Table III. ρ_{sk}(gem) (×10^4) for Each Molecular Orbital

	Molecule									
	C_2H_2O		C_2H_4		C_2H_6		C_2H_4		C_2H_6	
Basis Orbital	Localized		Localized		Localized		Canonical		Canonical	
	CH_4 (gem)	−10.16	CH_4 (gem)	2.03	CH_4 (gem)	−4.43	a_g	−1.63	a_{1g}	−1.16
	CH_3	0.09	CH_3	1.08	CH_3	0.26	b_{1u}	−6.03	a_{2u}	−2.52
	$CC_1 + CC_2$	0.03	$CC_1 + CC_2$	0.02	CC	0.00	b_{3u}	5.35	e_u	0.21
	$CO_1 + CO_2$	−1.22	$CH_5 + CH_6$	0.49	$CH_6 + CH_7 + CH_8$	0.05	a_g	−6.01	a_{1g}	−1.59
	$O_1 + O_2$	0.00			CH_5	−0.05	b_{2g}	11.94	e_g	0.90
							π	0.0		

in parent molecular orbitals k and l, and this is the SCF analog of the mutual polarizability equation given earlier. In fact it may be shown that the summations over k and l may be restricted to occupied and virtual orbitals only.

Thus the general spin density (ρ) arises from unequal mixing of α and β spin parent molecular orbitals (k,l) as measured by Δ_{kl} and, specifically, the spin density at the geminal 1s orbital (ρ_s(gem)) reflects this unequal mixing, but weighted by the "differential overlap" between molecular orbitals k,l, at the geminal 1s orbital ($c_{sk}c_{sl}$).[16] The form of the last equation suggests a possible interpretation of the mixing phenomenon.

$$\rho_s(\text{gem}) = \sum_{k}^{\text{occ}} \rho_{ks}(\text{gem})$$

That is, ρ_s(gem) is factored into one contribution from each occupied parent molecular orbital being mixed with *all* parent virtual molecular orbitals.

Table III shows the results of this kind of analysis of the geminal spin density for C_2H_6 and C_2H_4. The simplicity of the localized orbital scheme is quite apparent and ketene is seen to be very much like C_2H_6 but quite different from C_2H_4, again reflecting that the ketene and C_2H_6 geminal couplings are of the same sign.

Examination of the terms $c_{sk}c_{sl}\Delta_{kl}$ for different pairs k,l shows only three types of (occupied ↔ virtual) orbital mixing to be important. Mixing of the σ and σ^* orbitals of the same (geminal) bond produces spin densities of opposite signs for C_2H_4 ($+7.41 \times 10^{-5}$) and H_2C_2O (-86.14×10^{-5}) and alone is sufficient to determine the sign and approximate magnitude of ρ_s(gem) for ketene but not so completely for ethylene. Second, there is the cross mixing of the σ and σ^* orbitals of one CH bond with the σ^* and σ, respectively, of the other. These are of the same sign ($+12.43 \times 10^{-5}$ and $+3.94 \times 10^{-5}$) in both molecules but the cross interaction for ethylene is three times larger than in ketene and of the same importance as the same bond σ,σ^* mixing. Finally, there are orbital mixings involving the vicinal orbitals (4CH's in C_2H_4 and 4CO's in H_2C_2O) which contribute negatively in both molecules (-0.54×10^{-5} and -13.59×10^{-5}) but by a factor 25 times larger in ketene. The difference in vicinal bond contributions for C_2H_4 and H_2C_2O can be attributed *directly* to hyperconjugation in ketene while the differences in in-bond and cross-bond CH orbital contributions are only *indirectly* attributed to hyperconjugation. The most important effects, however, arise from the σ,σ^* orbitals of the CH_2 bonds and how these differ for α and β spin orbitals. It is this aspect of hyperconjugative control of $^2J_{HH}$ and the greater localization of $^2J_{HH}$ in the CH_2 group of ketene which will be the basis for further study, in the context of SCF-localized spin orbitals.

Acknowledgment. The authors wish to thank the National Science Foundation for partial support of the work (GP-28924). Further appreciation is expressed to the Kansas State University Computer Center for their support of this work.

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[16] This is one way ($c_{sk}c_{sl} \neq 0$) that localized orbital tails (due to intrinsic delocalization) can enter into the coupling constant problem. In Table III, small but nonnegligible contributions to ρ_s(gem) arise primarily when k or l selects either the geminal CH σ or σ^* orbital. The high degree of localization of the orbitals renders the $c_{sk}c_{sl}$ product very small for the other k,l pairs.

Localized Magnetic Susceptibility Anisotropies

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Received March 15, 1973

Abstract: A theoretical framework is given for partitioning the individual elements in the total magnetic susceptibility tensor (χ_{aa}, χ_{bb}, and χ_{cc}) into local contributions. Molecular data are analyzed to give local values of χ_{aa}, χ_{bb}, and χ_{cc} for either atoms or bonds. These values can be added to give the total molecular magnetic tensor elements for a wide range of nonstrained, nonaromatic compounds. The method is used to estimate relative aromaticities, interpret data from Cotton-Mouton experiments, and to gain information about molecular structure. The values given here are also of use in determining neighbor group effects in proton magnetic shielding.

The magnetic susceptibility tensor describes the quadratic response of a molecule to an external magnetic field. The evaluation of this quantity has been a problem of theoretical and experimental interest for many years. Although the measurement of the average value of the magnetic susceptibility is relatively straightforward, until recently the direct measurement of the magnetic susceptibility anisotropy has been possible only for limited classes of molecules. Susceptibility anisotropies have been very accurately determined for small molecules by molecular beam techniques[1] and less accurately determined for large aromatic molecules by single crystal measurements.[2] Indirect attempts to obtain susceptibility anisotropies for intermediate sized molecules have been made using data from Cotton–Mouton measurements[3] or nmr chemical shifts.[4] However, the recent development of high-resolution Zeeman-microwave spectroscopy has made possible a direct, accurate measurement of the susceptibility anisotropy for a wide variety of compounds.[5] In the last few years additional measurements have been carried out in this laboratory on nearly 100 different molecules.

It has been known for some time that the *average* magnetic susceptibility of a molecule can be well represented by the proper summing of group susceptibility terms.[6] These group susceptibilities may be assigned to the atoms or bonds of a molecule and have been found to be transferable over a wide range of compounds. A sufficient quantity of accurate data on susceptibility anisotropies has now been accumulated to make it apparent that an additivity scheme can be applied to the diagonal elements of the susceptibility tensor as well. In section I of this paper we present a theoretical basis for such an approach. In section II we present the results of our analysis which give reliable values for the diagonal elements of the total magnetic susceptibility tensor for atoms and bonds. In section III we suggest several applications in which these group values can be useful.

I. Theory

The quantum mechanical expression for the diagonal elements in the molecular magnetic susceptibility tensor has been given by Van Vleck[7] as shown in eq 1. Here e is the charge of the electron, m is the electron mass, and c is the speed of light. $\mathbf{I}$ is the unit tensor and cc stands for complex conjugate. $\mathbf{r}_i$ is the vector from the center of mass to the ith electron and $\mathbf{L}_i =$

$$\chi_{gg} = -\frac{e^2}{4mc^2}\langle 0|\sum_i(\mathbf{r}_i\cdot\mathbf{r}_i\mathbf{I} - \mathbf{r}_i\mathbf{r}_i)_g|0\rangle \times$$
$$-\frac{e^2}{4m^2c^2}\sum_{k>0}\frac{\langle 0|\sum_i(\mathbf{L}_i)_g|k\rangle\langle k|\sum_i(\mathbf{L}_i)_g|0\rangle + \text{cc}}{E_0 - E_k} \tag{1}$$

$-i\hbar\mathbf{r}_i \times \nabla_i$ is the angular momentum of the ith electron. $\langle 0|0\rangle$ is the average value over the ground electronic state while the sum over $|k\rangle$ is over all excited electronic states. E_k is the energy of the kth excited state.

The first term in the above equation is the diamagnetic susceptibility, χ^{d}, and the second term is the paramagnetic susceptibility, χ^{p}. When the susceptibility is written in this way there is no reason to expect that it can be decomposed into relatively constant atomic quantities which combine additively to give the molecular susceptibility. Indeed, both χ^{d} and χ^{p} can be seen to depend explicitly on molecular distances.

However, a procedure suggested by Gierke, Tigelaar, and Flygare[8] for evaluating dipole moments, quadrupole moments, and diamagnetic susceptibilities is useful here. The sum over the i electrons in eq 1 can be partitioned arbitrarily into groups of Z_n where Z_n is the atomic number of the nth nucleus in the molecule. No approximation is involved here since we have made no assumption about these electrons being localized in any region of space. If we now introduce the coordinate transformation

$$\mathbf{r}_i = \mathbf{r}_n + \boldsymbol{\varrho}_{i_n} \tag{2}$$

where $\mathbf{r}_n$ is the vector to the nth nucleus and $\boldsymbol{\varrho}_{i_n}$ is the vector from the nth nucleus to the ith electron, and make use of the relation

$$-\frac{m}{\hbar^2}(E_0 - E_k)\langle 0|x|k\rangle = \left\langle 0\left|\frac{\partial}{\partial x}\right|k\right\rangle \tag{3}$$

in the expression for χ^{p}, the values of χ^{d} and χ^{p} have the forms shown in eq 4a and 4b.

$$\chi_{gg}{}^{\text{d}} = -\frac{e^2}{4mc^2}\left\{\sum_n\left\langle 0\left|\sum_{i_n=1}^{Z_n}(\mathbf{r}_n\cdot\mathbf{r}_n\mathbf{I} - \mathbf{r}_n\mathbf{r}_n)_g\right|0\right\rangle + 2\sum_n\left\langle 0\left|\sum_{i_n=1}^{Z_n}(\mathbf{r}_n\cdot\boldsymbol{\varrho}_{i_n}\mathbf{I} - \mathbf{r}_n\boldsymbol{\varrho}_{i_n})_g\right|0\right\rangle + \sum_n\left\langle 0\left|\sum_{i_n=1}^{Z_n}(\boldsymbol{\varrho}_{i_n}\cdot\boldsymbol{\varrho}_{i_n}\mathbf{I} - \boldsymbol{\varrho}_{i_n}\boldsymbol{\varrho}_{i_n})_g\right|0\right\rangle\right\} \tag{4a}$$

$$\chi_{gg}{}^{\text{p}} = \frac{e^2}{4mc^2}\left\{\sum_n\left\langle 0\left|\sum_{i_n=1}^{Z_n}(\mathbf{r}_n\cdot\mathbf{r}_n\mathbf{I} - \mathbf{r}_n\mathbf{r}_n)_g\right|0\right\rangle + 2\sum_n\left\langle 0\left|\sum_{i_n=1}^{Z_n}(\mathbf{r}_n\cdot\boldsymbol{\varrho}_{i_n}\mathbf{I} - \mathbf{r}_n\boldsymbol{\varrho}_{i_n})_g\right|0\right\rangle\right\} - \frac{e^2}{4m^2e^2}\sum_n\sum_{k>0}\left\{\frac{\left\langle 0\left|\sum_{i_n=1}^{Z_n}(-i\hbar\boldsymbol{\varrho}_{i_n}\times\nabla_i)_g\right|k\right\rangle\left\langle k\left|\sum_{i_n=1}^{Z_n}(-i\hbar\boldsymbol{\varrho}_{i_n}\times\nabla_i)_g\right|0\right\rangle + \text{cc}}{E_0 - E_k}\right\} \tag{4b}$$

It is easily seen that the first two terms in χ^{d} and χ^{p} cancel removing all explicit dependences on molecular coordinates. (Hence, χ is "gauge invariant" while χ^{d} and χ^{p} are not.) What remains is

$$\chi_{zz} = \sum_n\left\{-\frac{e^2}{4mc^2}(\langle x^2\rangle_n + \langle y^2\rangle_n) - \frac{e^2}{4m^2c^2}\sum_{k>0}\frac{\left\langle 0\left|\sum_{i_n=1}^{Z_n}(l_i{}^n)_z\right|k\right\rangle\left\langle k\left|\sum_{i_n=1}^{Z_n}(l_i{}^n)_z\right|0\right\rangle + \text{cc}}{E_0 - E_k}\right\} = \sum_n(\chi_n{}^{\text{d}} + \chi_n{}^{\text{p}})_{zz} \tag{5}$$

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(1) F. Mehron, R. A. Brooks, and N. F. Ramsey, *Phys. Rev.*, **136**, A62 (1964), and previous work.

(2) A review of the available crystal data up to 1965 is given by A. A. Bothner-By and J. A. Pople, *Annu. Rev. Phys. Chem.*, **16**, 43 (1965).

(3) (a) D. Buckingham, W. H. Prichard, and D. H. Whiffen, *Trans. Faraday Soc.*, **63**, 1057 (1967); (b) M. P. Bogaard, A. D. Buckingham, M. G. Canfield, D. A. Dunmar, and A. H. White, *Chem. Phys. Lett.*, **12**, 558 (1972).

(4) Reference 2 also provides a fairly comprehensive review of work in this area.

(5) W. H. Flygare and R. C. Benson, *Mol. Phys.*, 20, 225 (1971).

(6) P. Pascal, "Chimie Generale," Masson et Cie, Paris, 1949.

(7) J. H. Van Vleck, "Electric and Magnetic Susceptibilities," Oxford University Press, New York, N. Y., 1932.

(8) T. D. Gierke, H. L. Tigelaar, and W. H. Flygare, *J. Amer. Chem. Soc.*, **94**, 330 (1972).

where we have defined

$$\left\langle 0 \middle| \sum_{i_n=1}^{Z_n} \varrho_{i_n}{}^2 \middle| 0 \right\rangle = \langle \varrho^2 \rangle_n$$

$$-i\hbar\varrho_{i_n} \times \nabla_i = l_i{}^n$$

It is well known that the total susceptibility is independent of a single origin for all operators. What we have shown here is that the gauge invariance also extends to a sum over several origins. These origins may be defined arbitrarily; we use atomic origins as the most intuitively useful.

The total molecular susceptibility has now been expressed as a sum over *operators* localized on the various atomic nuclei. But they operate on *wave functions* which extend over the whole molecule. This alone does not prove that the susceptibility can be found from a sum of transferrable group susceptibilities. If, however, the average values of these atomic operators meet two conditions they will be transferrable. If they are not greatly dependent on parts of the wave function far removed from the nucleus in question and if the relevant properties of the electron distribution around each nucleus are not much different for a given type of atom in different molecules, the terms within the sum over n in eq 5 will be independent and constant. They will, in short, be additive atomic susceptibilities which can be evaluated from measured molecules and used to predict the susceptibility of any desired molecule.

The applicability of the above two conditions to the first term of eq 5 has been thoroughly discussed.[8] The average values of the squared coordinates around a nucleus are dominated by the electron distribution near that nucleus and are relatively constant from molecule to molecule. In fact, these atomic values in molecules are nearly identical with the free atom values. As a result, $\chi_n{}^d$ can be evaluated accurately from atomic properties for almost any molecule.[8]

It is hard to show theoretically that the average values of the atomic angular momentum operators in $\chi_n{}^p$ of eq 5 are local in character. Physically this requirement can be understood to imply that there be no long-range circulation of electrons; in other words, that each electron circulation is confined to localized orbitals. The successful correlation of both bulk susceptibilities[6] and some susceptibility anisotropies[9] with additivity rules indicates that for many molecules $\chi_n{}^p$ is localized. However, the usual model for aromatic compounds which involves a molecular ring current would indicate that this class of molecules cannot be treated by localized theories. There is also question as to whether small strained rings meet this localization criterion. In conclusion, there is reason to believe that an attempt to construct a system of local rules for the diagonal components of the susceptibility tensor might succeed for nonstrained, nonaromatic molecules.

The preceding analysis was based on a partition of the electrons among the nuclei of the molecule. Much the same treatment could be given for any other reasonable partition of electrons, provided only that the two conditions of independence from the rest of the molecule and constancy from molecule to molecule are met. Indeed, most past attempts to calculate molecular properties from local contributions, including dipole moments,[10] electric polarizabilities,[11] and magnetic susceptibility anisotropies,[12] have chosen bonds as the basic unit. A problem with this approach is ambiguity about the origin to be assigned to a bond. For properties such as the diamagnetic susceptibility, the quadrupole moment, and the magnetic shielding which depend on origin, the atom value approach would seem to be preferred.[8] However, for a property such as the total susceptibility which depends only on the orientation of the groups, not their position, either approach should be equally effective.

Even though the two approaches to the evaluation of the susceptibility are equivalent, no detailed relationship exists between the parameters involved. The value of an atomic susceptibility depends on how the bonds to that atom are distributed between it and its neighbors. Similarly, the value of a bond susceptibility depends on how the electron density near a nucleus is divided among the bonds to that nucleus. Therefore, the only valid comparison of the methods is a comparison of the results they predict for entire molecules. In addition, agreement of the methods is a good check on the accuracy of the calculation.

II. Results

We have used rotational Zeeman effect measurements to determine accurate local group contributions to the elements of the molecular magnetic susceptibility tensor. For convenience in application we have obtained both atom and bond values. In the atom approach we have assumed that an atom in a particular bonding situation (particular hybridization) will always contribute the same amount to the molecular susceptibility. This contribution consists of the three principal components as shown in Table I. To evaluate the molecular susceptibility, the atom values are rotated into the principal inertial axis system (a, b, and c) of the molecule using the following equations

$$\begin{aligned}\chi_{aa} &= \chi_{xx}\theta_{ax}{}^2 + \chi_{yy}\theta_{ay}{}^2 + \chi_{zz}\theta_{az}{}^2 \\ \chi_{bb} &= \chi_{xx}\theta_{bx}{}^2 + \chi_{yy}\theta_{by}{}^2 + \chi_{zz}\theta_{bz}{}^2 \\ \chi_{cc} &= \chi_{xx}\theta_{cx}{}^2 + \chi_{yy}\theta_{cy}{}^2 + \chi_{zz}\theta_{cz}{}^2\end{aligned} \qquad (6)$$

where θ_{ax} is the cosine of the angle between the principal inertial axis a and the atomic axis x. In order to use the transformation in eq 6 we require the atom or bond values of χ_{xx}, χ_{yy}, and χ_{zz} in Table I to be the principal values. These atomic contributions are then summed to give the molecular result. The same procedure can be followed in the bond approach with the bond values shown also in Table I. Our atom and bond susceptibilities were determined by least-squares fitting the experimental molecular susceptibility components of 14 common nonstrained, nonaromatic molecules. The values so obtained are shown in Table I, and the least-squares fit of the experimental data is shown in Table II.

It is evident from the results in Table II that the molecular susceptibilities obtained from the local values in

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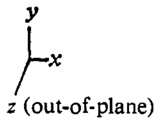
(9) C. L. Norris, R. C. Benson, P. Beak, and W. H. Flygare, *J. Amer. Chem. Soc.*, **95**, 2766 (1973).

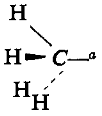
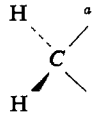
(10) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York, N. Y., 1955; "The Determination of Dipole Moments, Physical Methods of Organic Chemistry," Vol. III, A. Weissberger, Ed., Interscience, New York, N. Y., 1960.

(11) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

(12) J. Guy and J. Tillieu, *J. Chem. Phys.*, **24**, 1117 (1956).

Table I. Local Atom and Bond Susceptibilities



Atom	x	y	z
H—[a]	−2.0	−2.3	−2.3
	−9.5	−6.7	−6.7
	−6.5	−8.0	−7.1
O<[a]	−9.2	−8.8	−7.5
>C=[a]	−2.9	−3.5	−7.4
O=[a]	−0.1	−0.1	−6.3
—C≡[b]	−9.9	−7.4	−7.4
N≡[b]	−9.5	−4.5	−4.5
—N< (planar)[b]	−11.3	−14.8	−2.5
S<[b]	−18.7	−15.7	−16.8
S=[b]	+4.7	−13.1	−23.0
P≡[b]	−24.1	−17.9	−17.9

Bond	x	y	z
C—H[a]	−5.6	−3.1	−3.1
C—C[a]	−7.9	−0.2	−0.2
C=C[a]	−0.8	+4.0	−13.8
C—O[a]	−7.2	−6.7	−3.8
C=O[a]	−1.3	+2.2	−13.0
O—H[a]	−4.5	−7.5	−5.5
C—S[b]	−12.6	−11.3	−8.9
C=S[b]	+5.8	−11.0	−28.8
C≡C[b]	−13.7	−14.2	−14.2
C≡N[b]	−16.5	−11.6	−11.6
C≡P[b]	−30.4	−24.5	−24.5

[a] Determined from least-squares fit of molecules in Table II. [b] Determined from a limited number of molecules assuming the least-squares values for the other parameters.

Table I are in good agreement with experimental results. It is also gratifying to note that values of $\chi_{zz} - {}^1/_2(\chi_{xx} + \chi_{yy})$ calculated from the atom contributions in Table I agree quite well with past attempts to evaluate this quantity on a local basis.[9,13–15] However, the additional flexibility introduced in the present analysis by allowing hydrogen to have a small anisotropy and methyl and methylene carbons to have different anisotropies provides improved agreement with experimental molecular anisotropies. Of course either the atom or bond values have the further advantage of allowing the extraction of all three diagonal elements of the susceptibility tensor rather than just one anisotropy.

We feel confident that these local values can be used to predict the molecular susceptibility of nonstrained, nonaromatic compounds on which measurements are not available. These predictions should prove useful since some compounds (for example, those having no dipole moment) can in principle never be studied by Zeeman-microwave techniques. In addition, many other interesting compounds present practical problems such as low vapor pressure, rotating substituent groups, weak rotational transitions, or short lifetimes, which make their treatment by Zeeman-microwave spectroscopy difficult.

III. Applications

In this section we discuss the use of local group susceptibilities in quantifying the concept of aromaticity and in deriving other molecular properties. Although many criteria have been used for aromaticity,[16] probably the most widely accepted is that which defines an aromatic system as one which has $4n + 2$ π electrons which can be delocalized in a planar ring.[17] Since our local group susceptibility values are derived under the explicit assumption that all electron motions are localized, the difference between the observed magnetic susceptibility and that calculated from local group values should provide a quantitative measure of electron delocalization and hence aromaticity. Table III provides a comparison between experimental and calculated molecular susceptibilities in a number of ring compounds. It is apparent that the calculated and experimental in-plane susceptibilities are in good agreement. This indicates first that the data from crystal measurements are consistent with the data derived from Zeeman-microwave experiments. Further, it is evident that electron delocalization influences only the out-of-plane component of the susceptibility. This is consistent with the ring current model of aromaticity which postulates a free circulation of electrons around closed conjugated rings in the presence of a magnetic field.[18] This induced current should manifest itself as a large negative contribution to the out-of-plane component of the magnetic susceptibility which is what is observed.

The χ_{nonlocal} values in Table II provide a quantitative method of comparing aromaticities relative to some standard such as benzene if the link between aromaticity and electron delocalization is accepted. It would appear that thiophene and pyrrole are virtually as aromatic as benzene while furan is less so. Cyclopentadiene is nearly as aromatic as furan (as hyperconjugation would suggest), while fulvene shows less evidence of

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(13) R. C. Benson and W. H. Flygare, *J. Chem. Phys.*, **58**, 2366 (1973).

(14) C. L. Norris, R. C. Benson, and W. H. Flygare, *Chem. Phys. Lett.*, 10, 75 (1971).

(15) R. C. Benson, C. L. Norris, W. H. Flygare, and P. Beak, *J. Amer. Chem. Soc.*, **93**, 5591 (1971).

(16) For a discussion, see A. J. Jones, *Rev. Pure Appl. Chem.*, **18**, 253 (1968); P. Beak, *Tetrahedron*, **20**, 831 (1964).

(17) E. Hückel, *Z. Phys.*, **70**, 204 (1931); **72**, 310 (1931); **76**, 628 (1932).

(18) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959.

Table II. Comparison of Experimental and Calculated Molecular Magnetic Susceptibilities

	χ_{aa} χ_{bb} χ_{cc}			
	Calcd			
Molecule	Atom	Bond	Exptl	Ref
Methyl formate	−28.6	−28.1	−28.3 ± 0.5	5
	−29.8	−30.2	−30.9 ± 0.6	
	−36.7	−36.4	−36.7 ± 0.8	
Acetaldehyde	−21.3	−20.6	−20.0 ± 0.9	5
	−19.1	−18.0	−19.5 ± 0.9	
	−29.2	−28.9	−28.6 ± 1.5	
Propene	−28.5	−28.0	−30.9 ± 1.0	5
	−26.6	−25.9	−26.2 ± 1.0	
	−34.9	−35.9	−34.9 ± 1.1	
Acrolein	−18.1	−20.3	−16.0 ± 3.0	5
	−18.5	−18.5	−18.3 ± 3.0	
	−37.7	−39.4	−37.7 ± 4.0	
Maleic anhydride	−25.1	−27.0	−25.7 ± 1.5	13
	−27.5	−29.4	−28.2 ± 1.5	
	−54.3	−54.0	−53.5 ± 1.7	
Cyclopent-2-en-1-one	−37.0	−36.2	−33.1 ± 4.0	14
	−38.0	−37.6	−39.6 ± 4.0	
	−55.7	−52.8	−55.4 ± 6.0	
Cyclopent-3-en-1-one	−39.1	−38.1	−34.3 ± 4.5	14
	−35.9	−35.7	−40.0 ± 4.0	
	−55.7	−52.8	−53.9 ± 6.0	
Vinylene carbonate	−32.0	−34.1	−35.3 ± 4.0	5
	−32.0	−34.8	−30.5 ± 4.0	
	−48.1	−48.2	−47.4 ± 5.0	
2-Pyrone	−32.9	−35.2	−36.1 ± 4.0	15
	−34.5	−36.3	−34.4 ± 4.0	
	−60.0	−61.0	−60.0 ± 6.0	
4-Pyrone	−32.6	−37.4	−31.2 ± 4.0	15
	−34.8	−34.8	−31.9 ± 4.0	
	−60.0	−61.0	−54.5 ± 6.0	
Isoprene	−36.9	−36.1	−35.4 ± 4.0	5
	−39.7	−38.8	−34.5 ± 4.0	
	−54.3	−56.1	−52.8 ± 5.0	
Formic acid	−16.9	−17.9	−18.8 ± 1.5	5
	−16.3	−15.7	−16.8 ± 1.5	
	−25.8	−25.4	−24.2 ± 2.0	
Glycolaldehyde	−28.9	−29.4	−27.6 ± 4.0	5
	−27.8	−26.5	−23.7 ± 4.0	
	−37.1	−35.1	−38.6 ± 4.5	
Water	−13.0	−11.3	−12.2 ± 2.0	5
	−13.6	−12.7	−13.4 ± 2.0	
	−12.1	−11.0	−13.4 ± 2.5	

electron delocalization. Benzene rings connected by σ bonds are virtually additive in their aromaticity while those linked by π bonds (where increased conjugation is possible) show increased aromaticity. Fused benzene rings also show enhanced aromaticity as predicted from the ring current model. It is also interesting to note that carbonyl groups tend to decrease aromaticity, *e.g.*, quinone or naphthazarin and of course the pyrones and tropone.[9,15] In summary, we feel that this method of determining relative aromaticities offers a clear-cut comparison free of the ambiguities surrounding other criteria of aromaticity, though of course it depends for its validity on a willingness to define aromaticity in terms of electron delocalization.

Local susceptibility values are also useful in elucidating molecular structure. By comparing measured and calculated susceptibility elements it is possible to obtain the broad features of molecular conformation. For example, hexa-2,4-dienoic acid has been considered planar. From crystal measurements it has been determined that $\chi_{cc} = -44.0 \times 10^{-6}$ erg/(G^2 mol);[2] however, a calculation of χ_{cc} from local values gives $\chi_{cc} = -75.5 \times 10^{-6}$ erg/(G^2 mol). Hence, we conclude that the planar structure is not correct and at least one of the functional groups must be twisted with respect to the plane of the molecule. In molecules containing groups with very high anisotropy, such as aromatic rings, even more detailed structural information can be obtained by calculating molecular anisotropy as a function of twist angle. While this procedure is not useful in obtaining small variations in bond angles or bond lengths, it should be a useful tool in conformational analysis.

Magnetic susceptibility anisotropies are related to molecular g values and molecular quadrupole moments by[19]

$$Q_{aa} = -\frac{\hbar|e|}{8\pi M_{\rm p}}\left[\frac{2g_{aa}}{A} - \frac{g_{bb}}{B} - \frac{g_{cc}}{C}\right] - \frac{2mc^2}{|e|}(2\chi_{aa} - \chi_{bb} - \chi_{cc}) \quad (7)$$

where Q_{aa} is the molecular quadrupole moment along the a principal inertial axis, $M_{\rm p}$ is the proton mass, g_{aa}, g_{bb}, and g_{cc} are molecular g values, and A, B, and C are the rotational constants. Molecular g values can be measured in a number of small molecules by molecular beam techniques.[1,5] In many of these molecules an accurate measurement of the susceptibility anisotropy is difficult. Magnetic susceptibilities calculated by the methods of this paper can thus be combined with g values obtained by other methods to extract quadrupole moments. Alternatively, calculated susceptibility anisotropies can be combined with calculated quadrupole moments to yield the g values. For instance, Hartford, *et al.*,[20] recently used a series of substituted acetylenes and substituted cyanides to obtain the magnetic susceptibility of H—C≡C—H. Their result was $\chi_\perp - \chi_\parallel = (4.5 \pm 0.5) \times 10^{-6}$ erg/(G^2 mol) which is in excellent agreement with the values of $\chi_\perp - \chi_\parallel$ for acetylene obtained from Table I, which are 4.4 from the atom values and 4.5 from the bond values. Using $\chi_\perp - \chi_\parallel = 4.5$ and a reliable calculated quadrupole moment in HC≡CH, Hartford, *et al.*, were able to show that the g value in this molecule must be positive rather than negative as reported in the literature.[21]

Calculated magnetic susceptibility anisotropies may also find application in liquid crystal work. The ratio of the elastic constant to the volume susceptibility anisotropy of a liquid crystal can be measured with bulk techniques.[22] But without $\Delta\chi$ the elastic constant itself can be extracted only from microscopic measurements. While experimental determination of this anisotropy in liquid crystals is a formidable task, its calculation from local values is quite straightforward if the structure of the molecule is known.

Because the susceptibility anisotropy was nearly impossible to measure directly before the advent of Zeeman-microwave spectroscopy, most past work has centered around deriving approximate susceptibilities from approximate values for other molecular quantities. With the availability of accurate susceptibility anisot-

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(19) W. Hüttner, M.-K. Lo, and W. H. Flygare, *J. Chem. Phys.*, **48**, 1206 (1968).

(20) S. L. Hartford, W. C. Allen, C. L. Norris, E. F. Pearson, and W. H. Flygare, *Chem. Phys. Lett.*, **18**, 153 (1973).

(21) B. W. Cederberg, C. H. Anderson, and N. F. Ramsey, *Phys. Rev.*, **136**, A960 (1964).

(22) I. Haller, *J. Chem. Phys.*, **57**, 1400 (1972).

Table III. Comparison between Experimental and Calculated Magnetic Susceptibilities in Ring Compounds

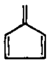
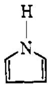
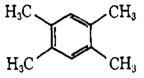
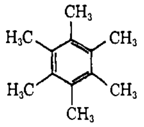
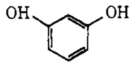
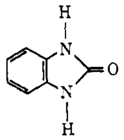
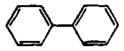
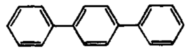
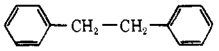
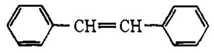
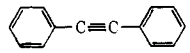
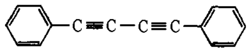
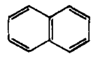
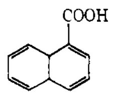
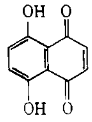
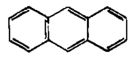
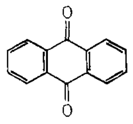
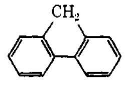
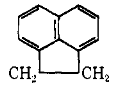
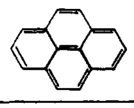
	χ(average in-plane)[a]		
	χ_{cc}[b]		
Molecule	Exptl[d]	Calcd[e]	χ_{cc}[c](nonlocal)
	−34.9 ± 2.0 −94.6 ± 2.5	−33.4 −59.4	−35.2
	−30.6 ± 2.0* −67.6 ± 2.5*	−33.4 −59.4	−8.2
	−33.3 ± 1.0* −67.5 ± 1.5*	−33.8 −50.5	−17.0
	−31.9 ± 1.5* −70.6 ± 2.0*	−31.3 −47.0	−23.6
	−40.7 ± 2.0* −90.8 ± 2.5*	−40.3 −56.8	−34.0
	−34.4 ± 2.0* −76.8 ± 2.5*	−34.5 −42.4	−34.4
	−79.8 −143.9	−80.4 −100.8	−43.1 = (−35.2) − 7.9[f]
	−101.9 −163.4	−107.0 −121.5	−41.9 = (−35.2) − 6.7
	−49.2 −103.2	−50.5 −71.1	−32.1 = (−35.2) + 3.1
	−25.0 −65.2	−28.8 −66.5	+1.3
	−60.0 −124.2	−59.8 −78.4	−45.8 = (−35.2) − 10.6
	−64.7 −183.8	−62.3 −113.0	−70.8 = 2(−35.2) − 0.4
	−92.5 −271.3	−91.2 −167.6	−103.7 = 3(−35.2) + 1.9
	−90.8 −202.3	−85.0 −135.0	−67.3 = 2(−35.2) + 3.3
	−70.0 −209.6	−73.2 −135.3	−74.3 = 2(−35.2) − 3.9
	−74.7 −198.3	−77.4 −124.5	−73.8 = 2(−35.2) − 3.2
	−92.4 −206.7	−87.2 −131.0	−75.7 = 2(−35.2) − 5.3
	−53.7 −173.5	−51.3 −93.7	−79.8 = 2(−35.2) − 9.4
	−64.7 −192.5	−63.5 −115.0	−77.5 = 2(−35.2) − 7.1
	−57.3 −140.1	−62.5 −116.5	−23.6 = (−35.2) + 11.6
	−69.2 −251.6	−69.2 −133.1	−118.5 = 3(−35.2) − 12.9
	−70.3 −217.6	−64.6 −135.1	−82.5 = 2(−35.2) − 12.1

Table III *(Continued)*

Molecule	Exptl^d	Calcd^e	$\chi_{cc}{}^c$ (nonlocal)
	$\chi_{\text{(average in-plane)}}{}^a$		
	$\chi_{cc}{}^b$		
	−68.0 −189.0	−69.1 −119.0	−70.0 = 2(−35.2) + 0.4
	−71.3 −185.5	−69.4 −116.8	−68.7 = 2(−35.2) + 1.7
	−80.6 −303.0	−74.2 −142.6	−160.4 = 4(−35.2) − 19.6

^{a} $\chi_{\text{(average in-plane)}} = \frac{1}{2}(\chi_{aa} + \chi_{bb})$. ^{b} χ_{cc} = out-of-plane component. ^{c} χ_{cc}(nonlocal) = χ_{cc}(exptl) − χ_{cc}(calcd). ^{d} Those values marked with * were measured by Zeeman-microwave techniques in this laboratory (see ref 5 and 13). The rest were measured by single crystal measurements. ^{e} These values are the average of those calculated using the atom and the bond contributions from Table I. ^{f} −35.2 is the χ_{cc}(nonlocal) for benzene.

ropies it has become profitable to reverse this procedure and use these susceptibilities to derive more accurate values for related molecular parameters.

Cotton–Mouton measurements provide a relationship among the magnetic susceptibility anisotropy ($\Delta\chi$), the electric polarizability anisotropy ($\Delta\alpha$), and a mixed hyperpolarizability anisotropy ($\Delta\eta$), according to[3]

$$_{\mathrm{m}}C = \frac{2}{135}\pi N\left[\Delta\eta + \left(\frac{2}{3kT}\right)\Delta\alpha\Delta\chi\right] \qquad (8)$$

where $_{\mathrm{m}}C$ is the molar Cotton–Mouton constant, N is Avogadro's number, k is Boltzmann's constant, and T is the absolute temperature. η is related to the variation of electric polarizability with magnetic field. Several attempts have been made to evaluate susceptibility anisotropies by measuring the Cotton–Mouton constant and the polarizability anisotropy and using eq 8 by assuming a value of zero for $\Delta\eta$.[3,23]

The assumption that $\Delta\eta$ is small has thus far been checked only for a few linear molecules, where it appears to be reasonably good.[24] We are now in a position to extend this check to two larger molecules. From the values in Table I, $\chi_\perp - \chi_\parallel$ for ethane can be calculated as $+6.2 \times 10^{-6}$ erg/(G^2 mol). In addition, the above discussion indicates that the single crystal value of $\Delta\chi = -59.7 \times 10^{-6}$ erg/(G^2 mol) for benzene is fairly reliable. These should be compared with the values of $\Delta\chi = +2.4 \times 10^{-6}$ erg/(G^2 mol) for ethane and $\Delta\chi = -53.9 \times 10^{-6}$ erg/(G^2 mol) for benzene calculated from eq 8 with experimental values of $_{\mathrm{m}}C$ and $\Delta\eta = 0$.[3] The contribution to the Cotton–Mouton constant from the temperature-independent hyperpolarizability in these two molecules seems to be significant, suggesting that susceptibility anisotropies derived from Cotton–Mouton measurements may not be totally reliable unless studies of the temperature dependence of the constant are done.

Finally, we turn to the most common source of derived magnetic susceptibility anisotropies: chemical shift measurements. McConnell[25] has derived an expression relating a part of the magnetic shielding to the susceptibility anisotropy of neighboring atoms or bonds. If the many other contributions to the shielding can be calculated, estimated, or canceled out, chemical shifts can be used to derive magnetic susceptibility anisotropies. Numerous such attempts appear in the literature,[4] but none of the values for group anisotropies derived from chemical shift measurements are in agreement with the values given in this paper. They are generally much smaller in magnitude and sometimes not even of the right sign. In addition, the proper origin to be assigned to a bond susceptibility when relating it to magnetic shielding is not clear. This uncertainty in a quantity believed to be small has led to the practice of ignoring susceptibility contributions in treatments of the chemical shift.

The fact that magnetic susceptibility anisotropies derived from chemical shifts agree so poorly with direct measurements would seem to indicate that some other contribution to the chemical shift has not been properly evaluated. It would therefore be worthwhile to reexamine the interpretation of magnetic shielding data in the light of a more accurate calculation of the neighbor group magnetic susceptibility contribution. The derivation in this paper of atom as well as bond susceptibilities makes possible an unambiguous choice of origin for such a calculation since the origin of an atom susceptibility is clearly the nucleus.

IV. Conclusion

In this paper we have decomposed the elements of the molecular magnetic susceptibility tensor into additive group contributions. We have demonstrated theoretically that such a decomposition is reasonable, and we have derived atom and bond values which successfully correlate the available experimental data. We believe that these values can provide accurate predictions of the magnetic susceptibility in many unmeasured molecules. We have used these local values to provide an unambiguous quantitative measure of electron delocalization and have shown how this can be related to the concept of aromaticity. Finally we have shown how calculated susceptibilities can be used to provide insight into other molecular properties.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

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(23) C. L. Cheng, D. S. N. Murthy, and G. L. D. Ritchie, *J. Chem. Soc., Faraday Trans. 2*, 10, 1679 (1972).

(24) See W. H. Flygare, R. L. Shoemaker, and W. Hüttner, *J. Chem. Phys.*, **50**, 2414 (1969), for a discussion of this type of evaluation for linear molecules.

(25) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).