

LONGITUDINAL RELAXATION TIME FROM MAXWELL EQUATIONS USING SPIN UP AND SPIN DOWN APPROXIMATION

By

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ABSTRACT

In this work Maxwell equations were utilized to derive an expression for the magnetic dipole moment. Treating the total dipole moment as resulting from spin up and spin down atoms, solution for the dipole moment and longitudinal relaxation time was obtained. It was found that relaxation time is related to the frequency and susceptibility.

ملخص

في هذا البحث استخدمنا معادلات ماكسويل لإستنباط معادلات العزم الثنائي المغناطيسي، وباعتبار أنّ العزم الكلي ناتج عن محصلة العزم اللفي العلوي السفلي للذرات. تم الحصول على حلول للعزم الثنائي المغناطيسي ولزمن الاسترخاء الطولي. ووجد أنّ هذا الزمن يعتمد على التردد والقابلية المغناطيسية.

RESONANCE DEFINITION [1, 2, 3, 4, 5, 6, 9, 13, ..., 17, 18, 19]

If a certain magnetic field is applied to a certain atom, each energy level splits into two or more sublevels, as proposed by Zeeman. In a simple case, each level splits into two levels where the spin up particles occupy the lower level, whereas the spin down particles occupy the upper level. When a photon of energy equals to the difference in energy between the two states is incident on this atom, resonance occurs and some particles from the lower state absorb the photon energy and are transferred to the higher state.

Resonance effect can also be explained on classical basis where each nucleus forms a very tiny magnetic dipole which, when placed in an external magnetic field, it tends to align itself along the field. Due to this interaction the magnetic moment tips away from

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the direction of the applied field and rotates around it with a certain frequency. When the frequency of the applied radio signal is equal to the precession frequency, the nucleus absorbs the radio energy and this is known as resonance.

Relaxation Time Phenomena ^[21] : Excitation of an equilibrium system always transfers the system to an unstable state. A similar unstable situation is created; the time required to the return to the equilibrium state is called the relaxation time.

The relaxation process is induced by field fluctuation due to molecular motion; relaxation may be defined as the lag in the response of a system to change in the force to which it is subjected. It is a very general phenomenon and its mechanism and rate depend upon the forces and upon the system.

Relaxation time is considered as the length of time taken by the nuclei to return to their original position that is aligned with the magnetic field. There are two types of relaxation times ^[24]

- 1- Longitudinal relaxation time T_1 , also known as spin-lattice relaxation time, is the time needed to align the protons in static magnetic field after being perturbed by an electromagnetic field.
- 2- Transfer relaxation time T_2 which is the time needed for the protons to lose coherent energy in an NMR* measurement.

Relaxations are exponential decays for which T_1 and T_2 are the time constants. Different mechanisms contribute to both T_1 and T_2 .

Initially this work was aimed at studying the longitudinal relaxation time T_1 . The longitudinal relaxation time T_1 represents the lifetime of the first order rate process that returns the magnetization to the Boltzmann equilibrium along the Z- axis. The longitudinal relaxation process T_1 governs the time interval between two transitions.

Attempts of Some Previous Studies to Find T_1 ^[7, 8, 9, 10, 11, 12]

Different attempts were made to solve T_1 problem. In Debye model T_1 is shown to be dependent on the frequency of the radiation. Solomon suggested a model in which T_1 depends on the interaction between the spin of the electron and the proton. In Korringa model

* NMR (Nuclear Magnetic Resonance).

T_1 depends on the density of the electronic state at Fermi level and on temperature.

Other attempts were also made to find T_1 , but the drawback of these attempts is due to the fact that these attempts do not reflect the experimentally observed dependence of T_1 on mass, magnetic field, and susceptibility.

Relaxation time plays an important role in magnetic resonance phenomena in physics, chemistry and medicine. Different attempts were made to find its dependence on the properties of the medium as well as on the applied external fields. These attempts are mainly based on classical grounds and show a dependence of the longitudinal relaxation time on frequency, temperature, and viscosity.

Maxwell equation is used to obtain the expression for the magnetization. The longitudinal relaxation time expressed from the magnetization due to the transition from one energy state to another. The treatment shows that the longitudinal relaxation time is related to the frequency and susceptibility.

EQUATION FOR MAGNETIC DIPOLE

Maxwell equations are regarded as the basic equations of the electromagnetic field.. The four field equations are as follows:

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0} \quad (a)$$

$$\nabla \cdot \mathbf{H} = \mathbf{j} + \frac{d\mathbf{D}}{dt} \quad (b)$$

$$\nabla \times \mathbf{E} = - \frac{d\mathbf{B}}{dt} \quad (c)$$

$$\nabla \times \mathbf{H} = \mathbf{j} + \frac{d\mathbf{D}}{dt} + \sigma \mathbf{E} \quad (d)$$

Where:

E is the electric field strength, H is the magnetic field strength B is the magnetic flux density, ϵ is the electric permittivity, σ is the conductivity.

The electric displacement and the magnetic flux density are related to the magnetic and electric field strengths by the polarization and the magnetization.

$$\mathbf{D} = \epsilon_0 (\mathbf{E} + \mathbf{M}), \quad \mathbf{B} = \mu_0 \chi_m \mathbf{H}, \quad \mathbf{B} = \mu \mathbf{H}, \quad \mathbf{M} = \chi_m \mathbf{H} \quad (1)$$

Where:

B is the magnetic flux density, μ_0 is the magnetic moment in vacuum, χ_m is susceptibility, μ is the magnetic moment, M is the magnetization, H is magnetic field strength.

Attempts at solving Maxwell Equations:

If the curl of the fourth Maxwell equation is taken one gets:

$$\nabla \times (\nabla \times H) = \epsilon \frac{d \nabla \times E}{dt} + \sigma \nabla \times E \quad (2)$$

The left hand side can be deduced to be:

$$\nabla \times (\nabla \times H) = \nabla (\nabla \cdot H) - \nabla^2 H \quad (3)$$

$$(\nabla \cdot H) = 0 \quad (4)$$

Equation (2) by using equation (3) and (4) can be obtained as:

$$-\nabla^2 H = \epsilon \frac{d \nabla \times E}{dt} + \sigma \nabla \times E \quad (5)$$

From the third law of Maxwell equations one gets:

$$\nabla \times E = -\frac{dB}{dt} \quad (6)$$

Substituting equation (6) into equation (5) to get:

$$-\nabla^2 H = -\epsilon \frac{d^2 B}{dt^2} - \sigma \frac{dB}{dt} \quad (7)$$

Where $\frac{d^2 B}{dt^2}$ is obtained through substituting for $\nabla \times E = -\frac{dB}{dt}$ inside the differential to get:

$$d \nabla \times E / dt = -d \left(\frac{dB}{dt} \right) / dt = -\frac{d^2 B}{dt^2}$$

The Derivation of Magnetization:

From the relation of the magnetic flux density:

$$B = \mu H \quad (8)$$

By substituting equation (8) into equation (7) one gets:

$$-\nabla^2 H + \mu \epsilon \frac{d^2 H}{dt^2} + \mu \sigma \frac{dH}{dt} = 0 \quad (9)$$

Multiplying equation (9) by χ_m one obtains:

$$-\nabla^2 \chi_m H + \mu \epsilon \frac{d^2 \chi_m H}{dt^2} + \mu \sigma \frac{d \chi_m H}{dt} = 0 \quad (10)$$

The magnetization M can be written as:

$$M = \chi_m H \quad (11)$$

By substituting equation (11) into equation (10) one gets:

$$-\nabla^2 M + \mu \epsilon \frac{d^2 M}{dt^2} + \mu \sigma \frac{dM}{dt} = 0 \quad (12)$$

ATTEMPTS AT SOLVING THE MAGNETIZATION

Try the solution for:

$$M = M_m(t) e^{i(kz - \omega t)} \tag{13}$$

$$dM/dt = (dM_m/dt) e^{i(kz - \omega t)} - i\omega M_m e^{i(kz - \omega t)} \tag{14}$$

$$d^2M/dt^2 = d^2M_m/dt^2 - i\omega dM_m/dt - i\omega dM_m/dt - \omega^2 M_m e^{i(kz - \omega t)} \tag{15a}$$

$$\nabla^2 M = -k^2 M_m e^{i(kz - \omega t)} \tag{15b}$$

By substituting the relations (14), (15a) and (15b) into equation (12) one obtains:

$$+k^2 M_m e^{i(kz - \omega t)} + \mu \epsilon [(d^2 M_m/dt^2) - I\omega dM_m/dt] e^{i(kz - \omega t)} + \sigma \mu [dM_m/dt - i\omega M_m] e^{i(kz - \omega t)} - \omega^2 \mu \epsilon M_m e^{i(kz - \omega t)} = 0 \tag{16}$$

Dividing equation (16) by $e^{i(kz - \omega t)}$ and setting $\sigma = 0$, one gets:

$$+k^2 M_m + \mu \epsilon [d^2 M_m/dt^2 - 2i\omega dM_m/dt - \omega^2 M_m] = 0 \tag{17}$$

Considering a slowly varying function:

$$d^2 M_m/dt^2 \ll dM_m/dt \tag{18}$$

Therefore any term containing $d^2 M_m/dt^2$ is neglected and one gets:

$$2i\omega \mu \epsilon dM_m/dt = [k^2 - \mu \epsilon \omega^2] M_m \tag{19a}$$

Rearranging equation (19a) one gets:

$$dM_m/M_m = [(k^2 - \mu \epsilon \omega^2) / (2i\omega \mu \epsilon)] dt \tag{19b}$$

By integrating equation (19b) one obtains:

$$\int dM_m/M_m = \int [(k^2 - \mu \epsilon \omega^2) / (2i\omega \mu \epsilon)] dt + M_1 \tag{20a}$$

where M_1 is the integration constant.

Integrating equation (20a) yields:

$$M_m(t) = M_0 e^{i[(\mu \epsilon \omega^2 - k^2) / (2\mu \epsilon \omega)]t} \tag{20b}$$

Therefore equation (13) becomes:

$$M = M_0 e^{-i[(i\omega + [(\mu \epsilon \omega^2 - k^2) / (2\omega \mu \epsilon)])t - kz]}$$

$$M = M_0 e^{ikz} e^{i[(\mu \epsilon \omega^2 - k^2 - \omega) / (2\mu \epsilon \omega)]t} \tag{21}$$

Taking the real part of equation (21) after setting $z = 0$, assuming that M is along z -axis, the real part becomes:

$$M_z(t) = M_z = M_0 \cos [(\mu \epsilon \omega^2 - k^2 - \omega) / (2\mu \epsilon \omega)]t \tag{22}$$

At $t = 0$: $M(0) = M_0$ That is because when $t = 0$, the angle becomes zero and then \cos zero = 1; which is the maximum value of the cosine.

Therefore:

$$M_{(0)} = M_0 \tag{23}$$

INTERPRETATION OF MAXIMUM AND MINIMUM MAGNETIZATION

The nuclei align themselves in one of two possible orientations, defined as the spin up directions (low energy state) or spin down direction (high energy state).

This observed phenomenon can be described in terms of a vector force M_z . The nuclei are constantly exchanging between spin up and spin down orientations, but they will quickly reach an equilibrium state where there is an excess number of nuclei in the spin up (lower energy state) alignment and the atom is referred to as being fully magnetized.

Thus the net magnetic vector M at equilibrium points upwards along the Z- axis as shown in (figure 1).

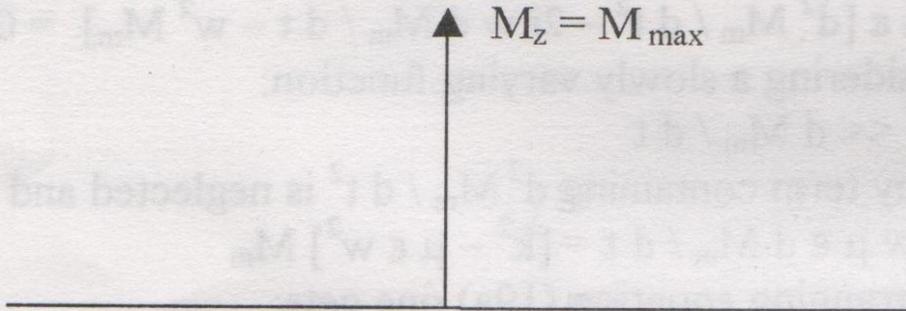


Figure (1) shows the maximum magnetization along the Z- axis

If we assume that each molecule (proton) have a magnetic moment M_p (p refer to proton), and the number of the molecules pointing upwards is N_a the magnetization M_z in case that all the protons are in the lower state, is given by:

$$M_z = N_a M_p;$$

as shown in figure (2).

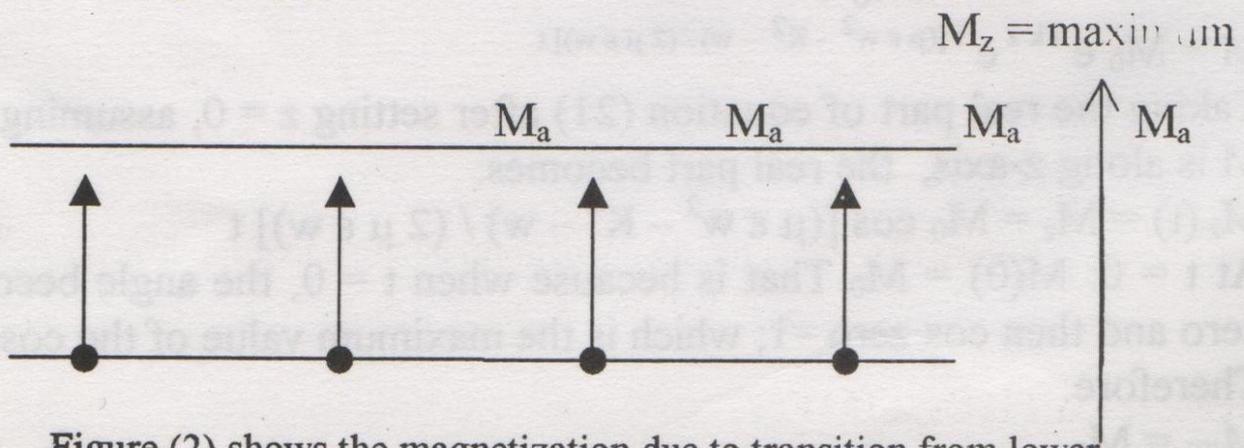


Figure (2) shows the magnetization due to transition from lower energy state to upper energy state

In this case M_z is maximum, and in view of equation (22) this occurs when $t = 0$.

$$\text{i.e., } M_z(0) = M_0 = N_a M_p \tag{24a}$$

On the other hand, M is minimum when:

$$t = T_1 = (\pi / 2)(2 \mu \epsilon w) / (\mu \epsilon w^2 - w - k^2) \tag{24b}$$

where:

$$M_z = M_0 \cos [(-w - k^2 + \mu \epsilon w^2) / \mu \epsilon w] \pi / 2 [(-w - k^2 - \mu \epsilon w^2) / \mu \epsilon w] = M_0 \cos \pi / 2$$

Since $\cos \pi / 2 = 0$, then:

$$M_z = 0 \tag{24c}$$

Equation (24c) means that magnetization M_z equals to zero when the number of nuclei (N_a) in the lower energy state equals the number of nuclei (N_b) in the upper energy state as shown in figure (3). The magnetization M_z due to the lower energy state is equal to:

$$M_z = N_a M_a \tag{25}$$

While the magnetization M_z due to the upper energy state is equal to:

$$M_z = N_b M_a \tag{26}$$

$$\text{When } N_a = N_b \tag{27}$$

From equations (25), (26), and (27) one gets:

$$M_z = (N_a - N_b) M_a \tag{28}$$

$$\therefore M_z = 0 \tag{29}$$

Equation (29) is described in figure (3). The time T_1 which is taken by M_z to drop to zero from its maximum value is called the longitudinal relaxation time.

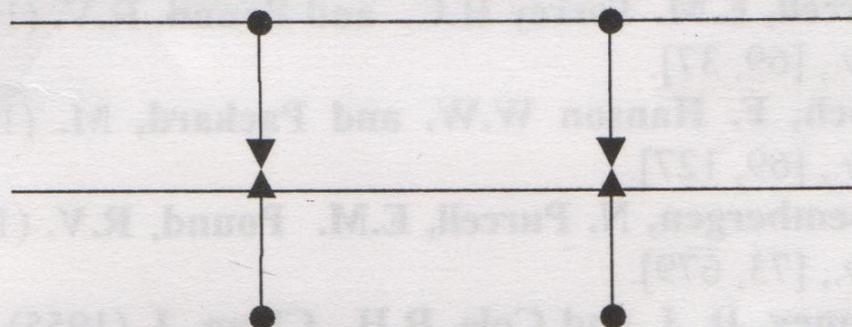


Figure (3) shows the magnetization due to equal number of nuclei in two energy states ($M_z = \text{zero}$)

RELAXATION TIME T_1

From equation (24b) the relaxation time T_1 can be expressed as:

$$T_1 = (\pi/2) [(2 \mu \epsilon w) / (\mu \epsilon w^2 - k^2 - w)]$$

$$= 2 \mu \epsilon w / w^2 (1 - 2 \mu \epsilon) + k^2$$

When $w \gg 1$, k^2 and w can be neglected. Then:

$$T_1 \cong \pi \mu \epsilon w / w^2 \mu \epsilon \tag{30}$$

$$\cong \pi / w$$

$$T_1 \sim 1 / w \tag{31}$$

The result in equation (31) shows that the relaxation time T_1 is inversely proportional to w , and we deduce that for very high frequency w the relaxation time is very short which is in conformity with the classical value.

CONCLUSION

The expression for the longitudinal relaxation time T_1 is shown to be inversely proportional to the frequency w , in complete agreement with the previous classical works and the common sense. It is also related to the susceptibility which also is in conformity with physical reality.

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DIRAC DELTA FUNCTION AND THE PROBABILITY DENSITY OF AN ELECTRON BOUND IN THE ANGULAR-MOMENTUM EIGENSTATES

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ABSTRACT

The Dirac delta function is shown to be an operator for the probability density. General expressions for these densities are presented and expressed in terms of multipole expansion found in most textbooks on electricity and magnetism. Some illustrative examples are given.

ملخص

عنوان البحث: دالة دلتا ديراك وكثافة الاحتمال للاكترونيات المقيدة في الحالات المميزة للاندفاع الزاوي.

تم التعبير عن دالة ديراك في شكل مؤثر لإيجاد كثافة الاحتمال. وعرضت التعبيرات العامة لهذه الكثافة بدلالة مفكوك متعدد الأقطاب موجود في معظم الكتب الدراسية في الكهربائية و المغناطيسية. وقد قدمت بعض الأمثلة التوضيحية بخصوص ذلك.

INTRODUCTION

In quantum mechanics the concept of probability density is essential. Classical theory state that the behavior of particle can be described in terms of two parameters, position and velocity. Quantum mechanics however, introduces only one parameter: the wave function Ψ which is associated with the motion of the particle. It is interpreted as probability amplitude of the particle's presence. For the stationary states, the quantity:

$$\rho(\mathbf{r}) = \Psi(\mathbf{r})^* \Psi(\mathbf{r}). \quad (1)$$

is interpreted as probability density. This may appear conceptually difficult, presumably for the reason, it is not associated to any distribution function (operators). There should be an operator in quantum mechanics which is associated to this quantity. Indeed the

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Dirac $\delta(\mathbf{r}' - \mathbf{r})$ "function" is the required one. Take the expectation value of the $\delta(\mathbf{r}' - \mathbf{r})$ function between the one-particle wave function $\Psi(\mathbf{r})$ and obtain:

$$\langle \Psi(\mathbf{r}') | \delta(\mathbf{r}' - \mathbf{r}) | \Psi(\mathbf{r}') \rangle = \int \Psi^*(\mathbf{r}') \delta(\mathbf{r}' - \mathbf{r}) \Psi(\mathbf{r}') d\mathbf{r}' \quad (2)$$

where \mathbf{r}' and \mathbf{r} are respectively the position vector of an electron and the point at which the density is calculated. Making use of properties of delta function:

$$\int \delta(\mathbf{r}' - \mathbf{r}) f(\mathbf{r}') d\mathbf{r}' = f(\mathbf{r}),$$

and the fact that the position functions are commutable. It is evidently seen that the integrand of the left right side of eq.(2) will produce the required result (right hand side of eq.(1)). One of the states of our interest will be the spin-orbit uncoupled eigenstate:

$$\Psi(\mathbf{r}) = | n l s m_l m_s \rangle = R_{nl}(\mathbf{r}) Y_m^l(\theta, \phi) | s m_s \rangle, \quad (3)$$

where $Y_m^l(\theta, \phi)$ the spherical harmonics, $| s m_s \rangle$ is the spin function and $R_{nl}(\mathbf{r})$ is the radial wave function. The radial wave function for the hydrogenic wave function, has the following expression [1]

$$R_{nl}(r) = \left[\alpha^3 \frac{(n-l-1)!}{n(n+l)!} \right]^{1/2} e^{-\alpha r/2} (\alpha r)^l L_{n-l-1}^{2l+1}(\alpha r) \quad (4)$$

Here $\alpha = 2Z/na_0$, a_0 is the Bohr radius, Z the atomic number and $L_{n-l-1}^{2l+1}(\alpha r)$ is the associated Lagurre polynomial which is defined by the relation

$$L_q^k(x) = \frac{e^x x^k}{q!} \frac{d^q}{dx^q} (e^{-x} x^{k+q}). \quad (5)$$

To get some explicit expression (multipole expansion) for the density of eq.(1) in the uncoupled single-electron eigenstates of eq. (3), one may expand the delta function [1] of eq. (2) in terms of spherical harmonics as:

$$\delta(\mathbf{r}' - \mathbf{r}) = \frac{1}{r^2} \delta(r' - r) \sum_{LM} Y_M^L(\theta', \phi') Y_M^{*L}(\theta, \phi), \quad (6)$$

and evaluate the expectation value with the Wigner-Eckrat theorem. Although this method can be easily extended to many-electrons

system [2], it requires some considerable knowledge of Wigner-Eckrat theorem. So it is better to get results directly from eq. (1).

MULTIPOLE EXPANSION OF THE PROBABILITY DENSITY IN UNCOUPLED SINGLE EIGENSTATES:

Substituting $\Psi(\mathbf{r})$ of eq. (3) in eq.(1) results in:

$$\rho(\cdot) = R_{nl}^2(r)(-1)^{m_1} Y_{-m_1}^{l_1}(\theta, \phi) Y_{m_2}^{l_2}(\theta, \phi). \tag{7}$$

To get this result we make use of the identity $Y_{-m}^{l_1}(\theta, \phi) = (-1)^m Y_{m}^{l_1}(\theta, \phi)$ and the fact that the spin functions are orthogonal. Equation (7) can be expressed in terms of a single spherical harmonics by expanding the product of the two spherical harmonics with the aid of

$$Y_{m_1}^{l_1}(\theta, \phi) Y_{m_2}^{l_2}(\theta, \phi) = (-1)^{l_1-l_2+M} \sum_{L=|l_1-l_2|}^{l_1+l_2} \sqrt{\frac{(2L+1)(2l_1+1)(2l_2+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix} \times \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} Y_M^L(\theta, \phi).$$

Consequently eq. (7) will reduce to

$$\rho(r) = R_{nl}^2(r)(-1)^m \sum_{L=0}^{2l} (2L+1) \sqrt{\frac{(2L+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} Y_M^L(\theta, \phi) \tag{8}$$

where $\begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}$ and $\begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix}$ are the 3j symbols which are closely related to the Celebesh-Gordan coefficients [6] and $M = -(m_1 + m_2)$. The 3j symbol $\begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}$ will impose the condition that L must be even ($L=0, 2, \dots, 2l$).

The spherical harmonics Y_M^L can be written as:

$$Y_M^L = (-1)^M \left[\frac{(2L+1)(L-M)!}{4\pi(L+M)!} \right]^{1/2} P_M^L(\cos\theta) e^{im\phi} \tag{9}$$

where $P_M^L(\cos\theta)$ are the associated Legendre function and $P_0^L = P_L$ the Legendre functions. We list here some expressions of the associated Legendre functions which are relevant to this article:

$$P_0 = 1, P_2 = \frac{1}{2}(3 \cos^2 \theta - 1), P_4 = \frac{1}{8}(35 \cos^4 \theta - 30 \cos^2 \theta + 3),$$

$$P_6 = \frac{1}{16}(31 \cos^6 \theta - 315 \cos^4 \theta + 105 \cos^2 \theta - 5). \tag{10}$$

Substitution of Y_o^L in eq. (8) after getting its value from eq. (9), we express the probability density of eq. (8) as:

$$\rho(r) = \frac{(-1)^m}{4\pi} (2l+1) R_{nl}^2(r) \sum_{L=0}^{2l} (2L+1) \begin{pmatrix} l & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & l & L \\ m & -m & 0 \end{pmatrix} P_L \tag{11}$$

MULTIPOLE EXPANSION OF THE PROBABILITY DENSITY IN SPIN ORBIT COUPLED EIGENSTATES

In this section we will extend the previous method of last section to get some expression for the probability density of spin-orbit coupled eigen-states. These eigenstates are conveniently represented as a spinor of the form

$$\Psi = \begin{pmatrix} \uparrow \\ \downarrow \end{pmatrix} \tag{12}$$

where [3]

$$\psi_l^\uparrow = R_{nl}(r) \sqrt{\frac{l-m}{2l+1}} Y_m^l$$

$$\psi_l^\downarrow = -R_{nl}(r) \sqrt{\frac{l+m+1}{2l+1}} Y_{m+1}^l \tag{13}$$

for low-lying spin-orbit coupled states and

$$\psi_h^\uparrow = R_{nl}(r) \sqrt{\frac{l+m+1}{2l+1}} Y_m^l$$

$$\psi_h^\downarrow = R_{nl}(r) \sqrt{\frac{l-m}{2l+1}} Y_{m+1}^l \tag{14}$$

for the higher-lying spin-orbit coupled state. Using the spinor of eq.(12), the probability density for the spin-orbit (so) coupled state is easily seen to be:

$$\rho_{so}(r) = \psi^{*\uparrow} \psi^\uparrow + \psi^{*\downarrow} \psi^\downarrow \tag{15}$$

Following the same procedure of obtaining eq. (11) in the last section we express the density for low-lying and high-lying spin-orbit eigenstate respectively as:

$$\rho_{sol}(r) = \frac{(-1)^m}{4\pi} R_{nl}^2(r) \sum_{L=0}^{2l} (2L+1) \begin{pmatrix} l & l & L \\ 0 & 0 & 0 \end{pmatrix} \left[\begin{matrix} (l-m) \begin{pmatrix} l & l & L \\ m & -m & 0 \end{pmatrix} \\ -(l+m+1) \begin{pmatrix} l & l & L \\ m+1 & -(m+1) & 0 \end{pmatrix} \end{matrix} \right] P_L \tag{16}$$

and

$$\rho_{soh}(r) = \frac{(-1)^m}{4\pi} R_{nl}^2(r) \sum_{L=0}^{2l} (2L+1) \begin{pmatrix} l & l & L \\ 0 & 0 & 0 \end{pmatrix} \left[\begin{matrix} (l+m+1) \begin{pmatrix} l & l & L \\ m & -m & 0 \end{pmatrix} \\ -(l-m) \begin{pmatrix} l & l & L \\ m+1 & -(m+1) & 0 \end{pmatrix} \end{matrix} \right] P_L \tag{17}$$

We list here some expressions of the 3j symbols [5] which are suitable for evaluation of the probability density for any hydrogenic wavefunction:

$$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = 1, \tag{18}$$

$$\begin{pmatrix} l & l & 0 \\ m & -m & 0 \end{pmatrix} = (-1)^{l-m} [2l+1]^{-1/2}, \tag{19}$$

$$\begin{pmatrix} l & l & 2 \\ m & -m & 0 \end{pmatrix} = (-1)^{l-m} \frac{3m^2 - l(l+1)}{[(2l-1)l(l+1)(2l+1)(2l+3)]^{1/2}}, \tag{20}$$

$$\begin{pmatrix} l & l & 2l-2 \\ m & -m & 0 \end{pmatrix} = -(2l-1) \left[\frac{2}{(4l+1)!} \right]^{1/2} \frac{[(2l-2)!]^2 [l^2 - 4lm^2 + m^2]}{(l-m)!(l+m)!}, \tag{21}$$

and

$$\begin{pmatrix} l & l & 2l \\ m & -m & 0 \end{pmatrix} = \frac{[(2l)!]^2}{(l-m)!(l+m)![(4l+1)!]^{1/2}}, \tag{22}$$

APPLICATION TO PARTICULAR STATES

We will give in this section two examples which are relevant to atomic magnetism [2] and which will serve as illustrations for the calculation of multipole expansion of the probability density. We will first evaluate the probability density for the uncoupled spin-orbit eigenstate $|n = 3, l = 2, m_l = 1, m_s = 1/2\rangle$. For this state $L=0, 2, 4$, and the radial part of the wavefunction is:

$$R_{32}(r) = \frac{\sqrt{30}}{1215 \sqrt{a_0^7}} r^2 e^{-r/3a_0} \tag{23}$$

Substitution of $l = 2, m_l = 1, L = 0, 2, 4$ and appropriate $3j$ symbols of eqs. (18)-(22) or of reference [4] in eq. (11) we get:

$$\rho(r) = \frac{R_{32}^2(r)}{4\pi} [P_0 + \frac{5}{7}P_2 - \frac{1}{7}P_4] \tag{24}$$

after making use of eq. (10) and (23), this equation will reduce to:

$$\rho(r) = \frac{r^4}{6561a_0^7} e^{-2r/3a_0} (\cos^2 \theta - \cos^4 \theta) \tag{25}$$

Panels (a), (b) and (c) of Figure 1 are respectively, the graphical representations of the radial part $R_{32}(r)$, angular part $[P_0 + \frac{5}{7}P_2 - \frac{1}{7}P_4]$ and the probability density $\rho(r)$ of eq. (24). The second example which we will consider here is the evaluation of the probability density for the low-lying spin-orbit coupled eigenstate $|n = 4, l = 3, j = 5/2, m_j = 5/2\rangle$. This state is important in magnetism, it is the ground state of Ce^{3+} . In this case $l = 3, m_l = m_j - 1/2 = 2, L = 0, 2, 4, 6$ and the radial part of the wave function is:

$$R_{43}(r) = \frac{\sqrt{35}}{26880 \sqrt{a_0^9}} r^3 e^{-r/4a_0} \tag{26}$$

Following the same procedure of obtaining the probability density for the previous state, we find the multipole expansion for this state as:

$$\rho_{\text{sol}}(r) = \frac{R_{43}^2(r)}{4\pi} [P_0 - \frac{10}{7}P_2 + \frac{3}{7}P_4] \quad (27)$$

This equation will reduce in a similar way to

$$\rho_{\text{sol}}(r) = \frac{r^6}{44040192a_0^7\pi} e^{-r/2a_0} (1 - 2\cos^2 \theta + \cos^4 \theta) \quad (28)$$

Panels (a), (b) and (c) of Figure 2 are respectively, the graphical representation of the radial part $R_{43}^2(r)$, angular part $[P_0 - \frac{10}{7}P_2 + \frac{3}{7}P_4]$ and the probability density $\rho(r)$ of eq.(28).

CONCLUDING REMARKS

Patterns of Figures 1 and 2 ((b) and (c)) reveal that the distribution of electron position over space is quite complicated. This conclusion destroys any naive idea of an electron orbiting in specified orbits around the nucleus. The behavior of an individual electron is random and the interpretation of this behavior in terms probability density is necessary. The electron cloud can explain this behavior. The angular distribution of the probability density of the first state is a double torrid. This is in accord with the findings [2] that, the magnetic field generated by this state is a reminiscent of the field lines produced by a Helmholtz pair (two equivalent coils spaced a radius apart). The angular distribution of the probability density of the second state consists of a single torrid which is much simpler than the previous one. The magnetic field generated in this case is also found to be a reminiscent of the field of a single loop. In summary, we have presented a general method of calculating the probability density of an electron bound in angular momentum eigenstates. This method is similar to the method of obtaining the multipole expansion for the electrostatic potentials. It has a merit of clarifying the concept of probability density.

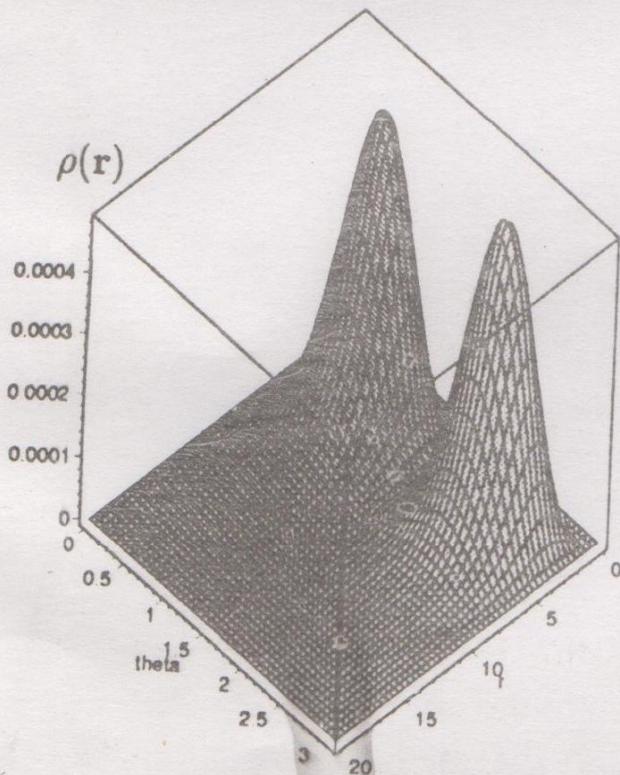
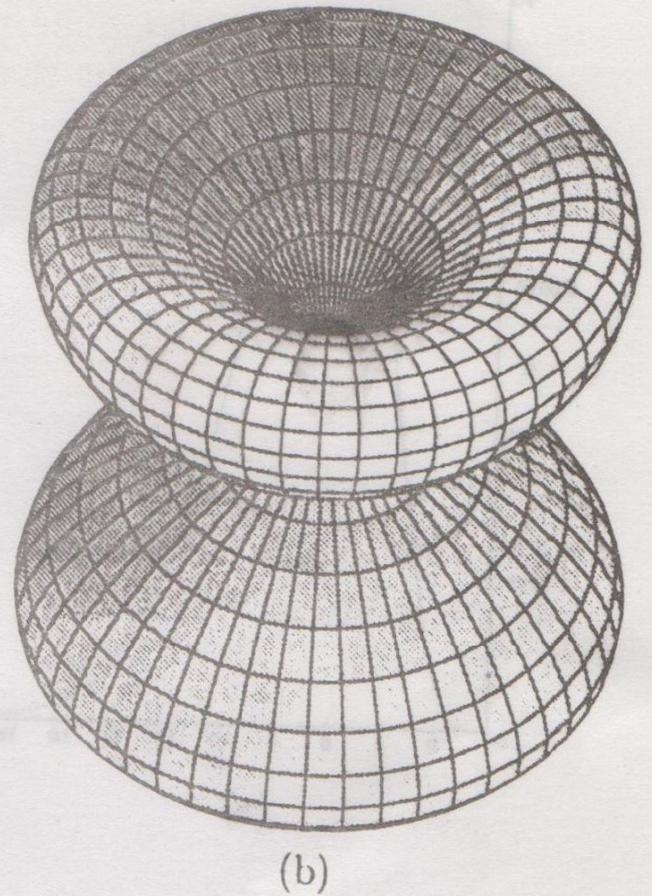
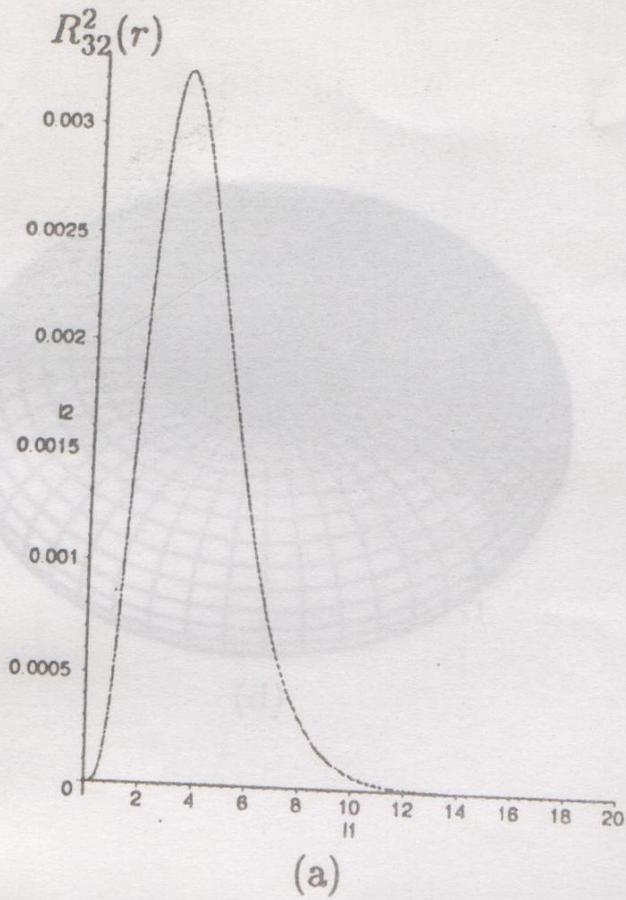


Figure (1): (a) The radial part of the probability density of eq. (24). (b) The distribution of the angular part in spherical coordinates (eq. (24)) and (c) The probability density (eq. (24)) plotted as function of r and θ .

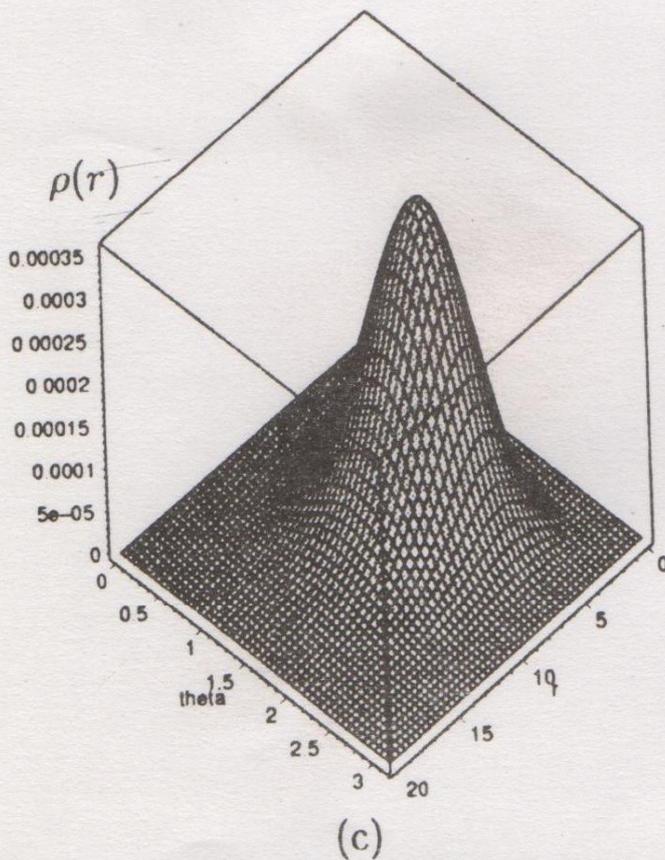
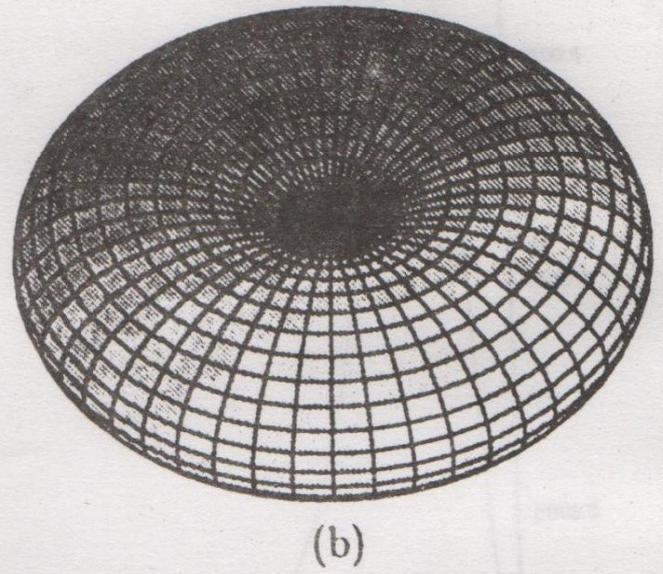
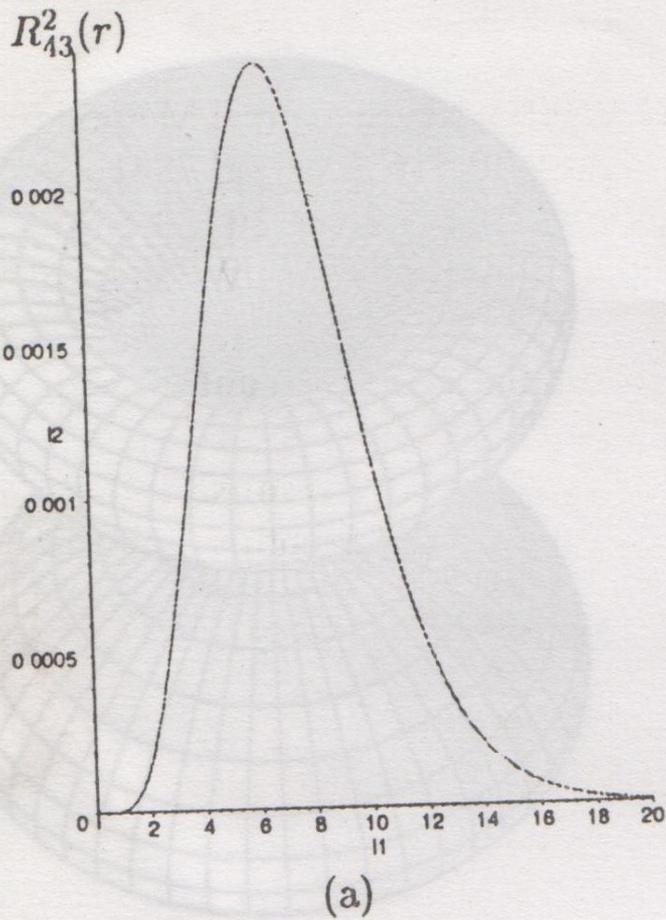


Figure 2: (a) The radial part of the probability density of eq. (27), (b) The distribution of the angular part in spherical coordinates (eq. (27)) and (c) The probability density (eq. (27)) plotted as function of r and θ .

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