

MAGNETIC SUSCEPTIBILITY, ELECTRON DELOCALIZATION AND AROMATICITY

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Since evaluations of aromatic character¹⁻³ are based on differences between observed properties of real molecules and estimated properties of hypothetical molecules, it is essential that the pertinent property of the model compound be clearly defined in any discussion of aromaticity.^{1,4} The need for such clarity is made especially evident by consideration of a recent suggestion of Palmer and Findlay⁵ that diamagnetic susceptibility anisotropy is not related to aromaticity on the basis of their calculation of the diamagnetic part of the susceptibility.

Earlier papers from this group^{6,7} have suggested that the presence of a non-local magnetic susceptibility anisotropy might serve as a measure of electron delocalization in ring compounds and hence, if aromaticity is defined in terms of electron delocalization,⁸ of aromatic character. Recently, it has been shown that it is only the out-of-plane component of the magnetic susceptibility which shows non-local effects in aromatic systems.⁹ By this criterion, a compound is judged to have delocalized electrons not because it has a large out-of-plane magnetic susceptibility but because it has a more negative susceptibility than that which would be predicted from a localized model.^{6,7,9} The advantages of the use of non-local molecular magnetic susceptibilities for evaluation of aromaticity lie in the reliability of the assignments of magnetic susceptibilities to the hypothetical localized models and in the theoretical relationship of non-local contributions to electron delocalization.

The magnetic susceptibility (or any of its molecular cartesian components) is a combination of a diamagnetic susceptibility, which can be calculated from a knowledge of the ground state molecular electronic wavefunction only, and a paramagnetic susceptibility, which can be calculated from a knowledge of the

ground and excited state electronic wavefunctions.[‡] Experimentalists commonly define a ground state property in terms of observations on molecules in the ground state. However, theoreticians often use the term ground state to mean a property which can be calculated solely from a knowledge of the ground state wavefunction. There are, however, many properties of the ground state which cannot be so calculated. In particular, any property which requires second order perturbation theory for its evaluation of necessity requires a knowledge of excited state wavefunctions. The claim that a non-local magnetic susceptibility is a measure of electron delocalization is essentially a statement that ground state molecules which possess delocalized electrons will behave in a particular way when subject to an external magnetic field and it is not surprising therefore that the calculation of this behavior requires more than the unperturbed wavefunction.

The work of Palmer and Findlay⁵ is subject to criticism on at least two counts. First, it makes no reference to a non-aromatic model and second, it considers the paramagnetic contribution to the susceptibility to be an excited state property which can be disregarded, although as we will show below, that term in fact contains the correlation with aromatic character. Finally, contrary to the claim of Palmer and Findlay, the measurement of the magnetic susceptibility anisotropy in molecules with less than C_{2v} symmetry is no more difficult than in any other molecule, so calculations do not have the power to reaching molecules which are experimentally inaccessible on the basis of lower symmetry.

The diamagnetic susceptibility is now a very well understood property. It has been clearly shown that the diamagnetic susceptibility tensor is relatively insensitive to the bonding in the molecule and can be calculated accurately by the method of atom dipoles¹¹ for either aromatic or nonaromatic systems. The diamagnetic susceptibility of a molecule can even be estimated to within 10% by calculation of this property for unbonded atoms with the same geometric configuration as the atoms in the molecule. Therefore, it

[‡]The term diamagnetic susceptibility has often been used in the literature for what is normally called¹⁰ the magnetic or total magnetic susceptibility. This misnomer has arisen because the negative diamagnetic contribution to the total susceptibility usually is larger than the positive paramagnetic contribution; thus, the term "diamagnetic molecule". However, the total susceptibility is usually only approximately 10% in magnitude of either the diamagnetic or paramagnetic contribution.

should not have been regarded as surprising⁵ that the anisotropy in the diamagnetic susceptibility is not a measure of aromatic character.

To illustrate this point, we have calculated the diagonal elements of the diamagnetic susceptibility tensor for several molecules considered by Palmer and Findlay by the method of atom dipoles. We list the results in Table 1. As can be seen, the method of atom dipoles (a ten-minute hand calculation) yields results of accuracy equal to the non-empirical wavefunction calculation of Palmer and Findlay. Comparable agreement between the method of atom dipoles and reliable SCF calculations of the diamagnetic susceptibility is generally observed.¹¹ Since the diamagnetic susceptibility can be calculated so accurately from a localized model, any non-local behavior in the total susceptibility of a molecule must be associated with the paramagnetic component.

Table 1. Comparison of the Experimental Diamagnetic Susceptibilities (χ_{oop}^d , Out-of-Plane; $(\chi_{ip}^d)_{av}$, average In-Plane) with those Calculated with the Atom Dipole Method (ref. 11) and those Calculated by Non-Empirical Methods. The Units are 10^6 erg/G² mole.

Source Molecule	Ref. 5		Exp [‡]		Ref. 11	
	$-\chi_{oop}^d$	$-(\chi_{ip}^d)_{av}$	$-\chi_{oop}^d$	$-(\chi_{ip}^d)_{av}$	$-\chi_{oop}^d$	$-(\chi_{ip}^d)_{av}$
Benzene	526, 304		508, 286		516, 295	
Fluorobenzene	739, 408		732, 402		741, 410	
Pyridine	492, 387*		481, 274		494, 282	
Pyrrole	343, 205		330, 196		315, 187	
Furan	328, 196		314, 186		314, 186	
Thiophene	445, 258		438, 256		443, 257	

* Presumably 287. The original references for the experimental diamagnetic susceptibilities are in reference 12.

This result can be understood on the basis of a simple model. The energy level pattern for the $4n + 2 \pi$ electron systems of an aromatic ring is identical to that for free particles in a ring.^{13‡} If the electrons in such an aromatic molecule were completely free to move in a cylindrically symmetric ring, there would be no

[‡] These arguments are not valid for $4n \pi$ electron systems where the energy level pattern is not analogous to that for free particles in a ring.

paramagnetic (positive) component perpendicular to the ring. As the electrons become progressively more localized (i.e., as the cylindrical symmetry is broken) the paramagnetic susceptibility perpendicular to the ring will increase. The diamagnetic (negative) susceptibility, which is proportional to the extension of the electron density in space, would not be expected to change. The observable result would be that the total out-of-plane susceptibility would have its most negative value for a completely delocalized system and would become progressively less negative as the electrons become more localized.

In summary, if the non-local contributions to molecular magnetic susceptibilities are considered to correlate with cyclic electron delocalization, then perforce these values provide one measure of aromatic character. Direct experimental measurements of magnetic susceptibilities such as those available from Zeeman microwave spectroscopy¹² free this measure from the complications^{9,14} involved in interpretations of nuclear magnetic resonance chemical shifts. Whether or not the magnetic susceptibility criterion will correlate with other criteria of aromaticity is a matter of continuing theoretical and experimental interest.^{1-4, 15}

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