Magnetized Materials: Contributions Inside Lorentz Ellipsoids

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Abstract: The Lorentz Sphere is a hypothetical spherical volume element, inevitably, invoked to take into account the demagnetizing effects (in the case of diamagnetic materials) while describing the contributions to the induced fields at a point inside magnetized materials. Till now, there have not been any compelling necessity to know the actual magnitudes of the contributions from within this sphere and, how exactly to demarcate this spherical part of the material by a concrete boundary, within the bulk material of the specimen. Not much emphasis could be given in the discussions on the significance of the Lorentz sphere, except that, it be defined as a semi-micro volume element. This situation seems to have been brought to prominence by the discussions requiring interpretation of the experimental results by the technique of Solid State High Resolution Proton Magnetic Resonance (HR PMR) in single crystals of organic molecules. It is this perspective which is being discussed in this paper.

1.Introduction

The widths of the Nuclear Magnetic Resonance (NMR) spectral lines in solids are large (can be up to 100 KHz) compared to the line widths in the NMR spectra (0.2Hz) obtained in liquid state [1]. The nuclear Shielding differences, to be measured as Proton Chemical Shifts, can be several orders of magnitude smaller than the relatively large widths of the spectral lines. Such large line widths are inherent due to the nuclear spin-spin (proton-proton magnetic dipolar) interactions in the solid-state PMR. In the liquid state because of the rapid tumbling motions of the molecules, the dipolar interaction averages out to zero and what is measurable experimentally as line width are merely the in-homogeneities of the externally applied static fields. Line-narrowing multiple-pulse NMR techniques are used in the solid state PMR, to appropriately and selectively average out the nuclear

magnetic dipole-dipole interactions for the determination of the **Shielding Tensor** of protons in single crystals of organic molecules [2]. The Shielding Tensor parameters thus obtained are useful in understanding the trends of the induced field contributions at the proton site due to electron circulations induced in the molecules in which the protons remain bonded while the molecules themselves occupy the symmetry related lattice sites. But to arrive at such intra-molecular contributions, it is necessary to recognize the criticality of the shapes of the specimens used in the measurements and the discrete nature of the contributions from the adjacent molecules. The induced field contributions at the proton site due to the bulk susceptibility would be specimen-shape dependent; while, the intermolecular contributions from the adjacent molecules would be reflecting the symmetry of the lattice with reference to the proton locations. All these various factors contribute essentially by the same field-inducing

mechanism and hence these contributions cannot be disentangled on the basis of mechanistic differences in the basic interactions. While arriving at the values for the intra-molecular shielding differences from the measurements made on macroscopic specimens, it becomes necessary to make measurements on specimens of well-specified shapes to quantitatively account for the macroscopic shape dependent contributions at the nuclear site. If this is accomplished, then the intermolecular contributions from the adjacent molecules have to be accounted for before arriving at the only intra-molecular contributions so that these could be interpreted for the variations in induced field attributable to the molecular structure and bonding.

Thus it became necessary to find out methods for calculating the contributions due to the adjacent molecules by a suitable discrete summation procedure. Such an effort could clearly establish that several of the discrepancies encountered till then (while interpreting proton shielding tensors in molecular systems), were mainly due to the fact that the discrete contributions from the other molecules were not properly taken into account even if the bulk susceptibility contributions from the farther continuum were reasonably taken into account.

2. Sample Shapes for HR PMR Studies

Since, the induced field contributions due to the bulk susceptibility at a proton site, and at any point within the specimen, is zero for a spherical macroscopic shape of the specimen; the proton HR PMR measurements are made with spherically shaped samples.

As an aside, it is necessary to mention at this point, that making spherically shaped specimens (from the shapes of the specimen with the shapes resulting from the crystal growing processes and the inherent morphological determining factors) is not a simple task, and hence is not a matter of routine. This restricts the utility of this technique which otherwise would be a method which can provide much greater structural and bonding details becoming a potential technique for the wealth of information obtainable. In fact, much of the effort to be described here

stands to be justified, first and foremost, for the possibility that the constraint on shape may become less stringent.

As stated above the spherical shape (of the specimen) has the preferential advantage, and, this is explainable on the following basis: the demagnetization factors are defined for the specific shape of the surface that can be depicted to be enclosing the material continuum with homogeneous magnetization. If a cavity is carved out "within" such a continuum, and, if the inner cavity shape is the same as the outer macroscopic shape, then the inner cavity can be assigned the same demagnetization factor value as for the outer surface but with an opposite sign. This is because of the fact that the inner surface encloses cavity without any material filling. In most of such discussions assigning a default demagnetization factor value depending only on the shape (and not on the size) was a matter of simple symmetry arguments [3] for the spherical shape. Thus, if the outer shape of the specimen is sphere (*with an assigned demagnetization factor D^{out}*) and, if a hypothetical spherical cavity inside is carved out (for which *the demagnetization factor D^{in} is equal to D^{out} but opposite in sign*) around the specific site, then the induced field would be zero. This is so because the demagnetization factor ($D^{out} + D^{in}$) occurs as a shape dependent pre-multiplying factor in the expression for induced fields within the specimen [4]. With these considerations the HR PMR experiments on single crystalline solids were carried out on spherically shaped specimens. Further, there was the prevailing practice of using spherical sample tubes for the HR PMR studies in solution and, thus, it was possible to obtain reliable corrections [4] for bulk susceptibility contributions in solutions. Because of these solution-state results, the following fact was not apparent to researchers, that, in solids the discrete contributions from within the sphere of Lorentz have to be explicitly calculated and subtracted from the experimental shielding tensor values to get the only molecular contributions evaluated [5]. This is a specific aspect, which makes this topic relevant exclusively for the solid state physicists in the context of studies on dielectric and magnetized materials. Several

efforts to account for the line-shapes and line widths of PMR lines have been documented in the literature [6]. In spite of all the efforts, it is only the HR PMR studies on single crystalline samples, which establishes the significance of contributions from within the Lorentz sphere. While pursuing the efforts to calculate the induced field contributions from the dipoles located within the Lorentz sphere, the following question had to be answered. *How far from the proton site should the dipoles be considered;* to be convinced that the induced filed contributions from **"Lorentz sphere"** have been taken into account completely; *and, none of the dipoles, which can be considered as part of the continuum, have to be included* in the discrete summation? A natural consequence of trying to calculate the contribution from within a sphere was that at an appropriate radius from the specified site, the summed up contributions reaches a limiting value, and increasing the radius beyond that value does not contribute to the sum significantly Fig.1.
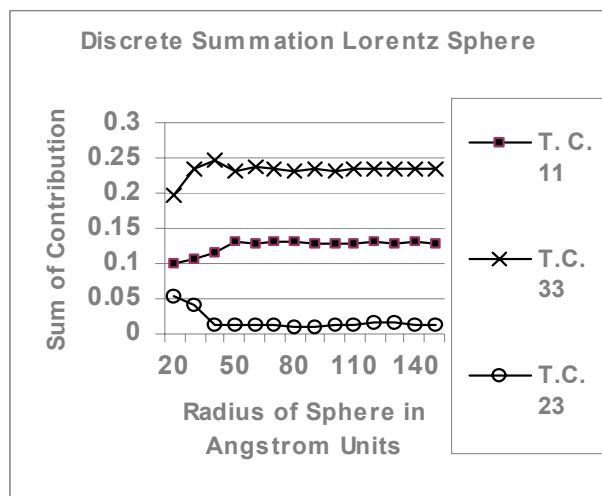
Fig.1 *The graphical plot of the sum of the contributions from within Lorentz sphere as a function of the radius of the sphere. The sum reaches a Limiting Value at around 50Aº. These are values reported in a M.Sc., Project (1990) submitted to N.E.H. University. T.C. stands for (shielding) Tensor Component*

Thus, there was a clear delineation possible for the Lorentz Sphere to be demarcated from the remaining bulk as depicted in Fig.2. This value of 50 Aº would vary from system to system but the fact remains that the discrete summation around the specified lattice point can unambiguosly indicate a definite numerical value for the radius of the Lorentz sphere for demarcation. This makes the Lorentz sphere a precisely defined sphere with a surface boundary line unlike the way it is to be left undefined as to the numerical values for the construction of a Lorentz sphere.
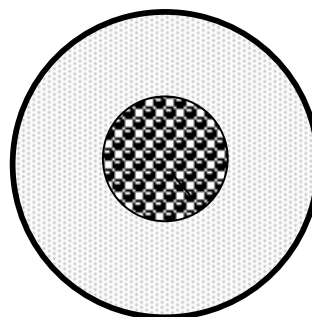
Fig.2. *The demarcation (~50Aº radius) of the inner Lorentz Sphere from the outer macroscopic continuum. The Lorentz Sphere is supposed to be semi-micro and the above depiction is an exaggeration for the size of the inner sphere.*

3. Calculations by Discrete Summation

As depicted in Fig.2 the molecules may be considered as located in lattice points within the Lorentz sphere and, by definition, this being of semi micro dimensions, the discreteness should be obvious as seen in the hypothetical arrangement in this figure. The size of the depicted molecules inside the Lorentz are on the scales of a view through a microscope as compared to what is depicted in the continuum of the material. It is the same molecule (chemical unit), which makes up the inner sphere as well as the outer continuum since it is a single crystal sphere of the given organic molecule. Each molecule can be assigned its due molecular susceptibility and in presence of an external magnetic field, and all of these individual molecular susceptibilities induce magnetic moments respectively at appropriate origin within the molecules. Then the magnetic moments approximated as point dipoles and at any specified proton site in a molecule at the center, the contributions to induced fields from the point dipoles of the other molecules can be calculated using a magnetic dipole model. Defining the susceptibility Tensor of a molecule by χ_i and the distance from the dipole origin to the specific proton as R_i with the corresponding distance vector being $\mathbf{R_i}$, then Equation 1 can be used for the

calculation of the contribution from the molecule 'i' and the summation would be over the index 'i' for all the other molecules. In the equation $[RR]_i$ is the dyadic formed from the Vector R_i.

$$\sigma = [1/R^3_i - (3 \cdot [RR]_i / R^5_i)] \cdot X_i \qquad (1)$$

A computer program is used to transform the susceptibity tensors from the respective principal axes system of the individual molecules into a common crystal axes system and the summation is carried out to result in the total Shielding tensor contribution in the crystal axes system from all the molecules. For each of the moment from which the contribution is calculated, [the 'i'th moment] dropping the index 'i', the illustration in Fig.3 indicates the details.

$$\sigma_T = \frac{\chi_T}{R^3} - \frac{3 \cdot [R_v R_v]_T \, \chi_T}{R^5}$$

σ_T = Shielding Tensor R_v = Radial vector from Nuclear Site to the point dipole

χ_T = Susceptibility Tensor $|R_v|$ = R Radial vector length

$R_v = i_u \, x + j_u \, y + k_u \, z$

$[R_v R_v]_T$ = Dyadic = $[x \ y \ z]\begin{bmatrix} x \\ y \\ z \end{bmatrix}$

$$\begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} = \frac{\begin{bmatrix} \chi_{xx} & \chi_{xy} & \chi_{xz} \\ \chi_{yx} & \chi_{yy} & \chi_{yz} \\ \chi_{zx} & \chi_{zy} & \chi_{zz} \end{bmatrix}}{R^3} - 3 \cdot \frac{\begin{bmatrix} xx & xy & xz \\ yx & yy & yz \\ zx & zy & zz \end{bmatrix}\begin{bmatrix} \chi_{xx} & \chi_{xy} & \chi_{xz} \\ \chi_{yx} & \chi_{yy} & \chi_{yz} \\ \chi_{zx} & \chi_{zy} & \chi_{zz} \end{bmatrix}}{R^5}$$
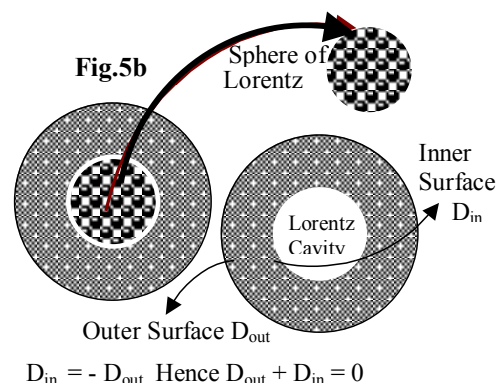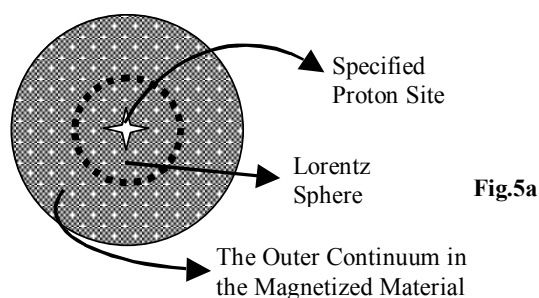
Fig.3. *Equation for calculation of Shielding (induced field) by discrete summation of the contributions from within the Lorentz sphere. Explicit expression in terms of the matrix indicating the required matrix multiplication steps for such calculation.*

In the Fig.4 below is a depiction of a typical molecule, which can be considered as placed in a lattice site.
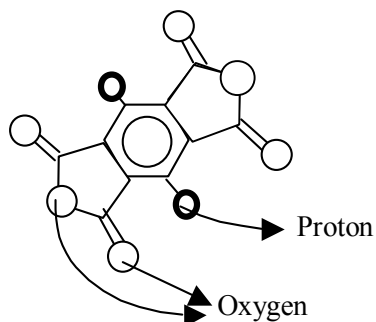
Fig.4. *A Typical Organic Molecule, which can be located in a Lattice Site in the Molecular Single Crystal. This molecule has a center of Inversion.*

This is a typical molecule, which has been studied by the Multiple Pulse HR PMR techniques in Solid State [7]. In this particular case, the molecule is planar-elongated shaped (approximate D_{2h} symmetry) with dimensions 6Aº x 3Aº in a crystal with unit cell dimensions of 10.79Aº x 10.79Aº x 7.41Aº in the P4$_2$/n space group and 4 molecules per unit cell and the Lorentz sphere could be conveniently estimated to be about 100Aº in radius. The summation beyond this radius does not add to the total contribution significantly any further, thus establishing a trend towards a converging value [7]. Suffices here to mention the result that this convergent Tensor value when subtracted from the experimentally determined Shielding Tensor value yields the tensor which truly reflects the only molecular contribution by conforming to all the symmetry requirements as determined by the molecular point group symmetry. Since this subtraction leads to such convincing result, the hypothetical Lorentz sphere enclosing the central molecule, becomes well defined Fig 5(a) &5(b).

Fig.5a

Specified Proton Site

Lorentz Sphere

The Outer Continuum in the Magnetized Material

Fig.5b

Sphere of Lorentz

Inner Surface D_{in}

Lorentz Cavity

Outer Surface D_{out}

$D_{in} = - D_{out}$ Hence $D_{out} + D_{in} = 0$

Fig.5 The *various demarcations required, in an Organic Molecular Single Crystalline Spherical specimen, to Calculate the Contributions to the induced Fields at the specified site.* **D** $_{out/in}$ *values stand for the corresponding Demagnetization Factors*

4. Excursions into the Necessity for Spherical Shape

As can be seen, in Fig.6 [a]&[b], different combinations of the sets of external macroscopic shape and inner semi micro volume elements can be envisaged. The requirement of a spherical shape for the specimen were stipulated for bulk susceptibility corrections only because conventionally the hypothetical inner volume element was considered as spherical since it is most conveniently envisaged shape with high symmetry, so that the shape dependent demagnetization factor can be inferred by simple arguments based on the spherical symmetry [3]. But as long as the macroscopic shape results in homogeneously magnetized specimen, it is only required that the inner volume element be of similar [proportionately same] shape
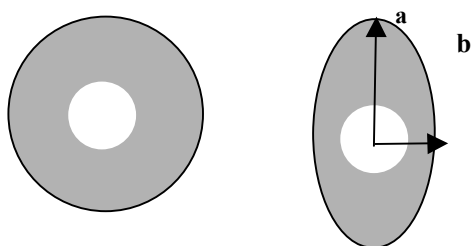
Outer a/b=1	outer a/b=0.25
Demagf=0.33	**D**emagf=0.708
inner a/b=1	inner a/b=1
Demagf=-0.33	**D**emagf=-0.33
0.33-0.33=0	*0.708-0.33=0.378*

Conventional combinations of shapes
Fig.6 [a]
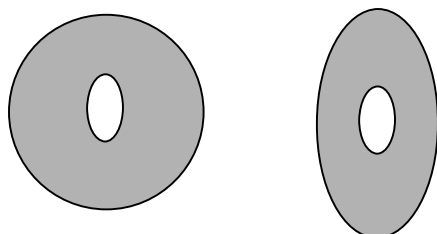
Current propositions of combinations

Outer a/b=1	outer a/b=0.25
Demagf=0.33	**D**emagf=0.708
inner a/b=0.25	inner a/b=0.25
Demagf=-0.708	**D**emagf=-0.708
0.33-0.708=-0.378	**0.708-0.708=0**

Fig.6 [b]

of a reduced dimension, for the induced field at the central point to be zero. The above statement can be further substantiated by the fact that the demagnetization factors available as tabulated values do not depend upon the real size of the specimen, but depend only on the relative ratios of the shape determining parameters, in the most general case of considered ellipsoidal shapes it is merely the elasticity that determines the demagnetization factor value and not the actual size in terms of absolute length units. Thus the possibility of outer ellipsoids with proportionately same inner hypothetical ellipsoidal cavity should result in the same conclusions, as it happens to be for spherically shaped specimen with inner hypothetical spherical Lorentz cavity. Thus for the induced field to be zero within the magnetized material medium, if the magnetization is homogeneous, then, around the specified site, it seems, it is necessary to carve out a cavity, which is a semi micro volume element, and its shape being proportionately the same (to have the same value for the demagnetization factor but opposite in sign to that of the outer surface) as the macroscopic specimen (outer) shape. This has been illustrated in Fig.6.

5. Further Insights for Solid State NMR

It is important to note that all these revelations about the Lorentz sphere comes about because of the fact that the angular dependence of the nuclear shielding is smaller in magnitude for protons compared to other nuclear systems for which similar magnetic resonance measurements are made. This is because of the fact that the differences in induced fields at the nuclear site depend on the number of electrons surrounding those nuclei. This is reflected even in the ranges of isotropic chemical shift (shielding) values for the various nuclei. For protons the range is about 10ppm (*for non-hydrogen bonded protons*). On the other hand, for the ^{13}C nuclei the range is about 250ppm for similar variations in the bonding and electronic structures in the molecules. Such orders of magnitude smaller values for protons compared to other nuclei amenable for NMR studies is mainly because the Hydrogen atom has only a

single electron around its nucleus and for a positive Hydrogen ion, there are no electrons in the outer atomic orbits. Thus for the case of protons the Shielding tensor anisotropies have relatively small values of about 6ppm whereas the anisotropy values can be orders of magnitude large for other nuclei. One can consider the magnitude of typical molecular diamagnetic susceptibility values and a point dipole generated in this diamagnetic molecule at its center in presence of external magnetic fields. At the usual intermolecular distances for the nearest neighbors in the molecular single crystals, the differences in induced field contributions and their angular dependences due to the molecular susceptibility tensor values can be comparable in magnitudes to the variations in the intramolecular shielding anisotropy. Whereas in the same molecular systems, the other nuclei present have shielding anisotropy values much larger but the intermolecular induced field contributions would be the same. All these are the considerations for the experiments and the results reported in the paper [7], which is the first instance, when this significance, as explained above, of intermolecular contributions could dramatically set the experimental results, disposed for an interpretation, appealing in terms of the interactions conforming to the demands of molecular symmetry. Since the solid state holds out a rigid lattice structure, the angular variations become tractable in single crystals.

When so much is said, all with the presumed spherical shape for the hypothetical Lorentz volume element, then the practical ordeal of having to make spherical single crystal specimen and to orient them for tractable angular dependences in terms of the known crystal structures makes the experimentalist look for possibilities of relaxing the stringent requirement for a spherically shaped specimen. Then with the propositions as in Fig 5 of the previous sections, it is necessary to find out the kind of convergence characteristics that would result for a summation within an ellipsoidal volume element instead of a summation within a Lorentz sphere. In fact results as reported in Fig.1 for convergence characteristics for a discrete lattice summation can be obtained for summations

within the "Lorentz ellipsoids" [8]. Equation (1) used for summation within spheres can be used also for summations within ellipsoids. This is because enclosing the same magnetic dipole among the neighbors within a sphere or within an ellipsoid does not alter the form of interaction of that individual point dipole and its induced field contribution at the specified nuclear site. The independence of every individual magnetic point dipoles from the neighboring dipoles must be ensured, since the dipole moment under consideration is the characteristic property of the molecule and the corresponding molecular magnetic susceptibility is not changed by the presence of neighboring molecules in a crystal lattice. Hence a computer program to take into consideration all the molecular magnetic point dipoles within a specified shape of the surface enclosing them, would give the result for a spherical volume or an ellipsoidal volume by setting appropriate boundary conditions with the flexibility to vary the size and the shape determining parameters. Following the criteria as above the convergence characteristics can be calculated for discrete summations in semi micro volume elements. These results thus obtained surprisingly indicate [9] that, even though the trends of the sums obtained for the ellipsoids (with a specified ellipticity) vary with the size of the ellipsoids around the central proton site, after a certain size the summation converged to the **same total value** as for the Lorentz sphere. Thus it seems that, when the ellipsoidal specimen shapes of Fig. 6a and 6b are considered, the discrete summation near the site would result in the same value for the intermolecular contribution for the two cases in spite of the fact that in Fig 6a inner shape is the conventional Lorentz sphere where as in Fig. 6b the inner volume element is a Lorentz ellipsoid. Since we have inner and outer shape as ellipsoid, shape dependent induced field would be zero. Hence, subtracting this intermolecular value (same for both the sphere and ellipsoid) from the experimental value should result in intramolecular value for the shielding tensor even if the shape of the macroscopic specimen is ellipsoidal. Besides the relevance of such results for the solid state physics, the prime

concern is whether it is possible to circumvent the necessity of having to practically make good spheres out of every single crystal which is to be studied by multiple-pulse line-narrowing technique for HR PMR results in solid state. This remains to be answered conclusively in spite of these investigations on Lorentz spheres and ellipsoids.

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9. http://geocities.com/saravamudhan1944/eenc_ampere_lille.html

Concluding remarks of referee for "Indian Journal of Physics" on this paper quoted below:

"Finally, I find the article interesting. It tries to deliver an important message pertaining to the very fundamental aspect in material studies The article should be published after modifying the same as per the above suggestions" {*Suggestions not reproduced here*}