CHEMICAL SCIENCES

MOLECULAR SUSCEPTIBILITY TENSOR AND THE SUSCEPTIBILITY TENSOR FOR MOLECUALR FRAGMENTS

S.ARAVAMUDHAN
Department of Chemistry, North Eastern Hill University, Shillong, 793022, Meghalaya

Key words: susceptibility tensor, molecular fragments, functional groups, spatial resolution, HR PNMR in single crystalline solids.

ABSTRACT
(101 words count)

Molecular Susceptibility Tensor values can be obtained by theoretical calculations based on quantum mechanical formalisms and by experimental methods. Once the molecular susceptibility tensor values are available, it may be possible also to obtain susceptibility tensor values for the molecular fragments which are transferable from one molecule to another. By appropriate combination of the molecular-fragment-tensors, it may become possible to obtain the molecular susceptibility tensor values. This possibility of *spatial resolution* of molecular susceptibility based on functional groups would be considered, indicating the requirements for obtaining consistent sets.

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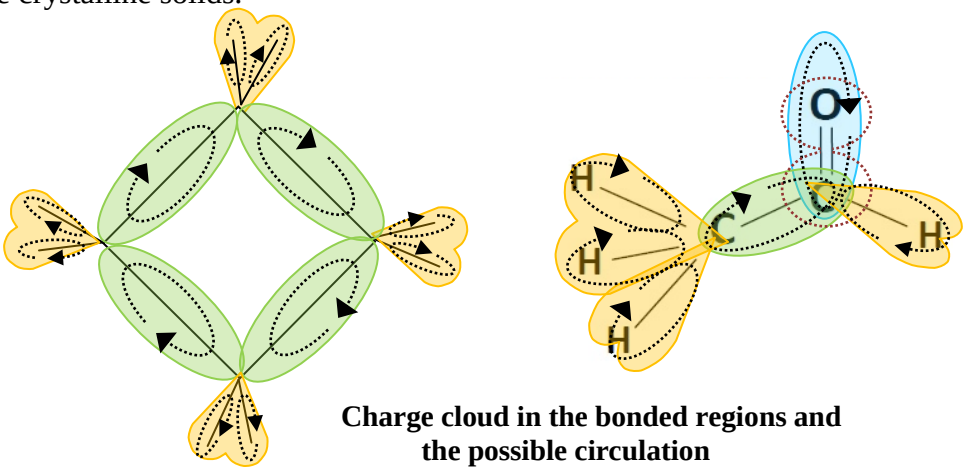
INTRODUCTION

In presence of an external magnetic field, magnetic susceptibility indicates the possible extent of change in the electron charge-cloud circulations (Fig.1). Changes in electron circulations result in changes in induced fields in the molecule and hence the NMR chemical shifts depend on the physical quantity susceptibility. In view of a more convenient method for calculating demagnetization factors, experimental determination of susceptibilities and chemical shifts together with the quantum chemical methods seem to provide a refreshing way to comprehend the electronic structure of molecules in particular the full proton shielding tensor values obtainable from High Resolution Proton NMR in single crystalline solids.



Charge cloud in the bonded regions and the possible circulation

Fig.1

Thus, experimental measurements lead to improve calculations for comparable values; and theoretical trends lead to look for novel variations in structures to study experimentally.

DESCRIPTION OF THE OBJECTIVE

Fragmentation of molecular susceptibility values is for the route in the middle of scheme (below Fig.2 Scheme.1) standing for the calculation of PMR shielding values starting from these fragmented molecular susceptibility values. First thing to remark is that in case the fragmented values are obtained from total molecular value by an empirical fitting, then, using such empirically derived quantity for calculating Shielding would mean

that the empirically derived values are the actual values for the physical quantities(1) in the molecule arising locally.

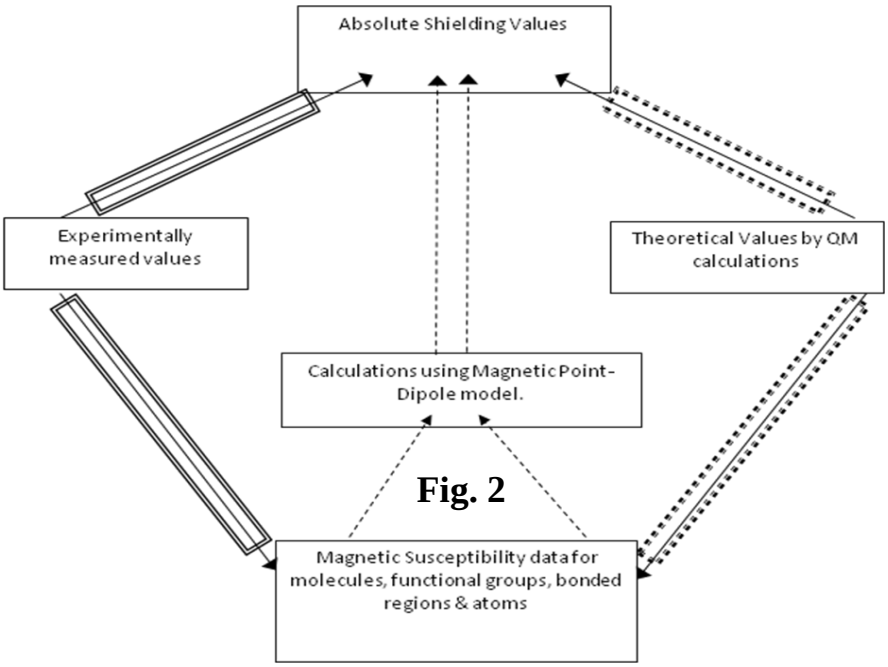


Fig. 2

Fig.2: Scheme.1: Possible routes to obtain Proton shielding tensor values

Even if it becomes possible to reconstruct the total molecular value from the fragmented values, it would in the limit mean that the mathematical procedures of arriving at empirical values are permitting reversibility to get back the original value. More specifically if the fragmented quantities are not representative of the typical electronic structure characteristic of the functional group, then such fragmented values may not be transferable parameters and also in some way or other there could be inconsistency encountered in the use of these values. The Proton NMR studies for intra molecular shielding tensor would stand to benefit if the intra molecular shielding parameters can be calculated using the fragmented susceptibility values on the basis of the classical point dipole model. However, Quantum Mechanical computational chemistry has formalisms and software for implementing these QM methods to obtain the calculated values for the shielding.

Thus the novel route to obtain intra molecular shielding values would require susceptibility tensor values which can be obtained experimentally and also by the QM theoretical methods. The classical route to calculate the intra molecular shielding tensor can be envisaged as an extension from the possibility to explain the neighbor group contribution to isotropic proton chemical shift (2). Flygare et al., (3) report that a set of bond (tensor) susceptibilities derived by an empirical fit from the set of TOTAL (experimentally determined) MOLECULAR SUSCEPTIBILITY TENSOR values and a set of atom (tensor) susceptibilities were derived by an empirical fit from the same set of TOTAL MOLECULAR TENSOR VALUES. Further, the set of Bond susceptibities thus derived could not be constructed from the similarly derived atom susceptibilities.

susceptibility value. As illustrated in the example of Acetaldehyde in Fig.2 & Table-1, the molecular value compares well with experimental value and the calculated from Atom susceptibility set and bond susceptibility set (from results of W.H.Flygare) .

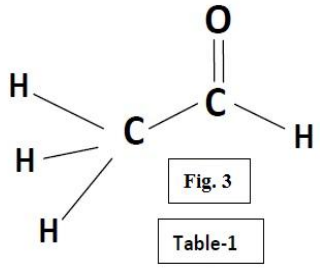


Fig. 3

Table-1

Molecule	Exptl molecular Susceptibility	Calcd from Atom	Calcd from Bond
Acetaldehyde	χ_{aa} -20.0	-21.3	-20.6
	χ_{bb} -19.5	-19.1	-18.0
	χ_{cc} -28.6	-29.2	-28.0

This observation thus, points out that the two *empirically derived "consistent sets"* are not *mutually consistent*. This requires an explanation on theoretical grounds. Since the susceptibility is a pervasive quantity because of the fact that it is the extent of charge (charge cloud) circulation that would be possible in presence a intense magnetic field for which susceptibility is a measure. When the total susceptibility tensor of a molecule is being fragmented, is it possible to identify a charge cloud volume carved out of the totality of charge cloud (undergoing a circulation)? When susceptibility or shielding tensor is calculated, the integral evaluations are done by dividing the entire charge cloud volume into small (infinitely small) shells of charge cloud and by the mathematical limiting theorems a continuity for the charge cloud is visualized. If infinitely small shells provide the necessary criterion for analytical/numerical integration, then what would be the constraint to envisage fragmented charge cloud volumes which correspond to the chemist's characterization of functional groups of the molecule? A closer look at this question for an answer would be the approach in this paper.

THE APPROACH AND RESULTS

The molecular fragments consist of electron circulations as can be determined from the bonding nature within the fragments. Typically the fragment can be a functional group which has characteristic properties attributable to the typical electronic structure prevailing within the group.

When there are many functional groups within the molecule (Fig.1), all related to one another by a symmetry element of the point group of molecule, then the question that would arise is: just because the atomic positions of the functional groups correspond to a symmetry related set, should the electron charge clouds of the characteristic groups would separate out into charge clouds which do not have any overlapping regions with the remaining part of the molecule? Inclusive of such possible inseparable overlapping charge clouds, the symmetry can be present. Thus separating the charge clouds from one part of the molecule with respect to another, cannot be entirely determined by symmetry of the molecule.

Thus the physical quantity of the whole molecule cannot be easily *fragmented* into symmetry compliant set of fragmented values. Further complication could be due to the fact that the fragments may have local symmetry axes with respect to a point within the fragment which does not coincide with the molecular axes system. Since, the diagonal form for the fragmented physical quantity must conform to local symmetry, either when the fragments of the physical quantity are obtained from the total molecular value or the total molecular value is obtained from the by the appropriate summing of values of the fragments, the retention of local symmetry and the molecular point group symmetries consistently could pose a problem that may not be resolvable in any simple manner. This comment is when the physical quantity is a Tensor of second rank, and a different type of difficulty has to be overcome when handling equations for the isotropic trace values of the molecular quantity and the fragmented quantities.

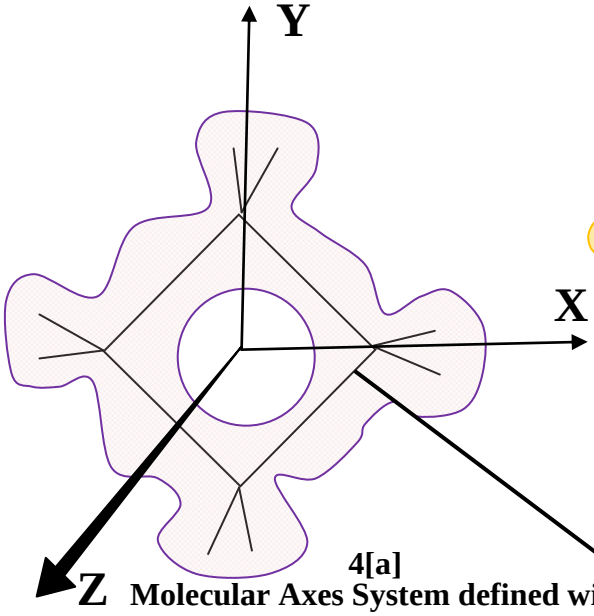
The molecular fragmented Physical Quantities are further substituted in equations to calculate related physical quantities. All these require a certain mathematical procedures which seemed to result in reasonable values justifying the fragmented values of the molecular quantity. In particular the context is the effort to calculate intra molecular proton shielding values reported in the previous sessions of the Indian Science Congress.

However there are certain limitations and there have been certain discrepancies reported earlier and now in this presentation an effort would be made to clarify and justify to the extent possible the considerations on the basis of the theoretical formalisms, whenever the fragmented values were obtained with empirical considerations or semi empirical considerations.

When the Total Molecular Tensor is calculated from the appropriate addition of the fragmented Tensor, then the property in the Local PAS for each of the fragments, should be transformed into values in the molecular axes system, and then added to get the total in the molecular axes system, which then would have to be diagonalized to get the property in molecular PAS.

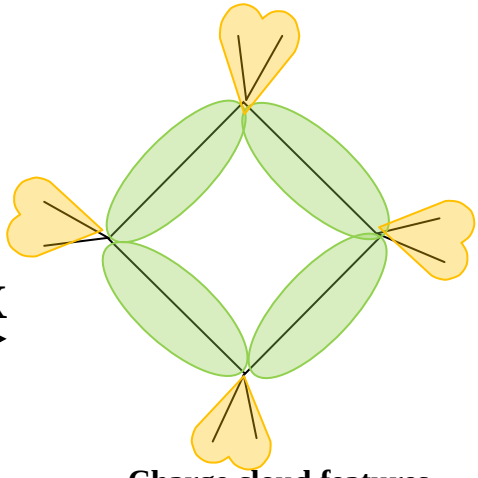
Thus if the functional group tensor values are transferable consistent sets, these set of functional group values may be generally used for arriving at Molecular property for different molecules.

Consider the situation when a functional group fragment Tensor is available. And, this would be a diagonalized tensor in the local symmetry axes system and hence the PAS would be conforming to the Local symmetry. Such a situation in Benzene molecule would be the C-C bonds, 6 of them. The diagonal components are given below in Fig.5. In the benzene molecule there are six such tensors and their disposition would be as illustrated in Fig. 6.



4[a]

Molecular Axes System defined with reference to conventional drawing of molecular geometric structure with the charge cloud distribution

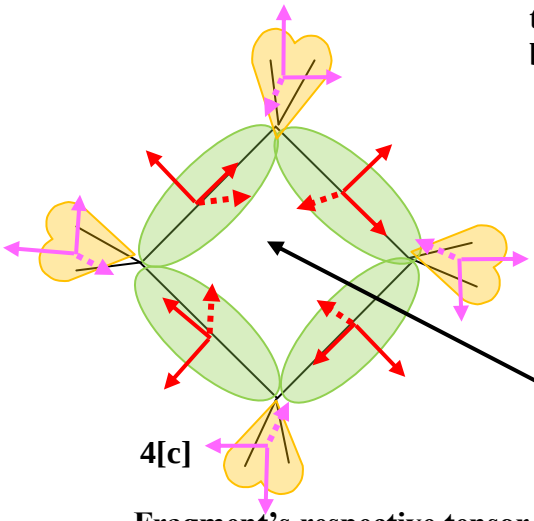


Charge cloud features (localized to the bond regions) represented for the molecular geometric structure

4[b]

When the molecular Tensor property is fragmented to correspond to the functional groups, then with the origin within the group the Tensor principal axes system (PAS) would be assigned to coincide with the Molecular PAS.

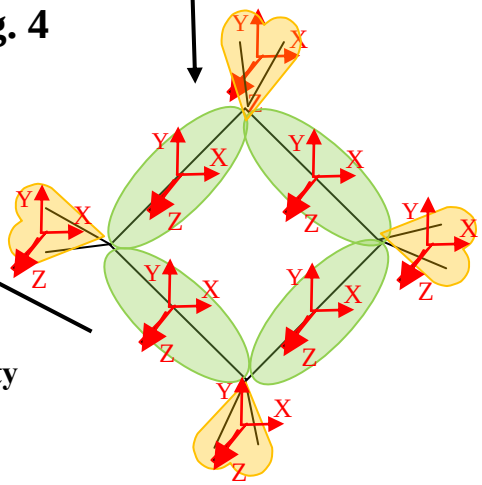
4[d]

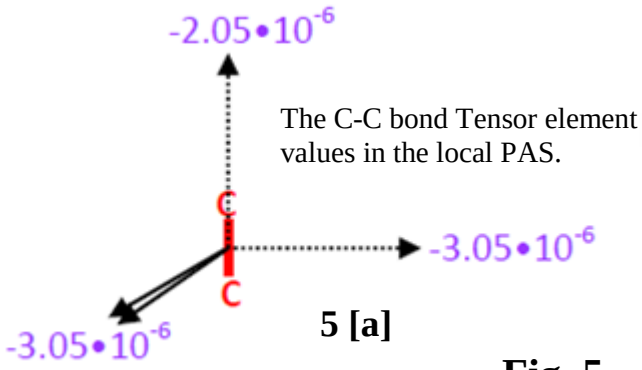


4[c]

Fragment's respective tensor property transformed to local symmetry.

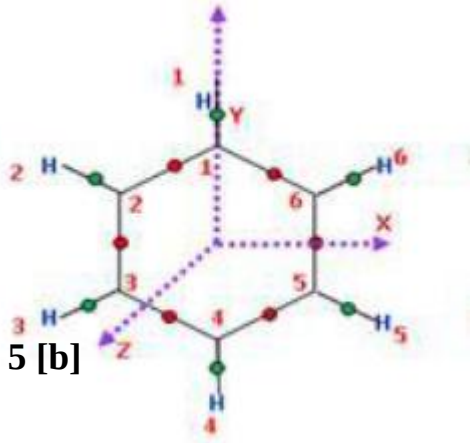
Fig. 4





The C-C bond Tensor element values in the local PAS.

5 [a]



5 [b]

Fig. 5

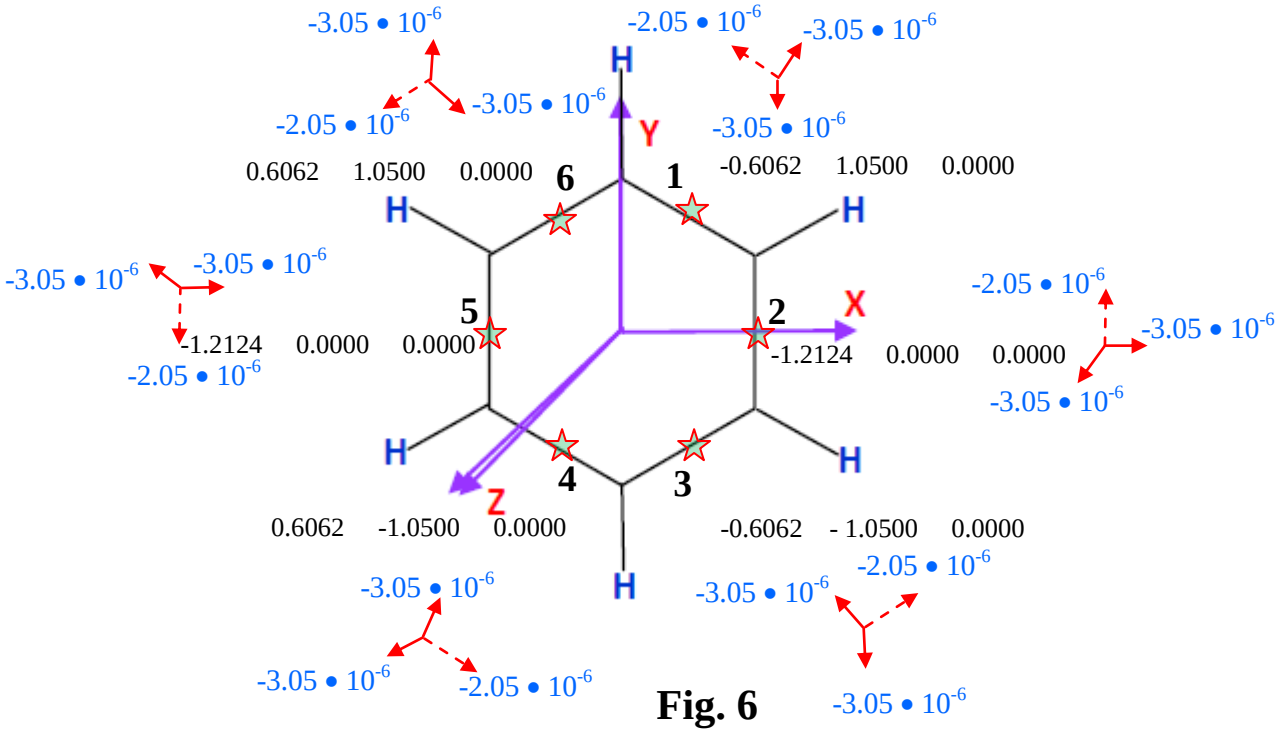


Fig. 6

Fragmented six C-C bond Tensors disposed relatively in conformity with the Molecular Symmetry

All the 6 tensors in the **local PAS** are given by the matrix elements of the form **(Fig.5- [a] & Fig.6)**:

$$\begin{pmatrix} -2.5 \times 10^{-6} & 0 & 0 \\ 0 & -3.5 \bullet 10^{-6} & 0 \\ 0 & 0 & -3.5 \bullet 10^{-6} \end{pmatrix}$$

Whereas for this C-C group **1 (Fig.5-[b])** the above tensor matrix for would be transformed to **Molecular PAS** would be as follows

$$\begin{pmatrix} -2.29\times10^{-6} & 0.43\times10^{-6} & 0 \\ 0.43\times10^{-6} & -2.79\times10^{-6} & 0 \\ 0 & 0 & -3.5\times10^{-6} \end{pmatrix}$$

Group **1**

$$\begin{pmatrix} -2.29\times10^{-6} & -0.43 & 0 \\ -0.43\times10^{-6} & -2.79\times10^{-6} & 0 \\ 0 & 0 & -3.5\times \end{pmatrix}$$

Group **3**

And obviously the tensor is not diagonal. Such a transformation, being merely a mathematical process, does not affect the charge cloud situations in the molecule. The geometrical representation of all the Tensor elements when the Tensor is in non diagonalized form is not as simple; particularly the off diagonal elements are difficult to track as simply by a geometrical representation. All the 6 C-C groups have the same principal axis values in their respective PAS (all oriented differently w.r.to each other), though the Molecular PAS system is the same for all the 6 groups transforming them from their local PAS to molecular PAS gives different tensors. It can be reassured that a simple mathematical transformation does not imply any redistribution of the charge clouds.

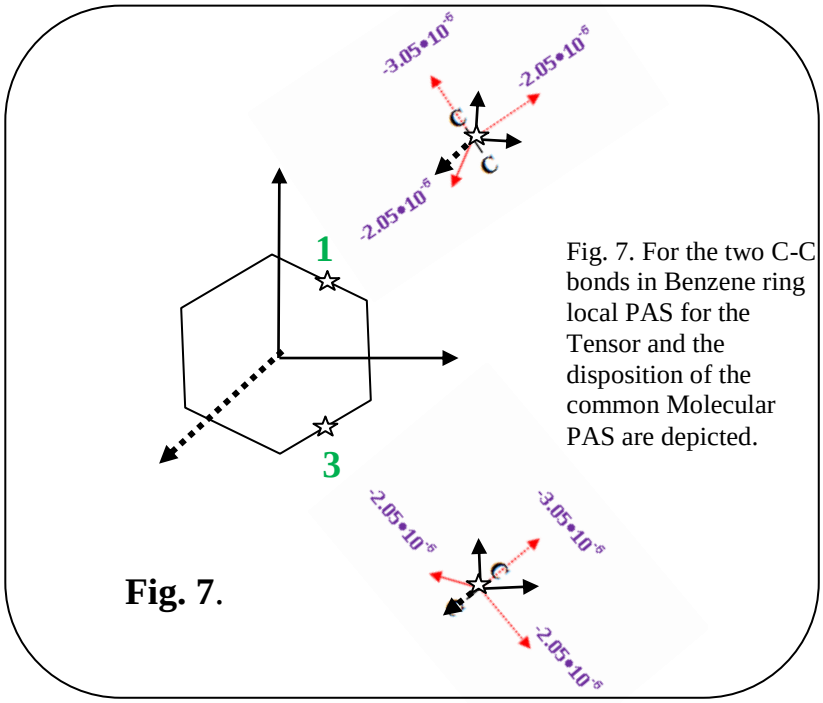


Fig. 7. For the two C-C bonds in Benzene ring local PAS for the Tensor and the disposition of the common Molecular PAS are depicted.

Fig. 7.

However, breaking a total into fragments or adding fragments to make up the total should be properly accounted for by the kind of charge distributions prevailing in the total electronic structure while delineating the separate fragments.

In particular while fragmenting a bond into two atoms or combining the atoms to make a bond in terms of the numerical divisions of tensor property may not be conserving the totality of the nature of charge cloud to preserve the significance of the physical property which the numerical values stand for.

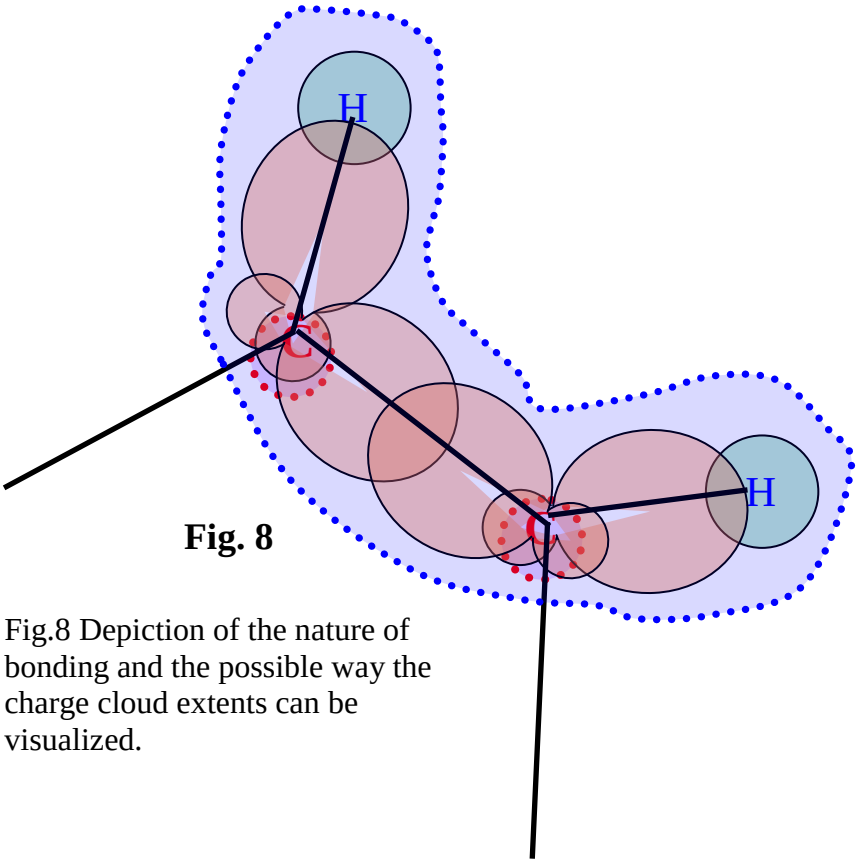


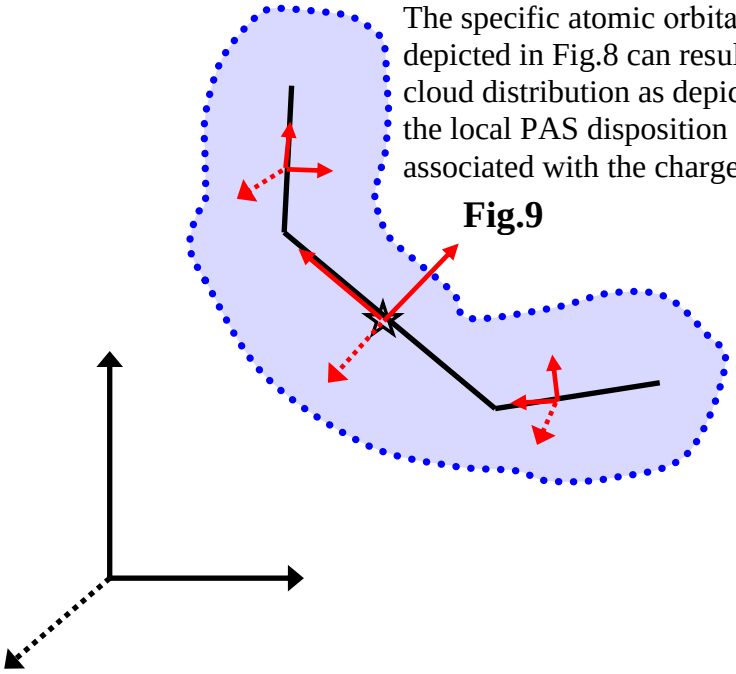
Fig. 8

Fig.8 Depiction of the nature of bonding and the possible way the charge cloud extents can be visualized.

For the explanation of the above Fig.8, it is the simplest depiction of the valence electron orbital charge clouds which participate in the sigma bonding in this part of the ring, the two carbon atoms and the two hydrogen atoms. Carbon atom valence electrons ($2s^2$ $2p^2$) are located in the three sp^2 hybridized (trigonal hybridization) orbital with one 2p electron forming the delocalized (aromatic) π system. The single electron of the hydrogen atom is in the corresponding atomic 1s atomic orbital. The carbon atom $1s^2$ electron system forms the core orbital and presumed to be (atomic core) not much contributing to the bonding. Since the aromatic pi system has a different symmetry compared to the sigma bonds, the σ part of the local fragmented tensor can be separated out. The tensor properties as depicted in Fig.7 are for the sigma contribution from the fragments. The blue colored superposed depiction bounded within the dotted line could be the overall charge cloud view of the sigma bonding in the fragment, which is in the Fig.9.

As mentioned in Pag-2 of this paper with the citation of Ref.3, the discrepancy with regard to the fragmented bond contributions and the fragmented atom (corresponding to that bond) contributions to the total molecular value can be followed with the

visualization by Fig 7, Fig.8, and Fig.9.. Considering one of the bonding carbon atom of the C-C bond, it can be seen that the carbon atomic Valence part contribution to the tensor must be arising in part from the C-H part and the C-C part.



The specific atomic orbital's overlapping as depicted in Fig.8 can result in a overall charge cloud distribution as depicted in Fig.9 along with the local PAS disposition of the Tensor property associated with the charge cloud distribution.

Fig.9

The two bonding contributions have PAS (local symmetries) are different with respect to each other and to the common molecular PAS. Thus if fragmenting from total results in Atomic values, a similar fragmenting from the same total gives the bonding values as well. But by empirical procedures for arriving at fragmented value may be consistent within the domain of all atomic fragments by virtue of a reversibility ensured by mathematical procedures. Same way consistency of the set of bond fragments can result. However, empirical procedure may not ensure the addition of atomic domain values to bond domain values with a kind of consistency as it happens to be within the domain.

There have been theoretical reports of calculating by QM methods the neighboring atom contributions, and these can be compared with the corresponding dipole model calculations, As of the situation now there does not seem to be any such type of QM calculations for the atomic fragment Tensor (susceptibility) values which is necessary to use a classical dipole model. Such calculations of Tensor values for small regions of localized electron circulations, which are part of the pervasive molecular charge cloud circulations, may not be achieved by any reasonable and simple enough approximations. In this context a recent paper of this author (**4**) on "QM Chemical Shift Calculations to infer on the Long-range Aromatic Ring Current-induced Field Contributions" might lead to certain indicative trends to be evolved. This much could be at this stage on the situation for the comment on the difficulties of reconciling with two consistent sets which are mutually inconsistent. Even to arrive at the possible source of such a peculiarity, it was necessary to calculate intra molecular shielding constant for a molecule using fragmented susceptibility with magnetic dipole model for comparison with *ab initio* QM calculation results. Benzene was a convenient system and important in the context of ring current effects (**4**) and the variety of transformations required and the significance of actual numerical magnitudes of fragmented tensor elements could also be to some extent discerned by such calculations on

benzene molecule to enable an insight into the context of possible shortcomings in the empirical methods of fragmentation approaches. While at this stage the possibilities available to obtain the Susceptibility Tensor values for the 25 fragments of the Benzene molecule have all been tried out with different combinations of such derived sets and an optimal set of fragmented values have been reported (**5**) till recently.

CONCLUSION

The numerical values of the Shielding Tensor thus calculated by the central route indicated in Fig.2, have been compared for ensuring the trends of variation and dependences. The completion of such trial and error approach could give the insight to comment on the bond-set values atom-set values with better confidence. Thus trying to get the fragmented Susceptibility Tensor values by the several trial methods and using them in the classical dipole model equation to calculate a related physical quantity Proton Shielding Tensor provides an indirect justification for the following inference: that, the adhoc procedures by which the Molecular Susceptibility Tensor value has been subjected to yield resolved information for the constituent functional groups could mean that such fragmented values of tensor correspond to what actually happens locally at the functional group in terms of electron charge circulations.

Thus in the previous papers at Science Congress Sessions (**5**) the calculation on benzene molecule was given an exposition. The summary of results reported in the previous Science Congress Session is displayed below in Fig.10. The macroscopic

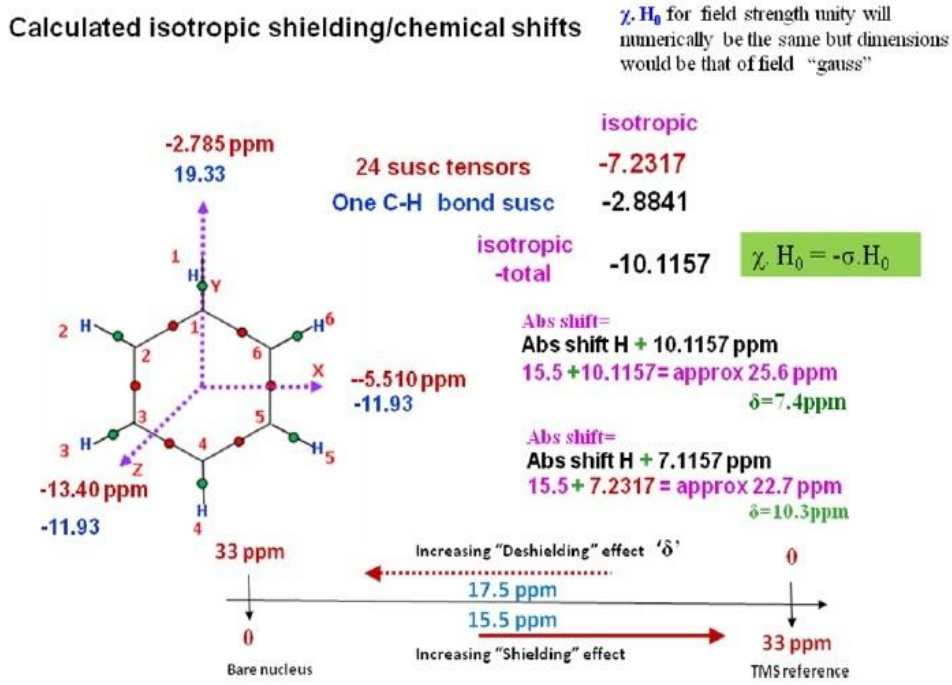


Fig.10 Summary of results on Calculation of Proton Chemical Shift in Benzene Molecule: Comparison of values obtained by Classical dipole model and experimental values. A similar comparison of the Classical model values with that by QM calculations was also part of earlier

demagnetization factor calculation methods could also be incorporated into intra molecular context to make it possible to arrive at exclusively a classical method of calculation of shielding as compared to QM methods. That the situation of molecular fragments making up the whole molecule is, in principle, the limit of close-packed inner volume elements make up the whole macroscopic specimen (**6**), is borne out. The fragmentation limit at much smaller intra molecular regional level of atoms and bonds poses a peculiarity unlike the macroscopic fragmentation into smaller volume elements.

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