

The magnetizability, rotational g tensor, and quadrupole moment of PF_3 revisited

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Abstract

The Hartree–Fock limit is determined for the molecular dipole moment (μ), the molecular quadrupole moment (Θ_{\parallel}), the magnetizability (ξ), and the rotational g tensor (g) of PF_3 . It is demonstrated that rotational London orbitals are crucial for obtaining reliable magnetic properties. Indeed, even with a basis set of augmented polarized triple-zeta quality, the signs of the rotational g tensor components are wrong when conventional basis functions are used. Using rotational London orbitals, the calculated components of the magnetizability tensor and the rotational g tensor agree with the experimentally observed quantities obtained from the doublet splittings of the rotational transitions, but not with the experimentally derived components of the g tensor nor with the experimental quadrupole moment. The Hartree–Fock limits of the different quantities are estimated to be: $\mu = 0.572 \pm 0.004$ a.u., $\Theta_{\parallel} = 0.690 \pm 0.010$ a.u., $g_{\perp} = -0.0643 \pm 0.0007$, $g_{\parallel} = -0.0383 \pm 0.0003$, $\xi = -6.61 \pm 0.06$ a.u., and $\Delta\xi = -0.33 \pm 0.02$ a.u.

1. Introduction

In recent years, the use of London atomic orbitals [1] for improving basis set convergence in ab initio calculations of molecular magnetic properties has become widespread. London atomic orbitals are now used routinely in calculations of nuclear magnetic shieldings for a wide variety of wave functions [2–6] and density functional theory (DFT) approaches [7,8].

Apart from nuclear magnetic shieldings, London atomic orbitals have also been used in the calculation of other molecular magnetic properties such as magnetizabilities [9], vibrational and electronic circular dichroism [10,11], Raman optical activity [12], and magnetizability and shielding hyperpolarizabilities [13]. In all cases, a significant improvement in the basis set convergence compared with conventional orbitals is observed.

In general, among all these properties, the magnetizability shows the most spectacular improvement in basis set convergence when London orbitals are introduced. This may be understood from the fact that the magnetizability represents the second-order response of the system to an externally applied magnetic field. Thus, for this particular property the London orbitals – which depend explicitly on the magnetic field – may respond to all perturbations applied to the system. In contrast, for nuclear shieldings the London orbitals respond to the external magnetic field only and not to the nuclear magnetic moments. Consequently, the basis set convergence of the shieldings is somewhat less satisfactory than for the magnetizability, which may be determined to within 2% of the Hartree–Fock limit using basis set of augmented polarized double-zeta quality [14].

In view of the ease with which molecular magnetizabilities can nowadays be calculated ab initio, it is

somewhat ironic that its unambiguous experimental determination remains problematic because of the difficulties associated with establishing an accurate calibration standard as well as the smallness of the effects associated with molecular diamagnetism. Indeed, the accuracy of the experimentally determined isotropic magnetizabilities published in the literature [15] remains unsettled, with recent strong evidence of systematic errors provided by accurate *ab initio* calculations [14].

A richer and more reliable source of information on molecular diamagnetism is provided by microwave spectroscopy measurements of magnetic properties, pioneered by Flygare and coworkers [16]. In microwave spectroscopy, no information on the isotropic part of the magnetizability is obtained but one may instead determine its anisotropy as well as the rotational g tensors. Both properties may be straightforwardly calculated by *ab initio* means, keeping in mind, however, their extreme sensitivity on the basis set if conventional orbitals are employed.

Recently, we introduced perturbation-dependent atomic orbitals – the rotational London atomic orbitals [17] – that significantly improve the basis set convergence of rotational g tensors by depending explicitly on the molecular angular momentum in a physically reasonable manner. Employing a combination of conventional magnetic (magnetic field dependent) London atomic orbitals and rotational (angular momentum dependent) London atomic orbitals, our basis set now responds physically to all perturbations involved in the measurement of rotational g tensors – that is, to the molecular rotation and to the external magnetic field. Consequently, the same excellent basis set convergence is now observed for the rotational g tensor as was previously observed for magnetizabilities calculated with magnetic London orbitals [9]. Comparing calculations with and without the use of rotational London orbitals, we found it to be almost impossible to reach the basis set limit of the rotational g tensor even for a small molecular system such as N_2 with conventional orbitals [17].

Recently, Fowler, Kelly and Sadlej carried out a theoretical study of the quadrupole moment of PF_3 [18], as experiment had indicated an anomalously large quadrupole moment for this molecule [19]. The work of Fowler et al., which indicates that the quadrupole moment in PF_3 is in fact not anomalous,

contains a thorough evaluation of the experimental data (magnetizability anisotropies and rotational g tensor). Based on their results for the rotational g tensor, the authors concluded that the sign assumed in the experimental investigation was in error and that the magnetizability anisotropy was some 10 times too small. However, all calculations of Fowler et al. were carried out using conventional orbitals. In view of the difficulties faced in reaching the Hartree–Fock limit with conventional orbitals [17], it seems timely to reinvestigate this system using rotational London atomic orbitals.

In the next section, a brief summary of the theory is given. In Section 3, we give the computational details, and Section 4 presents our results. Section 5 contains some concluding remarks.

2. Theory

The magnetizability, ξ , is the second-order response of a molecular system to an external magnetic field \mathbf{B} and is commonly given by the expression

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

where $\varepsilon(\mathbf{B})$ is the molecular energy in a magnetic field and atomic units have been used. \mathcal{I} is a 3×3 unit matrix. \mathbf{I}_O is the electronic angular momentum around the gauge origin O . The rotational g tensor, g , can in a similar fashion be given as the second derivative with respect to the magnetic field \mathbf{B} and the molecular angular momentum \mathbf{J} ,

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

Here I is the moment of inertia tensor, M_p is the proton mass, Z_K the charge of nucleus K , and \mathbf{R}_K the

distance vector from nucleus K to the center of mass. I_{CM} denotes the electronic angular momentum with respect to the center of mass.

The expressions for the magnetizability and the rotational g tensor given above apply to exact states. For ab initio calculations, we obtain the working expressions for the magnetizability and the rotational g tensor by differentiating the total energy with respect to the field twice (for the magnetizability tensor) and with respect to the field and the molecular angular momentum (for the rotational g tensor), having first extended the electronic Hamiltonian with the terms needed to describe the interaction of the electronic system with the molecular angular momentum. The resulting expressions can be evaluated by the standard techniques developed for the calculation of second-order molecular properties.

In order to ensure fast convergence towards the basis set limit, we employ for magnetizabilities and molecular g tensors a basis of rotational London atomic orbitals [17],

$$\omega_{\mu}(\mathbf{B}, \mathbf{J}) = \exp[-i(\mathbf{A}_{\mu}^B + \mathbf{A}_{\mu}^J) \cdot \mathbf{r}] \chi_{\mu}, \quad (3)$$

where χ_{μ} is an ordinary spherical Gaussian basis function, and \mathbf{A}_{μ}^B and \mathbf{A}_{μ}^J are defined as

$$\mathbf{A}_{\mu}^B = \frac{1}{2} \mathbf{B} \times \mathbf{R}_{\mu\text{O}}, \quad (4)$$

$$\mathbf{A}_{\mu}^J = \frac{1}{I} \mathbf{J} \times \mathbf{R}_{\mu\text{CM}}. \quad (5)$$

The effect of the phase factors in Eq. (3) is to transfer the common gauge origin (and rotational center) to the most suitable center for each atomic orbital – that is, to the nucleus to which it is attached. The interested reader is referred to Ref. [17] for further details about the theory and performance of the rotational London orbitals. Computationally, the complications introduced by the use of rotational London orbitals are similar to those associated with the use of nuclear-fixed atomic calculations of molecular Hessians.

From the expressions for the magnetizability tensor Eq. (1) and the molecular g tensor Eq. (2) for the exact states, we note the following simple relationship between these properties calculated with the gauge origin at the center of mass:

$$4\xi(\text{CM}) + \frac{I}{M_p} g(\text{CM}) = \text{Tr}(Q) - Q. \quad (6)$$

Here Q is the matrix of the second moment of the charge with respect to the center of mass,

$$Q = \sum_i q_i r_i^T r_i, \quad (7)$$

where the summation runs over all particles in the system and q_i is the charge of the i th particle. This relationship – which relates the diamagnetic parts of the molecular magnetizability tensor and the molecular g tensor to the components of the molecular quadrupole moment – holds also for approximate wave functions calculated with or without rotational London orbitals. The implementation of one of these properties therefore follows trivially from the other by the calculation of the components of the second-order moments.

3. Computational details

All calculations reported here have been carried out with the DALTON quantum chemistry program [20], which was recently extended to include rotational London atomic orbitals. We have used the augmented correlation-consistent basis sets by Dunning and coworkers [21–23], which have been shown to give good results for the calculation of magnetizabilities and rotational g tensors with perturbation-dependent orbitals [17].

We used the optimized Hartree–Fock geometry obtained with the aug-cc-pVDZ basis set for all calculations. The optimized structure ($r(\text{PF}) = 1.5883 \text{ \AA}$, and $\angle(\text{FPF}) = 96.68^\circ$) has a somewhat larger bond length, but a smaller bond angle than the corresponding geometry obtained with a 6-31G** basis set [18], as well as the experimental gas-electron-diffraction geometry of Morino et al. [24]. The difference in the angle is only 0.02° compared with the 6-31G** optimized geometry, whereas the bond length is some 0.025 \AA longer.

4. Results

In Table 1 the results obtained with the aug-cc-pVDZ basis set are collected. We have here included both results obtained with conventional orbitals and results obtained with rotational London atomic orbitals. For comparison, the results of Fowler et al. [18] ob-

Table 1

Results obtained with the aug-cc-pVDZ basis both with (Lon) and without (No-Lon) rotational London orbitals. The results of Fowler et al. [18] and the experimental results of Stone et al. [19] are also quoted. All numbers reported are in atomic units, and the experimentally determined quantities are listed first in the table

Property	Experiment [19]	This work		Fowler [18] et al.
		Lon	No-Lon	
μ	0.393 ± 0.004		0.601	0.470
$\Delta\xi$	-0.28 ± 0.04	-0.25	-3.66	-3.23
g_{\perp}	-0.0659 ± 0.0003	-0.0618	0.0845	0.0714
$ 7g_{\perp} - g_{\parallel} $	0.3798 ± 0.006	0.3948	0.5025	0.423
ξ^{para} ^a	38.96	37.49	27.74	28.34
Experimentally derived properties				
Θ_{\parallel}	17.9 ± 2.3	0.757	0.757	0.561
ξ^{dia} ^a	-46.83	-44.29	-44.29	-43.87
ξ	-7.87	-6.80	-16.55	-15.53
g_{\parallel}	-0.0815 ± 0.002	-0.0378	0.0890	0.0768

^a The diamagnetic term is the same for both the London and conventional atomic orbital basis sets, and the paramagnetic term is defined as the difference between the total magnetizability and the diamagnetic term, as suggested by Gauss et al. [17].

tained with Sadlej's polarized basis set [25,26] and the experimental results of Stone et al. [19] are also given.

The difference between the results obtained with and without London orbitals is striking. The isotropic magnetizability is reduced to approximately one half of its value when London orbitals are employed in the calculation, whereas the magnetizability anisotropy is reduced to less than a tenth of the value obtained without perturbation-dependent orbitals, bringing the London orbital result into excellent agreement with experiment. Even more striking is the change in sign of the rotational g tensor components when going from the conventional to the rotational London orbital basis set. The rotational London orbitals support the experimentally chosen sign, whereas the no-London calculation agrees with the sign-reverse suggested by Fowler et al. [18].

Comparing with experiment, we note that our calculations as well as those of Fowler et al. agree with the experimentally observed molecular g tensor quantities $|g_{\perp}|$ and $|7g_{\perp} - g_{\parallel}|$. In contrast, for the experimentally observed component of the magnetizabil-

ity tensor $\Delta\xi$, our calculations agree with experiment whereas the result of Fowler et al. is an order of magnitude larger. Concerning the quadrupole moment, our calculations as well as those of Fowler et al. indicate that the anomalously large experimentally derived parallel component of the quadrupole moment is in error by at least an order of magnitude. We note that although there are some differences between the dipole and quadrupole moments calculated by us and by Fowler et al., these differences are not large enough to undermine the conclusion that the experimentally derived quadrupole moment is in error.

We now examine the reasons for the unphysically large experimental quadrupole moment in PF_3 , derived from the expression

$$Q_{\parallel}^{\text{derived}} = -\frac{1}{M_p} (g_{\parallel} I_{\parallel} - g_{\perp} I_{\perp}) - 4 (\xi_{\parallel} - \xi_{\perp}) \quad (8)$$

Fowler et al. suggest that it is the smallness of the observed magnetizability anisotropy of -0.28 a.u. which is the cause of the large derived quadrupole moment, basing their suggestion on their calculated anisotropy of -3.66 a.u. This appears not to be the case, however. Our calculations agree with *all* the experimentally observed quantities needed to derive the quadrupole moment and yet our calculations yield a quadrupole moment some 24 times smaller than the experimentally derived quadrupole moment. Instead, we shall demonstrate that it is the relative magnitudes of g_{\perp} (observed) and g_{\parallel} (derived) that are wrong, and that the wrong ordering of these components is the cause of the anomalously large quadrupole moment.

In Table 2, we have collected our results for the basis sets aug-cc-pVXZ ($X = \text{D, T, Q, 5}$). The convergence of the isotropic magnetizability, the magnetizability anisotropy and the rotational g tensor components are depicted in Figs. 1–3. The table and the figures are revealing. They show that Hartree–Fock limit results cannot be hoped for with any conventional basis set of manageable size. Even for the aug-cc-pV5Z basis set – with 512 basis functions – the isotropic magnetizability is still some 15% off the results obtained with the aug-cc-pVQZ basis set and London orbitals. From an inspection of Table 2 it is clear that only significant enlargements in basis set size may help in discovering any basis set dependency in the magnetic properties.

We note from Table 2 that Fowler et al. were rather unfortunate with their choice of basis set. At the aug-

Table 2

Basis set convergence of the properties investigated both with (Lon) and without (No-Lon) London orbitals. All numbers reported are in atomic units

Property	aug-cc-pVDZ		aug-cc-pVTZ		aug-cc-pVQZ		aug-cc-pV5Z
	No-Lon	Lon	No-Lon	Lon	No-Lon	Lon	No-Lon
μ		0.601		0.582		0.576	0.572
θ_{\parallel}		0.757		0.709		0.699	0.690
$\theta_{\parallel}^{\text{derived}}$	0.764	0.757	0.709	0.708	0.701	0.699	
$\xi_{\text{dia}}^{\text{a}}$	-44.29	-44.29	-44.24	-44.24	-44.22	-44.22	-44.21
$\xi_{\text{para}}^{\text{a}}$	27.74	37.49	32.74	37.57	35.16	37.61	36.55
ξ	-16.55	-6.80	-11.50	-6.67	-9.06	-6.61	-7.66
$\Delta\xi$	-3.66	-0.25	-0.77	-0.32	0.48	-0.33	-0.28
g_{\perp}	0.0845	-0.0618	0.0159	-0.0636	-0.0181	-0.0643	-0.0461
g_{\parallel}	0.0890	-0.0378	0.0162	-0.0380	-0.0181	-0.0383	-0.0274
$ 7g_{\perp} - g_{\parallel} $	0.5025	0.3948	0.0951	0.4072	0.1086	0.4118	0.2953

^a See footnote in Table 1.

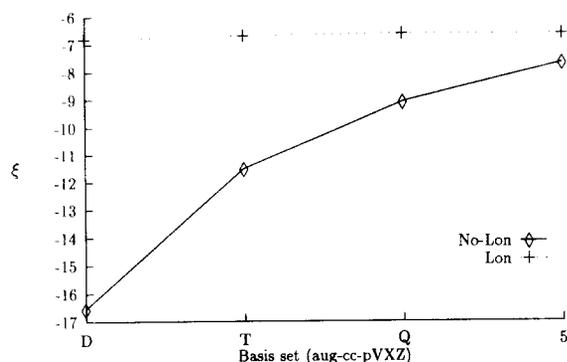


Fig. 1. The isotropic magnetizability (ξ) obtained with (Lon) and without (No-Lon) London atomic orbitals. The London orbital result for the aug-cc-pV5Z basis set has been set to the value obtained with the aug-cc-pVQZ basis set.

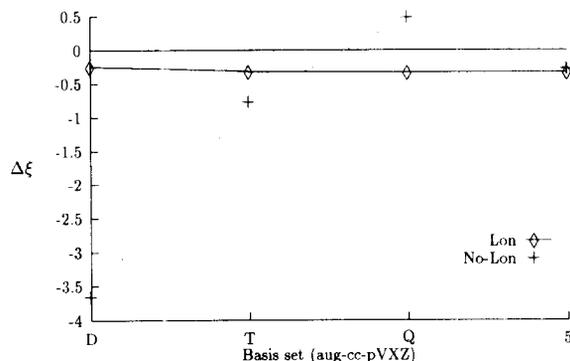


Fig. 2. The magnetizability anisotropy ($\Delta\xi$) obtained with (Lon) and without (No-Lon) London atomic orbitals. The London orbital result for the aug-cc-pV5Z basis set has been set to the value obtained with the aug-cc-pVQZ basis set.

cc-pVDZ level (which is of comparable size to the polarized basis set of Sadlej), the results are consistent with the experimentally determined quantities also without London atomic orbitals (with the noticeable exception of $\Delta\xi$). This agreement is destroyed, however, when the basis set is increased to the aug-cc-pVTZ level and for larger basis sets. Clearly, extreme care need to be taken when calculating magnetic properties without rotational London orbitals.

From Table 2 and Figs. 1 and 2, it appears that the magnetizability and rotational g tensors will converge to the same values, but that the convergence of the

conventional orbital results is slow. As for N_2 [17], it appears impossible to reach basis set saturation with conventional orbitals for the magnetic properties of PF_3 . An interesting artifact of the conventional calculations is the observation that, for the aug-cc-pVQZ basis set (with 324 basis functions), the rotational g tensor becomes isotropic. Furthermore, for this basis set the magnitudes of the magnetizability components change order, so that the magnetizability anisotropy becomes positive.

Our results support the experimentally chosen sign for the rotational g tensor and indicate that the change

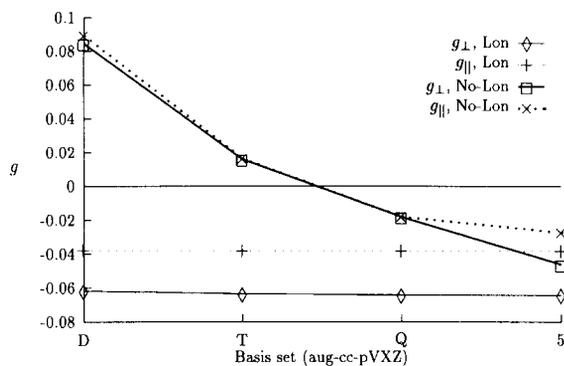


Fig. 3. The rotational g tensor components (g_{\perp} and g_{\parallel}) obtained with (Lon) and without (No-Lon) rotational London atomic orbitals. The London orbital result for the aug-cc-pV5Z basis set has been set to the value obtained with the aug-cc-pVQZ basis set.

of sign for the rotational g tensor suggested by Fowler et al. is an artifact of the calculation arising from basis set incompleteness. Furthermore, our results do not support their for using a value of -3.23 a.u. for the magnetizability anisotropy. On the contrary, our best estimate is almost within the experimental error bar for the magnetizability anisotropy. The results obtained with conventional orbitals and the aug-cc-pV5Z basis set support this conclusion.

There still remains some disagreement between the isotropic magnetizability reported by Stone et al. [19] and our result obtained using London orbitals. As correlation in general modifies Hartree–Fock isotropic magnetizabilities by less than 2% [14] and since we are close to the Hartree–Fock limit, we consider our isotropic magnetizability to be more accurate than the experimentally derived one. Furthermore, we note that our results for the dia- and paramagnetic contribution is in fair agreement with the experimental estimates.

Finally, we note that there is a fairly large discrepancy between the experimental and theoretical result for the quantity $|7g_{\perp} - g_{\parallel}|$. However, it is noteworthy that in order to obtain a reasonable sign and magnitude for the quadrupole moment, g_{\perp} must be larger (in absolute value) than g_{\parallel} . We thus believe that the main problem in the experimental investigation of Stone et al. [19] is the value of $|7g_{\perp} - g_{\parallel}|$, which we believe should be closer to our London orbital result. This will lead to what we believe is a correct ordering of g_{\perp} and g_{\parallel} , and in combination with the small value for $\Delta\xi$ a more reasonable quadrupole moment will be obtained.

5. Conclusion

Despite the substantial increase in computer power in the last few years, the ab initio computation of molecular magnetic properties remains a challenging task. In particular, thorough basis set convergence investigations need to be undertaken if magnetic properties are calculated with conventional orbitals in order to avoid misleading results and conclusions. As we have shown, an easy way of circumventing these obstacles when calculating magnetic properties is to use orbitals that respond to the perturbations applied. Indeed, for a molecular system of the size of PF_3 , it does not appear to be possible to obtain reliable results without the use of perturbation-dependent basis sets.

Our investigation has shown that the sign chosen in the experimental investigation of Stone et al. [19] is the correct one, and that the sign change previously suggested on the basis of coupled-perturbed Hartree–Fock calculations using a double-zeta basis [18] is not correct. Furthermore, our results for the magnetizability anisotropy indicate that the experimental results of -0.28 ± 0.04 a.u. is correct, whereas the result in Ref. [18] is some 10 times too large due to basis set incompleteness. However, our results indicate that the experimental determination of $|7g_{\perp} - g_{\parallel}|$ is inaccurate, giving a value for $|g_{\parallel}|$ that is too large by a factor of two and consequently a quadrupole moment in error by a factor of twenty or more.

As a by-product of this investigation, we have determined the Hartree–Fock limit for the dipole moment, quadrupole moment, rotational g tensor and magnetizability of PF_3 at the aug-cc-pVDZ optimized geometry. Whereas we believe the results obtained for g and ξ to be quite insensitive to correlation and to rovibrational averaging [14,27], the dipole moment and in particular the quadrupole moment may change significantly when correlation and rovibrational effects are added. The estimated Hartree–Fock limit results are (with the errors referring to the uncertainty of the Hartree–Fock limit and not to experiment): $\mu = 0.572 \pm 0.004$ a.u., $\Theta_{\parallel} = 0.690 \pm 0.010$ a.u., $g_{\perp} = -0.0643 \pm 0.0007$, $g_{\parallel} = -0.0383 \pm 0.0003$, $\xi = -6.61 \pm 0.06$ a.u., and $\Delta\xi = -0.33 \pm 0.02$ a.u.

It has been pointed out to us by Professor D.H. Sutter, that the analysis of the rotational spectrum of PF_3 by Stone et al. [19] is based on an incomplete

Hamiltonian, where the Lorentz effect associated with molecular translation is neglected. Engelbrecht and Sutter have shown that, for symmetric top molecules, the Lorentz effect may lead to corrections in experimental g tensor components larger than the experimental error bars [28]. A reinvestigation of the experimental spectrum using a complete Hamiltonian is difficult due to the lack of information about the experimental conditions.

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