MAGNETIC RESONANCE IN CHEMISTRY, VOL. 36, 92–97 (1998)

Atomic Magnetizability Tensors of Benzene and Fluoro- and Chlorobenzenes

Per-Olof Åstrand* and Kurt V. Mikkelsen

Chem. Lab. III, H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen Ø, Denmark

Received 31 March 1997; revised 6 August 1997; accepted 14 August 1997

ABSTRACT: Calculation of the contribution to the chemical shift of molecules in solution arising from the magnetizability anisotropy of the neighbouring molecules requires a distributed representation of the molecular magnetizability tensor. A partition scheme of the molecular magnetizability into atomic magnetizability tensors is discussed and atomic magnetizabilities of benzene and fluoro- and chlorobenzenes are calculated. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: atomic magnetizability tensors; benzene; fluorobenzenes; chlorobenzenes

INTRODUCTION

Chemical-shift non-equivalences of molecules in solution are of different origins. The electrostatics of the surroundings alter the intramolecular geometry and polarize the charge distribution, there is a dispersive contribution and the magnetizability anisotropy of the nearby molecules or subgroups in the same molecule also shields the atom of interest. The solvent shift δ_{solvent} may be partitioned by adopting perturbation theory:[1,2]

$$\delta_{\text{solvent}} = \delta_{\text{E}} + \delta_{\text{w}} + \delta_{\text{a}} + \delta_{\text{b}} \tag{1}$$

where δ_{E} is the electrostatic contribution, δ_{w} is the van der Waals (dispersion) term and δ_{a} is due to the magnetizability anisotropy of the nearby molecules; δ_{b} is proportional to the magnetic susceptibility of the bulk and vanishes if the sample is spherical,[3] otherwise it is normally corrected for in the experiment. The electrostatic and dispersion shifts may be obtained from shielding polarizabilities by considering both the external magnetic field and the intermolecular interactions as perturbations and adopting regular perturbation theory.[1,2,4,5] A perturbation approach based on first principles has recently been used for calculating the electrostatic and van der Waals contributions of the gas-to-liquid chemical shifts of liquid water.[6,7]

Solvent effects on chemical shieldings have been studied by computational methods by considering the surroundings as a continous dielectric medium[8–10] and by studying clusters[8,11–13] (sometimes within a dielectric medium[14]). Molecular dynamics simulations have been used to calculate some contributions of Eqn (1), but empirical parameters have mostly been employed.[15,16] Intramolecular effects in large molecules such as proteins have been considered by different empirical relations that sometimes are related to Eqn (1).[17–26] The shifts arising from the magnetizability anisotropy of the neighbouring molecules are expected to be important in for example aromatic systems where ring-current effects are large[27] and for proteins where peptide bonds are present.[28] Consequently, this term has to be calculated if we wish to model NMR spectra of, e.g., peptides and proteins. If perturbation theory is adopted, the term arising from the anisotropy of the magnetizability may be calculated as[2]

$$\delta_{\text{a}} = \sum_{j} -\tfrac{1}{3}R^{-5}(3r_{\alpha}r_{\beta} - R^{2}\delta_{\alpha\beta})\xi^{j}_{\alpha\beta} \tag{2}$$

where $\xi_{\alpha\beta}$ is a tensor component of the magnetizability of a neighbouring molecule j and r_{α} is a component of the intermolecular distance R. Since the magnetizability is a molecular property, the distance R has to be large compared with the molecular dimensions for the perturbation expansion to converge, which in most cases is not true for a liquid. Furthermore, in macromolecules, the dominant contribution may arise from other parts of the same molecule. A procedure for calculating local magnetizabilities distributed to different parts of the molecule is therefore required. An important example is the magnetizability anisotropy of the peptide bond, which has been calculated by Pauling.[28]

The remarkable additivity properties of the magnetizability have been known for a long time[29,30] and several theoretical investigations of the additivity property have been carried out.[31–36] These schemes deal, however, mostly with the isotropic magnetizability, whereas we are interested in its anisotropy.

METHOD

Any partition scheme of the molecular magnetizability tensor into local contributions is arbitrary because it is not possible to measure a local contribution to a property in an experiment. Furthermore, to be able to use Eqn (2) we also have to choose a set of expansion

* *Correspondence to:* P.-O. Åstrand, Chemistry Laboratory III, H. C. Ørsted Institute, University of Copenhagen, DK-2100 København Ø, Denmark.

Contract/grant sponsor: Danish Natural Research Council (SNF).

CCC 0749-1581/98/020092–06 $17.50

points. It is reasonable to expand a property in atomic contributions since the wavefunction is normally expanded in basis functions placed at atomic positions. Atomic magnetizability tensors have been calculated by carrying out calculations of molecular magnetizabilities of benzene and some fluoro- and chlorobenzenes and assuming that the atomic magnetizabilities are transferable from one molecule to another. The molecular magnetizability is therefore given as a sum of atomic contributions. We included 18 molecules in this investigation: benzene, all 12 fluorobenzenes, chlorobenzene, all three dichlorobenzenes and *p*-fluorochlorobenzene. The atomic magnetizability tensors were fitted by minimizing the mean square deviation (*msd*) of the molecular magnetizabilities as

$$msd = \sqrt{\left[\sum_{i=1}^{N}\sum_{\alpha,\beta}(\xi_{\alpha\beta,i}^{\text{fitted}} - \xi_{\alpha\beta,i}^{\text{HF}})^2 \Big/ N-1\right]} \qquad (3)$$

where N is the number of molecules.

All the calculations were performed at the Hartree–Fock level and with the atomic natural orbital (ANO) basis sets by Widmark *et al.*,[37,38] The carbon and fluorine basis sets were contracted to [4s3p2d], the hydrogen basis set to [3s2p] and the chlorine basis set to [5s4p3d2f]. The molecular magnetizabilities were calculated by adopting response theory and London atomic orbitals.[39] The DALTON program package was employed in all calculations.[40]

All tensors are presented as if the particular atom is situated in (0, *y*, 0). The *z*-axis is chosen as the out-of-plane axis. The in-plane components are, however, presented as $\xi_{aa} = \frac{1}{2}(\xi_{xx} + \xi_{yy})$ and $\xi_{bb} = \frac{1}{2}(\xi_{xx} - \xi_{yy})$ since ξ_{aa} is invariant to rotation around the *z*-axis.

RESULTS

In our first patition scheme, we assign a magnetizability tensor to each of the elements C, H, F and Cl. The tensors of H, F and Cl are restricted to as the atoms are part of linear molecules, i.e. $\xi_{xx} \equiv \xi_{zz}$. The fitted magnetizability tensors are given in Table 1 and the fit of the in-plane (*aa* and *bb*) and out-of-plane (*zz*) components in Fig. 1. It is noted that the fit is excellent.

If only one tensor is used for each element in the fit, all the molecules with the same number of fluorine (chlorine) atoms will have the same value, which is noted in Fig. 1. Furthermore, since benzene and fluorobenzene have almost the same *zz*-component, all the fluorobenzenes have approximately the same value for ξ_{zz} in the fit.

One way to deal with this is to partition the carbon parameters into different sets of parameters. However, if only two types of carbon parameters are employed, one for carbons bonded to fluorine or chlorine atoms (labelled $C_{F,Cl}$) and one for carbons bonded to hydrogen atoms (labelled C_H), the problem would persist. The results of such a fit are also given in Table 1. It is noted that the *msd* is dramatically decreased.

If C_H is furthermore partitioned into one type of carbon which has a $C_{F,Cl}$ carbon as a neighbour (labelled C_H^n) and another type which only has hydrogen carbons as neighbours, the problem is solved for the difluorobenzenes but not for the molecules with three or four fluorine atoms. As equivalent partitioning of $C_{F,Cl}$ into neighbours of C_H^n carbons and all other $C_{F,Cl}$ carbons resolves the problem for the tetrafluorobenzenes, but 1,2,4-trifluorobenzene and 1,3,5-trifluorobenzene still have the same set of parameters. If, however, we partition the $C_{F,Cl}$ carbons into one type which has another $C_{F,Cl}$ carbon (labelled $C_{F,Cl}^n$) as a neighbour and one type which only has C_H^n carbons as neighbours, this problem is also resolved. The carbon atoms are thus described with four parameters.

We carried out a fit where we retained the values for H, F and Cl from the second fit in Table 1 and optimized only the carbon parameters. The results of the fit are given in Table 2 and Fig. 2. When a full optimization of all components was carried out, we found that the parameters obtained were sensitive to the chosen set of molecules.

It is noted that the fit has become substantially better, which of course is expected since the number of fitting parameters has been increased. In Table 2, it is noted, however, that the effects on the actual parameters from the further partitioning of the carbon parameters are small. The stability of the values between the two fits and within the set of carbon parameters in the

Table 1. Atomic magnetizability tensors (ppm cm^3 mol^{-1})

	Four atom types			Two types of C		
Atom	ξ_{aa}	ξ_{bb}	ξ_{zz}	ξ_{aa}	ξ_{bb}	ξ_{zz}
H	−1.42	−1.42	−2.85	−2.65	−2.12	−4.77
F	−5.87	1.50	−4.37	−2.93	−2.93	−5.86
Cl	−17.52	1.19	−16.33	−14.98	−2.01	−16.99
C	−5.13	—[a]	−14.00			
C_H				−3.61	−3.00	−12.68
$C_{F,Cl}$				−8.38	−0.42	−11.90
		msd = 3.11			*msd* = 1.57	

[a] ξ_{bb}^C will sum to zero for these molecules.

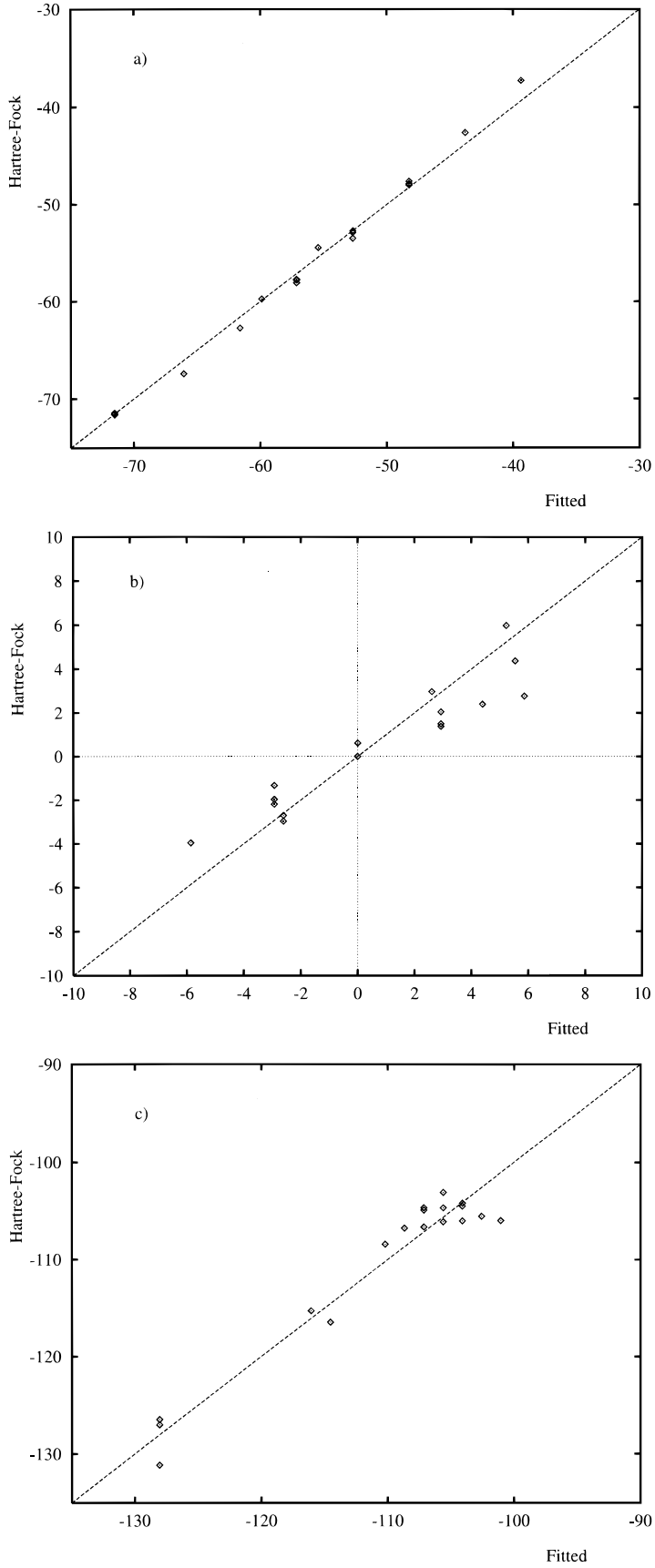

Figure 1. Molecular magnetizabilities. One type of carbon. (a) *aa*-component; (b) *bb*-component; (c) *zz*-component.

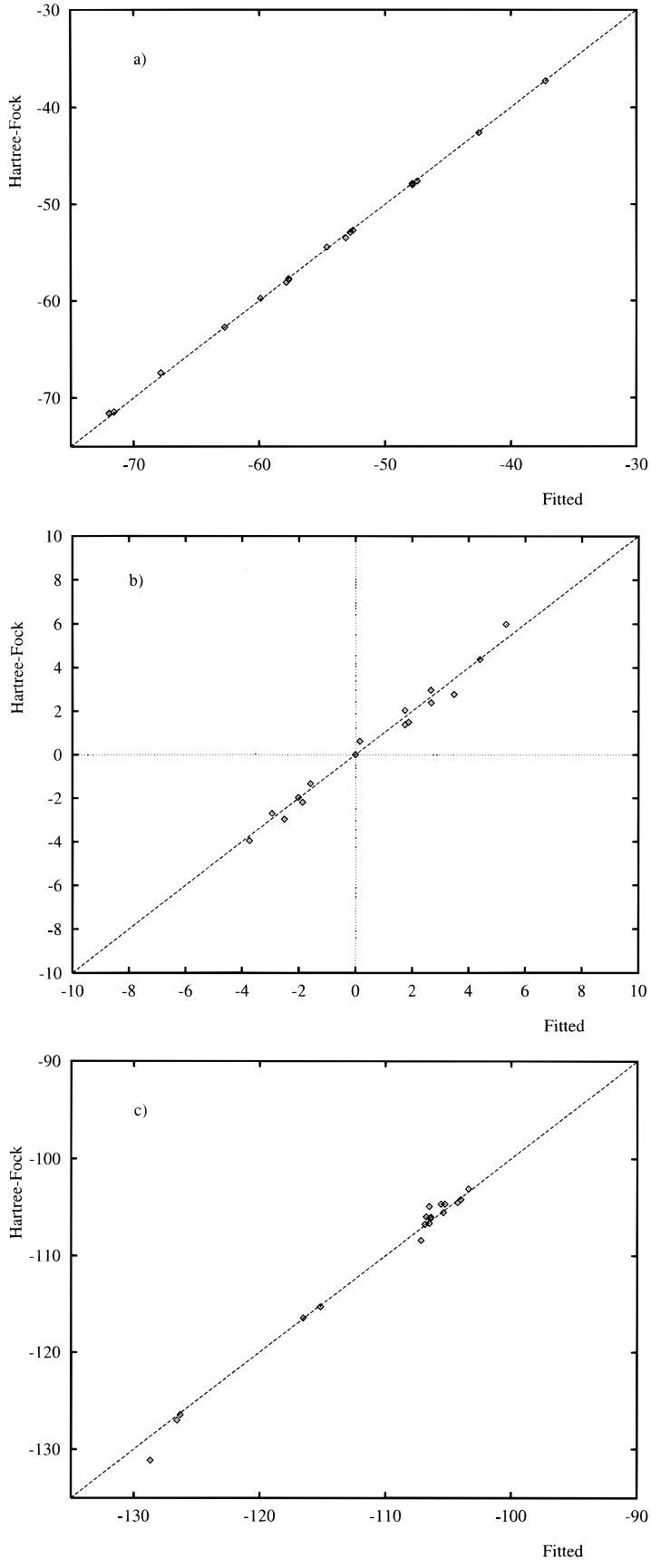

Figure 2. Molecular magnetizabilities. Four types of carbons. (a) *aa*-component; (b) *bb*-component; (c) *zz*-component.

Table 2. Atomic magnetizability tensors (ppm cm^3 mol^{-1})

Atom	ξ_{aa}	ξ_{bb}	ξ_{zz}
C_H	−3.56	−2.77	−13.03
C_H^n	−3.57	−2.92	−12.77
$C_{F,Cl}$	−8.56	−0.37	−11.08
$C_{F,Cl}^n$	−8.38	−0.24	−12.01
		$msd = 1.05$	

second fit indicates that the atomic magnetizabilities have a physical meaning and are not just results of a fitting procedure.

DISCUSSION AND CONCLUSIONS

It has been demonstrated that it is possible to represent the molecular magnetizability tensor of benzene and the fluoro- and chlorobenzenes with a set of atomic magnetizability tensors, which is important for modelling chemical shifts arising from the magnetizability anisotropy of aromatic compounds. The parameters obtained here may be used for describing the magnetizability in aromatic rings and also provide an estimate of the corresponding contribution to the chemical shift. It is noted that for the set of aromatic compounds included in this study, the σ-space (in-plane components) is easier to partition into atomic magnetizabilities than the π-space.

However, more rigorous methods are needed for calculating distributed magnetizabilities for most molecules. The set of molecules studied here is advantageous owing to the large number of molecules which may be used for fitting a small number of parameters. One may use methods available for calculating distributed polarizabilities such as the uncoupled Hartree–Fock approximation[41] or the coupled Hartree–Fock approach.[42,43]

The partition scheme adopted here is different from Pascal's rule since we use atomic magnetizability tensors and we thereby include the deviation from Pascalian additivity for aromatic compounds in our parameters. Musher[44] also used atomic magnetizabilities for aromatic compounds, $\xi_{aa}^C = -3$ cgs and $\xi_{zz}^C = -12.5$ cgs, which are in good agreement with our values of about −3.6 and −12.7 cgs for C_H, respectively. Perhaps it would be useful to adopt a similar approach as for polarizabilities, where the molecular polarizability has been calculated from a set of interacting isotropic point polarizabilities.[45,46] The magnetizability and electrostatics of the other atoms in the molecule would induce a magnetic moment at an atom that will couple to all other magnetic moments in a self-consistent way. Such a model would reduce the number of parameters and may give large molecular magnetizability anisotropies and explain the deviations from Pascal's rule and be an alternative to ring-current models.

It should also be noted that the surrounding medium will perturb the anisotropy of the magnetizability and thus indirectly alter the chemical shift. Especially electric field effects arising from nearby charged groups in a peptide will be important. These effects may be estimated in a perturbative fashion by calculating magnetizability polarizabilities, as for example has been carried out by Rizzo *et al.*[47]

Acknowledgements

Grants from the Danish Natural Research Council (SNF) are gratefully acknowledged.

REFERENCES

1. M. J. Stephen, *Mol. Phys.* **1**, 223 (1958).
2. A. D. Buckingham, T. Schaefer and W. G. Schneider, *J. Chem. Phys.* **32**, 1227 (1960).
3. W. C. Dickinson, *Phys. Rev.* **81**, 717 (1951).
4. A. D. Buckingham, *Can. J. Chem.* **38**, 300 (1960).
5. A. D. Buckingham, *Adv. Chem. Phys.* **12**, 107 (1967).
6. T. M. Nymand, P.-O. Åstrand and K. V. Mikkelsen, *J. Phys. Chem. B* **101**, 4105 (1997).
7. T. M. Nymand and P.-O. Åstrand, *J. Chem. Phys.* **106**, 8332 (1997).
8. D. B. Chestnut and B. E. Rusiloski, *J. Mol. Struct. (THEOCHEM)* **314**, 19 (1994).
9. P.-O. Åstrand, K. V. Mikkelsen, K. Ruud and T. Helgaker, *J. Phys. Chem.* **100**, 19771 (1996).
10. K. V. Mikkelsen, P. Jørgensen, K. Ruud and T. Helgaker, *J. Chem. Phys.* **106**, 1170 (1997).
11. J. F. Hinton and D. C. Bennet, *Chem. Phys. Lett.* **116**, 292 (1985).
12. J. F. Hinton, P. Guthrie, P. Pulay and K. Wolinski, *J. Am. Chem. Soc.* **116**, 292 (1992).
13. V. G. Malkin, O. L. Malkina, G. Steinebrunner and H. Huber, *Chem. Eur. J.* **2**, 452 (1996).
14. K. V. Mikkelsen, K. Ruud and T. Helgaker, *Chem. Phys. Lett.* **253**, 443 (1996).
15. I. M. Svishchev and P. G. Kusalik, *J. Am. Chem. Soc.* **115**, 8270 (1993).
16. E. Y. Lau and J. T. Gerig, *J. Chem. Phys.* **103**, 3341 (1995).
17. G. Wagner, A. Pardi and K. Wüthrich, *J. Am. Chem. Soc.* **105**, 5948 (1983).
18. K. Ösapay and D. A. Case, *J. Am. Chem. Soc.* **113**, 9436 (1991).
19. T. Asakura, E. Nakamura, H. Asakawa and M. Demura, *J. Magn. Reson.* **93**, 355 (1991).
20. M. P. Williamson and T. Asakura, *J. Magn. Reson.* **94**, 557 (1991).
21. J. D. Augspurger, C. E. Dykstra and E. Oldfield, *J. Am. Chem. Soc.* **113**, 2447 (1991).
22. J. Augspurger, J. G. Pearson, E. Oldfield, C. E. Dykstra, K. D. Park and D. Schwartz, *J. Magn. Reson.* **100**, 342 (1992).
23. J. D. Augspurger and C. E. Dykstra, *J. Am. Chem. Soc.* **115**, 12016 (1993).
24. A. C. de Dios, J. G. Pearson and E. Oldfield, *Science* **260**, 1491 (1993).
25. A. C. de Dios and E. Oldfield, *J. Am. Chem. Soc.* **116**, 7453 (1994).
26. P. E. Hansen, J. Abildgaard and Aa. E. Hansen, *Chem. Phys. Lett.* **224**, 275 (1994).
27. C. W. Haigh and R. B. Mallon, *Nucl. Magn. Reson. Spectrosc.* **13**, 303 (1980).
28. L. Pauling, *Proc. Natl. Acad. Sci. USA* **76**, 2293 (1979).
29. S. Henrichsen, *Wied. Ann.* **34**, 180 (1888).
30. P. Pascal, *Ann. Chim. Phys.* **18**, 5 (1910).
31. V. C. G. Trew, *Trans. Faraday Soc.* **49**, 604 (1953).
32. H. F. Hameka, *J. Chem. Phys.* **34**, 1996 (1961).
33. P. S. O'Sullivan and H. F. Hameka, *J. Am. Chem. Soc.* **92**, 1821 (1970).

34. W. H. Flygare, *Chem. Rev.* **74**, 653 (1974).
35. R. F. W. Bader and T. A. Keith, *J. Chem. Phys.* **99**, 3683 (1993).
36. K. Ruud, H. Skaane, T. Helgaker, K. L. Bak and P. Jørgensen, *J. Am. Chem. Soc.* **116**, 10135 (1994).
37. P.-O. Widmark, P.-Å. Malmqvist and B. O. Roos, *Theor. Chim. Acta* **77**, 291 (1990).
38. P.-O. Widmark, B. J. Persson and B. O. Roos, *Theor. Chim. Acta* **79**, 419 (1991).
39. K. Ruud, T. Helgaker, K. L. Bak, P. Jørgensen and H. J. Aa. Jensen, *J. Chem. Phys.* **99**, 3847 (1993).
40. T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen, H. Ågren, T. Andersen, K. L. Bak, V. Bakken, O. Christiansen, P. Dahle, E. K. Dalskov, T. Enevoldsen, B. Fernandez, H. Heiberg, H. Hettema, D. Jonsson, S. Kirpekar, R. Kobayashi, H. Koch, K. V. Mikkelsen, P. Norman, M. J. Packer, K. Ruud, T. Saue, P. R. Taylor and O. Vahtras, *DALTON, an Ab Initio Electronic Structure Program.*
41. G. Karlström, *Theor. Chim. Acta* **60**, 535 (1982).
42. A. J. Stone, *Mol. Phys.* **56**, 1065 (1985).
43. J. G. Ángyán, G. Jansen, M. Loos, C. Hättig and B. A. Hess, *Chem. Phys. Lett.* **219**, 267 (1994).
44. J. I. Musher, *J. Chem. Phys.* **43**, 4081 (1965).
45. J. Applequist, J. R. Carl and K.-F. Fung, *J. Am. Chem. Soc.* **94**, 2952 (1972).
46. B. T. Thole, *Chem. Phys.* **59**, 341 (1981).
47. A. Rizzo, T. Helgaker, K. Ruud, A. Barszczewicz, M. Jaszuński and P. Jørgensen, *J. Chem. Phys.* **102**, 8953 (1995).

