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Magnetizability of Hydrocarbons

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Abstract: The magnetizability of a large number of hydrocarbons—saturated, unsaturated, and aromatic—have been investigated by *ab initio* methods at the Hartree–Fock level. Gauge-origin independence and size extensivity are imposed by the use of London atomic orbitals (also known as gauge-invariant atomic orbitals). Using a standard basis set adapted for magnetizabilities, results close to the Hartree–Fock limit are obtained. Correlation has a moderate effect on the magnetizabilities. Using an overall scaling factor for the Hartree–Fock results, we obtain magnetizabilities within the experimental error bars for most of the molecules considered. The calculations suggest that the observed gas-phase magnetizabilities contain a calibration error.

I. Introduction

One of the most remarkable additivity schemes is perhaps the additivity of the magnetic susceptibility, known as Pascal's rule. This scheme is also one of the oldest, as Henrichsen at the University of Christiania (now Oslo) in 1888 noticed that there seemed to be an almost constant contribution to the magnetic susceptibility from the methylene group in a wide range of organic molecules, irrespective of the neighboring groups.[1] This notion was further elaborated through systematic investigations, carried out mainly by Pascal and Pacault.[2–4] Several schemes based on atomic susceptibilities as in Pascal's original work[3–6] or by assigning "magnetic moments" to larger functional units have been proposed.[7–10] The latter approach has recently been given a theoretical foundation by Bader and Keith in their work on the additivity of the magnetizability using the theory of atoms in molecules.[12] [We refer to measurements on bulk properties as magnetic susceptibility, and measurements/theoretical calculations on the molecular property as magnetizability. We use SI units for the magnetizabilities (J T^{-2}), as recommended by, for example, Bishop *et al.*[11]]

Although there has been considerable theoretical interest in the magnetizability of molecules, most calculations have been hampered by the need for large basis sets to ensure gauge-origin-independent results.[13–15] Several schemes have been proposed to overcome this problem. Most commonly the gauge origin is chosen according to some predefined set of rules, thereby eliminating any ambiguity in the choice of gauge origin for each particular molecule.[16–20] Although unambiguous, there is no guarantee that this choice of origin is the best, and large basis sets are generally needed for near Hartree–Fock limit results.[21] Furthermore, these methods are not size extensive.

Despite the great efforts put into the work of eliminating the gauge-origin problem in quantum chemical calculations, the problem was in principle solved in 1937 by London, who proposed to attach field-dependent complex phase factors to the individual atomic orbitals.[22] In this way each individual atomic orbital has its own local gauge origin: the nucleus to which it is attached. The London atomic orbitals—commonly known as gauge-invariant atomic orbitals (GIAOs)—are physically motivated by the fact that they are correct through first order in the magnetic field for a one-electron one-center problem.[23]

The use of London orbitals in *ab initio* calculations was pioneered by Hameka[24–27] in the 1950s and 1960s and by Ditchfield[28] in the 1970s. Efficient implementations have only recently been presented, first for self-consistent field (SCF) shieldings by Wolinski, Hinton, and Pulay.[29] The use of London orbitals has now become widespread, and Häser *et al.* have, for example, presented a direct program for the calculation of nuclear shielding constants.[30] Correlated shieldings have been calculated by Gauss[31,32] at the second-order Møller–Plesset (MP2) level and by Ruud *et al.*[33] at the multiconfigurational self-consistent field (MCSCF) level. Ruud, Helgaker, and co-workers have presented calculations of magnetizabilities at the SCF[34,35] and

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MCSCF levels,[36] and Bak, Jørgensen, and co-workers have used London orbitals in calculations of vibrational circular dichroism (VCD)[23,37] and electronic circular dichroism (ECD)[38] at the SCF and MCSCF levels.

In the London orbital approach the field-dependent phase factors are attached to the atomic orbitals. An alternative method has been presented by Kutzelnigg and Schindler, who in the IGLO (individual gauges for localized orbitals) method[39,40] attach phase factors to localized molecular orbitals. This method has recently been extended to direct calculations[41] and to MCSCF wave functions.[42] In the IGLO method, the calculation of a certain class of two-electron integrals is avoided by the use of the completeness relation. Although this approximation is usually regarded as a good one, comparisons with the London method have revealed that IGLO is more sensitive to the size of the basis set.[34]

Because of these difficulties, very few magnetizability calculations have been carried out for larger molecules. Some IGLO calculations on hydrocarbons have been presented,[43] although the additivity of the magnetizability for most of the larger molecules was implicitly assumed (the IGLO INCREMENT method). In a recent study of the normal alkanes from methane to pentane using the IGAIM (individual gauges for atoms in molecules) method, Bader and Keith confirmed the almost constant contribution to the magnetizability from the methylene group.[12]

With our newly developed GIAO MCSCF program we are able to calculate magnetizabilities of relatively large molecules accurately with modest basis sets. We therefore decided to carry out an extensive study of the magnetizabilities of hydrocarbons. Our aim is 2-fold: to study Pascal's rule for hydrocarbons, and to compare Hartree–Fock magnetizabilities with experimental values. We have focused our attention on linear and cyclic hydrocarbons with at most six carbon atoms and no more than two double bonds. In addition we have investigated benzene, four heterocyclic aromatic compounds, and two molecules containing triple bonds. In total more than 30 molecules have been studied. All magnetizabilities have been calculated at the optimized Hartree–Fock geometries.

No theoretical background for the calculation of magnetizabilities using London orbitals is given. We refer instead to the paper describing our program and the method used in these calculations.[34] We only note that the calculated magnetizabilities correspond to the second derivatives of the total energy with respect to the magnetic field, and are obtained using standard techniques of analytical derivative theory.[44] Computational details are given in section II, and the calculated magnetizabilities are compared with experiment in section III. Section IV contains a discussion of Pascal's rule, and in section V we compare the magnetizabilities of normal alkanes and cycloalkanes. Section VI contains some concluding remarks.

II. Computational Details

Table 1. Hartree–Fock Energies (hartrees) of the Geometry Optimized Molecules Investigated

molecule	energy	molecule	energy
hydrogen	−1.128 826	cyclobutene	−154.915 322
methane	−40.199 331	cyclobutadiene	−153.660 300
ethane	−79.236 399	*n*-pentane	−196.351 388
ethene	−78.042 318	cyclopentane	−195.180 255
ethyne	−76.828 287	cyclopentene	−193.996 349
propane	−118.274 799	cyclopentadiene	−192.813 142
propene	−117.085 073	*n*-hexane	−235.389 645
cyclopropane	−117.069 164	cyclohexane	−234.228 698
cyclopropene	−115.835 215	1,3-cyclohexadiene	−231.855 770
propadiene (allene)	−115.875 412	1,4-cyclohexadiene	−231.858 230
propyne	−115.877 137	benzene	−230.726 384
n-butane	−157.313 146	thiophene	−192.813 142
trans-2-butene	−156.126 663	1,3-dioxol-2-one	−339.374 961
cis-2-butene	−156.124 222	furan	−192.813 142
s-trans-1,3-butadiene	−154.938 384	pyridine	−246.721 354
cyclobutane	−156.110 300		

Dahle *et al.*[45] have carried out an extensive investigation of basis set effects for London magnetizabilities. Their recommendation is to use a modification of the augmented *cc*-pVDZ basis of Dunning and co-workers,[46–48] obtained by removing the outermost s and d orbitals on all atoms except hydrogen. The resulting [5s2p|3s2p] and [9s5p1d|3s3p1d] basis sets have been shown to give London magnetizabilities within 2% of the Hartree–Fock limit. Moreover, Dahle *et al.* found that if the Hartree–Fock magnetizabilities are scaled by a factor of 0.925, the results are within 1.5% of experiment for all molecules. For many molecules this gives an error bar smaller than the experimental uncertainties. This procedure was successfully used in a recent study of the magnetizability anisotropy of small fluorine-containing molecules.[35]

For a consistent treatment of the magnetizability, we have optimized the geometries of all molecules using the second-order method described in ref 49. The integrals were generated by HERMIT[50] and the wave functions by the SIRIUS program.[51] The gradients and Hessians (needed for the optimization of the geometry) and the magnetizabilities were calculated using the ABACUS program.[52] Except for the noble gases, all calculations were carried out at the Hartree–Fock level of theory.

The energies of the geometry-optimized molecules are listed in Table 1 and the magnetizabilities in Table 2. For comparison we have included in Table 2 the IGLO results of Schindler and Kutzelnigg[43] and the IGAIM results of Bader and Keith.[12]

The IGAIM calculations of Bader and Keith were carried out using the 6-311++G(2d2p) basis,[53–55] but for pentane the diffuse functions on hydrogen were deleted because of disk limitations.[12] This basis is rather large compared to ours. IGAIM results for smaller basis sets have not been reported.[56,57]

The three basis sets (DZ, H I, and H II) used in the IGLO calculations are based on Huzinaga's compilation.[58] The H I basis is a triple-ζ set with a single set of polarization functions. The slightly larger H II set is identical to H I except that the p shells on the first-row atoms are less heavily contracted. As noted in Table 2, some of the IGLO results have been obtained with the IGLO INCREMENT method. These results are based on calculations carried out with a variety of basis sets and are not strictly *ab initio*.

As discussed below, we have carried out correlated calculations on helium, neon, and argon. For He we performed a full CI calculation

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Table 2. Isotropic Magnetizabilities (10^{-30} J T^{-2}) Using Different Theoretical Models Compared with Experimental Values Where Such Exist

molecule	GIAO	GIAO scaled	IGLO[a]	IGAIM[b]	experiment
hydrogen	−66.5	−61.5 ± 0.8			−66.4[c]
methane	−315.3	−292 ± 4	−322 (H II)	−302.2	−310[d] −289 ± 13[e]
ethane	−493.2	−456 ± 6	−513 (H II)	−473.2	−455 (l)[f] −445 ± 13[e]
ethene	−356.3	−330 ± 4	−375 (H II)		−327[d] −312 ± 13[e]
ethyne	−386.5	−358 ± 5			−345 ± 13[e]
propane	−693.3	−641 ± 9	−837 (DZ)	−671.0	−673[f] −641 ± 13[e]
propene	−551.7	−510 ± 7	−593 (H I)		−510 ± 13[e]
cyclopropane	−703.8	−651 ± 9	−805 (DZ)	−689.6	−662[f] −651 ± 13[e]
cyclopropene	−481.3	−445 ± 6			
allene	−482.9	−447 ± 6	−529 (H II)		−420 ± 13[e]
propyne	−574.6	−532 ± 7			
n-butane	−891.8	−825 ± 11	−940 (INC)	−866.7	−835 ± 13[e]
s-trans-1,3-butadiene	−614.7	−566 ± 9	−674 (H I)		−533 ± 13[e]
trans-2-butene	−742.1	−686 ± 11	−895 (DZ)		−719[g] (l)
cis-2-butene	−747.1	−691 ± 11	−901 (DZ)		−707[g] (l)
cyclobutane	−753.2	−697 ± 9			−664 ± 13[e]
cyclobutene	−611.9	−566 ± 8			
cyclobutadiene	−273.2	−219 ± 3			
n-pentane	−1088.7	−1007 ± 14	−1157 (INC)	−1055	−1021 ± 17[e]
cyclopentane	−1020.1	−944 ± 13			−933 ± 13[e]
cyclopentene	−863.4	−799 ± 13			
cyclopentadiene	−786.6	−728 ± 10			
n-hexane	−1287.3	−1191 ± 16			−1222[g] (l) −1255[h] (l)
cyclohexane	−1158.0	−1071 ± 14			−1081[g] (l) −1111[h] (l)
1,3-cyclohexadiene	−891.3	−825 ± 13			−807[i] (derived)
1,4-cyclohexadiene	−845.5	−782 ± 13			
benzene	−859.0	−795 ± 13			−910[j] (derived)

[a] Unless otherwise stated, the results are taken from ref 43. [b] Taken from ref 12. [c] Cited in ref 66. [d] Taken from refs 71 and 72. [e] Taken from ref 66. [f] Taken from ref 73. [g] Taken from ref 74. [h] Taken from ref 75. [i] Taken from ref 76. [j] Taken from ref 77.

using the ANO set of Widmark *et al.*,[59] decontracted completely to give [9s4p3d]. To this we added three diffuse s orbitals with exponents 0.020 115 17, 0.007 040 2, and 0.002 464 1, two diffuse p orbitals with exponents 0.068 278 26 and 0.002 389 74, and finally a diffuse d orbital with exponent 0.2176. This gives [12s6p4d] with a total of 50 basis functions.

For Ne we used the [10s8p6d4f] basis set of Maroulis and Thakkar[60] and a complete active space consisting of the 2s, 2p, 3s, 3p, and 3d orbitals. The 1s orbital was kept inactive. This basis set and active space have been used successfully for calculating the magnetic hyperpolarizability anisotropy of the neon atom.[61] For argon we used a similar active space (consisting of the 3s, 3p, 3d, 4s, and 4p orbitals) and a [17s13p6d3f1g] basis, as recommended in ref 62 for calculating hyperpolarizabilities.

III. Comparison with Experiment

The experimental determination of diamagnetic magnetizabilities is a difficult task. Because of the very small effect of the susceptibility of diamagnetic molecules, most measurements have been carried out on liquid samples. This is unfortunate, since *ab initio* magnetizabilities cannot be compared directly to bulk susceptibilities. The experimental determination of the magnetizability of gaseous molecules is further complicated by the large permanent magnetic moment of molecular oxygen. Small amounts of oxygen may dominate the measured magnetizability, and the presence of as little as 10 ppm in the sample will make the measured susceptibility more paramagnetic by about 6 × 10^{-30} J T^{-2}. A final difficulty is the sensitivity of the measurements on the calibration standard, making experimental susceptibilities prone to systematic errors.

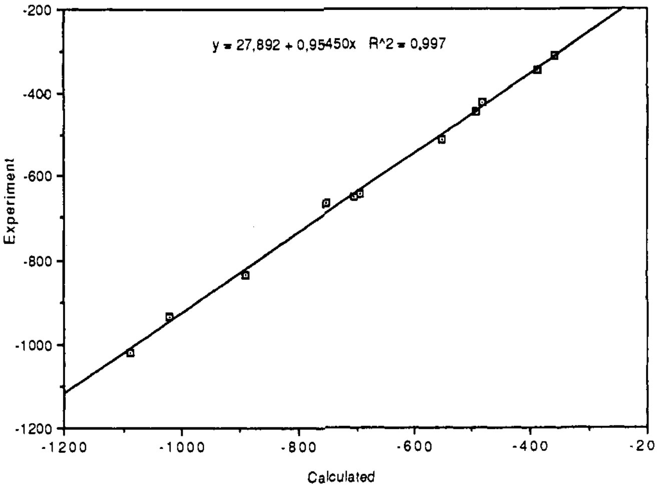

Figure 1. Experimental gas-phase measurements of Barter *et al.*[66] plotted against Hartree–Fock magnetizabilities. Units are 10^{-30} J T^{-2}. See Table 2.

An alternative to the direct measurement of the isotropic magnetizability is a semiexperimental approach using microwave spectroscopy, pioneered through the work of Flygare and coworkers.[63–65] In this technique, the paramagnetic part of the magnetizability is determined by experiment and the diamagnetic part is calculated by, for example, *ab initio* methods.

The experimental magnetizabilities are listed in Table 2. Results obtained from liquid-phase data are tagged with (l), and values derived from microwave spectroscopy are identified as (derived). All other measurements are in the gas phase. The scaled London magnetizabilities in Table 2 are in excellent agreement with at least one of the experimental numbers for all molecules for which experiment has been carried out. With the exception of *s-trans*-1,3-butadiene and cyclobutane, our scaled values with uncertainty bars fall within the range of the experimental uncertainties. Note that there are few gas-phase data for the larger hydrocarbons.

With two exceptions, all gas-phase magnetizabilities listed have been obtained by Barter *et al.*[66] These measurements were carried out in the early 1960s and still represent the standard compilation of experimental gas-phase magnetizabilities of hydrocarbons. Since the measurements of Barter *et al.* were carried out in a uniform manner using a single calibration standard, they are particularly suitable for comparison with the Hartree–Fock magnetizabilities.

In Figure 1 we have plotted the gas-phase measurements by Barter *et al.* against the unscaled Hartree–Fock magnetizabilities. The slope of the linear fit is approximately 0.95. The need for a scaling factor may be attributed to the neglect of electron correlation in the calculations, but it may also arise from the use of an incorrect calibration standard in the experiments.

In a recent paper by Cybulski and Bishop,[67] the magnetizabilities of a series of small molecules are studied at the Hartree–Fock and MP2 levels using large basis sets. The correlation corrections are found to be fairly small for the nine molecules considered. In six cases the corrections are diamagnetic with a mean value of 3.4%; the remaining three corrections are

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Table 3. Isotropic Magnetizabilities (10^{-30} J T^{-2}) of the Noble Gases

	He	Ne	Ar
our work	−31.406	−125.61	−343.08
Glick[a]	−31.405		
Reinsch and Meyer[b]	−31.38	−127.0	−344.7
Jaszuński *et al.*[c]			−343.04
Barter *et al.*[d]	−33.5 ± 1.3	−115.6 ± 2.3	−320.8[e]

[a] Hylleraas functional. See ref 68. [b] Using the CEPA approach. See ref 69. [c] MCSCF linear response using the same active space as we have, but a larger basis set (17s13p7d5f3g). See ref 70. [d] See ref 66. [e] This number is taken as the average of three other experimental investigations[78-80] and used as a calibration standard.

paramagnetic by 2.3% on average. In mean, therefore, the correlation corrections are diamagnetic by about 1.5%. If the scaling factor of 0.95 in Figure 1 is attributed to the neglect of electron correlation only, we are forced to conclude that the correlation corrections for hydrocarbons are paramagnetic by about 5%. This is highly unlikely in view of the results of Cybulski and Bishop. The factor of 0.95 therefore cannot be explained by neglect of correlation alone, and we decided to investigate the possibility of a calibration error in the measurements of Barter *et al.*

The calibration standard chosen by Barter *et al.* is argon. Their reference value of -320.8×10^{-30} J T^{-2} was obtained as the average of measurements carried out by three different groups in the 1930s. Since atomic calculations are considerably simpler than those on molecules—particularly for magnetizabilities—the magnetizabilities of the noble gases may be calculated to high accuracy. We have calculated the magnetizabilities of helium, neon, and argon using large basis sets and large correlation spaces. The results are given in Table 3, where we have also listed the reference value for argon employed by Barter *et al.*, as well as the helium and neon measurements based on this standard. There are significant discrepancies between the experimental and measured magnetizabilities.

For helium we obtain -31.4×10^{-30} J T^{-2}, which agrees with the value obtained by Glick using a 20 term Hylleraas wave function.[68] The measurement of Barter *et al.* is 7% more diamagnetic. Our calculations on neon and argon agree well with calculations by Reinsch and Meyer using CEPA (coupled electron-pair approximation) wave functions[69] and with a recent calculation on argon by Jaszuński, Jørgensen, and Rizzo.[70] For neon the experimental values are about 8.5% more paramagnetic than the calculated magnetizability, and for argon the standard employed by Barter *et al.* is about 7% more paramagnetic than our result. We do not see how any of the approximations in our calculations (truncation of orbital and configuration spaces) can give errors as large as this, and we are thus lead to the conclusion that the calibration standard employed by Barter *et al.* is in error.

Assuming that the calculated magnetizability of argon is correct, the measurements of Barter *et al.* must be multiplied by 1.07 to give the final magnetizabilities. If we now fit the Hartree–Fock magnetizabilities to the corrected experimental numbers, the scaling factor becomes 1.02 rather than 0.95. This means that the Hartree–Fock magnetizabilities are in general more *paramagnetic* than the true magnetizabilities by about 2%, in agreement with the result of Cybulski and Bishop.

As mentioned in section II, we have previously advocated a scaling factor of 0.925 for Hartree–Fock magnetizabilities.[45] This factor was in fact obtained by comparing theoretical calculations with gas-phase measurements of Barter *et al.* for a range of small molecules, carried out using the same calibration standard as for hydrocarbons. Since these experimental values would be affected by the same systematic errors as those considered in this paper, there is no inconsistency between our old and new scaling factors.

Independent gas-phase measurements exist for methane and ethylene. Oldenziel and Trappeniers have measured the magnetizabilities of these molecules by high-resolution nuclear magnetic resonance (HRNMR) spectroscopy[71] and obtained -310×10^{-30} and -327×10^{-30} J T^{-2}, respectively. This is significantly different from the values of $(-289 \pm 13) \times 10^{-30}$ and $(-312 \pm 13) \times 10^{-30}$ J T^{-2} obtained by Barter *et al.* Scaling the values of Barter *et al.* by 1.07, we obtain -309×10^{-30} and -334×10^{-30} J T^{-2}, in good agreement with the results of Oldenziel and Trappeniers.

In Figure 1 there is also a constant term of about 28×10^{-30} J T^{-2} added to the calculated magnetizabilities of all molecules, irrespective of their size. It is difficult to see how this difference can be understood in terms of the approximations made in the wave function, for example, neglect of electron correlation. A more likely explanation is a systematic error in the measurements. For example, the presence of 40 ppm of oxygen may account for this discrepancy, but according to Barter *et al.* there was in no case found as much as 10 ppm of oxygen in the samples after the measurements. We will not speculate further on the reasons for the additivity term. More accurate calculations—for example, at the MP2 level—or new measurements are needed to settle this problem.

Comparing the London method with the other theoretical approaches, we notice that IGLO yields results that are too diamagnetic. However, although the absolute error compared to experiment increases with the size of the molecule, the relative error remains constant. IGLO therefore appears to be size extensive, and the error related to the use of the completeness relation does not seem to become larger as the size of the molecules increases. It is instead governed by the incompleteness of the basis on the individual atoms.

Interestingly, the IGAIM results fall between our calculated and scaled values, indicating that the method is size extensive and gives results closer to the (unscaled) experimental values. The reasons for this are not clear. IGAIM is based on Hartree–Fock, so the discrepancies cannot be attributed to electron correlation effects. They may arise from a different treatment of the interaction between the molecule and the external field. On the other hand, if the experimental values are scaled by 1.07 as suggested above, we find that our GIAO magnetizabilities are closer to experiment than IGAIM.

For benzene, we notice that there is a rather large difference between our calculations and experiment. It should be noted, however, that the experimental number for benzene has been obtained by combining microwave measurements of the paramagnetic contribution with an estimate of the diamagnetic part calculated from quadrupole moments. Such a procedure is less satisfactory than a direct measurement of the magnetizability, and may lead to errors larger than that of the experimental numbers for the other molecules.

Another possibility is that Hartree–Fock is less capable of giving the correct magnetizability of aromatic systems. We therefore carried out additional calculations for other planar molecules with different degrees of aromaticity to see whether Hartree–Fock is capable of reproducing the experimental trends for aromatic systems. Our results are collected in Table 4, where we compare them with the available experimental data. Un-

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Table 4. Energies (hartrees) and Isotropic and Anisotropic Magnetizabilities (10^{-30} J T^{-2}) of Some Planar Aromatic Systems

molecule	theor		exptl[a]
	ξ_{iso}	ξ_{aniso}	ξ_{aniso}
benzene	−859.0	−681.3	−991
thiophene	−786.6	−536.8	−832
1,3-dioxol-2-one	−692.6	−230.5	−239
furan	−755.0	−637.3	−643
cyclopentadiene	−786.6	−536.8	−568
pyridine	−883.8	−1060.4	−953

[a] Taken from ref 65.

fortunately, only measurements of anisotropic components are available for these molecules.

As known from other studies, the anisotropic components of the magnetizability are more difficult to calculate than the isotropic part.[34,35] However, it appears from Table 4 that the Hartree–Fock approximation does not give correct anisotropic magnetizabilities for aromatic molecules. We suspect that this to some extent also applies to the isotropic part. Although several of the anisotropies are close to experiment, this may be accidental as the other results are either too diamagnetic (pyridine) or too paramagnetic (benzene and thiophene). It is likely that the inclusion of electron correlation is important for the magnetizability of aromatic systems.

IV. Pascal's Rule

As noted in the Introduction, Pascal's rule states that the magnetic susceptibility of a given compound may be calculated as the sum of atomic susceptibilities arising from the individual atoms. Thus, the magnetic susceptibility is regarded as a bulk property to which each atom in the sample gives a constant contribution irrespective of its chemical environment. There is, however, no reason why this principle should not apply microscopically to molecular magnetizabilities. We have therefore fitted our results to this simple model (using atoms as the parameters), as well as a model with functional groups (CH_2, CH_3, and so on) as parameters (as suggested, for example, by Spieckermann[10]).

If the total magnetizability of the hydrocarbons is expressed as a linear function of the numbers of carbon and hydrogen atoms (Pascal's original scheme), linear regression gives atomic contributions of $(-68 \pm 12) \times 10^{-30}$ J T^{-2} for carbon atoms and $(-63 \pm 7) \times 10^{-30}$ J T^{-2} for hydrogen atoms. In this fit we have included all hydrocarbons in Table 2. In Table 5 we compare the calculated (unscaled) Hartree–Fock magnetizabilities with those obtained using Pascal's rule with the above two parameters. In Figure 2 we have plotted the calculated and predicted magnetizabilities of Table 5 against each other. The plot shows that the magnetizabilities of the hydrocarbons are well predicted within a two-parameter Pascal model (slope −0.999 and $R^2 = 0.967$).

We have also tried to express the total magnetizabilities of the molecules as a linear function of the functional groups $-CH_3$, $=CH-$, $-CH_2-$, and $=CH_2$. Although the number of independent parameters is now four, there is little gain in accuracy as measured in percentage error between the linear interpolation and the calculated magnetizability. For hydrocarbons, therefore, Pascal's original two-parameter model is better than a model based on functional groups, since it gives about the same accuracy with fewer parameters. It should be noted that this conclusion is based upon a rather limited number of molecules. For instance, a scheme based on atomic contributions alone will never be able to predict differences between isomeric compounds such as cyclopropene, allene, and propyne. To a smaller extent, this deficiency is also present in models based on functional groups, as they will not predict any difference between, for example, *cis*- and *trans*-2-butene or 1,3- and 1,4-butadiene.

Table 5. Theoretical Magnetizabilities and Magnetizabilities Predicted with Pascal's Rule from Theoretically Optimized Parameters (10^{-30} J T^{-2})

molecule	calcd	Pascal's rule	dev
methane	−315.3	−319	−4
ethane	−493.2	−512	−19
ethene	−356.3	−387	−31
ethyne	−386.5	−261	+126
propane	−693.3	−705	−12
propene	−551.7	−580	−28
cyclopropane	−703.8	−580	+124
cyclopropene	−481.3	−455	+26
allene	−482.9	−455	+28
propyne	−574.6	−455	+120
n-butane	−891.8	−898	−6
trans-2-butene	−742.1	−773	−31
cis-2-butene	−747.1	−773	−26
s-trans-1,3-butadiene	−614.7	−648	−33
cyclobutane	−753.2	−773	−20
cyclobutene	−611.9	−648	−36
cyclobutadiene	−273.2	−523	−250
n-pentane	−1088.7	−1092	−3
cyclopentane	−1020.1	−966	+54
cyclopentene	−863.4	−841	+22
cyclopentadiene	−786.6	−716	+71
n-hexane	−1287.3	−1285	+2
cyclohexane	−1158.0	−1160	−2
1,3-cyclohexadiene	−891.3	−909	−18
1,4-cyclohexadiene	−845.5	−909	−64
benzene	−859.0	−784	+75

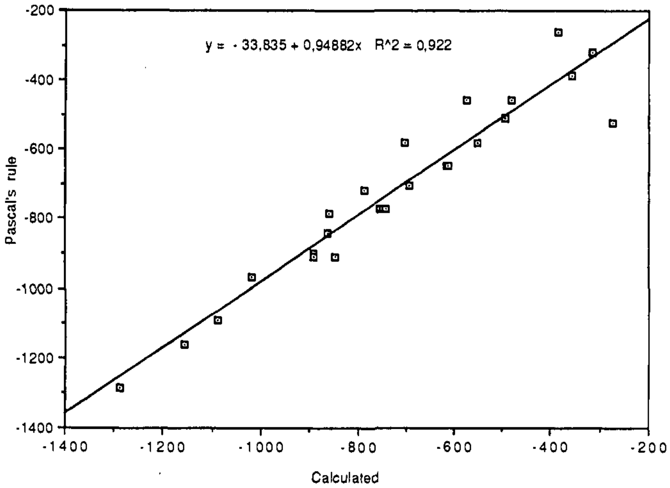

Figure 2. Magnetizabilities predicted by Pascal's rule against the calculated magnetizabilities at the Hartree–Fock level. Units are 10^{-30} J T^{-2}. See Table 5.

From Table 5 we conclude that strain has an important influence on isotropic magnetizabilities, and that the magnetizabilities of highly strained molecules cannot be predicted by a simple modification of Pascal's rule. Triple bonds, too, are not well predicted by this model. In conclusion, Pascal's rule gives a good estimate of the magnetizability of several molecules, but fails to describe special bonding situations as well as configurational and conformational variations in the magnetizabilities.

It is interesting to note that Pascal's rule may be regarded as an application of semiempirical electronic structure theory to the calculation of magnetizabilities. Indeed, Hameka has derived semiempirical expressions for molecular magnetizabilities that are similar to those employed for Pascal's rule.[8] By fitting the adjustable parameters of the semiempirical model to experiment, Hameka[8] and O'Sullivan and Hameka[9] have reproduced the experimental magnetizabilities of a large number of hydrocarbons to within 0.5%. We note, however, that any systematic errors in the experimental magnetizabilities would be incorporated in this model and thus not affect the agreement with experiment.

V. Normal Alkanes and Cycloalkanes

We first restrict our attention to the normal alkanes and fit the magnetizabilities of ethane, propane, butane, pentane, and

Table 6. Comparison of Calculated/Measured Magnetizabilities (10^{-30} J T^{-2}) with Prediction from the Respective Pascal's Rule Constants

	theor		exptl	
molecule	calcd	Pascal's rule	exptl	Pascal's rule
ethane	−493.2	−494.1	−445	−452
propane	−693.3	−692.5	−641	−646
butane	−891.8	−890.9	−835	−840
pentane	−1088.7	−1089.2	−1021	−1034
hexane	−1287.3	−1287.6	−1222	−1229
cyclopropane	−703.8	−595.1	−651	−582
cyclobutane	−753.2	−793.4	−664	−776
cyclopentane	−1020.1	−991.8	−933	−971
cyclohexane	−1158.0	−1190.2	−1081	−1165

hexane with the functional groups CH_2 and CH_3; see Table 6. The fit is almost perfect for the theoretical magnetizabilities; the largest difference between calculated and predicted magnetizabilities is 0.2% (ethane). For the experimental values the fit is not as good, the largest difference being 1.6%, again for ethane. Thus, the theoretical calculations give a clearer picture of the almost perfect additivity of the methylene group in normal alkanes, free of experimental noise.

It is interesting to compare the theoretical and experimental values of the magnetizabilities for the two functional groups. The fit to the unscaled Hartree–Fock magnetizabilities gives −247.1 and −198.4 × 10^{-30} J T^{-2} for methyl and methylene, respectively. The corresponding experimental numbers are −226.1 and −194.1 × 10^{-30} J T^{-2}. There is a factor of 0.96 between the experimental and theoretical parameters for methylene, as expected from our overall scaling factor of 0.95 for all hydrocarbons. The difference between the values of the methyl group is larger, however, with the experimental parameter being more paramagnetic. This is in agreement with our discussion of the additivity constant observed in Figure 1. Since the methylene parameter only describes differences between the normal alkanes, any constant contribution to all molecules would be absorbed entirely in the methyl parameter.

To see the effects of cyclization, we compare the magnetizabilities of the cycloalkanes with the predictions based on the parameters obtained from fits to the normal alkanes. In Figure 3, we have plotted the difference between the magnetizabilities obtained from the Hartree–Fock calculations and from Pascal's rule based on the normal alkanes. This is the same as the difference between the second and first columns in Table 6 for cyclopropane, cyclobutane, cyclopentane, and cyclohexane.

We observe an oscillatory behavior: Cycloalkanes with an odd number of carbon atoms are more diamagnetic than expected from Pascal's rule; those with an even number of carbon atoms are more paramagnetic. As the size of the ring increases, we expect this difference to disappear as strain is reduced and the freedom of movement of the methylenes approaches that of the normal alkanes. Figure 3 agrees with this expectation, although the effect of cyclization decreases less rapidly than expected.

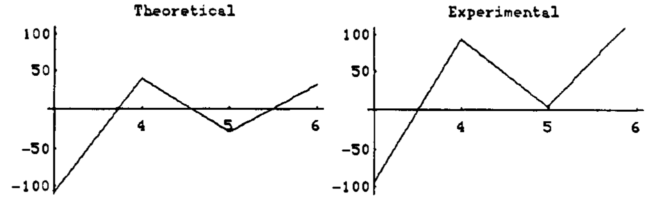

Figure 3. Differences between the magnetizabilities of cycloalkanes and the predictions made using Pascal's rules based on the magnetizabilities of the normal alkanes. Units are 10^{-30} J T^{-2}. The figure on the left is based on Hartree–Fock calculations of the cycloalkanes and the normal alkanes. The figure on the right is based on measurements.

In Figure 3 we have also made the corresponding plot for the experimental magnetizabilities of Barter *et al.* Again we find that the cycloalkanes behave in an oscillatory manner, but cyclopropane is now the only compound more diamagnetic than expected from Pascal's rule. This behavior has already been observed by Barter *et al.* Also, the convergence toward the magnetizabilities of the normal alkanes is less pronounced than in the Hartree–Fock case.

We would like to make the observation that any error in the measurements that shift all magnetizabilities equally (such as, for example, the presence of oxygen) would be absorbed entirely in the parameter for the methyl group since the methylene parameter only describes differences between the normal alkanes. Since the cycloalkanes contain methylene groups only, the *predicted* magnetizabilities for the cycloalkanes should be completely unaffected by any such error, even though the methylene parameters are based on the measured magnetizabilities. For example, the presence of oxygen in the samples would shift the experimental plot in Figure 3 upward, and this may explain some of the difference between the *ab initio* and experimental plots. However, the difference may also arise from deficiencies in the Hartree–Fock model.

VI. Concluding Remarks

We have presented an extensive series of calculated magnetizabilities for hydrocarbons and some planar ring systems. Due to the fast basis set convergence of the London orbital approach, we can calculate accurate magnetizabilities even for quite large molecules at a moderate cost of computer time. The scaled Hartree–Fock magnetizabilities are in good agreement with experiment.

Our results indicate that it may be worthwhile to reinvestigate the isotropic magnetizability of small hydrocarbons in the gas phase, as there may be calibration errors in the experimental numbers. For small molecules with strained bonding, the use of London orbitals in *ab initio* calculations may prove to be a useful alternative to Pascal's rule for predicting the isotropic magnetizability of molecules in the gas phase.

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