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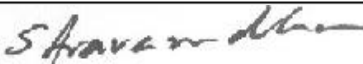
Title of Paper **Line Shapes in Magnetic Resonance and the Average Static Magnetic Field in the Medium : The Role of Discreteness and Continuum within the Material**

**NOTE: alteration in title: "...Average Static Magnetic Field in the Medium ..."**

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## ABSTRACT

*The magnetic material properties can be measured by taking into account the influence of the given sample of material, on the field distributions surrounding the specimen in regions external to the sample. In such a case it may be possible to consider a typical average value for the static field within the magnetized bulk of the material, to stand for the field at any of the given site within the medium. This presumed uniform value would suffice for bulk properties provided the averaging procedure is based on a proper rationale to separately account for the contributions from 1) the near-neighbor magnetic moments and 2) the moments in the remaining bulk of the material. When the structure of the magnetic material is to be inferred by the induced field distributions, then it is necessary to experimentally observe the actual magnetic field value at every one of the sites within the sample. Magnetic resonance measurements can probe this field distribution within the material medium at the nuclear sites over the entire extent of the sample. The HR PMR studies in [diamagnetic solid] single crystal specimen of organic molecules has provided the possibility to enquire into the properties related to bulk of the material starting from the results obtained in the medium for the molecular properties constituting the solids. Thus an enquiry as to whether the magnetization is homogeneous or not can be ascertained from the spectral features manifest; being mainly shift of (positions of) spectral lines, or there are line shape and width changes also occurring in the observed spectra. As it is well documented, inhomogeneous magnetization of homogeneous materials can be accounted for by the shape dependent bulk susceptibility contributions to induced fields within the material medium. In the light of the demagnetization effects and NMR Chemical shifts known till now, the possibility of a **conceptual clarification on the role of discreteness and continuum within the material medium is being pointed out in this paper.***

## INTRODUCTION

If the near-neighbor contributions around the site can be separated, then the bulk susceptibility effects can result in homogeneous magnetization within a magnetized material only when the macroscopic specimen shape is a sphere or an ellipsoid (an ellipsoid of revolution is the shape usually encountered in the discussions). Quantitative measurement of the chemical shifts would thus require that the bulk susceptibility effects be taken into account quantitatively to obtain the chemical shifts of nuclei in Nuclear Magnetic Resonance experiments [NMR]. The chemical shifts observed originate from changes in the electronic charge circulations within a molecule in presence of an externally applied large magnetic field (typically 7-14 Tesla in current NMR spectrometer systems). The presence of bulk susceptibility effects (continuum regime) and the intra molecular contributions (discrete regime) to induced fields seem to be of particular interest [1] in the case of High Resolution Proton Magnetic Resonance studies on diamagnetic single crystals of organic molecules. This interesting aspect thus mentioned is the perspective of molecules to materials [2]. This perspective concerns itself with trying to account for the experimentally measured chemical shift tensor parameters in terms of the break ups attributable to *a) the bulk susceptibility (contribution from the bulk, farther continuum), b) inter-molecular (contributions from discrete near neighbors) and c) the intra molecular contribution.*

Invariably it is the field distribution due to the presence of a magnetic dipole which accounts for the induced field at a neighboring or farther site. If point dipole approximation can be held valid, then a dipole moment can be attributable at convenient (as per the approximation)

locations and the cumulative value at any given site due to dipoles at all other points can be calculated. However the equation  $\{\chi_i \cdot (1-3 \cdot \cos^2 \theta_i)\} / (R_i)^3$  - [Eq.1] for calculating the dipolar (*point dipole*) field distribution contains the distance parameter to the site from the point dipole occurring in the denominator of the equation. Thus while estimating the fields using this equation it becomes necessary to set up the equations in such a way that in the denominator the distance parameter is never set to zero. This makes it necessary to describe a sphere around the considered site (every one of all the sites in turn) which includes the region where the point dipole approximation cannot be held valid [Fig.1]. The region [the **Inner Volume Element I.V.E.**] is considered by an explicit discrete summation to conveniently leave out the coordinates of the point which results in zero value in the denominator. And, the region outside this (semi micro) sphere can be treated conveniently as a continuum for evaluating the induced field contributions and it has been found that even for the simplest case of homogeneous magnetization, the evaluations are possible only with complicated functions and the corresponding integration of complicated functions. This restricted the sample shapes to be spherical and regular ellipsoids of revolution. Because the evaluations require certain type of equations to be setup, instead of starting with magnetic susceptibility, it becomes necessary to start out with charge circulations, the current densities from the circulating charge densities thus resulting in associated distributed magnetic moments expressed in terms of infinitesimal quantities (and the infinitesimal magnetic moments there of) to integrate over appropriate variables for the induced fields. Handling arbitrary cases of inhomogeneous situations could be only for certain specified regular shapes; no generalized approach was tangible which retains the visualization of the physical picture of field distribution around the magnetic point dipole. ***This generalized situation is where the line width and line shape variations become predominant in NMR as described in the Fig. 2.***

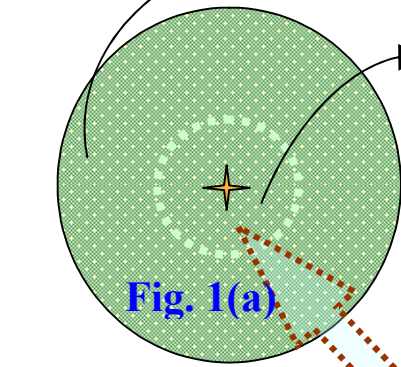
Since the NMR spectral features are determined by the induced field values at every one of the resonating nuclei which is in a way distributed all over the macroscopic extent of the sample, it is essential to first of all to determine whether, if an IVE is described around every one of the nuclear sites, the intermolecular contribution would be the same at every site. The first convincing criteria in this regard is in typical cases within a radius of  $100 \text{ \AA}$  for the IVE, the sum total converges to such a sum total value that the contribution from further outer shells do not add anything significant. And since the macroscopic specimens typically can be of the order of 5mm, conveniently almost around every resonating nuclear site the same IVE can be carved out in the single crystal. This means whether the magnetization is homogeneous or not, as far as the IVE contribution of the intermolecular nature would be the same and to this extent all the nuclear spins would be resonant at the same field value including the intermolecular contribution (3). Thus at this field value a single sharp line can be obtained as indicated also in Fig.2. Now what is left out in this description is that the IVE can be now considered as a cavity of this radius size of about  $100 \text{ \AA}$ . And this cavity occurs at points distributed all over the sample (the single crystal specimen) as before. But if the induced field due to the bulk susceptibility is inhomogeneous due the specimen shape, then, the induced field values at the center of the cavity due to the continuum outside the IVE would not be the same unlike the intermolecular contributions. Hence this part of it would be resulting in a line shape change and line width variations.

**'Continuum'**: Bulk region of the magnetized material. Concerns bulk susceptibility demagnetization effects.  $\sigma_{bulk}$

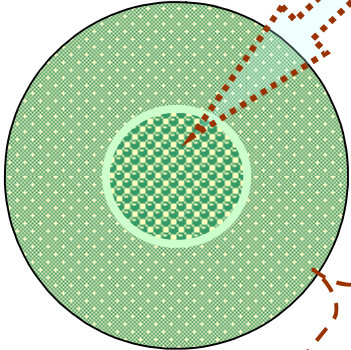
**FIG. 1** Magnetized Material medium and the relevant regional demarcations

Location of the site: molecule with specified proton. Concerns: **'intra'** molecular contributions.  $\sigma_{intra}$

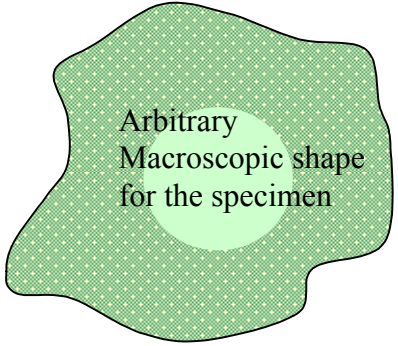
Sphere of 'Lorentz'. Inner Volume Element [I.V.E] of spherical shape. Near-neighbor, 'discrete' region; Concerns **'inter'** molecular contributions.  $\sigma_{inter}$



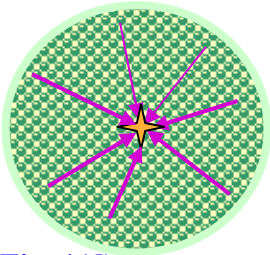
**Fig. 1(a)**



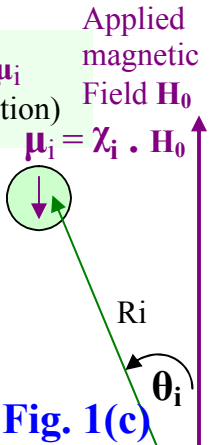
**Fig. 1(b)**



Smallest unit magnetic moment  $\mu_i$  from within IVE (enlarged depiction)



**Fig. 1(d)**



**Fig. 1(c)**

Lorentz Cavity / Inner Volume Elemental spherical Cavity and the spherical macroscopic specimen shape

Outer surface:  $D_{out}$

Inner Surface:  $D_{in}$

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

$\sigma = \sum \sigma_i = \sum \{ \chi_i \cdot (1 - 3 \cdot \cos^2 \theta_i) \} / (R_i)^3$

$\{ \chi_i \cdot (1 - 3 \cdot \cos^2 \theta_i) \} / (R_i)^3$

## Macroscopic shape

1. Sphere: Magnetization (zero) within specimen homogeneous
2. Ellipsoids: Magnetization homogeneous; not same value as for sphere
3. Other shapes: Magnetization Inhomogeneous

## NMR spectral feature

Narrow line

Narrow line: position shifted from that of sphere

Broadened Line shapes

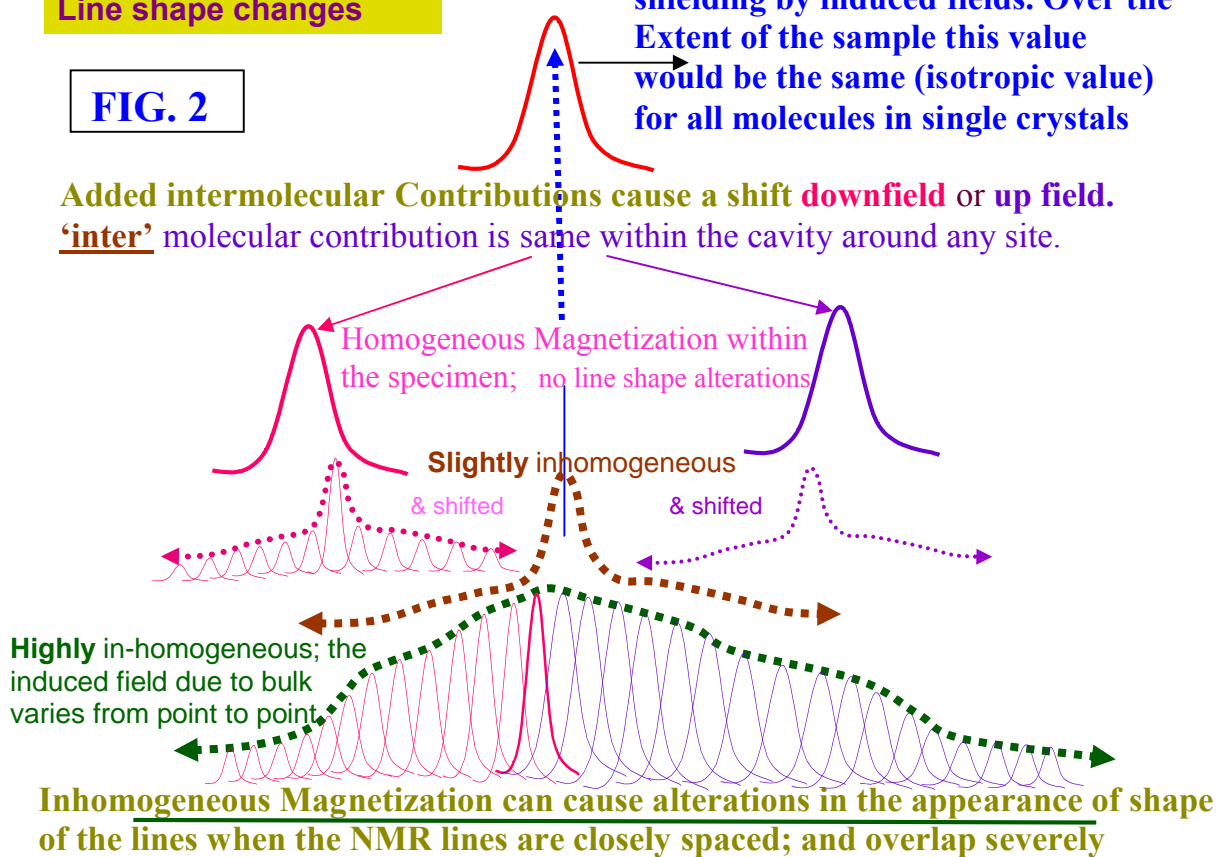
**Task:** Calculate point by point values of the induced field due to bulk susceptibility within the material medium. At each value place an NMR line when there is a proton located. Calculate the overall shape.

Line (position) shifts & Line shape changes

FIG. 2

NMR Line for only 'intra molecular' shielding by induced fields. Over the Extent of the sample this value would be the same (isotropic value) for all molecules in single crystals

Added intermolecular Contributions cause a shift downfield or up field. 'inter' molecular contribution is same within the cavity around any site.



For small in homogeneities the sharp line observed as in homogeneous case might be discernible. But if the in-homogeneities are large the intermolecular value (same) at every site would be added with a field characteristic of the location of that site. This can result in a broadened line with shapes which are not of the known descriptions. This consequence in

general has not been tractable for simulation and calculations particularly in cases of strong internal fields.

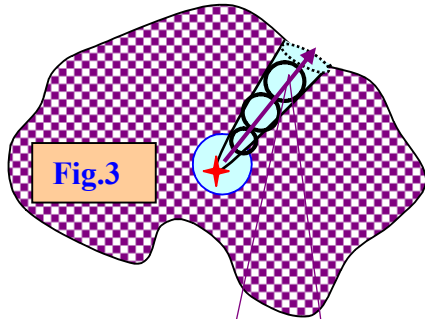
## ON BULK SUSCEPTIBILITY EFFECTS AND DEMAGNETIZATION FACTORS

Estimating the intermolecular contributions to the induced field at a site in a single crystal can be accomplished by appropriately obtaining a molecular susceptibility value and using the equation for dipolar field distribution under the point dipole approximation. As pointed out in the previous section, the evaluation of the demagnetization (factors) effects due the bulk continuum in the medium requires setting up equations which involves complicated functions and the corresponding evaluation of integrals from the considerations on the contributions from infinitely small volume elements of the medium. The restrictions resulting from these factors could be overcome to a large extent by evolving an alternate mathematical procedure to reproduce the hitherto tabulated demagnetization factors. The simplicity of this procedure has been described in an earlier occasion [4]. For the present topic under discussion the simplicity of the alternate procedure can be summarized as follows.

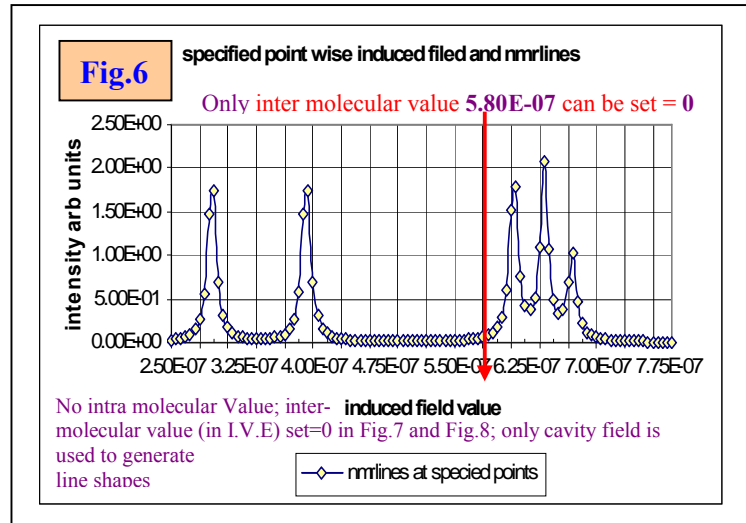
Consider a single crystal specimen of arbitrarily macroscopic shape [Fig.3]. A spherical V.E is carved out which is effectively a cavity since the contributions within are taken into account by discrete summation independently. This cavity can be placed around any other point within the medium and the contributions within the cavity at the center would be the same. A conical element is considered which is characterized by specific polar coordinate values for the axial radial vector to the base of the cone. This cone is one of the cones carved out at equal intervals of a specified solid angle interval  $\Delta\Omega$ . The conical V.E thus described account for the entire material of the specimen. Each sphere within this cone are placed in such a way that their radius 'r' and distance 'R' from origin at site, bear a constant ratio placed along the axis of the cone. If this ratio has a fixed value, the number of spheres can be calculated which can be closely placed along the distance from the surface of the Cavity (I.V.E) to the surface of the macroscopic specimen. And, each one of such spheres would contribute the same value of induced field at the center of the I.V.E. Thus estimating the contribution from the material along the conical VE is simple to evaluate. From every one of such cone with its specified polar coordinates the value is calculated to obtain the sum total contribution (4). This procedure is simple enough to be programmed for calculations. The contribution from any specific part of the specimen at any specified site becomes a simple calculation to evaluate. If this method can be used for evaluating the induced fields at various points sampled conveniently within the sample, then a sorting out can be made as to the values of induced fields and all the site coordinates where this field occurs. A plot of induced field versus the (number of incidences) frequency of occurrence in the table of sampled sites, would result in the required line shape obtainable for the specimen. Using the method as illustrated from Fig. 3, a calculation of the induced field values has been possible along an axial line for a Spindle (TOP) shape (Fig.4 (a)) and cylindrical shape (Fig.4 (b)) of the specimen as depicted in the graphical figure Fig. 5. Corresponding NMR lines are in Fig.6.

Thus using the Summation Procedure induced fields within specimen of TOP (Spindle) shape and Cylindrical shape could be calculated at **various points** and the trends of the inhomogeneous distribution of induced fields could be ascertained. These are EXACT calculations for the induced fields.



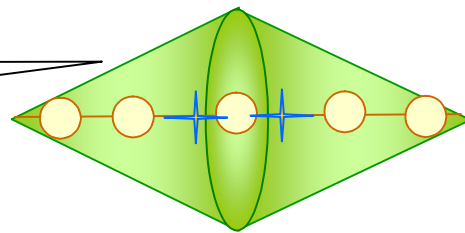


**Fig.3**  
Radial Vector with polar coordinates:  $r, \theta, \phi$ . Look up Ref. 3 for details



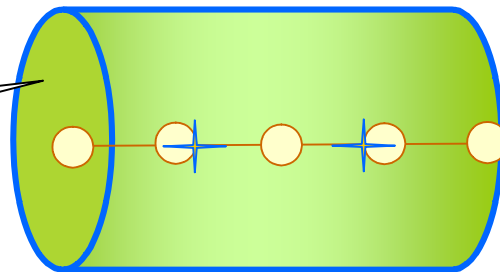
Spindle or Top shaped Specimen (Green line in the plot below)

**Fig.4a**



A cylinder shaped specimen (Blue line in the plot below)

**Fig.4b**

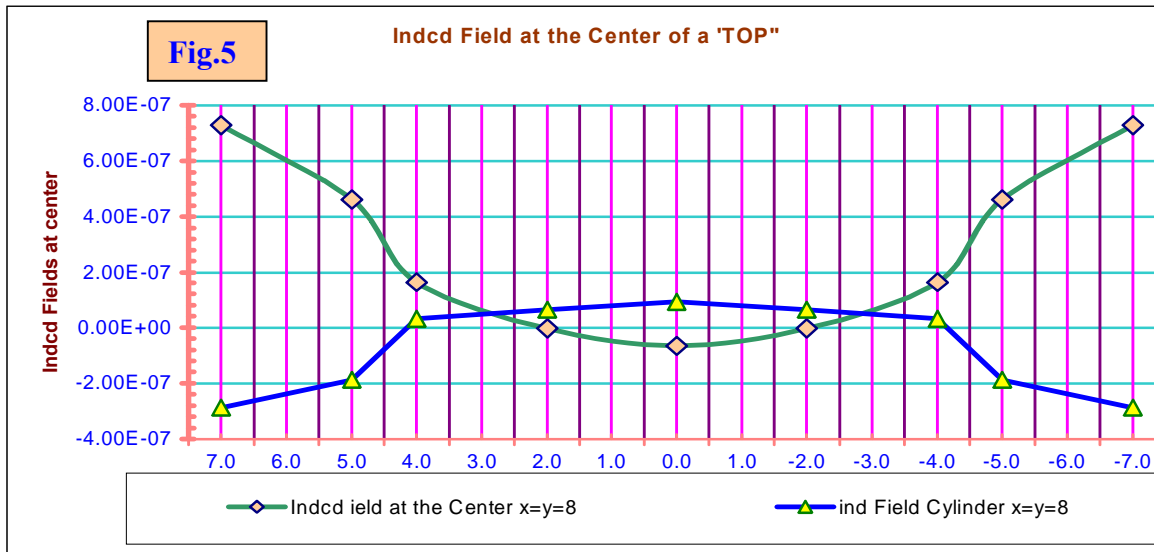


+ Zero ind. Field Points

## GENERATING LINESHAPES

The field values are on the y-axis. To convert this into a line shape spectrum, weight factors (frequency of occurrence of each value of induced field) for each field value have to be associated with the induced field values and plot should be made with the frequency factor (multiplied by the amplitude calculated from a line shape function) on the y-axis and induced field values on the x-axis. In the above result, the value at 0.0 distances corresponds to the middle of the line joining the vertices and as an example a frequency factor corresponding to the variation of distance from the spindle surfaces can be used approximately as area of a circle with increasing radius towards the middle point of the specimen.

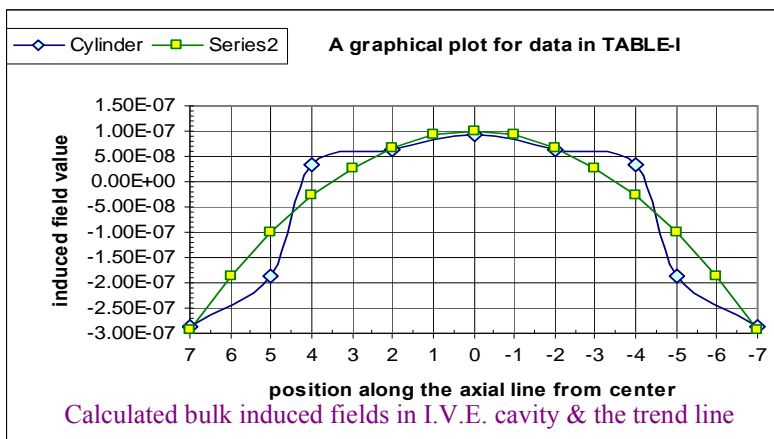
A line shape corresponding to the calculated field values is depicted in Fig.6. The frequency factors are the proportional values to the area of the circular cross section. This rationale at this point is only an illustration of a possibility of getting a line shape, but it would be possible to calculate the actual weight factors for the shapes using this type of induced field calculations for a shape which is not regular but only which can be approximated partly or fully to a regular shape.



The calculation of such line shapes would be the tasks set to be accomplished. Fig 6 for the frequency factors calculated for the shape of a cylinder. A procedure to Calculate would be illustrated by a step by step construction from the simple intermolecular contribution in spherically shaped specimen to the cylindrical case data plotted above. In the following, instead of using the summation procedure to cover all the points, trend lines are used on the basis of a stated reasoning. *MS Excel* application was used for these line shape simulations.

Cylinder Refer to plot on Right		
	From Plot	Trend line
7	-2.87E-07	-2.9E-07
6		-1.9E-07
5	-1.87E-07	-1E-07
4	3.25E-08	-2.8E-08
3		2.8E-08
2	6.45E-08	6.8E-08
1		9.2E-08
0	9.35E-08	1E-07
-1		9.2E-08
-2	6.45E-08	6.8E-08
-3		2.8E-08
-4	3.25E-08	-2.8E-08
-5	-1.87E-07	-1E-07
-6		-1.9E-07
-7	-2.87E-07	-2.9E-07

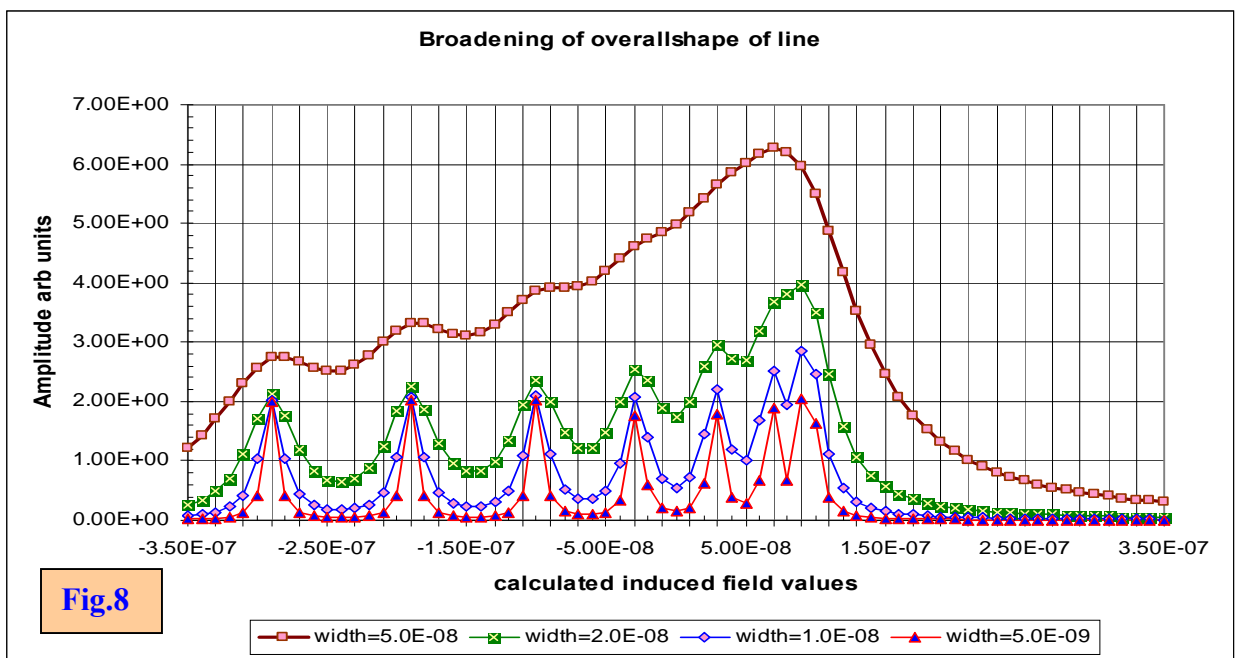
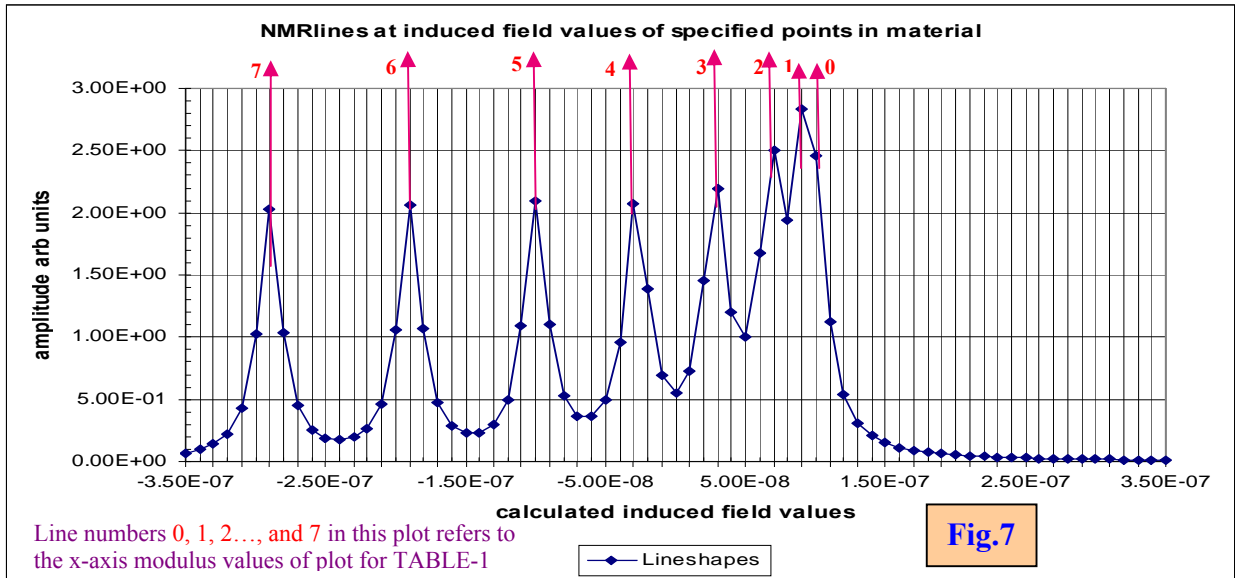
On the left side is the table (Table.1) of values of induced fields for the cylindrical specimen as read out from the graphical plot (Blue line). A trend line (Green line) gives by interpolation the values in between points.



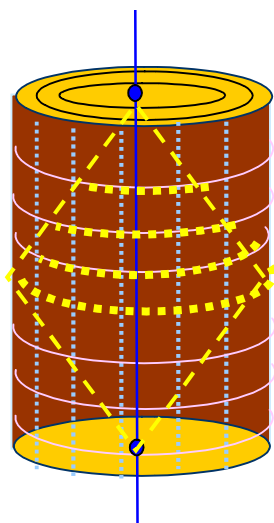
The intermolecular value for the induced field is set equal to the zero so that the bulk induced field values can be the actual resonance field values. Hence for the 8 points from 7 to 0 in the table above, at the trend line values a NMR line appears in the plot in Fig.7. The intensity of lines at positions 7-1 are multiplied by two for the induced field values from -1 to -7 also are the same as for 1 to 7. The lines at **position 1** (intensity 2) and **position 0** with (intensity 1) overlap and merge for proximity reasons compared to the line widths. Thus only seven distinct



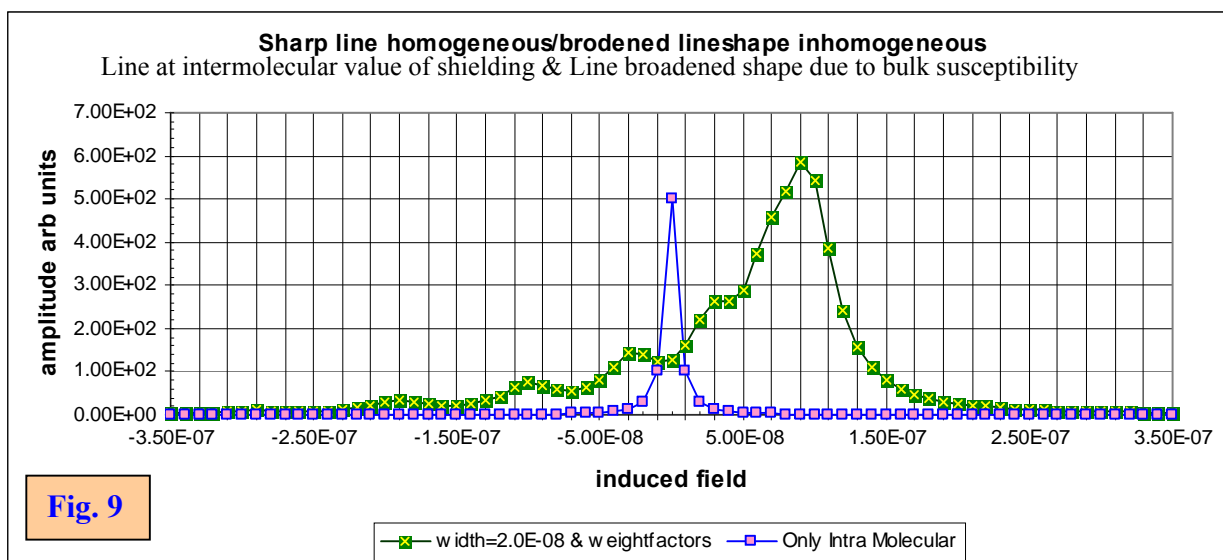
lines are countable. The appearance of the seven lines (in Fig.7) further changes with increase in line widths of the component lines and this corroborates the line width effects and the resulting overlapped line shapes alluded to earlier. The top most line (brown) in the plot of Fig.8 is for the maximum width which is set large compared to the line separations in the calculations.



Equation used for simulating the line shapes:  $\sum_{j=0,7} Y_i = (\text{width})^2 / [(\text{width})^2 + (x_i - x_j)^2] + \sum_{i=1,7} Y_i = (\text{width})^2 / [(\text{width})^2 + (x_i - x_j)^2]$



The simulations as in Fig.8 have been made taking into considerations the induced field values along the axis of the cylinder with a trend line fitted for getting more points. For the points within the **cylinder** surrounding the axis a weight factor is used and multiplied to account for the increased points with the same induced field values. A **trapezoidal weight factor varying as the distance from the center of cylinder** was used thus giving less weight factor for end of the cylinder than at the middle. When this is included to the Green line in the plot above (for width  $2.0E-08$ ) then as in plot in the next page, a broadened line results. And, the un-broadened line at (zero induced field) intermolecular value is also plotted in Fig. 9



## CONCLUSION

Even though weight factors and certain interpolation procedures do not have any *a priori* reason, it has been the observation during the several of the induced field calculations by this procedure, that the induced field values vary continually from the center to the surface and in most cases it has a parabolic shape for the variations. And, to take into account the necessary frequency of occurrence of the specific value of induced field, a weight factor of the type used here is only for illustration. A more rigorous exact calculation at sampled points for the actual induced fields over the extent of the microscopic extent is necessary. According to the experience with this method and procedures till now, soon an actual calculation of line shapes for regular shapes must be obtainable and then the case of more arbitrary shapes can come under the purview of coverage by this method. All this being with diamagnetic specimen, the extension then to the materials with strong internal fields would be well within the reach by these procedures. There have been efforts to define and setup equations for average demagnetization factors when the sample is in-homogeneously magnetized. But even for evaluating trends among

in-homogeneously magnetized specimen these cannot be without ambiguity as can be inferred from the fact that, if the average demagnetization factors must be anywhere close to actualities, then the corresponding NMR feature should be a single sharp line at the given field value derived from the single average demagnetization factor for the sample. Considering the broad line shape illustrated in this paper, it would be highly unrealistic to replace this broad, almost featureless NMR lines, with single sharp line as if the field distribution can be well characterized by a single sharp line even if that corresponding single resonance field is derived by taking into account the field distribution. In NMR experiments it would not be possible to observe a single sharp line for a featureless broad line. However, currently there are several line narrowing techniques developed and are in use in several contexts. It might be interesting to find out any of the line narrowing (effective averaging of field distributions) can result in a single resonance field value that can be derived by the equations setup for average demagnetization factors. Even for this context, this method of quantitatively accounting for discrete intermolecular contribution and the bulk continuum contribution is the way. It is yet to be investigated, of the several works reported for the line shapes in the case of magnetic materials ( with large internal fields) , which are the contexts where the discrete region is explicitly taken into account over which the continuum is allowed to prevail. This is all in static field distributions in solids and the case of I.V.E. in the liquid state is much less tractable since the time and space averages have to be considered. If this recent method of treating the continuum bulk contribution is extended to liquid state and by subtracting its effect from the experimental value, it would be possible to ascertain the contribution of I.V.E (discreteness is out of the purview in liquids) can be estimated. Since this summation method simplifies handling non regular shapes, it might be providing more insights into the IVE contributions in liquids.

## REFERENCES

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2. S.Aravamudhan, *Bulk Solid Specimen Shape Dependences in the Molecular Chemical-shift Tensor Determinations*, Proceedings of ICMM2006 March 3-6, 2006, Section on Materials for the Future page 13-18; Article # 2.3. This full paper has been posted by this author in the webpage URL: [http://nehuacin.tripod.com/pre\\_euromar\\_compilation/](http://nehuacin.tripod.com/pre_euromar_compilation/)
3. Download the PowerPoint file documented at the “jump to MRSFall2006” links of URL: <http://nehuacin.tripod.com/id1.html> and view the animated slide show for further elaborations.
4. URL: <http://nehuacin.tripod.com/id1.html> Sheets 06-08 displayed in the poster **P-174** presented by S.Aravamudhan at the EUROMAR2006, York, UK on 20th July 2006. The early stages of the evolution of the recent alternate procedure for the calculation of demagnetization factors have been documented at <http://saravamudhan.tripod.com/>