Bulk solid specimen shape dependences in the molecular, chemical-shift tensor determinations

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Abstract

*Determination[1] of the chemical shift tensors (measured with respect to a 'reference' chemical-compound) require using single crystals of organic molecules and these are diamagnetic specimen. The chemical shifts arise due to variations in induced fields at a proton (nuclear) site within a molecule, due to the changes in the electron charge circulations within the molecules when placed in a strong external magnetic field. The solid-state **High Resolution Proton Magnetic Resonance** (HR PMR) techniques yield tensor values measured experimentally, but it becomes necessary to calculate and take into consideration the intermolecular contributions to the chemical shifts to retrieve the only 'intra molecular' shift tensor values. The intermolecular contributions in principle can be contribution beginning from the molecule which is immediate neighbor and the other molecules which are distant neighbors extending to the entire extent of the macroscopic specimen. Thus it raises the questions pertinent for taking into consideration the induced fields from the entire bulk of the specimen at a point within the specimen which typically are the issues in the study of magnetic materials. Seeking answers to such questions as is necessary to validate the procedures used for the retrieval of the intra molecular values as mentioned above. These questions and, the answers seem to pave the way to secure certain clarifications pertaining to field distributions within magnetized materials. Thus evolving a criterion to correct for the bulk specimen shape dependences in the context of the measurement of proton Chemical Shift Tensor paves the way to unravel the consequences of induced field distributions within the material medium. This path-way, from molecule to materials, seem to be refreshing the understanding of the requirements laid out for the specifications of local fields at points within a specimen with bulk magnetization features.*

1.INTRODUCTION

In diamagnetic molecules the electrons, which are all spin-paired, undergo circulatory motions centered on the atomic nuclei in the molecular frame-work. In the case of diamagnetic molecular systems, there are two electrons in each of the occupied molecular orbital. The occupancies in molecular orbitals entails the possibility that the charge circulations of the electrons in the orbitals can be in the opposite directions. Thus even though there are continuous circulations of electrons there can be cancellations of the induced fields because of the circulations in opposite directions. When an external magnetic field is applied, there can be preferences established for circulations in one direction over the other alternative direction and there could be changes in the velocity of circulations and the circulation paths. Such effects in the environment of bonded atoms can have varying effects significant enough to indicate the electronic structures. It is primarily these differences in induced fields which are of interest to chemists while investigating spectroscopically, and, in particular using the NMR Spectroscopic tool.

The situation described above, for a diamagnetic molecule, is entirely with respect to the intra molecular perspectives for induced

fields at the site of nuclei. What compounds this description of induced field at particular site is the fact that there are contributions to induced fields from other molecules. There are molecules which are in the immediate vicinity as well as from the distant locations in a continuous distribution over the entire macroscopic extent of the specimen, which at any particular instance, can be a single crystal of organic molecule. Under the influence of external magnetic field the electronic circulations prevailing are the same in every one of the independently identifiable equivalent molecules which are present in the crystal. The induced fields due to a molecule at a given site differ depending upon whether that specified site is occupied by a proton bonded to that molecule or in any molecule located in any of the other the lattice sites.

It is a fact that the induced fields arising at a site, *due to the specified repeating-unit of* the electronic structure in *the lattice* (which is a molecule in the particular case), *must be considered always inseparably with the induced fields from the other lattice site uni*ts. This makes the estimation of induced fields for a given site to become complicated and laborious to evaluate. While approximations are resorted to, then the uncertainties in the calculated estimates in conjunction with the accuracies of experimental measurements render the interpretations to be less conclusive.

2. HR PMR EXPERIMENTS

The High Resolution Proton Magnetic Resonance (**HR PMR)** experiments in Solids have been well described in the literature[2]. It is reiterated here that the single specimen used for the measurements in HR PMR in solids have been spherically shaped; for reasons that the bulk susceptibility contribution to induced fields within the specimen is zero for the spherical shape of the specimen. This limits the utility of this technique since it is not always possible that the given organic molecular single crystal can be shaped into a sphere for the convenient use for measurement by HR PMR techniques. The current experimental efforts being made to reduce the experimental constraints in making spheres are posted in the WebPages[3] of this author. Fig.1 below depicts the situation for the disposition of the

experimentally measured principal axis directions of the chemical shift tensor for the proton attached to the aromatic ring and the deviation from the molecular symmetry is obvious in the Fig.1 (a) and when the intermolecular contribution is subtracted then the principal directions conform better to the molecular symmetry requirements
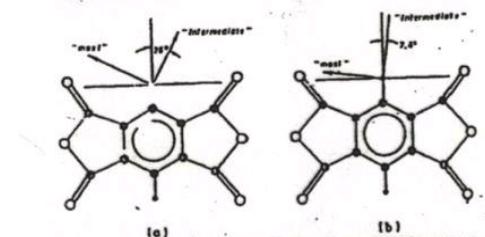

Fig.1.*The experimentally measured chemical shift tensor principal directions. Only molecular in-plane directions are shown with respect to the c-h bond disposition in the molecule (a) the in plane tensor principal directions are turned 27°away from bond direction. (b) when the intermolecular contributions have been subtracted. The third principal direction remains more or less parallel to the perpendicular to the molecular plane.*

3. PERSPECTIVES FOR CONSIDERATIONS OF THE SPECIMEN CONSEQUENTIALLY AS MATERIAL

The considerations which are also pertinent to consequences in magnetic material begin with this effort by which the intermolecular contributions were calculated by rigid lattice summation procedures.
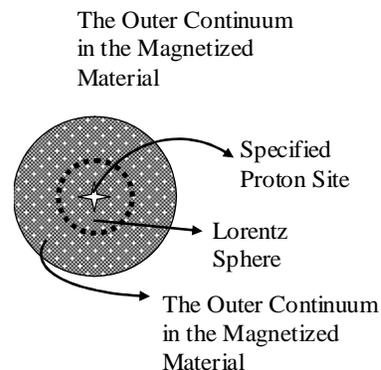

Fig.2. *The hypothetical division of the spherical sample for consideration from the perspectives of a material medium*
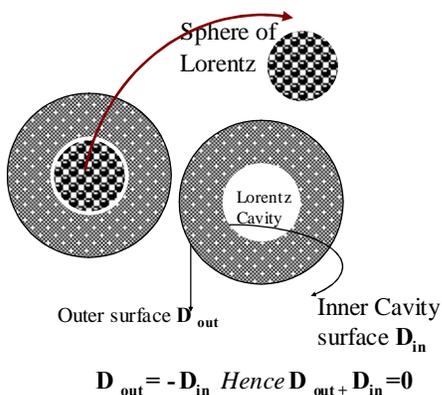
Fig.3. *Explaining the consequence of zero induced field inside the spherical specimen. The **D** with subscripts stand for the demagnetization factors of the corresponding boundary surfaces-inner & outer*

Fig.5 *Equation for calculation of Shielding (induced field) by discrete summation of the contributions from within the Lorentz sphere. Explicit expression in terms of the matrix indicating the required matrix multiplication steps for such calculation*

(a) Experimental determination of Shift tensors by HR PMR techniques in single crystalline solid state, require Spherically Shaped Specimen. The bulk susceptibility contributions to induced fields is zero inside spherically shaped specimen

(b) The above criterion requires that a semi micro **spherical volume element is carved out** around the site within the specimen and around the specified site this carved out region is a cavity which is called the **Lorentz Cavity**. Provided the Lorentz cavity is spherical and the outer specimen shape is also spherical, then the criterion 1 is valid.

(c) In actuality the carving out of a *cavity is only hypothetical* and the carved out portion contains the atoms/molecules at the lattice sites in this region as well. The distinction made by this hypothetical boundary is that all the materials outside the boundary is treated as a continuum. For matters of induced field contributions the materials inside the Lorentz sphere must be considered as making discrete contributions.

Fig.4. *(a) Spherical sample specimen (b) The Lorentz spherical cavity (c) & The Lorentz sphere in place as discrete region, within the extent of continuum.*

The equation 1 above is used to calculate the discrete sum over the lattice points within the Lorentz sphere. The Fig.5 (below equation 1) depicts the form of the above equation when the tensor elements are written explicitly in arrays.

The Sections 2 & 3 of the reference 2 contain the relevant discussion to explain well the preliminaries required to proceed towards the induced fields at points within in bulk of the material medium

4. THE ELLIPSOIDAL SEMI MICRO VOLUME ELEMENTS INSTEAD OF SPHERES FOR THE DISCRETE SUMMATION

The sections 4 & 5 of reference 2 contain the discussions for this aspect. It has been argued out that as much as there is reason for induced field to be zero within the magnetized spherical specimen, there is equally a valid argument as to why the induced fields within an ellipsoidal specimen also can be zero. However, this point of view has till now not been brought forward and it is in the context of intermolecular contributions in HR PMR in solids the ground could be laid for these reasons to be brought to stay. To gain better insight into the arguments and reasons for prevailing practices it became necessary to investigate the trends and final limiting values for convergence of the sum of contributions within the semi micro ellipsoidal volume elements. Such calculations indicate that even if during the summation the summed

values are different for spheres and ellipsoids after a critical value for the spherical radius and the major axis length value for the ellipsoids the limiting values are the same. Which means for the sphere the value being zero for cubic lattice for the ellipsoidal element also the sum goes to zero after a certain size of the ellipsoid and for several values of ellipticities indicating that ellipsoidal elements for all constants and types of lattices, can be replaced by a an effectively spherical volume element. That shape dependent factor which is supposed to be the value of such a summation over the entire set of lattice points in the macroscopic specimen seems inexplicable from this result that the discrete summation results in the same sum total value for induced field contribution within sphere and ellipsoids of any shape factor (ellipticity). Thus why does the demagnetization factor different? Only because outer shape and inner shapes are different? Even this can be argued that the inner contribution not being dependent upon shape can be replaced with any shape that the macroscopic specimen has and the dimensions being of semi micro ranges.

In such an event a certain trends indicated that the contributions from inside the semi micro volume element seem to dominate in value over the entire contribution from the remaining bulk of the specimen by several orders of magnitude that, the importance of macroscopic shape is relative and the demagnetization factor is only a multiplicative factor for the shape and when the multiplied value is less in magnitude than the semi micro volume element contribution, the dependences on shape factors may not be important for practical purposes for the induced field values at any particular site within the macroscopic specimen. Since this is all the arguments for diamagnetic specimen, similar calculations for paramagnetic and other magnetic materials seem warranted and in the presentation this point of view would be emphasized and highlighted.
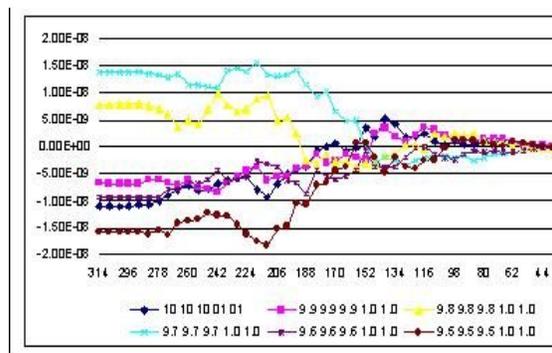

Fig.6 *A graphical display of the trends of summed values as a function of the radius in angstrom units from the proton site. Isotropic susceptibility is used. Cubic lattice with varying lattice constants indicated by the difference in the color of lines. Horizontal axis is increasing (from right to left) radius of sphere. All values on Y-axis are of the order of 10^{-8} or less. This order of magnitude seems to be taken as zero for practical considerations*

Thus from the above graphical plot it seems it is obvious

That the sum of contributions of induced field at the centre of a sphere is zero for typical variety of cubic lattice constants.

It is possible to compare the situation for inner sphere (semi micro) and the inner ellipsoid the remaining factors remaining the same. This is shown in **Fig.7.** The graph on top of Fig.7is the same as in Fig.6.The lower graphical plot is for the same cubic lattice parameters but the sphere radius is scaled with required ellipticity and each color represents an ellipticity. The lowest line is corresponding to cubic lattice and for all values of the radius the value is zero. Note that the Y-axis values are ranging from 10^{-8} to 10^{-3}. Hence what were appearing to be very different values in the top right all seem to be contained along the x-axis line for zero in the lower plot. This is precisely it was earlier remarked that all the values in the above are said to be practically zero. Thus a variation in ellipticity from 1.0 (sphere-the lowest dark blue line) to 1.25 the top green line on the x-axis when the radius measures from 48 to 186 angstroms there is significant increase in the sum with ellipticity. Beyond 186 there is a sharp variation in the summed values for all ellipticities. And, by 240 angstroms all the lines (for all ellipticities) have dropped to coincide with zero line. This

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establishes the observation that ellipsoid has the same sum total value as sphere for cubic lattices. The **Fig.8** to follow contains the results for summing for non-cubic lattice and the inner semi micro element for discrete summation is a sphere. The y-axis values range from 10^{-8} to 10^{-3} as in the previous case and the different lines for different lattice constants. This can be provided a comparison with an inner ellipsoid. In **Fig.8** the pink line has been made a special mention of at the caption. It is the lattice constant value corresponding to the pink colored line which is chosen and held fixed for the next plot as in **Fig.9**. Thus the Y-axis value for this pink line in **Fig.8** will be the convergent value for all the lines in the graph of **Fig.9** as on the Y-axis.
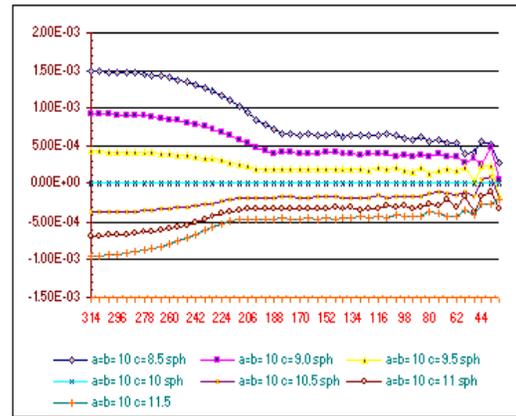

Fig.8. *INNER Element is Spherical and Convergence trends are indicated. The Pink Line corresponds to the case of a=b=10 c=9.0 Spherical inner element radius increases from 44 to 314 Aº. As the 'C' axis lattice constant value changes from 8.5 t0 11.5 Aº, The convergence value gradually decreases [through 'zero' for cubic case] to negative.-Ref.5*
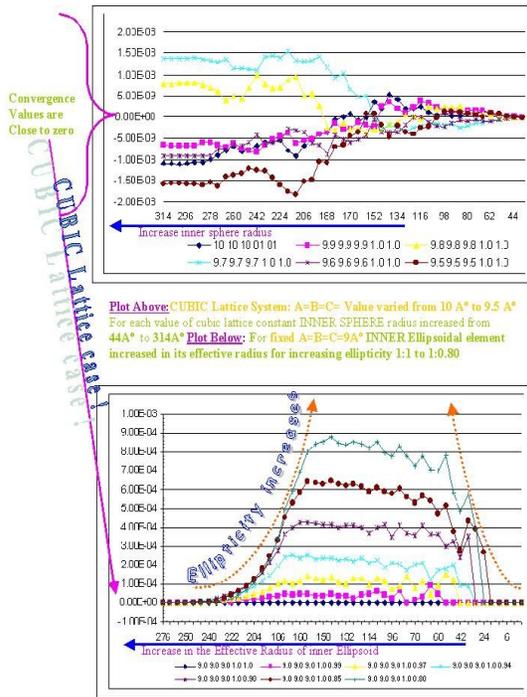

Fig.7. *(above) the same as **Fig.6** for inner sphere. (below)ellipsoidal inner volume element. Below the different colors correspond to varying ellipticity (dark-blue line ε=1.0; green line ε=1.25. More discussion in the text above. Also see Ref. 4*

The Plots below corresponds to the CASE of Pink Line in the previous page. The NON CUBIC Lattice parameter value are constant through out and only the ellipticity values are increased for Prolate (bottom) and Oblate (top) ellipsoidal cases. Since a=b=9Aº and c=10Aº all through it is clearly found that they all converge to the same value but in the region of effective radius 44 to 175 Aº the deviations increase as the ellipticity increases. As it would be evidenced in the next pages, these convergence values are the same for Spherical cases of inner volume element but the trends in the regions before convergence are different. Thus it seems possible to conclude that the Convergence values for Lorentz Ellipsoids do not depend on the ellipticity of the inner volume elements and they are as good as Spheres !
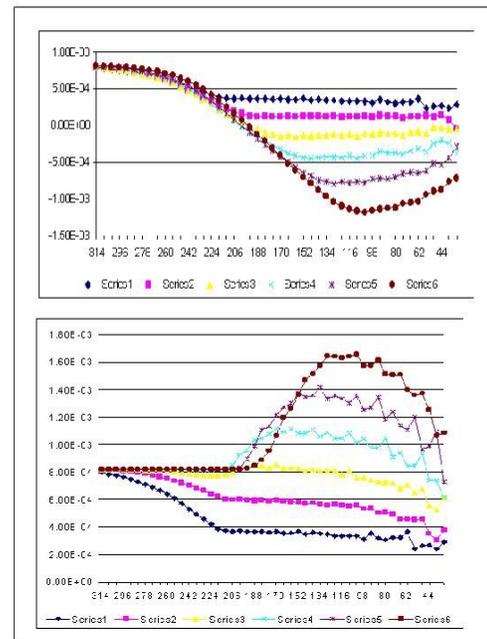

Fig.9. *Ellipsoidal inner volume element. varying ellipticity. All the lines converge to the same value as the value for inner sphere in Fig.8 (pink line for a=b=c=10)-Ref.6*

5. CONCLUDING REMARK

In this full paper preceding the presentation, it has been the effort to systematically document the salient results of the calculations which are taking the course from molecule to material. The ellipsoidal shapes are the ones which have the homogeneous magnetization for homogeneous susceptibility. Hence the case of inhomogeneity is yet to be discussed. More over when it is of importance to consider point by point summed contribution within the inner sphere, it must be obvious that even in the case of the favourable zero induced filed cases, the sum total of the discrete summation varies significantly from one point to other. If this summed value is significant compared to the bulk continuum contribution, then the assertion that the magnetization is homogeneous for spherical & ellipsoidal specimen would have to be reconsidered and ensure that it is only an average[7] picture which is being refereed which includes averaging the discrete summing of point to point. This being so for diamagnetic specimen what would be the criteria set for magnetic materials where the internal fields are large? These points would be enumerated while presenting the material. The references cited here are mainly for the documentations made for the calculations made by this author. More references of much earlier efforts to handle internal field values at specific sites would also be referred and yet another version of this manuscript would become due after the presentation. The computer programs used by this author (written by the author himself in FORTRAN) are posted[8] in the web pages. More over a simpler summation procedure could be evolved for the calculation of the shape dependent demagnetization factor. This is available as described in a manuscript posted in Ref.9

REFRENCES:

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