A INVITED ARTICLE REVIEWED BY THE JUORNAL "CONCEPTS IN NMR"

AND THE CHIEF EDITOR FOUND THAT THIS ARTICLE IS BETTER SUITED TO BE SENT TO A DIFFERENT JOURNAL.

NUCLEAR PRECESSION PICTURE FOR A QUADRUPOLAR NUCLEUS INTERACTING WITH ELECTRIC FIELD GRADIENT

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Abstract

In this paper a geometrical representation is suggested for describing the Nuclear Quadrupole Resonance (NQR) phenomenon. This would enable the depiction of the Nuclear Spin Precession for the interaction of nuclear electric Quadrupole Moment (QM) with the Electric Field Gradient (EFG).Similar to the well known precession of the Nuclear Magnetic dipolar moment with magnetic field.. A consideration of the essential differences of such classical vector description of NQR phenomenon and the NMR phenomenon would also be presented.

INTRODUCTION

The Nuclear Quadrupole Coupling Constant in frequency units is given **(1)** by

$$\omega_Q = \mathbf{e^2qQ/ \hbar} \qquad \textbf{[1]}$$

where, **e** is the charge on the electron

$$\mathbf{eq = V_{zz} = \partial^2 V/ \partial z^2} \qquad \textbf{[2]}$$

is the Electric Field gradient EFG, and **eQ** is the electrical nuclear Quadrupole Moment QM of the nucleus. All the nuclei with I≥1 possess, in addition to their Magnetic Moment μ_I an electrical Quadrupole Moment **eQ**, which measures the deviation of the distribution of the nucleus' positive charge from spherical symmetry.

The **Eq.[1]** is a consequence of the interaction of the nuclear QM with the EFG as given by the Hamiltonian:

$$\mathcal{H}_Q = 1/ 6 \, [\, \Sigma_{K,J} \, V_{JK} \, Q_{KJ}^{(op)} \,] \qquad \textbf{[3]}$$

A consideration **(2)** of the origin of this interaction, and the forms of Hamiltonians indicate that for a nucleus possessing electric QM and magnetic dipole moment, there is no well specified direction (value for an angle) for the Spin Angular Momentum with respect to the electric QM. However, several texts state these two are collinear in certain circumstances **(6)**.

To describe the NQR phenomenon in a manner analogous to the precession description of the NMR, it is required to assign a fixed direction for the Spin Angular Momentum Vector of the nucleus with respect to the nuclear QM. This assignment is made by trying to specify a line and associate this line with the nuclear QM (**eQ**) **[see Box 1]** . We then state (without specifying the actual value for the angle) that the nuclear Spin Angular Momentum Vector of the nucleus has a fixed angle with respect to the line associated with eQ (**Fig.2)**. The conventional direction of the largest component V_{zz} of the Principal Axes System of the EFG tensor determines (in the absence of an external DC magnetic field) the quantization axis for the Spin Angular momentum while the QM interacts with the EFG.

Hence by understanding that the interaction of the **eQ** with **eq(**V_{zz}**)** sets up the necessary energy of interaction and , that, this causes an alignment of the Spin Angular Momentum Vector which gets quantized along the z axis of EFG, it would become possible to provide a precession description for the qudrupolar nuclei interacting with EFG.

A quadrupolar system of charges can be formed in a manner similar to the forming of a dipole from two isolated charges of equal magnitude and opposite sign. To form a quadrupole system begin with two well separarted equivalent set of dipoles and bring them close enough so that neither of the dipoles can be said to be far from the influence of the other dipole. Bringing them to such a proximity to each other that the four charges (a pair of positive charges and a pair of negative charges) in a given configuration cannot be delineated only in terms of well defined dipoles.

A possible arrangement of such a set of four charges is shown in Figure 1(a) where the four charges are placed at the corners of a regular square.

From the principles of classical electricity and magnetism **(3,4)** , it is possible to get an equation for the electric quadrupole moment of such a system of four charges, in terms of the magnitude '**q**' of the set of equal charges and the distance of separaration '**a**' of the charges. Similarly the four charges can also be placed as shown in **Fig.1(b)** along a straight line. In this case also a quadrupole moment can be defined in terms of 'a' and 'q'.

In fact, by appropriately altering the magnitudes of ‘a’ and ‘q’, a square planar configuration of the charges with a given magnitude of QM can be rearranged to a linear configuration yielding the same MAGNITUDE (VALUE) FOR QM.

Thus if it is at all known that a “quadrupolar system” with a QM is present, in certain cases it should be possible to consider a set of four charges equal in magnitude and a linear arrangement for them to obtain that specified value of QM, provided variations in the arrangement of charges can be tolerated for particular context and situations.

It is this type of argument as above which would lead to a possible association of a line with the nuclear quadrupole moment, shown in **Fig.1(b).** Several possible lines can be drawn for **Fig.1(a).**

DIPOLEMOMENT IN EXTERNAL FIELDS AND LINEAR QUADRUPOLEMOMENT IN EXTERNAL FIELD GRADIENTS

Fig.3(a) depicts the situation of a Dipolemoment placed in a Uniform Field and **Fig. 3(b)** depicts the situation of a linear Quadrupolemoment placed in a uniform field. As is known from the principles of classical electricity and magnetism, there would be a couple acting on the dipole moment where as from the diagram it is clear and it is to be understood that there would be no resultant force acting on the quadrupolemoment in a homogeneous Field.

On the other hand for the magnetic dipole in a linearly varying field (linear gradient **Fig. 3(c))**, there can also be a translational motion (displacement) of the dipole in addition to the rotational motion. Similarly when the above quadrupole moment is placed in a linear field gradient (**Fig.3(d)**), it leads to a rotational motion. This rotational motion arises due to the fact that the two dipoles will have equal resultant forces acting at different points in space in the opposite direction.

DEVIATION OF NUCLEAR CHARGE DISTRIBUTION FROM SPHERICAL SYMMETRY AND THE POSSIBILITY OF LINEAR ELECTRIC QUADRUPOLE MOMENT

When the nuclear charge distribution deviates **(5)** from spherical symmetry the resulting shape of the charge distribution, most often , is that of an ellipsoid. Consider the possibility of representing, even if it be hypothetically, this deviation from spherical symmetry as accountable by adding two pairs of positive and negative charges of appropriate magnitudes. These added charges are placed conveniently at different points in and around the spherical shape. The magnitudes of these charges and their locations may be chosen so as to result in the same magnitude of quadrupole moment as it becomes equal to the known Quadrupole Moment of the nucleus.

This hypothetical construct can more easily be visualized considering the corresponding two dimensional analogues: **circle** and **ellipse**

Consider a total positive charge '**C**' distributed uniformly over the circular area as in **Fig.4(a).** Let **'q'** be a magnitude of charge much smaller than the value **'C'.** Consider the addition of two **'+q'** charges and two **'-q'** charges to the circular charge distribution as shown in **Fig.4(b).** Thus the net result is an elliptical charge distribution.

This rectangular placement of charges can be further rearranged to result in a linear Quadrupolar placement of charges to obtain the same value of the Quadrupole Moment effectively as depicted in **Figs.4(c) & (d).**

This illustration seem convincing enough to extend it to the case of three dimensions.The requirements of a Quadrupolar System of charges to account for the magnitude of the Quadrupole Moment and the required geometrical arrangement for the charges seems feasible**.**

LINEAR QUADRUPOLAR SYSTEM IN AN ELECTRIC FIELD GRADIENT AND THE PRECESSION PICTURE

Let the Quadrupolar system be represented as in **Fig.5(a)** with charge magnitudes **'q'** and distances of separation **'a'.**

The Dipole Moment of each of the above dipoles in **Fig.5(a)** is given by

$$\mathbf{P = a\,q} \quad \text{------------} \quad [4]$$

The quadrupolar system above would have a net Quadrupole Moment

$$\mathbf{Q = 2\,a^2\,q} \quad \text{-----------} \quad [5]$$

Consider as in **Fig.5(b)** that the linear Quadrupolar System has been placed in a Linear Electric field gradient $\mathbf{V_{zz}}$ which is in the direction of **Z-**axis. Let the two dipole moments be represented by $\mathbf{p_1}$ **&** $\mathbf{p_2}$ and the forces acting on the charges can be depicted as in **Fig.5(b).**

The center of gravity of each pair of dipoles is the midpoint of separation of the two unlike charges. And the distance of separation of the two centers of gravity would be **'a'** with reference to **Fig.5(b).**

Let a Spin Angular Momentum **I** ħ be placed along the line **(6)** of the linear Quadrupole system of charges.As can be obtained from the classical Electricity & Magnetism:

$$\mathbf{F_1 = -\,(P_1 \cdot grad)\,\tilde{E}_1} \quad \text{where } \mathbf{\tilde{E}_1} \text{ represents the Electric Field} \quad \text{-----} \quad [6]$$

$$\mathbf{F_2 = -\,(P_2 \cdot grad)\,\tilde{E}_2} \quad \text{where } \mathbf{\tilde{E}_2} \text{ represents the Electric Field} \quad \text{------} \quad [7]$$

$\mathbf{F_1}$ and $\mathbf{F_2}$ are equal in magnitude and opposite in direction and do not act at the same point, thus forming a couple. Let $\mathbf{F_1 = F_2 = F}$ ----------------- **[8]**

The rate of change of Angular Momentum **dI/dt** can be given by

$$\mathbf{dI/dt = (½)\, a \times F} \quad \text{-----------------} \quad \mathbf{[9]}$$

with **'I'** quantized along the **z**-axis.

$$\mathbf{F = (P \bullet grad)\, \tilde{E} = aq\, V_{zz}} \quad \text{---} \quad \mathbf{[10]}$$

$$\mathbf{dI/dt = (½)\, a\, aq\, V_{zz}\ \sin\theta = (½)\, a^2\, q\, V_{zz}\ \sin\theta} \quad \text{------------------} \quad \mathbf{[11]}$$

Since QM $= \mathbf{Q = 2\, a^2\, q}$, $\mathbf{dI/dt = (¼)\, Q\, V_{zz} \sin\theta}$ -------------------- **[12]**

From the above the energy of interaction can be obtained as

$$\mathbf{\Delta E = (¼)\, Q\, V_{zz}\ \cos\theta} \quad \text{--} \quad \mathbf{[13]}$$

If the Qudrupole Moment is written as **eQ** instead of '**Q**' to explicitly express in terms of the magnitude of the unit charge **e** and the Field Gradient $\mathbf{V_{zz}}$ is written as '**eq**' with the conventional symbols for the electronic charge and the maximum field-gradient component, then the energy of interaction can be obtained in the form

$$\mathbf{\omega_Q = Constant \bullet\ e^2\, qQ/\hbar} \quad \text{--------------} \quad \mathbf{[15]}$$

the proportionality constants must be appropriately accounted for and redefined as may be necessary. This is the resonance frequency at which the line of Quadrupole Moment can precesss.

A COMPARISON OF THE NMR AND NQR LEVEL SEPARATIONS, LEVEL DEGENERACIES AND THE CORRESPONDING RESONANCE PHENOMENA

As mentioned earlier the required constants would get incorporated in the equation for **'ω_Q'** when the Quadrupole Moment **'Q'** is expressed in the operator form **' $Q^{(op)}$ '** and substituted in the Hamiltonian and the energy for the resonance is calculated. For the case of spin **I ≥ 1**, the interaction with Magnetic Field would result in equally speced energy levels for the components of I_z, i.e., the different possible **'m'** values. For example for the integral Spin value **I = 2**, the energy level scheme as in **Fig 6(a)** can be drawn.

For this nucleus the Quadrupole Moment interacting with the Electric field gradient would result in the unequal energy level separations **(1)** and this interaction cannot lift the degeneracy completely as it happens in the case of the interaction of its Magnetic Moment interacting with a Magnetic Field but the '± m' levels would remain degenerate for all the possible 'm' values. Thus the energy level scheme of the type in **Fig. 6(b)** would result.

Hence the precession frequency for the description of NQR levels is not the same for all **Δm=±1** transitions since the energy differences have an **'m'** dependence for the energy values. Since it is well known that for **'I=2'** case there would be two NQR signals, for each one of the precession frequencies a precession picture can be provided which can be independent of the other. These would differ only in the **'ω_Q'** values with the other features remaining the same as for the case of **'I=½'** which is for the splitting in Magnetic Field.

Once these differences are well made aware of, then the classical vector description of the nuclear Spin Precession of the individual nuclear spin can be used for describing the NQR phenomena as well. The consequences, of the differences between NMR and NQR, for the macroscopic Magnetization vector descriptions and the effectiveness of both the rotating components of the linearly polarized applied RF perturbing field, have all been dealt with elaborately in the earlier papers on NQR phenomena for both CW and PULSED NQR detections.

ACKNOWLEDGEMENTS

I thank Prof.Anil Kumar for his keen interest in the contents of this article and for the discussions as and when I could make progress with this manuscript for "Concepts in Magnetic Resonance", mainly to insist upon the presentation being simple. Further, I sincerely acknowledge the hospitality extended to me during my stay at the Indian Institute of Science, Bangalore, at some stages of finalising the draft – manuscript.

Question: In the case of NMR, the precessional torque can be related to the rate of change of Nuclear Spin Angular Momentum because of the possible relation **μ = γħI** ,so that

$$\mathbf{dI/dt = \mu \times H = \gamma\hbar I \times H}$$

In the case of NQR, the rate of change of Angular Momentum

$$\mathbf{dI/dt = (1/4)\, Q\, V_{zz}\, \sin\theta}$$

does not find an expression for **Q** as simply relatable to **I** since $\mathbf{Q^{(op)}} \propto$ $\mathbf{(3I_z^2 - I^2)}$ for its dependence on Spin Operators. In this instance stating that precessional frequency can be equal to $\boldsymbol{\omega_Q}$ is not straight forward to explain. Find a rationalization for this difference and ensure the validity of the contention of the precession at $\boldsymbol{\omega_Q}$.

Answer: The most elegant way to go about convincingthe above point of view is to follow the discussion in the paper by Feynman, Vernon and Hellwarth : Journal of Applied Physics, Vol.28, No:1, page 49. And study the arguments in the application of the Geometrical representation of the Schrödinger equation to the Beam type Maser Oscillator.

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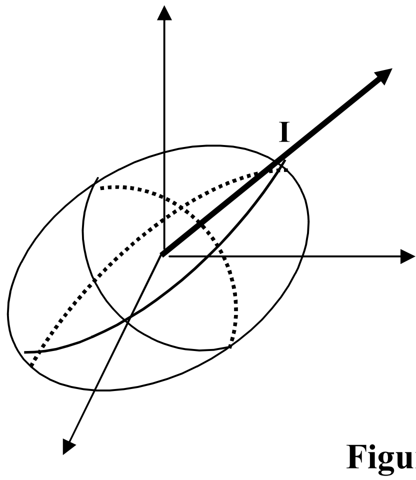
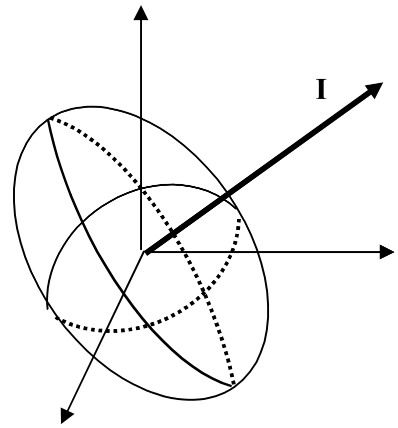
6. Hedvig P. Experimental Quantum Chemistry. NY: Academic Press; Pages 220-222. An excerpt below

Excerpt from Page 221: In the particular case when the charge distribution is axially symmetric and the main principal axes coincide with the direction of the SPIN, the quadrupole Moment is scalar. This situation is visualized in the **Figure**, where the positive charge of a nucleus is distributed as a revolution ellipsoid. When **Q > 0** the long axis of the ellipsoid is directed along nuclear spin **I** and **μ.** When **Q < 0** the ellipsoid is oblate with respect to the direction of the SPIN.





Figure

7. (a) Bloom M. Free Magnetic Induction in Nuclear Quadrupole Resonance.Physical Review, 1955; 97: 1699-1709. (b) Uma Maheswari Somayajula. Nuclear Quadrupole Resonance Study of Randomly Quenched Disorder in Structurally Incommensurate Systems. A Thesis Submitted for the award of the Degree of Doctor of Philosophy, School of Physics, University of Hyderabad, Hyderabad 500 046, India; October 1998. Chapter 3, Sec.1; p 88.

FIGURE CAPTIONS

Figure 1. (In Box) Arra ngements for the four charges to form a Quadrupolar System of Charges: (a) Regular Square and (b) Linear Arrangemenhts.

Figure 2. An Illustration for specifying fixed angle ‘ **β**’ for a possible linear quadrupole moment of the nucleus with respect to the Spin Angular Momentum of the Nucleus: both relatively disposed at fixed angles with respect to the Z axis of the EFG in the Principal Axis System.

Figure 3. (a) Dipole in a Homogeneous Field (b) (Linear) Quadrupole in a Homogeneous Field (c) Dipole in a Linear Field Gradient (d) Linear Quadrupole in a Linear Electric Field Gradient.

Figure 4. (a) A Total Charge **‘C’** distributed uniformly over a circular area (b) Addition of two (equal) positive and two (equal) negative fractional charges around the circular area (causing deviation from circular distribution) and the depiction of a possible resultant distribution of ‘**C**’ over an elliptical area. (c) A rearrangement of the two of the fractional charges to result in a Linear geometrical configuration for the additional charges. (d) Thus resulting Linear Quadrupolar System of Charges.

Figure 5. (a) Linear Quadrupolar System of charges. (b) When the Linear Quadrupolar System is placed in a Linear EFG, illustration of the equal and opposite forces acting at the midpoint of each of the two dipole moments which are equal and mutually in opposite directions.

Figure 6. (a) Energy level Scheme for the Interaction of Magnetic Moment of a Spin 2 Nucleus with external constant magnetic field. (b) The energy level scheme for the interaction of the Quadrupole Moment of the same Spin 2 Nucleus with Electric Field Gradient

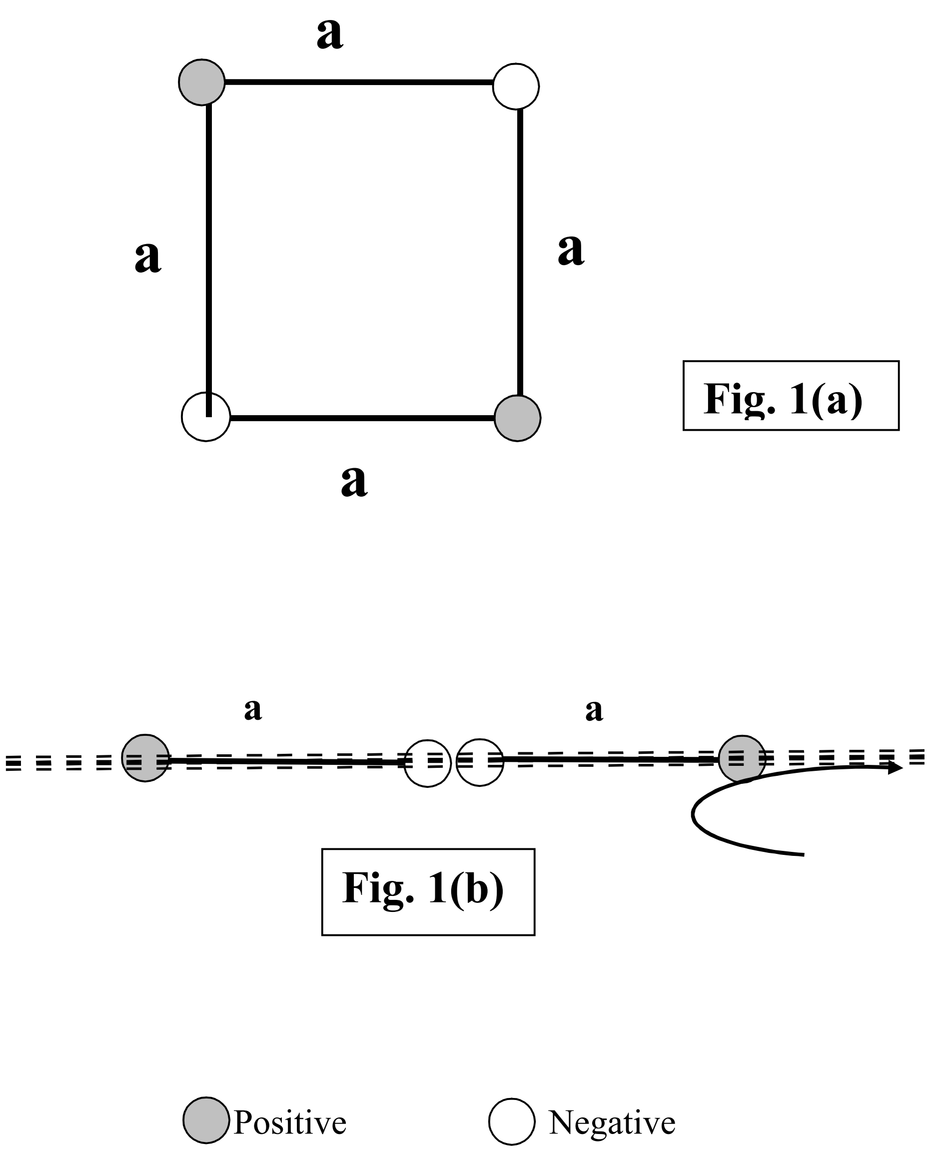


Fig. 1

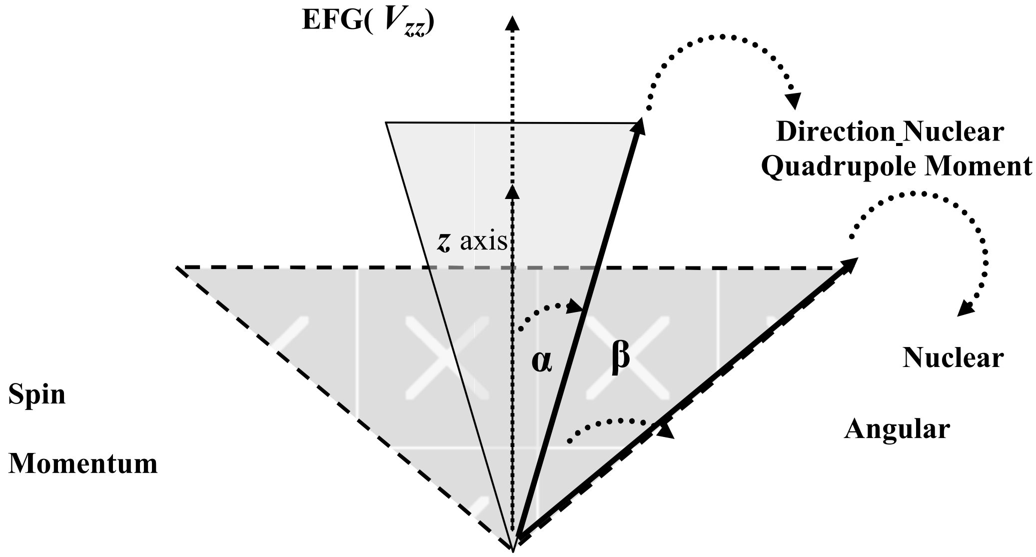

EFG(V_{zz})
Direction Nuclear
Quadrupole Moment
z axis
α
β
Nuclear
Spin
Angular
Momentum

Fig. 2

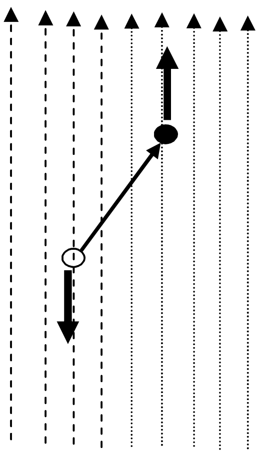


Fig. 3(a)

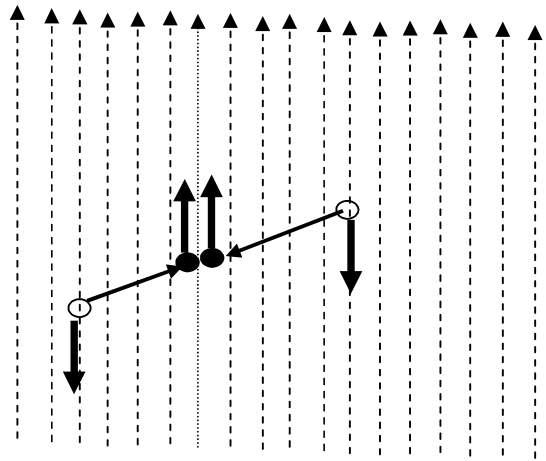


Fig. 3(b)

Fig. 3(c)

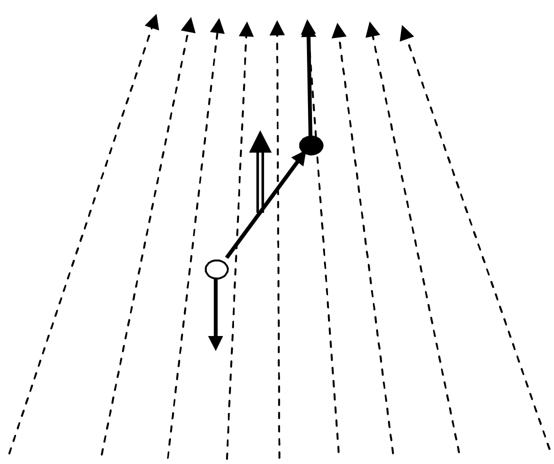
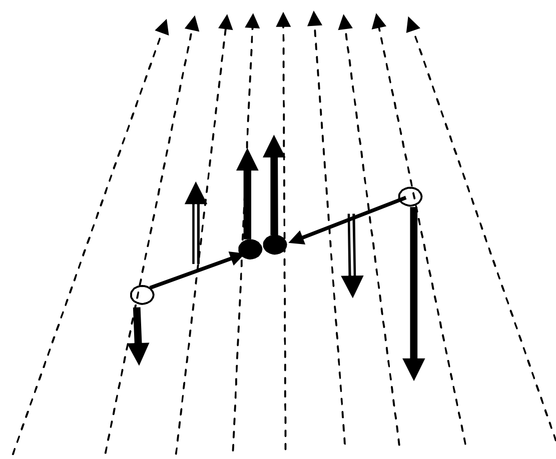


Fig. 3(d)



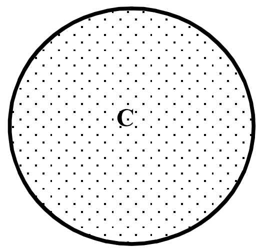


Fig.4(a)

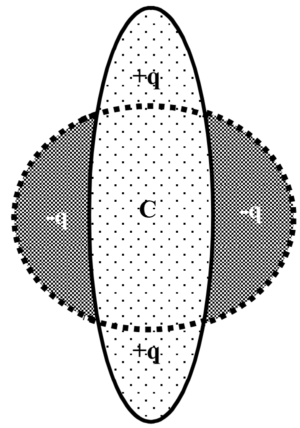
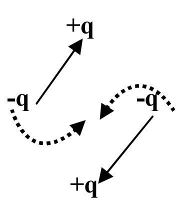


Fig.4(b)



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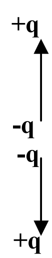

Fig.4(d)

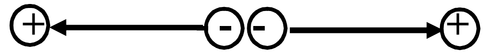

Fig.5(a)

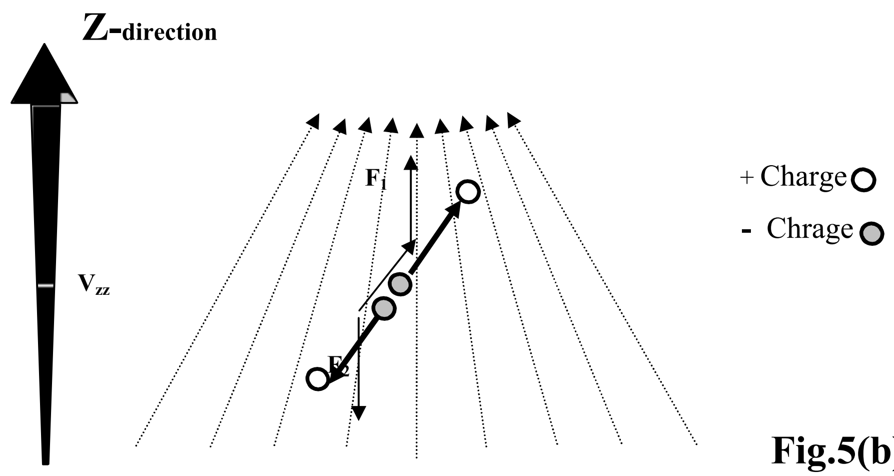

Fig.5(b)

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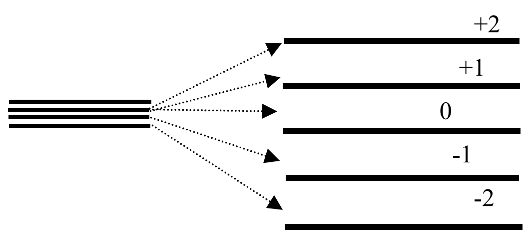

Fig. 6(a)

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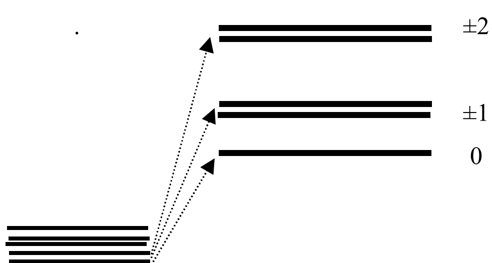

Fig.6(b)