZVPPall all-electron TURBOMOLE basis sets [37].

Specifically, in the calculations labelled ‘aug-pVDZ’, we employ the SVPall iodine basis in combination with the aug-cc-pVDZ boron basis. Likewise, in the

‘d-aug-VDZ’ calculations, we combine the d-aug-cc-pVDZ boron basis with a modified SVPall iodine basis, having added a set of diffuse functions of each angular momentum. The exponents of the diffuse functions (0.0405 for s and p , 0.0842 for d) were chosen in an even-tempered manner, based on the most diffuse exponents of the original basis.

In the ‘aug-pVTZ’ calculations, we use the TZVPall basis for iodine, with the f functions taken from the aug-cc-pVTZ-PP basis [38]. In the ‘d-aug-VTZ’ calculations, diffuse functions were added to the TZVPall basis (with exponents 0.0514 for s , 0.0334 for p , 0.1112 for d , and 0.08399 for f). Finally, in the calculations labelled ‘aug-VQZ’, we use the TZVPPall basis for iodine, but with the f and g functions taken from the aug-cc-pVQZ-PP basis and augmented with functions of exponents 0.05144, 0.0215, and 0.00895 for s , 0.3344, 0.0117, and 0.00409 for p , 0.0961, 0.0487, and 0.02468 for d , 0.03783 for f , and 0.07032 for g .

4. Results and discussion

The results obtained in this study for molecular Zeeman properties of the boron trihalides are presented and discussed with reference to table 1 (BF_3), table 2 (BCl_3), table 3 (BBr_3), and table 4 (BI_3), which also contain previous calculated and experimental results. Before beginning our discussion, we note that we have made no attempt at calculating vibrational or relativistic corrections to the molecular Zeeman properties examined here.

4.1. Basis-set convergence

The largest basis set used for all molecules and all levels of theory is the aug-cc-pVQZ basis (cc-pVQZ for BI_3). A comparison of the aug-cc-pVQZ results with the results obtained with smaller cardinal numbers (for all molecules) and with the aug-cc-pV5Z basis (available for BF_3) indicates that convergence with respect to the cardinal number has been achieved to within 0.01 a.u. for the magnetizability, to within 0.1×10^{-3} for the g tensor, and to within 0.02 a.u. for the quadrupole moment. In general, convergence is faster for BF_3 , BCl_3 , and BBr_3 than for BI_3 . For BBr_3 , there is a very slight oscillation of ξ_{\parallel} in the KT2/aug-cc-pVXZ series, with an associated oscillation of the anisotropy (-0.37 , -0.34 , -0.41 a.u.). For comparison, the KT2/d-aug-cc-pVQZ value is -0.41 a.u.

With regard to diffuse functions, we note that the addition of an extra set of such functions (from aug-cc-pVQZ to d-aug-cc-pVQZ) changes the magnetizability by no more than 0.01 a.u., the g tensor by no more than 0.1×10^{-3} , and the quadrupole moment by

Table 1. Magnetizability (a.u.), rotational g tensor (10^{-3}), and electric quadrupole moment (a.u.) of BF_3 .

Model	Basis	ξ_{\perp}	ξ_{\parallel}	ξ_{iso}	ξ_{ani}	g_{\perp}	g_{\parallel}	g_{iso}	g_{ani}	Θ_{\parallel}
HF	aug-cc-pVDZ	-5.78	-6.15	-5.90	-0.37	-37.5	-23.9	-33.0	-5.1	3.24
	aug-cc-pVTZ	-5.74	-6.07	-5.85	-0.33	-37.4	-24.7	-33.2	-6.1	3.43
	aug-cc-pVQZ	-5.73	-6.06	-5.84	-0.33	-37.4	-24.8	-33.2	-6.1	3.42
	aug-cc-pV5Z	-5.72	-6.05	-5.83	-0.33	-37.4	-24.9	-33.2	-6.1	3.42
	d-aug-cc-pVDZ	-5.81	-6.03	-5.89	-0.22	-36.7	-25.4	-32.9	-7.1	3.31
	d-aug-cc-pVTZ	-5.74	-6.06	-5.85	-0.32	-37.3	-24.8	-33.1	-6.2	3.42
	d-aug-cc-pVQZ	-5.72	-6.06	-5.84	-0.33	-37.5	-24.8	-33.2	-6.1	3.42
	aug-cc-pCVTZ	-5.74	-6.07	-5.85	-0.33	-37.3	-24.7	-33.1	-6.1	3.43
B3LYP	aug-cc-pVDZ	-5.67	-6.13	-5.82	-0.46	-41.5	-23.5	-35.5	-2.7	2.79
	aug-cc-pVTZ	-5.66	-6.09	-5.81	-0.43	-41.3	-24.3	-35.6	-3.7	3.00
	aug-cc-pVQZ	-5.65	-6.08	-5.79	-0.42	-41.3	-24.4	-35.7	-3.8	2.99
	aug-cc-pV5Z	-5.65	-6.07	-5.79	-0.42	-41.3	-24.4	-35.7	-3.8	2.98
	d-aug-cc-pVDZ	-5.73	-6.12	-5.86	-0.39	-40.2	-23.9	-34.8	-3.8	2.89
	d-aug-cc-pVTZ	-5.66	-6.08	-5.80	-0.42	-41.2	-24.4	-35.6	-3.8	2.98
	aug-cc-pCVTZ	-5.66	-6.09	-5.80	-0.43	-41.3	-24.3	-35.6	-3.7	3.00
KT2	aug-cc-pVDZ	-5.59	-6.05	-5.74	-0.46	-40.9	-22.3	-34.7	-1.9	2.48
	aug-cc-pVTZ	-5.59	-6.00	-5.73	-0.41	-40.6	-23.3	-34.8	-3.0	2.69
	aug-cc-pVQZ	-5.58	-6.00	-5.72	-0.42	-40.6	-23.3	-34.8	-3.0	2.68
	aug-cc-pV5Z	-5.58	-5.99	-5.72	-0.41	-40.6	-23.3	-34.9	-3.0	2.68
	d-aug-cc-pVDZ	-5.64	-6.01	-5.76	-0.36	-39.8	-23.1	-34.2	-3.2	2.57
	d-aug-cc-pVTZ	-5.61	-6.02	-5.75	-0.41	-40.1	-23.1	-34.4	-3.0	2.68
	aug-cc-pCVTZ	-5.59	-6.01	-5.73	-0.42	-40.6	-23.2	-34.8	-2.9	2.69
HF ^a	H III	-5.81	-6.14	-5.92	-0.33					
MP2 ^b	Huz-sv									3.21
Experiment				-5.66 ^c						2.81 ± 0.16^d 2.50 ^e

^aRef. [39]. IGLO calculation.^bRef. [2].^cEstimated from Pascal's constants in [41].^dRef. [1]. This value was modified in [8] to include temperature-independent contributions, yielding 2.72 ± 0.15 a.u.^eRef. [42]. Extrapolated from measured dipole moments of van der Waals complexes containing BF_3 .

no more than 0.01 a.u. The addition of core functions (from aug-cc-pVTZ to aug-cc-pCVTZ) has a slightly larger effect, changing the magnetizability by 0.03 a.u., the g tensor by 0.2×10^{-3} , and the quadrupole moment by 0.05 a.u. However, we attribute the larger changes observed with the addition of core functions to the fact that these functions are added to a smaller (triple-zeta) basis.

4.2. Magnetizabilities

For the magnetizability, the agreement with the available experimental data is very good for the KT2 functional, the isotropic component never differing by more than 1% from the experimental value. For the B3LYP functional, the errors are about three times larger, while the largest Hartree–Fock error is 7%. These results are in agreement with previous

observations—namely, that the KT2 functional performs very well for properties that involve an external magnetic field and that the Hartree–Fock model typically is in error by 5–10% for magnetizabilities. However, in making these comparisons, we should keep in mind that we have not accounted for the effects of vibrations and relativity. We also emphasize that only the BCl_3 magnetizability has been observed directly; the BF_3 and BI_3 magnetizabilities have been inferred from experimental measurements and empirical rules. In the case of the directly observed BCl_3 magnetizability, the KT2 functional is in all cases within the estimated error bar of 0.1 a.u. For BF_3 , our Hartree–Fock magnetizabilities are in reasonable agreement with the IGLO (individual gauge for localized molecular orbitals) Hartree–Fock values of Fleischer and Schindler, the differences being attributable to different basis-set and gauge-origin treatments [39].

Table 2. Magnetizability (a.u.), rotational g tensor (10^{-3}), and electric quadrupole moment (a.u.) of BCl_3 .

Model	Basis	ξ_{\perp}	ξ_{\parallel}	ξ_{iso}	ξ_{ani}	g_{\perp}	g_{\parallel}	g_{iso}	g_{ani}	Θ_{\parallel}
HF	aug-cc-pVDZ	-13.42	-14.09	-13.65	-0.67	-19.5	-8.5	-15.8	1.3	1.25
	aug-cc-pVTZ	-13.31	-14.00	-13.54	-0.69	-19.7	-8.5	-16.0	1.4	1.20
	aug-cc-pVQZ	-13.30	-13.98	-13.52	-0.68	-19.7	-8.5	-16.0	1.4	1.15
	d-aug-cc-pVDZ	-13.42	-13.96	-13.60	-0.53	-19.4	-8.8	-15.9	0.9	1.17
	d-aug-cc-pVTZ	-13.31	-14.01	-13.54	-0.70	-19.7	-8.4	-16.0	1.4	1.18
	d-aug-cc-pVQZ	-13.29	-13.98	-13.52	-0.68	-19.7	-8.5	-16.0	1.4	1.15
	aug-cc-pCVTZ	-13.30	-13.97	-13.53	-0.67	-19.7	-8.5	-16.0	1.4	1.15
B3LYP	aug-cc-pVDZ	-12.80	-13.60	-13.07	-0.80	-22.8	-9.4	-18.3	2.0	0.93
	aug-cc-pVTZ	-12.71	-13.50	-12.97	-0.80	-23.2	-9.5	-18.6	2.1	0.87
	aug-cc-pVQZ	-12.68	-13.47	-12.95	-0.79	-23.2	-9.5	-18.7	2.1	0.82
	d-aug-cc-pVDZ	-12.81	-13.52	-13.05	-0.71	-22.6	-9.6	-18.3	1.7	0.89
	d-aug-cc-pVTZ	-12.70	-13.51	-12.97	-0.80	-23.2	-9.5	-18.6	2.1	0.84
	aug-cc-pCVTZ	-12.68	-13.46	-12.94	-0.78	-23.3	-9.6	-18.7	2.1	0.82
KT2	aug-cc-pVDZ	-12.62	-13.27	-12.83	-0.65	-22.9	-9.6	-18.5	1.9	0.50
	aug-cc-pVTZ	-12.53	-13.16	-12.74	-0.64	-23.3	-9.8	-18.8	1.8	0.50
	aug-cc-pVQZ	-12.51	-13.15	-12.72	-0.65	-23.4	-9.8	-18.8	1.9	0.46
	d-aug-cc-pVDZ	-12.62	-13.19	-12.81	-0.57	-22.8	-9.8	-18.5	1.6	0.47
	d-aug-cc-pVTZ	-12.50	-13.17	-12.72	-0.67	-23.5	-9.8	-18.9	2.0	0.48
	aug-cc-pCVTZ	-12.49	-13.14	-12.71	-0.64	-23.5	-9.9	-18.9	1.9	0.45
MP2 ^a	Huz-sv									1.18
Experiment		-12.4 ± 0.1^a	-13.1 ± 0.1^a	-12.6 ± 0.1^b	-0.71 ± 0.09^a				1.4 ± 0.3^a	1.52 ± 0.7^c

^aFrom [2].^bFrom [43].^cRef. [5]. Derived from MW pressure broadening observations. See text for discussion.Table 3. Magnetizability (a.u.), rotational g tensor (10^{-3}), and electric quadrupole moment of BBr_3 (a.u.).

Wave function	Basis	ξ_{\perp}	ξ_{\parallel}	ξ_{iso}	ξ_{ani}	g_{\perp}	g_{\parallel}	g_{iso}	g_{ani}	Θ_{\parallel}
HF-SCF	aug-cc-pVDZ	-19.04	-19.71	-19.26	-0.66	-9.4	-3.9	-7.6	0.8	0.27
	aug-cc-pVTZ	-18.90	-19.64	-19.15	-0.74	-9.6	-3.9	-7.7	0.9	0.36
	aug-cc-pVQZ	-18.89	-19.63	-19.13	-0.74	-9.6	-3.9	-7.7	0.9	0.35
	d-aug-cc-pVDZ	-19.03	-19.59	-19.22	-0.56	-9.4	-4.0	-7.6	0.7	0.16
	d-aug-cc-pVTZ	-18.90	-19.63	-19.15	-0.73	-9.6	-3.9	-7.7	0.9	0.35
	d-aug-cc-pVQZ	-18.88	-19.63	-19.13	-0.74	-9.6	-3.9	-7.7	0.9	0.35
B3LYP	aug-cc-pVDZ	-18.21	-18.89	-18.44	-0.67	-10.9	-4.6	-8.8	0.9	-0.03
	aug-cc-pVTZ	-18.09	-18.80	-18.33	-0.70	-11.1	-4.6	-9.0	0.9	-0.02
	aug-cc-pVQZ	-18.07	-18.78	-18.31	-0.71	-11.2	-4.6	-9.0	1.0	-0.03
	d-aug-cc-pVDZ	-18.21	-18.81	-18.41	-0.59	-10.9	-4.6	-8.8	0.8	-0.11
	d-aug-cc-pVTZ	-18.10	-18.79	-18.33	-0.70	-11.1	-4.6	-9.0	0.9	-0.03
KT2	aug-cc-pVDZ	-17.99	-18.35	-18.11	-0.37	-11.1	-4.9	-9.0	0.7	-0.53
	aug-cc-pVTZ	-17.86	-18.21	-17.98	-0.34	-11.3	-5.0	-9.2	0.6	-0.45
	aug-cc-pVQZ	-17.85	-18.26	-17.99	-0.41	-11.3	-5.0	-9.2	0.7	-0.44
	d-aug-cc-pVDZ	-17.98	-18.32	-18.10	-0.34	-11.1	-4.9	0.0	0.7	-0.60
	d-aug-cc-pVTZ	-17.85	-18.18	-17.96	-0.33	-11.3	-5.1	-9.3	0.6	-0.45
MP2	Huz-sv									0.04
Experiment				-18.0^b						

^aRef. [2].^bRef. [44].

Table 4. Magnetizability (a.u.), rotational g tensor (10^{-3}), and electric quadrupole moment (a.u.) of BI_3 . For a description of the basis sets, see section 3.

Model	Basis ^a	ξ_{\perp}	ξ_{\parallel}	ξ_{iso}	ξ_{ani}	g_{\perp}	g_{\parallel}	g_{iso}	g_{ani}	Θ_{\parallel}
HF	aug-pVDZ	-28.58	-29.14	-28.77	-0.56	-7.0	-3.0	-5.7	0.5	-1.02
	aug-pVTZ	-28.38	-28.86	-28.54	-0.48	-7.4	-3.3	-6.0	0.4	-1.05
	aug-pVQZ	-28.32	-28.82	-28.49	-0.49	-7.5	-3.3	-6.1	0.4	-0.57
	d-aug-pVDZ	-28.63	-28.96	-28.74	-0.32	-7.2	-3.2	-5.9	0.4	-1.13
	d-aug-pVTZ	-28.36	-28.84	-28.52	-0.47	-7.4	-3.3	-6.1	0.4	-0.53
	d-aug-pVQZ	-28.33	-28.83	-28.49	-0.50	-7.5	-3.3	-6.1	0.4	-0.56
B3LYP	aug-pVDZ	-27.33	-27.56	-27.41	-0.23	-7.8	-3.5	-6.4	0.4	-1.47
	aug-pVTZ	-27.13	-27.21	-27.16	-0.08	-8.3	-4.0	-6.9	0.2	-0.97
	aug-pVQZ	-27.08	-27.09	-27.09	-0.01	-8.5	-4.1	-7.0	0.1	-0.83
	d-aug-pVDZ	-27.41	-27.37	-27.40	0.04	-8.1	-3.9	-6.7	0.2	-1.14
	d-aug-pVTZ	-27.12	-27.15	-27.13	-0.03	-8.5	-4.1	-7.0	0.2	-0.80
KT2	aug-pVDZ	-26.98	-26.50	-26.82	0.48	-8.2	-4.2	-6.9	-0.1	-2.04
	aug-pVTZ	-26.76	-26.09	-26.53	0.67	-8.5	-4.4	-7.1	-0.2	-1.46
	aug-pVQZ	-26.65	-25.97	-26.43	0.69	-8.7	-4.6	-7.3	-0.2	-1.28
	d-aug-pVDZ	-27.01	-26.25	-26.76	0.76	-8.2	-4.3	-6.9	-0.2	-1.70
	d-aug-pVTZ	-26.66	-25.97	-26.43	0.69	-8.7	-4.6	-7.3	-0.3	-1.26

^aCorrelation-consistent basis set for boron, modified SVPall, SVPall, TZVPall, and TZVPPall TURBOMOLE basis sets [37] for iodine; see section 3.

As expected, the isotropic magnetizability increases with increasing atomic number of the halides. Thus, with the KT2 functional, we obtain -5.7 , -12.7 , -18.0 , and -26.4 a.u., respectively, for the magnetizabilities of BF_3 , BCl_3 , BBr_3 , and BI_3 . For the anisotropic component, the corresponding values are -0.4 , -0.7 , -0.4 , and 0.7 a.u., respectively. The magnetizability is therefore nearly isotropic (in particular for the larger molecules), with a slightly dominant parallel component $|\xi_{\perp}| < |\xi_{\parallel}|$ except for BI_3 .

From the measured negative magnetizability anisotropies of the planar molecules BCl_3 , CH_3BF_2 , and $\text{CH}_3\text{B}_3\text{O}_3$, Ritchie and co-workers surmised that B–X bonds are less magnetizable along rather than across the internuclear axis—that is, that $|\xi_{\perp}| < |\xi_{\parallel}|$ [3]. The same trend had previously been noted for C=X bonds, whereas the opposite is observed for C–X bonds [11, 40]. On this basis, Ritchie concluded that, in the absence of further experimental data, B–X bonds are similar to C=X bonds. Since our results for BX_3 indicate that $|\xi_{\perp}| < |\xi_{\parallel}|$ for F, Cl and Br but that $|\xi_{\perp}| \geq |\xi_{\parallel}|$ for I, it may be concluded that the degree of electron delocalization and partial double-bond character decreases from F to I.

4.3. Rotational g tensors

The only reported experimental g -tensor element for the boron trihalides is the anisotropy of BCl_3 , which has been measured at 0.0014 ± 0.0003 [3]. Our calculated results are in agreement with this value, the

Hartree–Fock, B3LYP, and KT2 values all being within three times the experimental uncertainty. In this particular case, the Hartree–Fock value of 0.0014 is in better agreement with experiment than is the KT2 value of 0.0019. However, based on our knowledge about the relative performance of Hartree–Fock theory and the available density functionals for magnetic properties, we shall consider the KT2/aug-cc-pVQZ results as the most accurate.

As expected, the g value (i.e. the isotropic part of the g tensor) decreases with increasing molecular weight (in units for 10^{-3}): -34.8 for BF_3 , -18.8 for BCl_3 , -9.2 for BBr_3 , and -7.3 for BI_3 . The observed reduction by a factor of 4.8 from BF_3 to BI_3 occurs partly because of a smaller charge-to-mass ratio for the heavier atoms but mostly because of a more complete cancellation of the nuclear and electronic contributions for such atoms. For example, for the perpendicular component g_{\perp} at the KT2/aug-cc-pVQZ level of theory, the nuclear and electronic contributions in BF_3 are 0.477 and -0.518 , respectively, while the corresponding contributions in BI_3 are 0.421 and -0.429 . By contrast, the perpendicular component of the magnetizability increases in magnitude by a factor of 4.6 from BF_3 (-6 a.u.) to BI_3 (-27 a.u.). Separately, the diamagnetic and paramagnetic contributions to the magnetizability change from -35 to -455 a.u. and from 29 to 428 a.u., respectively, again illustrating the importance of cancellation in heavier systems.

As the boron trihalides become heavier, the anisotropy of the g tensor becomes smaller (in units

of 10^{-3}): -3.0 for BF_3 , 1.9 for BCl_3 , 0.7 for BBr_3 , and -0.2 for BI_3 . In relative terms, the anisotropy is 9% of the isotropic value in BF_3 but only 3% in BI_3 . We also note the sign change of the anisotropy (negative for BF_3 and BI_3 , positive for BCl_3 and BBr_3).

4.4. Electric quadrupole moments

The most recent experimental data for the quadrupole moment of the boron trihalides is 2.81 ± 0.16 a.u. for BF_3 [1] and 1.52 ± 0.07 a.u. for BCl_3 [5]. In [8], a critical analysis of these data is made, using state-of-the-art *ab initio* theory. In particular, the revision of BF_3 leads to a much more likely ‘experimentally derived’ value of 2.72 ± 0.15 a.u., whereas the best estimate for BCl_3 , neglecting vibrations and relativity, gives 0.71 a.u. For BF_3 , our DFT calculations, both B3LYP and KT2, are in good agreement with these values, both staying within three error bars, with KT2 (2.68 a.u.) closer to the center of distribution of the revised experimental value. In general, the KT2 functional performs less well for electric properties than for magnetic ones. On the other hand, the study of Rizzo *et al.* [8] shows that the best *ab initio* estimates, obtained with high-level coupled-cluster models, place the quadrupole moment of BF_3 without vibrational corrections around 3.00 a.u., in remarkably good agreement with B3LYP (2.99 a.u.). Thus, the apparently better performance of KT2 may, in this case, arise from the neglect of vibrational contributions. In the following, therefore, we shall consider the B3LYP quadrupole moments to be more reliable than the KT2 values. We also note that, for BF_3 , the Hartree–Fock quadrupole moment of 3.42 a.u. is much too large.

By contrast, for the quadrupole moment of BCl_3 , our results are in poor agreement with experiment, the B3LYP and KT2 functionals underestimating the observed value of 1.52 a.u. by 46 and 70%, respectively. However, serious objections have previously been raised towards the experimental value for BCl_3 [6, 8]. In view also of the conclusions of [8], we believe that the B3LYP value (0.82 a.u.) is closer than the experimental value (1.52 a.u.) to the true quadrupole moment of BCl_3 . In this connection, we note the previous second-order Møller–Plesset (MP2) results of Ritchie and coworkers: 3.21 a.u. for BF_3 , 1.18 a.u. for BCl_3 , and 0.04 a.u. for BBr_3 [2, 3]. These values are all larger than the corresponding B3LYP values and also larger than the experimental value for BF_3 (possibly because of the use of a too small basis set), further suggesting that the true value of the quadrupole moment of BCl_3 is smaller than 1.18 a.u.

Comparing the different trihalides, we find that the quadrupole moment becomes smaller and more

negative with increasing charge (and decreasing electronegativity) of the halide: 2.99 a.u. for BF_3 , 0.82 a.u. for BCl_3 , -0.03 a.u. for BBr_3 , and -1.83 a.u. for BI_3 . The positive sign of the quadrupole moment for the two smallest molecules indicates that the electronic charge has been shifted away from the central boron atom towards the electronegative halogen atoms. Apparently, in BI_3 , the situation is different, with no charge transfer towards the iodine atoms, in spite of their greater electronegativity (2.7 for iodine vs. 2.04 for boron), but probably related in some manner to the large size of the iodine atom (the only halide with a larger atomic radius than that of boron).

4.5. Relationships between Zeeman properties

In section 2, we gave two relationships, equations (14) and (17), between the molecular Zeeman properties that are sometimes used to derive new properties from measured ones. Let us first consider equation (17), which expresses the diamagnetic contribution of the anisotropic magnetizability $\xi_{\text{ani}}^{\text{dia}}$ in terms of the molecular quadrupole moment and molecular structure.

At the KT2/aug-cc-pVQZ level of theory, the calculated value of $\xi_{\text{ani}}^{\text{dia}}$ is -21.3 a.u. for BF_3 , -69.2 a.u. for BCl_3 , -167.9 a.u. for BBr_3 , and -316.3 a.u. for BI_3 . As seen from tables 1–4, the quadrupole-moment contributions to these anisotropies are very small: -0.7 a.u. for BF_3 and 0.3 a.u. for BI_3 . In other words, the diamagnetic contribution to magnetizability is, especially for large systems, largely determined by the nuclear framework of the system and independent of our description of the electronic structure. This is not true for the total magnetizability, however, which, for large systems, arises from a subtle balance between a large, negative diamagnetic contribution and a large, positive paramagnetic contribution.

According to the other exact relation equation (14), only two of the three listed terms ξ_{ani} , g_{ani} and Θ_{\parallel} in tables 1–4 are independent. This observation may seem to contradict our previous statement that, for the magnetic properties ξ_{ani} and g_{ani} , we trust the KT2 model over the B3LYP model, whereas, for the electric property Θ_{\parallel} , we trust the B3LYP model over the KT2 model. There is no contradiction here, however, since only the diamagnetic and nuclear contributions to the magnetizability and g tensor, respectively, contribute to equation (14), the sum-over-states contributions cancelling out from the relation. For Zeeman properties such as the magnetizability and the g tensor, it is the sum-over-states contribution that is difficult to calculate accurately and which is sensitive to our choice of computational model.

Concerning the three contributions to the relation equation (14), an inspection of the results for the four trihalides considered here shows that none of the terms dominate or may be neglected. Specifically, we note that the quadrupole-moment term is largest in magnitude for BF_3 and that the magnetizability term is largest for BCl_3 and BI_3 . Interestingly, for BBr_3 in the aug-cc-pVQZ basis, the magnetizability and rotational g -tensor terms very nearly cancel with the B3LYP functional (corresponding to a Θ_{\parallel} of 0.03 a.u.). The KT2 functional determines the magnitude of the g -tensor term to be greater than the magnetizability term (with a positive Θ_{\parallel} of 0.44 a.u.), whereas Hartree–Fock theory predicts the magnetizability term to be larger (with a negative Θ_{\parallel} of -0.35 a.u.).

The delicate balance between the anisotropies in the magnetizability and g tensors in equation (14) is readily illustrated by the KT2 results for BCl_3 . For example, a change in the anisotropy of the g tensor by 0.0008 (to -0.0038) alters the derived traceless quadrupole moment from 2.68 to 2.98 a.u. It appears, therefore, that this relation, although experimentally useful, is less useful for the purpose of analysis of the calculated Zeeman properties, even for a series as systematic as the boron trihalides.

5. Conclusions

We have calculated molecular Zeeman properties (i.e. the magnetizability, the g tensor, and the quadrupole moment) of the boron trihalides BF_3 , BCl_3 , BBr_3 , and BI_3 using Hartree–Fock theory and Kohn–Sham DFT with the B3LYP and KT2 functionals. The results are discussed both in relationship to available experimental and theoretical data and with respect to trends among the boron trihalides. In all cases except the quadrupole moment of BCl_3 , the agreement with experiment is good, when comparisons are made with the KT2 results for magnetic properties and with the B3LYP results for electric properties, keeping in mind that we have neglected the effects of molecular vibrations and relativity (for the heavier members of the series).

While the isotropic magnetizability of the trihalides increases with increasing charge of the halide (from -5.7 a.u. for BF_3 to -26.3 a.u. for BI_3), a decrease is seen for the g value (from -34.8×10^{-3} for BF_3 to -7.3×10^{-3} for BI_3). For both properties, these values arise from two large terms (dia- and paramagnetic terms for the magnetizability, nuclear and electronic terms for the g value), the cancellation of which becomes more complete for larger and heavier systems. The anisotropy of the magnetizability and the g tensor

is small and changes less smoothly in the trihalide series, with sign changes observed through the series.

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