Perspectives On The POINT-DIPOLE *Approximation:*
for the
Prospective INTUITIVE-CHEMISTS' *Approaches*

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ADDRESSES FOR SOME OF THIS AUTHOR'S WEBPAGES WHERE MATERIALS RELEVANT TO THE TOPIC HERE ARE DOCUMENTED.

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Explaining the trends of Nuclear Shielding caused by Magnetic moments related to Susceptibilties

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WebSite URL (IV) : http://geocities.com/amudhan_nehu/graphpresent.html

ABSTRACT

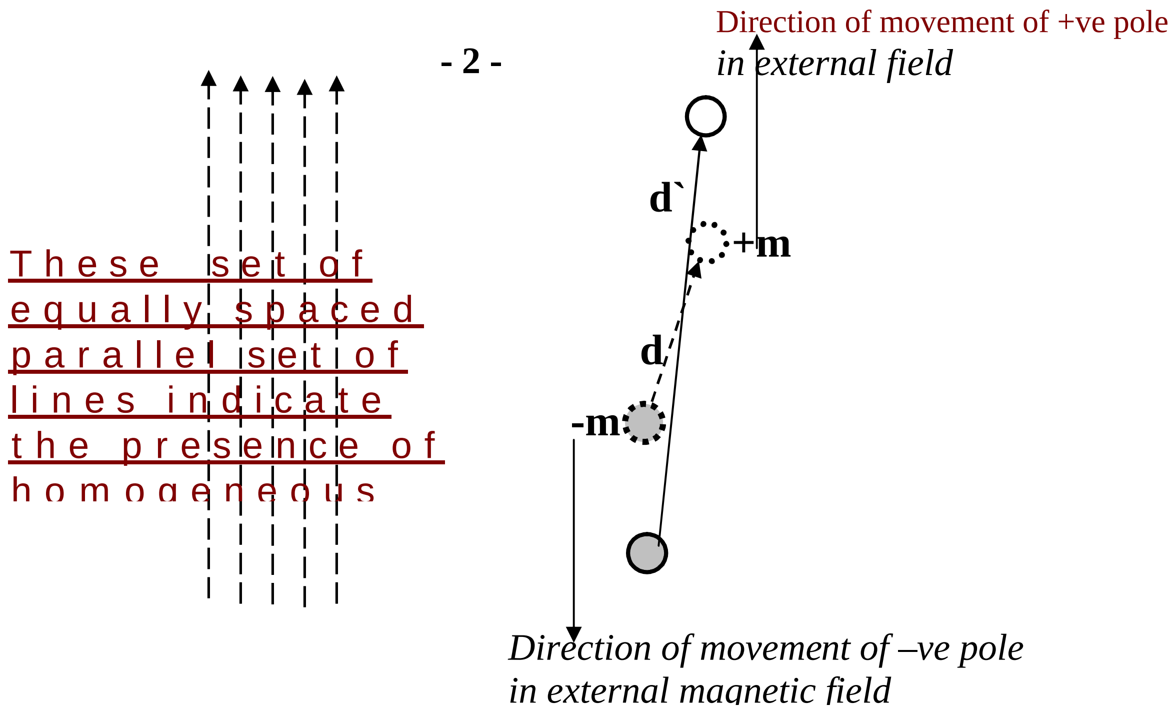
A dipole by definition **[SHEET_2**] consists of two unlike poles but equal in magnitude (pole strength) separated by a finite distance '**d'**. When the point (where this dipole's effect is) being considered is located at such large distances 'R' from the dipole that **'d'** is negligible compared to **'R'** [d<< R(as in **SHEET_8 and 9**)], the point-dipole approximation is said to be valid. When **'R'** becomes nearly equal (comparable in magnitude) to **'d',** then the point dipole-approximation would not be reliable.

Then, by [1] hypothetically considering [**SHEET_10**]each of the poles to be made up of 'n' number of equally divided polestrengths and [2] placing each of this divided poles separated from the correspondingly divided unlike-pole, and, further , [3] this distance of separation being equal to **d' = d / n**, a set of 'n' smaller dipoles can be constructed all these dipoles being centered at the same Electrical Centre of Gravity as the original undivided, single dipole. The value of 'n' can be so chosen that the distances of separation **d'** is negligible compared to the value **R**. This would enable the point dipole approximation to be valid for each of the divided, smaller dipoles and their effect at a point at distance 'R' can be calculated. Since all the 'n' number of divided dipoles are identical their contributions will all be the same and having calculated the effect of one of the dipoles, the effect of 'n' dipoles can be obtained by a multiplication by 'n'[***A critical question 'n' or 'n^2'***]. This should yield the effect of the single dipole within the frame work of point dipole approximation. Does this mean that dividing and multiplying by 'n'[***or 'n^2'***] [***effectively the multiplication factor is '1' or 'n'***] makes it a valid description that which was originally not reliable ? This procedure would be providing an argument to say the same numerical values are reliable eventhough at the outset this result could have been discarded as unreliable.

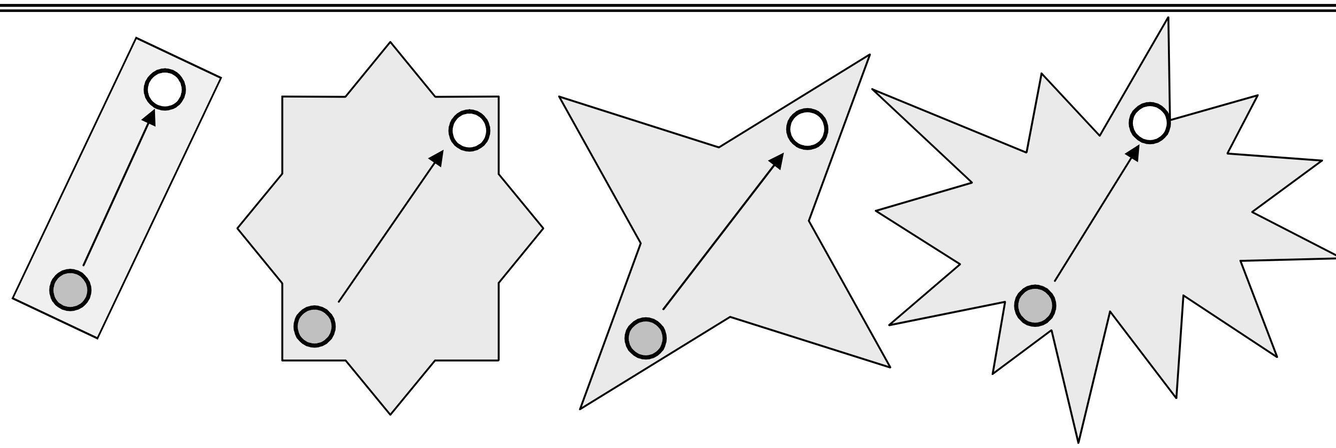
Since this is an argument which can lead a chemist astray while trying to interpret the results, it is intended in this poster presentation to address this question in greater detail so as to enable a confident handling of the point-dipole approximation which is inevitably the beginners' approach in chemical contexts.

INDEX to the Display SHEETS

SHEET_2 and SHEET_3 : *Definition of dipole, Dipole Moment* **SHEET_4 and SHEET_5** : *Charge cloud descriptions, Circulation and movement of Charges and associated CURRENT FLOW. Flowing Current as source of Magnetic Dipole Moment* **SHEET_5 and SHEET_6:** *Rotational Motions of Electrons (Orbital and Spin) and spin of Nuclei: The associated angular momenta and the Magnetic Moments.\: as is well evidenced in the description of the Magnetic Resonance Phenomena.* **SHEET_7:** *Such Magnetic Moments, Occurrence, Origin and consequences in Physical Chemistry* **SHEET_8:** *A Consideration of the POINT-DIPOLE Approximation: Criteria for its validity* **SHEET_9,10:** *How to make the Point-Dipole approximation more valid while the determining factors become critically uncompromisable.* **SHEET_10,11 :** *General indications of Induced Fields Due to circulation of electrons causing demagnetizing and Shielding effects* **SHEET_12:** *Summary and Conclusions*



The two poles, equal in magnitude and oppsit in sign, are not held fixed in a non-flexible and hard frame-work. Hence in external fields the two poles can be moving independent of each other and hence the inter-pole distance d is not a constant. Thus the two poles cvnnot be said to be forming a "dipole" with a well defined value for the <u>*" dipole moment".*</u>



In the above set of illustration the pair of poles are held by non-flexible and hard FRAME-work and the inter-pole distance d cannot alter in presence of the external field. When a movement is required the two poles move together with fixed distance between them. When no trnslational motion can provide the rewuired change to the minimum potential energy situation, the minimization occurs by a rotation of the line (imaginary) connecting the two poles. This is said to align the "dipole" or the <u>"Dipole moment"</u> gets disposed along the direction of the external field.

Image (1) of the 2 images for this display

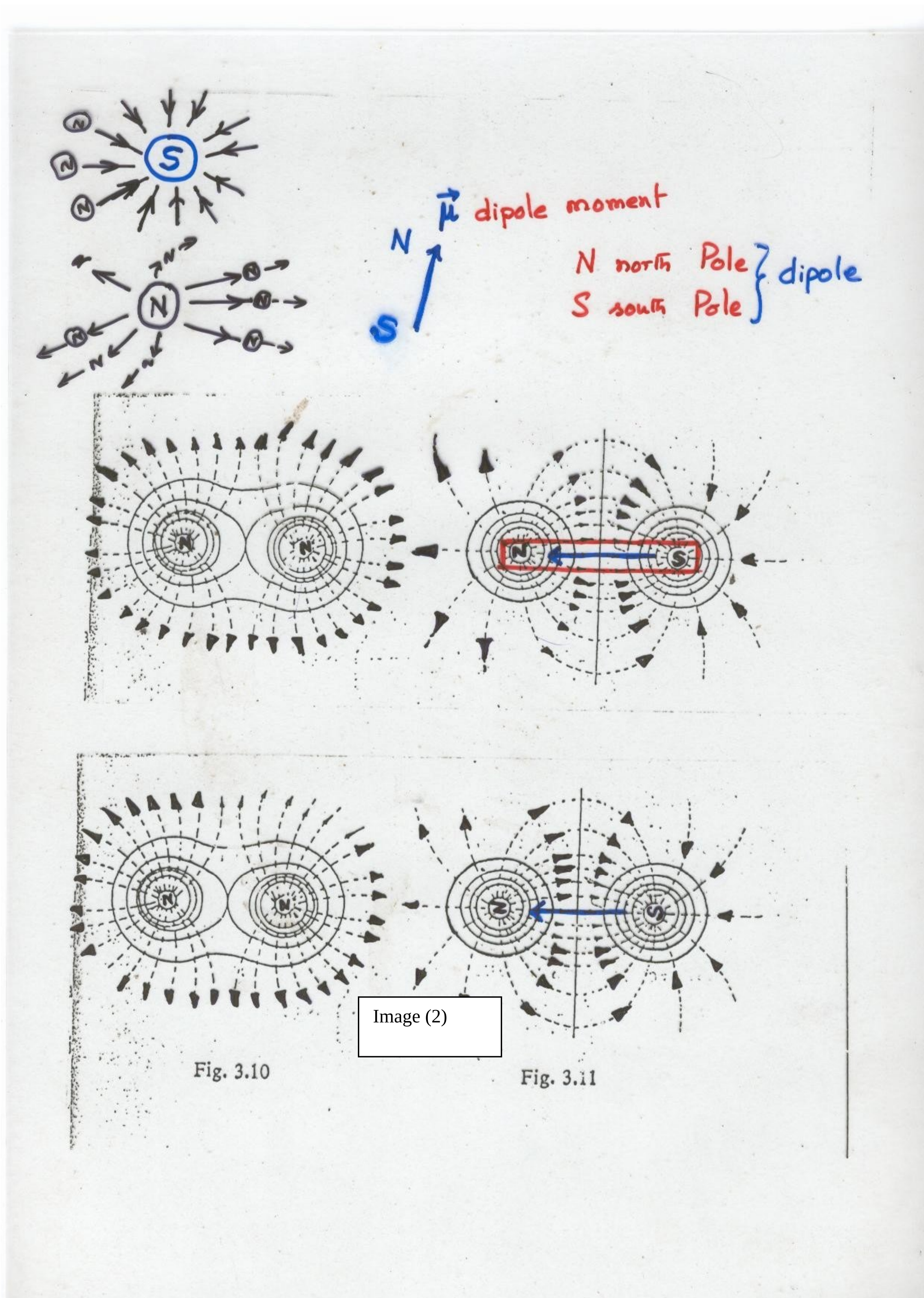
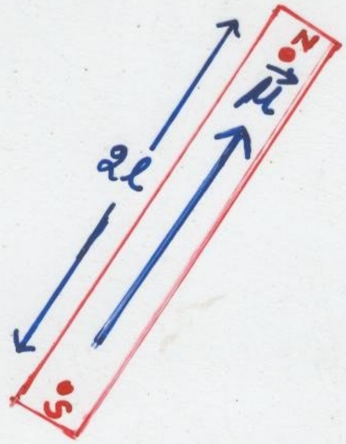


Fig. 3.10

Fig. 3.11



strength of north pole = m
strength of South pole = m

MAGNETIC DIPOLE MOMENT = $\vec{\mu}$

$\vec{\mu}$ POINTS from S to N INSIDE THE BAR MAGNET

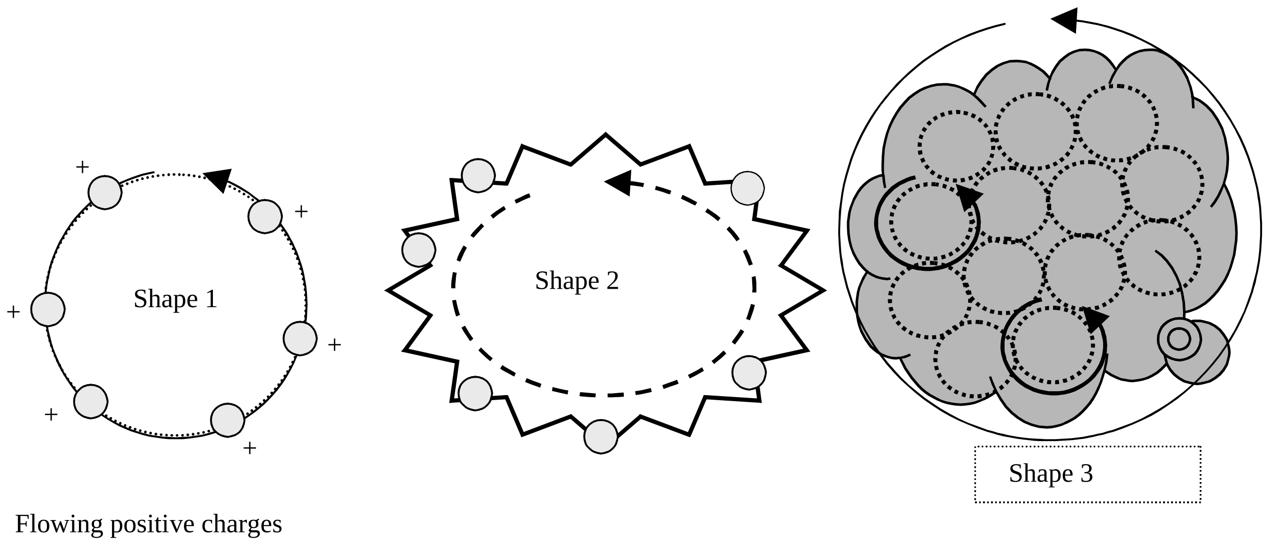
magnitude $|\vec{\mu}| = 2\ell m$

All the magnetic field effect representations can be done by simply considering the magnetic dipole moment vector $\vec{\mu}$ instead of picturising the bar magnet with its north pole and south pole.

Thus $\vec{\mu}$ represents the dipole characteristics.

While explaining the presence of a **"dipole moment"** by considering the poles which, depending on the context, the poles may be the "electrical (positive and negative) charges" or the ["magnetic charges"] magnetic "north" and "south" poles. In either case a dipole moment can be defined: in the former case it would be *electrical dipole moment* and in the latter case it would be *magnetic dipole moment*

In the case of flowing electrical charges, the current thus flowing can cause a magnetic field, which can be associated with the flow characteristics and the amount of the electrical charges. The magnetic field thus arising can be calculated and the direction of the field determined. This can be the attribute "dipolemoment" for the flowing charge systems.

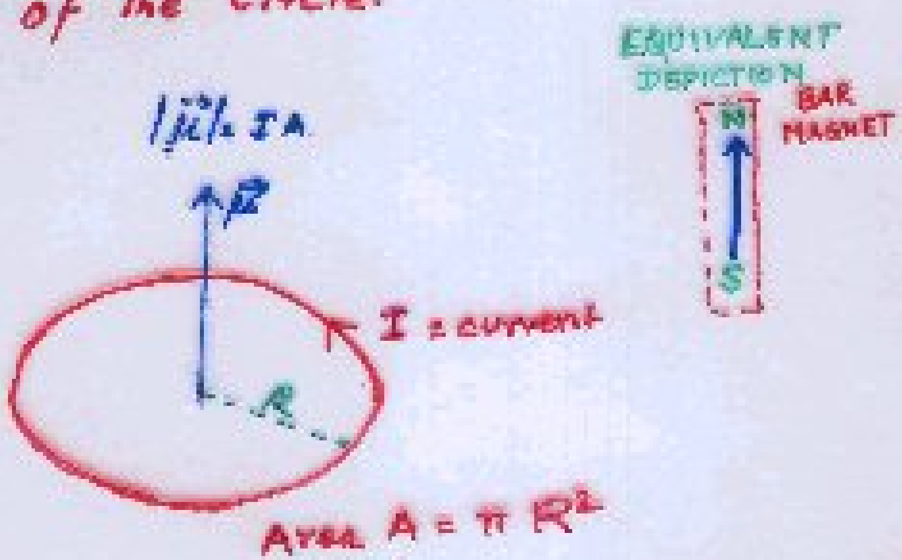


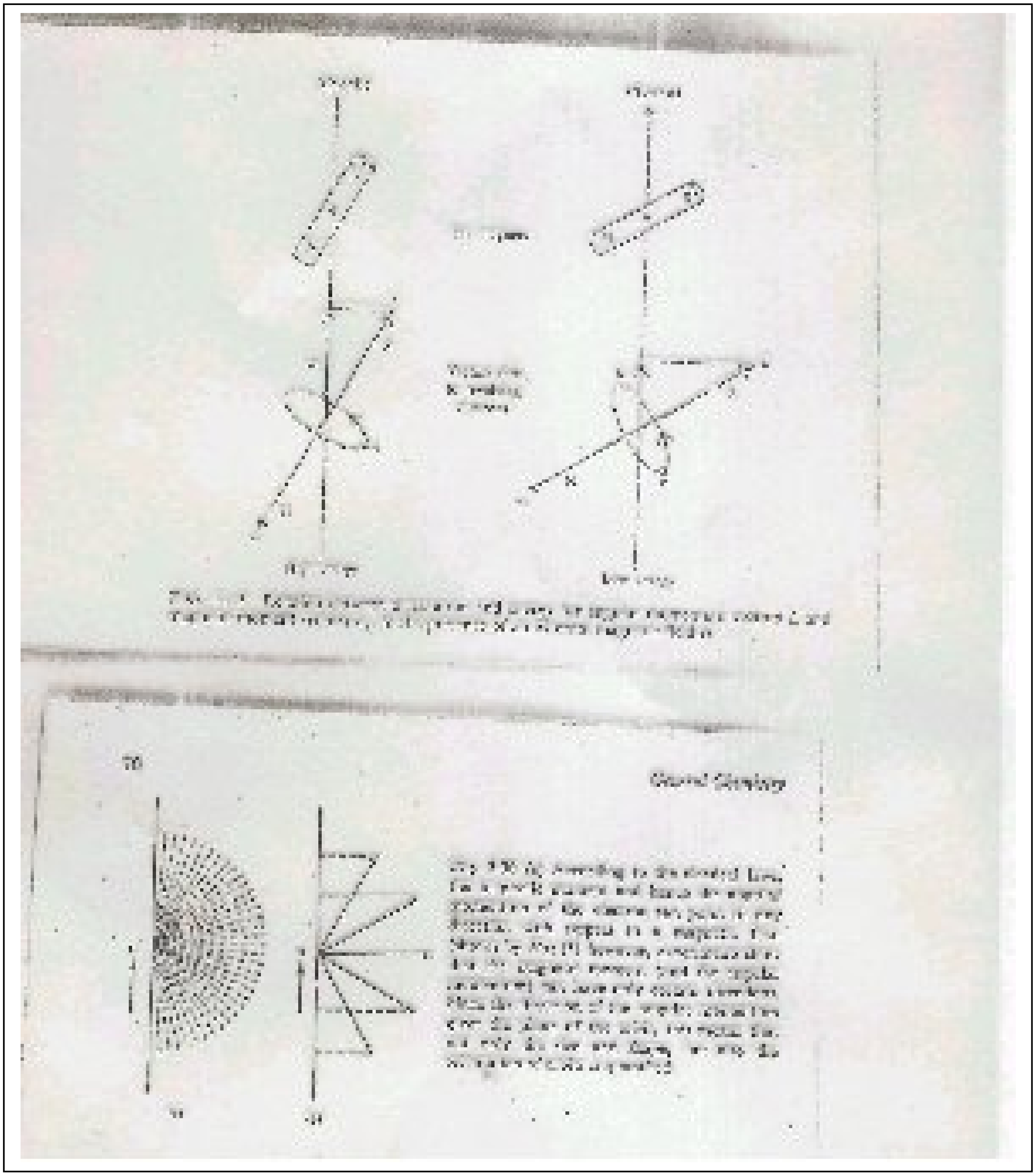
In each of the above cases a magnetic moment can be attributed for the charge flow. In the case of SHAPE 3 the charge cloud is depicted. The total charge cloud can be considered as small, charged, volume elements inside the charge cloud. These volume elements each can be attributed a small dipole moment and the total dipole moment associated with currents in the charge cloud can be obtained by a vector addition of the individual elemental dipole moments.

IF THE PARTICLE UNDERGOING A ROTATIONAL MOTION ALSO HAS AN ELECTRICAL CHARGE, THEN THE ROTATIONAL MOTION OF THE CHARGE — i.e., a flowing charge — WILL PRODUCE A MAGNETIC FIELD.

IT IS WELL KNOWN THAT IF A CURRENT 'I' FLOWS THROUGH A CIRCULAR COIL AND IF THE AREA OF THE CIRCLE IS 'A', THEN THE MAGNETIC FIELD PRODUCED IS GIVEN BY $\mu = I A$

and the magnetic field is at the center of the circle.





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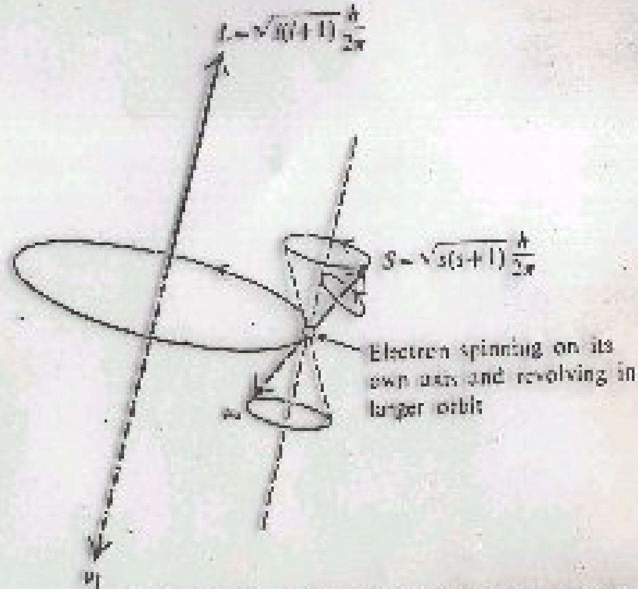

FIG. 10-20 An idealized classical picture of the relationship between the orbital angular momentum vector L and the spin angular momentum vector S, which is shown in the higher energy form of its two allowed positions. In the lower energy position, the S vector points downward at the same angle of precession.

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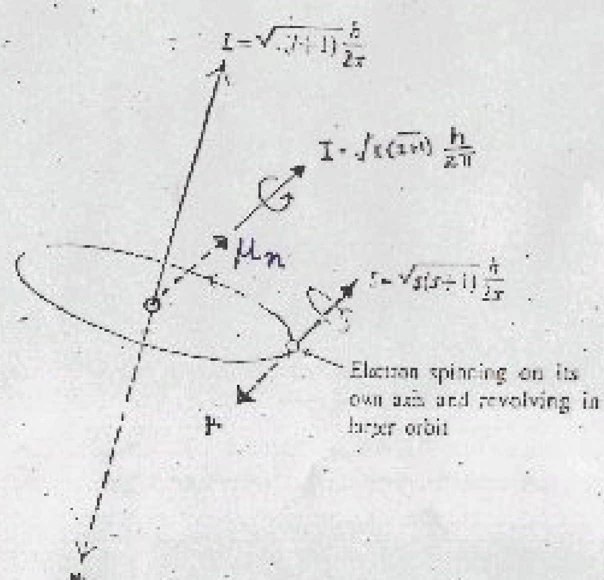

FIG. 10-20 An idealized classical picture of the relationship between the orbital angular momentum vector L and the spin angular momentum vector S, which is shown in the higher energy form of its two allowed positions. In the lower energy position, the S vector points downward at the same angle of precession.

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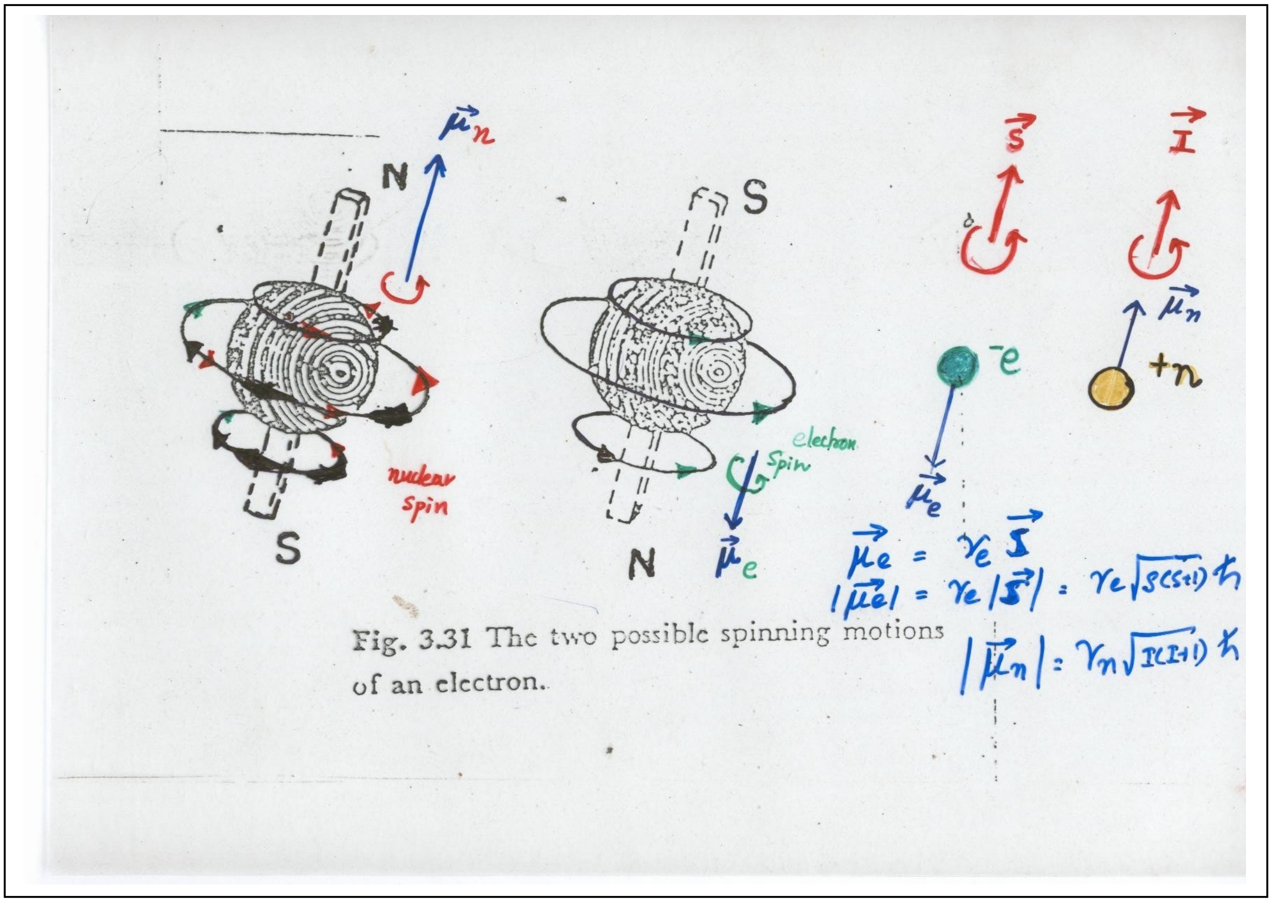
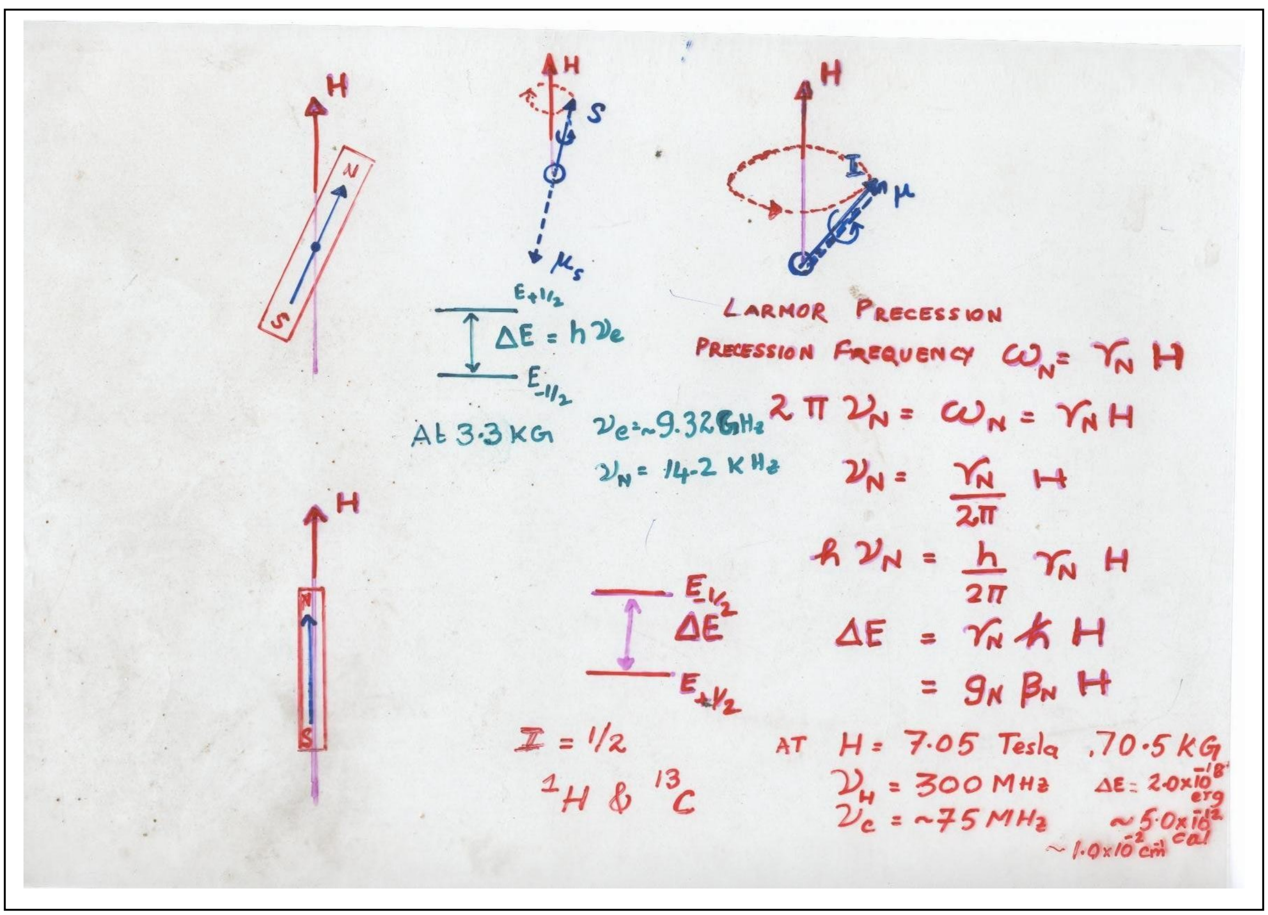
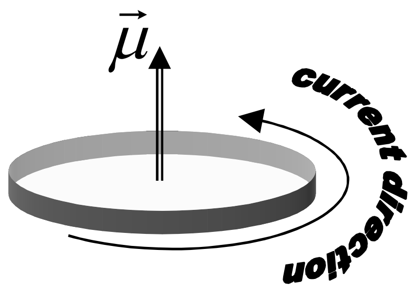
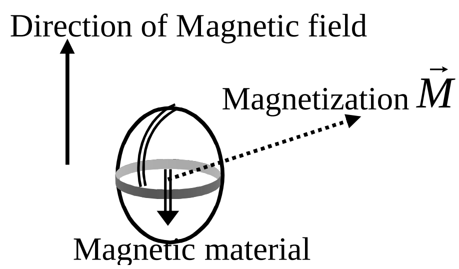


Fig. 3.31 The two possible spinning motions of an electron.

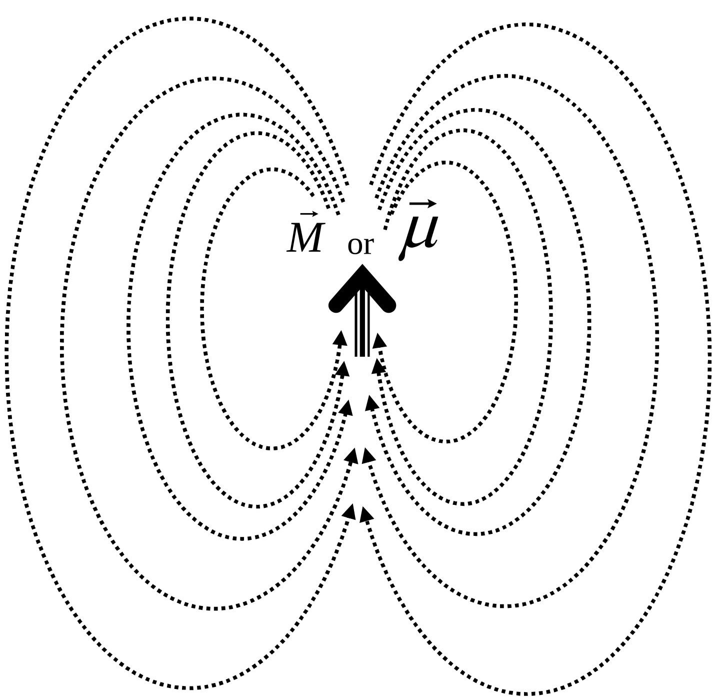


When electron circulations cause a magnetic field it can be described as the magnetic moment $\vec{\mu}$ associated with the moving charge (flowing current). In terms of the descriptions in magnetic materials it may be said that this magnetic field thus induced is said to magnetize the material and it is then a magnetization $\vec{M}$. In such a case, this magnetization if it is due to the fact that it is being caused by the applied magnetic field is expressed as that the contributions to the electron circulations is described as due to the sucesptibility χ of the material . Then the Magnetization $\vec{M}$ can be related to the strength of the Magnetic Field $\vec{H}$ by the equation $\vec{M} = \chi \bullet \vec{H}$





When the induced magnetization is opposite in direction to the Magnetic Field then the material is said to be Diamagnetic, otherwise it is Paramagnetic. All these magnetic vector quantities are amenable to Magnetic Dipole Moment descriptions similar to the case of a bar magnet. The electric dipole moment analogues can be understood in terns of descriptions similar to these.



Dipole Moment and the Field distributions due to the dipole moment

It is the intensity of the filed due to this $\vec{\mu}$ which is of interest in applications in Chemistry and Physics.
The approximations associated with these considerations can lead chemists astray if not well versed. This can make the chemists seek complicated or tedious approaches to explain observations while if dipole approximations are well understood then, there can be simpler ways of grasping the situations.

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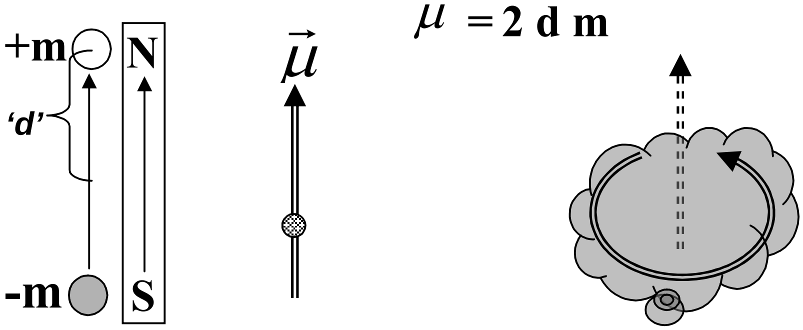
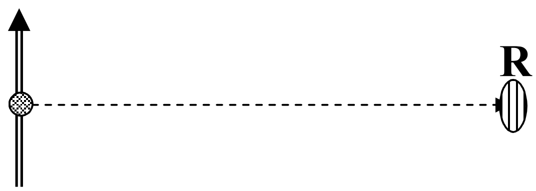
$\vec{\mu} = 2\,\mathbf{d}\,\mathbf{m}$



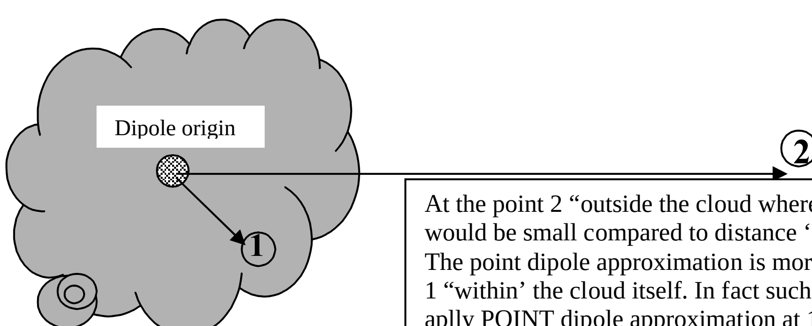
The approximated radius of this charge cloud has to be taken into account while deriving the "distance" factor **d**

In case of either the electrical or the magnetic dipole moments a simple arrow can serve the purpose to indicate the presence of a "Dipole" as located at a given point ●



While considering the Field due to the dipole moment at 'R' it is possible to consider the two poles separately and find the contribution from each pole and sum up to get the total.

Instead of each time considering the poles of dipoles separately , it is possible to get an equation for this total at R by a single equation using the dipole moment. This implies that the distance **d** has to be considered while calculating the field at a distance **R.** It turns out that if $\mathbf{d} \cong \mathbf{R}$ then, the calculations result in unrealistic values. For reasonable application the value of $\mathbf{R} \gg \mathbf{d}$. This means $\mathbf{R} \geq 10 \bullet \mathbf{d}$. This is referred to as the POINT-DIPOLE approxomation. It is a consideration as to at what values of the distance **R** the given dipole can be arising from a single point and not from the consideration of the length **d** characteristic for the value of the moment $|\mu|$.



At the point 2 "outside the cloud where the 'radius' would be small compared to distance 'R' to the point The point dipole approximation is more valid than at 1 "within' the cloud itself. In fact such an approach to aplly POINT dipole approximation at 1 would be not at all justifiable.

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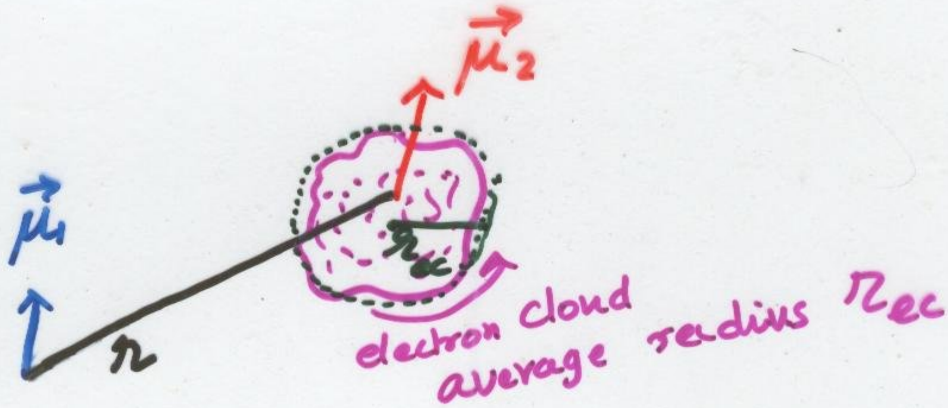
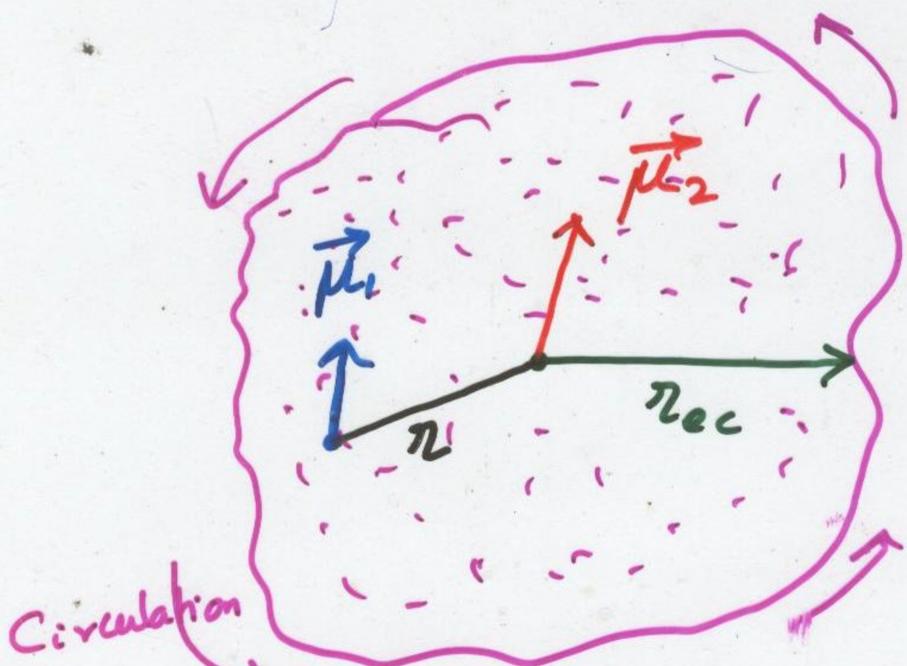


$r >> r_{ec}$

for the point-dipole approximation
to be a good approximation.



$r < r_{ec}$

point-dipole approximation
NOT VALID

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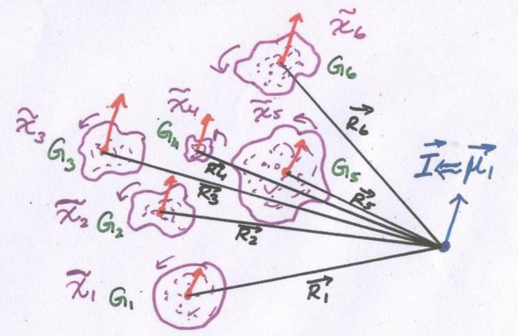


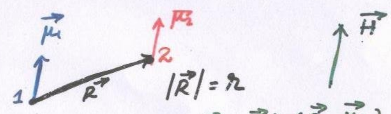
$|\vec{R}_i| = r_i$

Each group electron cloud circulation is independent of every other cloud circulation

i.e each tensor $\tilde{\chi}_i$ interacts with $\vec{I}$ independent of the presence of other susceptibility tensor

Hence Total $\tilde{\sigma}$ contribution at nucleus 'I' is sum of contribution from each electron cloud $\tilde{\sigma} = \sum_{i=1}^{6} \sigma_i$

$$\tilde{\sigma} = \sum_{i=1}^{6} \sigma_i = \sum_{i=1}^{6} \frac{\tilde{\chi}_i}{r_i^3} - \frac{3(\vec{R}_i\vec{R}_i)\cdot\tilde{\chi}_i}{r_i^5}$$

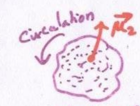


$$E = \frac{\vec{\mu}_1\cdot\vec{\mu}_2}{r^3} - 3\,\frac{(\vec{\mu}_1\cdot\vec{R})(\vec{R}\cdot\vec{\mu}_2)}{r^5}$$

Site - 1 $\vec{\mu}_1$ is a nuclear magnentic moment

$\vec{\mu}_1 = \gamma\hbar\vec{I}$ $\quad |\vec{I}| = \sqrt{I(I+1)}$

Site - 2 $\vec{\mu}_2$ Originates from electron cloud Circulation in presence of $\vec{H}$



$\vec{\mu}_2 = \tilde{\chi}\cdot\vec{H}$

$\tilde{\chi}$ Magnetic Susceptibility Tensor

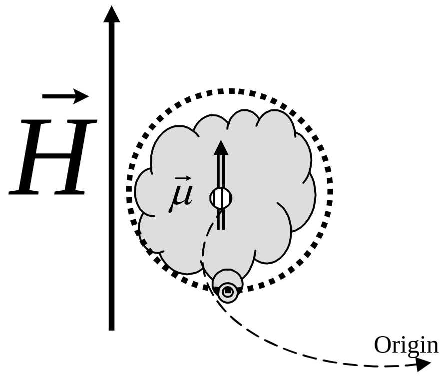
$\vec{\mu}_1 = \gamma\hbar\vec{I}$ $\quad \vec{\mu}_2 = \tilde{\chi}\cdot\vec{H}$

$$E = \frac{\gamma\hbar\vec{I}\cdot\tilde{\chi}\cdot\vec{H}}{r^3} - 3.\frac{(\gamma\hbar\vec{I}\cdot\vec{R})(\vec{R}\cdot\tilde{\chi}\cdot\vec{H})}{r^5}$$

$$= \frac{\gamma\hbar\vec{I}\cdot\tilde{\chi}\cdot\vec{H}}{r^3} - 3.\frac{\gamma\hbar\vec{I}\cdot(\vec{R}\vec{R})\cdot\tilde{\chi}\cdot\vec{H}}{r^5}$$

$$\gamma\hbar\vec{I}\cdot\tilde{\sigma}\cdot\vec{H} = \gamma\hbar\vec{I}\cdot\underbrace{\left(\frac{\tilde{\chi}}{r^3} - \frac{3.(\vec{R}\vec{R})\cdot\tilde{\chi}}{r^5}\right)}_{\cong\ \tilde{\sigma}}\cdot\vec{H}$$

$\vec{I}\cdot\tilde{\sigma}\cdot\vec{H}$



In presence of a magnetic field the entire charge cloud / magnetic material give rise to an effective total magnetic moment which has to be originating at some point within the specimen. Where to place such an origin within a specimen when the extent of the specimen cannot be approximated to be a mere point (relatively) is a matter which can be inconclusively debated at length.

How to resolve the above conflict ? *A trial with the two-poles definition of the dipole moment is given below:*

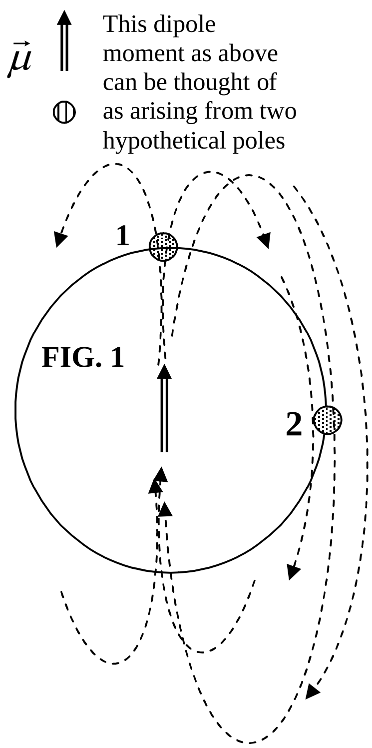
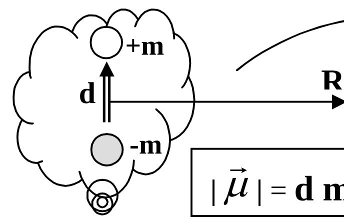


FIG. 1

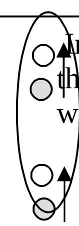


$|\vec{\mu}|$ = **d m**

When point dipole approximation is not valid, **then**

Arrangement-I

d/2 m/2 each moment is of value= **d.m/4** Thus for two moments resultant= **d.m/2**



In this case also the total moment would be **d.m/2**

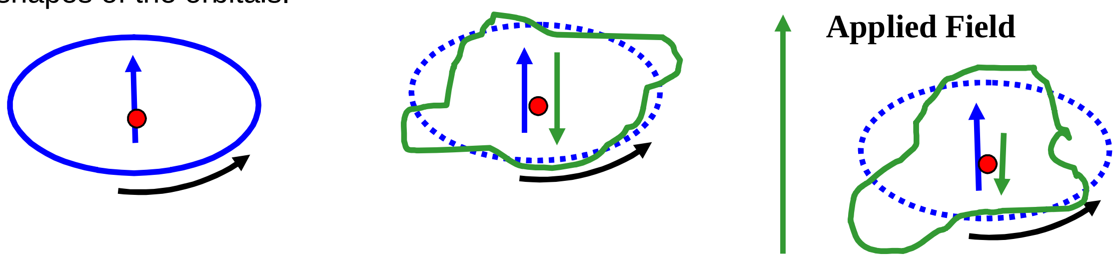
Arrangement-II

Consider **'n'** number of small dipoles such that the resultant magnetic dipole moment is equal to the same as above. Let n=2. When pole strength is retained as 'm' and distance made d/2, then for the two dipole moments the total strength of poles of each sign would be '2m'. This would not conserve the total pole strength available. Hence the poles have to be divided equally and the distance 'd' as well

For the case of 'n' = 2, both the arrangement above have only half the magnetic moment value than the original moments. However the effective field at a distance 'R' when calculated by the point dipole approximations would be more valid than in the original case since for the same 'R' the pole distance is only 'd/2' instead of 'd'

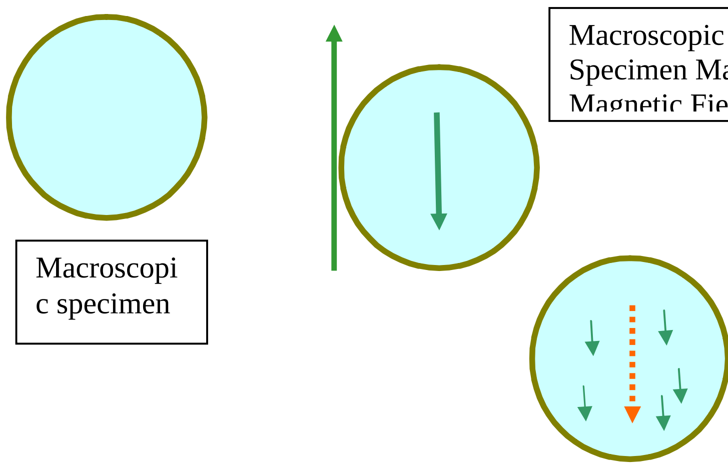
For the **FIG .1** consider the field strength at two points 1 and 2. At point 1 the value would be **'2.d.m/R'** where as at point 2 the field value would be **' –d.m/R'.**
Correspondingly for the divided dipoles with **'Arrangement-I'** the value at pint 1 would be **'d.m/R' .** For **'Arrangement-II'** there should be two values for **'R'** assignable to the two divided moments. Let them be **'R+r'** and **'R-r' .** Then the field value would be **'(d.m)/2.(R+r)'** and **'(d.m)/2.(R-r)'.** Will the sum of these two be the same as **'d.m/R' as** it is for **Arrangement-I ?** After subdividing and arriving at the total for the divided moments, in the above case the calculated total should be multiplied by **'n=2'** since the division resulted in a total moment of only half of the total originally present.

In Atoms and Molecules the electrons are in constant revolution in Orbitals which should be constituting a constantly flowing currents . These flowing currents should be inducing magnetic fields at the center where the nuclei are located in atoms,for example. Thus at the nuclear site there would be induced magnetic fields whether there is an externally applied magnetic fields or not. Applying the external ,large,steady fields alters the way the electrons were flowing in the system before the application field and it is these changes in induced fileds which are manifest while measuring the Shielding effects as the Chemical Shift parameter. The alteration of the flow of electrons could be either a change in the velocity of electrons or the shapes of the orbitals.



Alterations of shape of orbitals *can come about because they are bonded in molecules i.e., in different bonding situations. Thus for the same applied field strength, the* **changes in the induced fields in presence of external field** ***can be different. According to Lenz's Law these induced fields have directions opposite to the direction in which the Magnetic field is applied. Paramagnetic and diamagnetic chemical shift contributions must be related to the sense in which circulations are altered relatively and whether changes can be accounted for by the deviations from spherical symmetries***.

Macroscopic Diamagnetic Specimen Magnetized in Magnetic Field



The induced magnetic moment represented at the center of the specimen is due to its inherent magnetic susceptibility. Whether the magnetic moment induced should be at the center of the specimen or not cannot be answered in any simple way. The single moment at the center can be ***hypothetically***

Sub divided into several small components and distributed into several locations within the specimen the total adding upto the same value. Then the net induced fields due to this small moment are the same as that of the total placed at center? If not should an interaction between these subdivided moments be considered which would be absent if only the single total was considered?

CONCLUSIVELY the present situation on the POINT-Dipole Approximation and its validity can be SUMMARIZED thus:

When efforts are made to improve the applicability of Point Dipole approximation mainly taking Cognizance of the volume magnitudes for the extent of the source of dipole moments and appropriately fragmenting to conserve the sum-total of the dipolemoment magnitudes, simultaneously monitoring the physical and chemical considerations do not throw a beginner's comprehension astray, it has become possible to device rather elegant methods of calculating even the demagnetization factor values with great accuracy by a simple summation process for calculating induced fields. The various efforts and applicabilities are enumerated below:

To enumerate the cumulative impacts of the topic on which papers are being contributed at international conferences it is necessary to recall that the poster presented at the ***Joint ISMAR-CA'98*** was the material presented at the *NMRS(India) Symposia at IIT/Delhi (1997) and at IISc., Bangalore (1998)* which even in India evoked an interest and later found acceptable alsoto be presented at International conference. This work has yet to be pursued for better results to be conclusive. This effort was to use a Magnetic dipole model for Shielding (Induced Fields) calculations and the results till now on this could further substantiate the reproducibility of the Deagnetization factor Calculations by using the same approach and equations for induced field calculations with an additional constraints and equations used for summing over semimicrovolume elements for the whole macroscopic specimen.

While presenting these approaches for the Macroscopic Magnetized Specimen in India at the ***Dehradun,IIP (1999) Symposium*** the abstract could be presented giving the rationale for the necessity of semimicro volume elements and the derived equations inquiring as to whether all these are only a mere mathematical simplification OR can there be more to it. Later the interest from the audience and viewres of posters resulted in presenting the Full explanations and calculation of Demagnetization factor and its reproducibility and these were the considerations at the *NMRS Symposia at TIFR,Mumbai (2000) and at Chennai,CLRI/IITM (2001)* which were summarised as POSTER presentation at the ***2nd Alpine Conference on Solid State NMR ,Chamonix Mont-Blanc,France (2001)***. Soon after there were messages received from the participants expressing much interest in the material and these materials are being more carefully studied by them as per the messages, from the point of view of the posiible applications indicated.
The presentations at ***XIII International Biophysics Congress, New Delhi (1999) and in the XIV IBC at Buenos Aires,Argentina (2002)*** have highlighted and explained the induced fields and their calculations from the point of view of Membrane transport studies by NMR methods and further efforts to improve the applicability are being pursued. The purpose of all the national and international presentations are being more and more substantiated by the interest of the Organizers (National &International) of Conferences. The explanations for the workability of this simple procedure for induced calcu;ations raises a few questions which must be clarified and explained before detailed application of the method.
In ***Feb 2003 in the National Symposium on Biophysics***, a typical consideration of a aromatic-ring susceptibility tensor was used to illustrate the consequences of induced fields calculated in the tensor form at a point nearby the ring.
On the basis of the simple procedure being used for the calculation of Induced Fields due to the magnetized specimen in the regions inside and outside this Uniformly magnetized Specimen and the inferences based on the already known demagnetization effects, an inquiry was put forth as to what really are the criteria for the specimen shape and the shape for the semimicro volume element (a cavity) would apply to know the trends of field distributions inside a magnetized specimen. This was the content of the oral presentation at the ***NMRS2003 in IISc., Bangalore***. A suggestion could be made in these considerations that if the Lorentz cavity is chosen to be a nonspherical shape , an ellipsoid for that matter, then within this volume element the discrete dipoles would contribute at a nuclear site inside induced fields and, will these trends be the same as it is for spherically shaped Lorentz Cavity?
At the ***3rd Alpine Conference on Solid State NMR, France during Sept 14-18,2003*** the above question could be certain extent answered from the numerical trends from a simple lattice sum calculations for CUBIC & NONCUBIC lattices when a spherical and nonspherical (ellpsoidal) inner volume elements are considered. it seems the Lorentz Cavity need not be only spherical since even for an ellipsoidal shape of comparable semimicro volume element the discrete poit dipoles yielded the same limiting sum value for the total contribution from all the dipoles within the volume element. Hence the Lorentz cavity need not be only of spherical shape. Then for the same dimensions for allcases the CUBIC lattice yielded the same numerical value indicating a near zero contribution but for noncubic lattice the limiting sum varied significantly depending on the relative ratios/magnitudes of the lattice parameters. And even in this ellipsoidal case the limiting values did not depend on the ellticities for the ellipsoids and all values were close to the nonzero values obtained for the spherical case.
Thus having carified forthe situations with regard to the intermolecular lattice contributions at proton sites in the single crystal specimen, now it seems more confidence can be placed while using the magnetic dipole model (the Joint ISMAR CA'98 POSTER prentation) for the intramolecular shielding calculations since the comparison with experimentally measured Shielding tensor values would be available with much more certainty.

These results can be familiarized with from what stands documented in the Web Pages listed out in the SHEET_1 and the links provided therein