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Model for a Physiological Magnetic Compass

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1. Introduction

The observation that magnetic fields in the range 10 - 100 gauss can influence chemical and biochemical reactions with biradical intermediates[1,2] lead us to inquire if in principle such reactions can explain the molecular origin of the magnetic sense in higher animals. However, before such reactions are envoked one needs to adress two questions: (1) Can the hyperfine mechanism, which bears a dependence of biradical reactions on the absolute magnitude of an external magnetic field, also induce a dependence on the orientation of an external field? (2) Can such dependence also be produced by fields as low as the earth's magnetic field?

The first question can be answered immediately to the affirmative by pointing to the observations of Merrifield et al.[3] and Michel-Beyerle et al.[4] which proved that electron transfer reactions at a solid surface, i.e. between a dye and a crystal of organic molecules, shows a dependence on the magnitude as well as on the orientation of the external magnetic field. The origin of this effect is the anisotropy of the hyperfine coupling between nuclear and electronic spins.

In the following we will provide a positive answer also to the second question showing that fields which are weaker than the earth's magnetic field can induce an orientational dependence of a biradical biochemical reaction[5]. There is one important physical consideration which limits this possibility. The magnetic interaction between fields as weak as the earth's magnetic field measures only about 10^{-9} eV. For such small energies to influence a physical process quantum mechanics dictates the process to last a microsecond or longer. Such long reaction times are unusual for radical pairs, however, they have been realized by Turro and coworkers[6] and by Steiner[7] for such reactions occurring in micellar systems. In fact, the micellar reactions observed show a very pronounced magnetic field dependence at low field strengths.

We are, of course, aware of the fact illustrated by Fraenkel and Kirschvink in these proceedings[8] that the magnetic sense of some lower life forms is explained simply by the mechanical torque which the earth's field exerts on magnetite material in living cells. Granting that magnetite is rather ubiquitous in living tissues and, in particular, has been found in the sculls of migratory birds with magnetic

sensory capabilities, one might wonder if there is any reason for alternative explanations.

Our reason for considering an alternative explanation for the magnetic sense of higher organisms are the following. First, we note that the role of magnetite in the chain of physiological processes which lead to magnetosensory responses is very uncertain. In fact, it is still not known where in the body the primary magnetic sensory organs are located[9]. The best evidence in this respect are neurophysiological recordings of Semm which indicate that the retina may be involved[10]. Advocating a role of magnetite one would need to explain how the nerve system records the weak mechanical torque exerted by the earth's field and how the recording is computed into a behavioural response. A corresponding organ has not been discovered. Granting that such organ might exist some puzzling problems still remain: Why are magnetic sensory abilities of birds restricted to a narrow window of field strengths, i.e. deviate in their dependence on the field strength completely from the Langevin function type of behaviour expected for a mechanical torque mechanism[11]? Why do birds require light for their magnetic sensory responses[12]? Why can birds not differentiate between magnetic north and south, except on the basis of the inclination of the field lines[12]? Finally, why do organisms also show magnetic field effects on the products of physiological reactions, e.g. melatonin synthesis[13]?

Certainly, even if one seeks to envoke the magnetite hypothesis one could contrive answers to the questions posed above. However, at this point of uncertainty about the details of the magnetosensory mechanism it appears to be promising to also explore alternative explanations which may yield natural answers to the above questions. Actually one should bear the possibility in mind that the final explanation of the magnetosensory apparatus in higher animals may as well envoke both a magnetic field dependent biochemical reaction and magnetite, the role of the latter being to alter the magnetic field at the site of the actual sensory organ, e.g. the retina. Such role of magnetite may involve magnetite fixed to the organism, for example, in the scull[14] or magnetite which is free to orient relative to the organism.

2. Model: Biradical Reaction Induced by an Anisotropic Hyperfine Interaction

We consider a reaction which follows the following scheme:

$$^1X \xleftarrow[k_x]{} {}^1Z - {}^1 \underset{k_s}{\overset{k_i}{\rightleftarrows}} {}^1(^2R_1 +^2 R_2) \longleftarrow \text{magnet. int.} \longleftrightarrow {}^3(^2R_1 +^2 R_2) \xrightarrow[k_t]{} {}^3T \quad (2.1)$$

The reaction starts with a singlet precurser ^1Z which might be an excited singlet state $^1(^2R_1 +^2 R_2)$ generated by the absorbtion of a photon. The precurser can either decay to the product ^1X, e.g. a ground state molecule, or dissociate into two radicals $^2R_1 +^2 R_2$. The singlet pairing of the radical pair $^1(^2R_1 +^2 R_2)$ can reform the precursor. The triplet pairing of the radical pair $^3(^2R_1 +^2 R_2)$ forms a triplet product ^3T which is supposed to be chemically distinct from both ^1Z and ^1X. Examples of such reactions are presented in the contribution by K. Schulten in these proceedings.

It is important to note that the reaction scheme assumed here is one which has been observed in numerous studies of magnetic field dependent chemical reactions[15]. Yet it is by no means clear which physiological reaction might have corresponding properties. In case one interprets the evidence in Refs. 9,10 to imply that the primary magnetosensory process occurs in the outer segments of the visual receptors the physiological process in question might be identified with one of the steps in the cyclic-GMP reaction cycle[16]. Since the reaction system needed to be in a fixed orientation relative to the organism, i.e. should be located at the disk membranes of the outer segments, the most likely candidate would be one of the reaction steps connected with bleached rhodopsin or iodopsin at the meta$_{II}$ stage, i.e. the exchange of GTP for GDP on the GTP binding protein or the phosphorylation of meta$_{II}$-rhodopsin or its iodopsin equivalent. In this respect it is of interest to note that the other organ for which magnetic sensitivity has been reported (see for example Ref. 13) appears to contain rhodopsin kinase, i.e. the enzyme which phosphorylates meta$_{II}$-rhodopsin[17]. Unfortunately, little is known about the mechanisms of phosphorylation reactions. Possibble mechanisms have been reviewed recently by Kozlov and Skulachev[18].

In order to predict in how far a reaction governed by the scheme (1) can produce the desired orientational magnetic field dependence we follow the same

theory which had been employed previously to predict and analyze magnetic field effects involving solely a dependence on the strengh of an external field. For this purpose we describe the reaction (1) by the von Neumann equation

$$\partial_t \rho = -i[H, \rho(t)]_- + \frac{k_s Z(t) Q_s}{Tr Q_s} - \frac{1}{2}[Q_s, \rho(t)]_+ - \frac{1}{2} k_t [Q_t, \rho(t)]_+ \qquad (2.2)$$

where ρ is the electron-nuclear spin density matrix for the radical pair, Q_s, Q_t are the projection operators onto the singlet and triplet electron spin substates, and H is the Hamiltonian operator which governs the electron-nuclear spin motion. For details see the contribution by K. Schulten in these proceedings and references therein. $Z(t)$ denotes the concentration of the singlet precursor molecules which obeys the equation

$$\partial_t Z(t) = -(k_x + k_i) Z(t) + \frac{1}{2} k_s Tr[Q_s \rho(t)]_+ \qquad (2.3)$$

These equations can be solved analytically for $k_S = k_T = k$. One determines for the total fraction of products ^3T formed for each initial molecule ^1Z

$$\phi_T = 1 - \frac{1}{Tr Q_s} \sum_{m,n} \frac{|(m|Q_s|n)|^2}{1 + \frac{1}{k^2}(\epsilon_m - \epsilon_n)^2} \qquad (2.4)$$

where $|m,n)$ denote the eigenstates and $\epsilon_{m,n}$ the eigenvalues of the spin Hamiltonian H. Our aim is to study the dependence of ϕ_T on the orientation of the external magnetic field. We expect that such dependence is brought about by an anisotropic hyperfine coupling interaction between electron spins and nuclear spins. A simple model which allows to study the effect of such hyperfine coupling involves one nuclear spin on each of the two radicals, i.e. on $^2R_1$ and on $^2R_2$. The corresponding model is described by the electron-nuclear spin Hamiltonian

$$H = H_1 + H_2; \quad H_i = \vec{B} \cdot \vec{S}_i + \vec{I}_i \cdot \mathrm{A}_i \cdot \vec{S}_i \quad i = 1,2. \qquad (2.5)$$

Here $\vec{S}_i$ and $\vec{I}_i$ denote the electron and nuclear spins on ^2R_i, A_i is the hyperfine coupling tensor for which we assume a diagonal form with elements a_{ix}, a_{iy} and a_{iz}. We will assume that $\vec{B}$ is oriented perpendicularly to the y-axis, i.e. that it has the components $B_x = B sin\theta, B_y = 0$ and $B_z = B cos\theta$.

In a first demonstration we consider the particular hyperfine coupling $a_{1x} = a \neq 0$, $a_{1x} = a_{1y} = a_{2x} = a_{2y} = a_{2z} = 0$. In this case the z-component of the nuclear spin $I_{1z} = \pm\frac{1}{2}$ is conserved and the Hamiltonians are represented by the two matrices

$$H_1 = \begin{pmatrix} B_z \pm a & B_x \\ B_x & -(B_z \pm \frac{a}{2}) \end{pmatrix}, \quad H_2 = \begin{pmatrix} B_z & B_x \\ B_x & -B_z \end{pmatrix}. \qquad (2.6)$$

where the corresponding basis set of electron-nuclear spin states are $|S_{1z} = \frac{1}{2}, I_{1z} = \pm\frac{1}{2}>$, $|S_{1z} = -\frac{1}{2}, I_{1z} = \pm\frac{1}{2}>$, and $|S_{2z} = \frac{1}{2}>, |S_{2z} = -\frac{1}{2}>$, respectively. The eigenvalues of these two matrices are

$$\epsilon_{1\pm} = \pm\sqrt{B^2 \pm aBcos\theta + \frac{a^2}{4}}, \quad \epsilon_{2\pm} = \pm B \qquad (2.7)$$

If the eigenvalues of both Hamiltonians are equal, the two electron spins evolve in phase, and the radical pair, which is initially formed in the singlet state $^1(^2R_1 + ^2R_2)$, will not reach the triplet state $^3(^2R_1 + ^2R_2)$, i.e. will not form triplet products ^3T. However, even a slight difference in the eigenvalues $\epsilon_{i\pm}$ will destroy the in phase motion of the electron spins, at least after many precessions of the two electron spins. Therefore, if the reactions of $^2R_1 + ^2R_2$ are slow enough, like in micellar systems[6], then one can expect the formation of ^3T, even for very small differences of $\epsilon_{i\pm}$. The accidental degeneracies of $\epsilon_{i\pm}$ occur for field strengths B and angles θ, which obey the relation

$$cos\theta = \frac{a}{4B}. \qquad (2.8)$$

At these B and θ values $\phi_T(B,\theta)$ vanishes. Near such tuples of B, θ values $\phi_T(B,\theta)$ should vary rapidly with either B or θ. This expectation is, in fact, borne out by a numerical calculation as shown in Figure 1.

The B,θ dependence presented in Fig. 1 is actually generic for a broader class of hyperfine coupling tensors. This is demsonstrated by Figure 2 which shows $\phi_T(B,\theta)$ for $a_{1y} = 13$ Gauss, $a_{1z} = 15$ Gauss, $a_{2y} = 7$ Gauss, $a_{2z} = 5$ Gauss and $a_{ix} = 0$. Figure 3 presents the dependence on the magnetic field strength B of a system as in Figure 2 which, however, would assume random spatial orientations

relative to the external field $\vec{B}$. The observable $\phi_T(B)$ shown in Fig. 3 has been obtained from the results in Fig. 2 by taking the average over the angle θ. The resulting magnetic field dependence is typical for biradical reactions with long reaction times, i.e. those reacting in micellar systems. The corresponding $\phi_T(B)$ increases first to a maximum value and then decrease to a saturation value which is distinctly below the value $\phi_T(B=0)$. It is noteworthy that $\phi_T(B)$ assumes its maximum value at a field value B_{max} which is only about a tenth of the magnitude of the average hyperfine coupling $\bar{a} = \frac{1}{3}\sum_i (a_{ix} + a_{iy} + a_{iz}) \approx 13 Gauss$. Figure 4 shows that the θ -dependence of $\phi_T(B,\theta)$ differs strongly for the cases $B < B_{max}$, $B \approx B_{max}$, $B > B_{max}$ and $B >> B_{max}$. For this demonstration we have chosen the external field strength B = .5, 1, 2, 10 Gauss. The results show that for field strengths near the value B_{max} the triplet yield ϕ_T depends rather sensitively on the orientation θ, but for field values which are some multiples of B_{max} $\phi_T(B,\theta)$ is essentially independent of the orientation.

3. Summary

We conclude from the results of this paper that biochemical reactions involving biradical intermediates can show an orientational dependence in the earth's magnetic field. This conclusion is based on the fact that biradical reaction intermediates with average hyperfine coupling values $\bar{a}$ around 10 Gauss exist (see, for example Ref. 5). If the biradical reaction is spin-dependent and slow, i.e. the reaction rate is about 1 microsecond or slower, than external fields somewhat lower than $\frac{1}{10}\bar{a}$ can induce an orientational dependence. Hence, known organic reactants can be employed to realize a biochemical compass. If such reactants would play a role in one of the steps of the transduction of photon absorption in the rods and cones of the eye the orientation with respect to the geomagnetic field might be percieved by magnetic sensitive biological species as an apparent light intensity or color variation which moves when the geomagnetic field lines alter their orientation relative to the eye's optical axis[19]. The main value of our suggestion derives from the fact that we involve only the observed behaviour of 'in vitro' reaction systems. The search for the magnetoreceptor in higher species should concentrate therefore also on physiological processes.

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FIGURE CAPTIONS

1. Magnetic field strength and orientational dependence of the yield of triplet products ${}^3T$ for the reaction system (2.1) for $k_s = k_t = 10^6 s^{-1}$ and the hyperfine tensor described in the text.

2. Magnetic field strength and orientational dependence of the yield of triplet products ${}^3T$ for the reaction system (2.1) for $k_s = k_t = 10^6 s^{-1}$ and the hyperfine tensor described in the text.

3. Magnetic field dependence of the triplet yield of Figure 2 averaged over all orientations.

4. Orientational dependence of the triplet yield of Figure 2 at fixed field strengths: .5, 1, 2 and 10 Gauss.

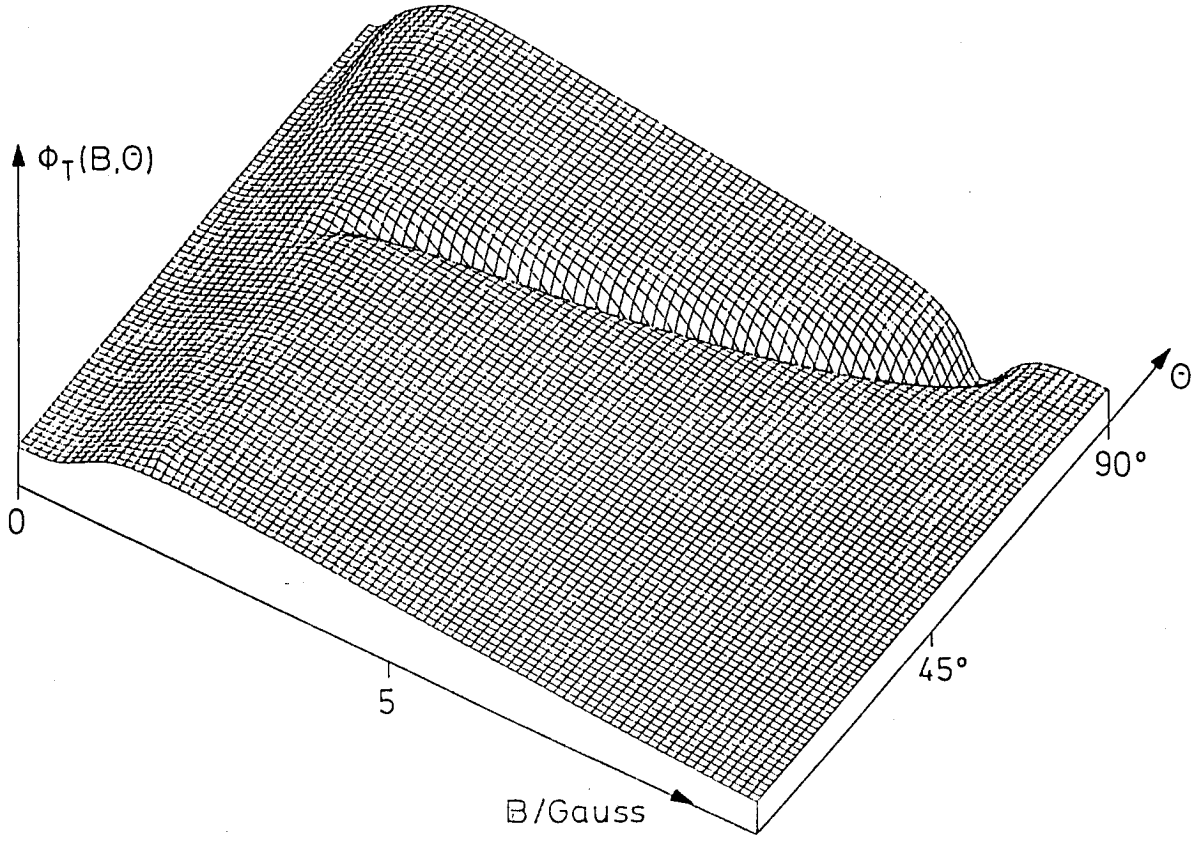

Figure 2

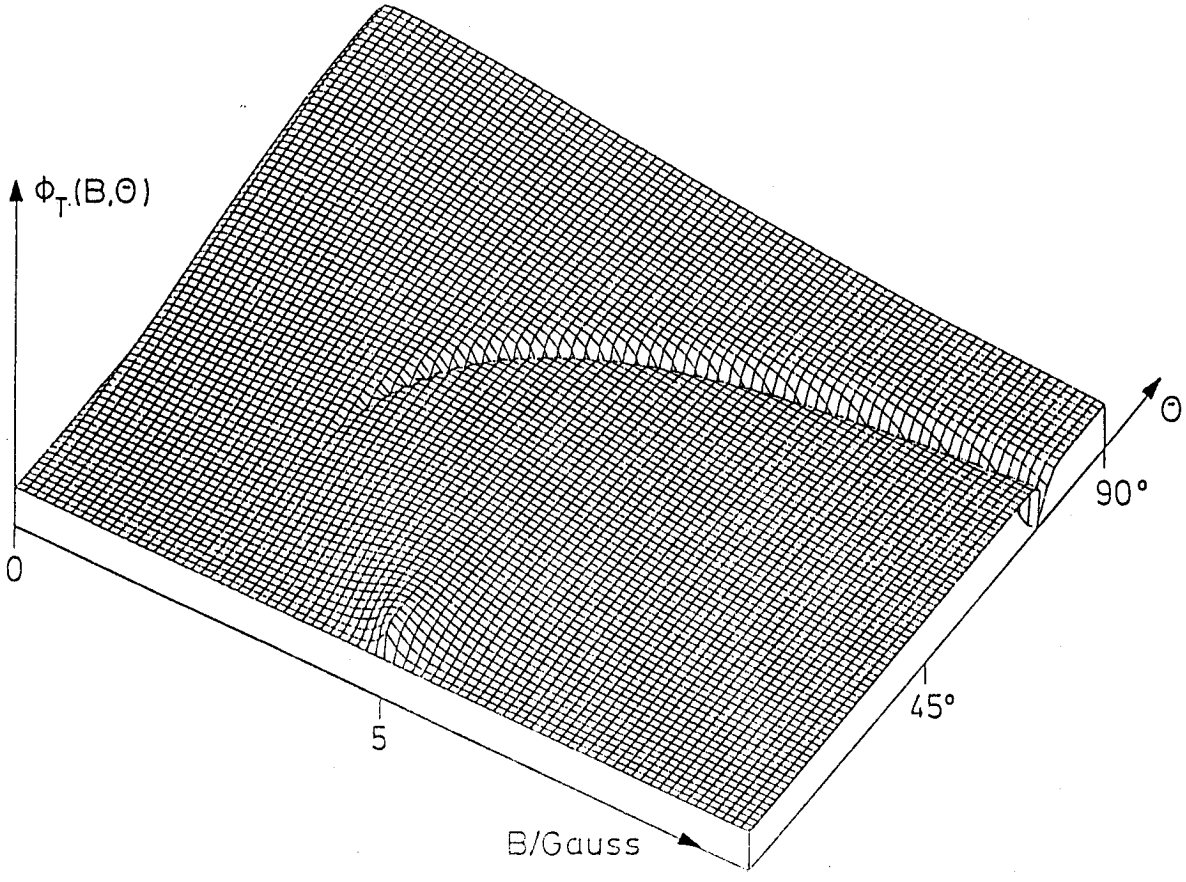

Figure 1

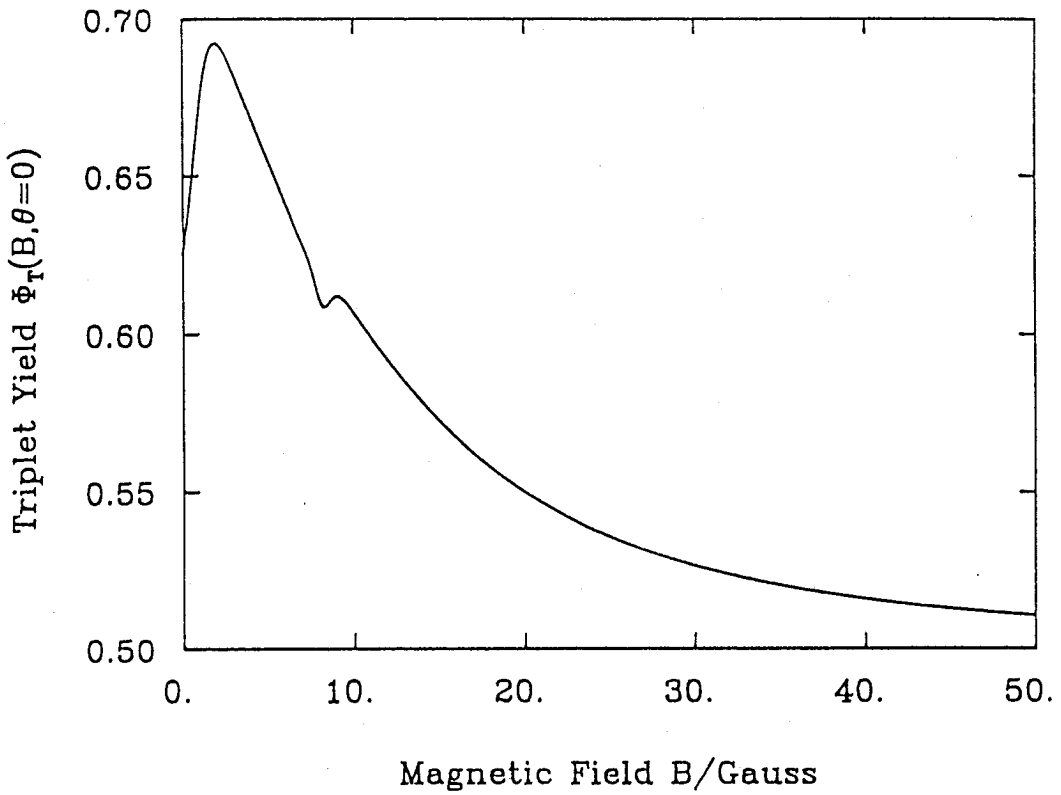

Figure 3

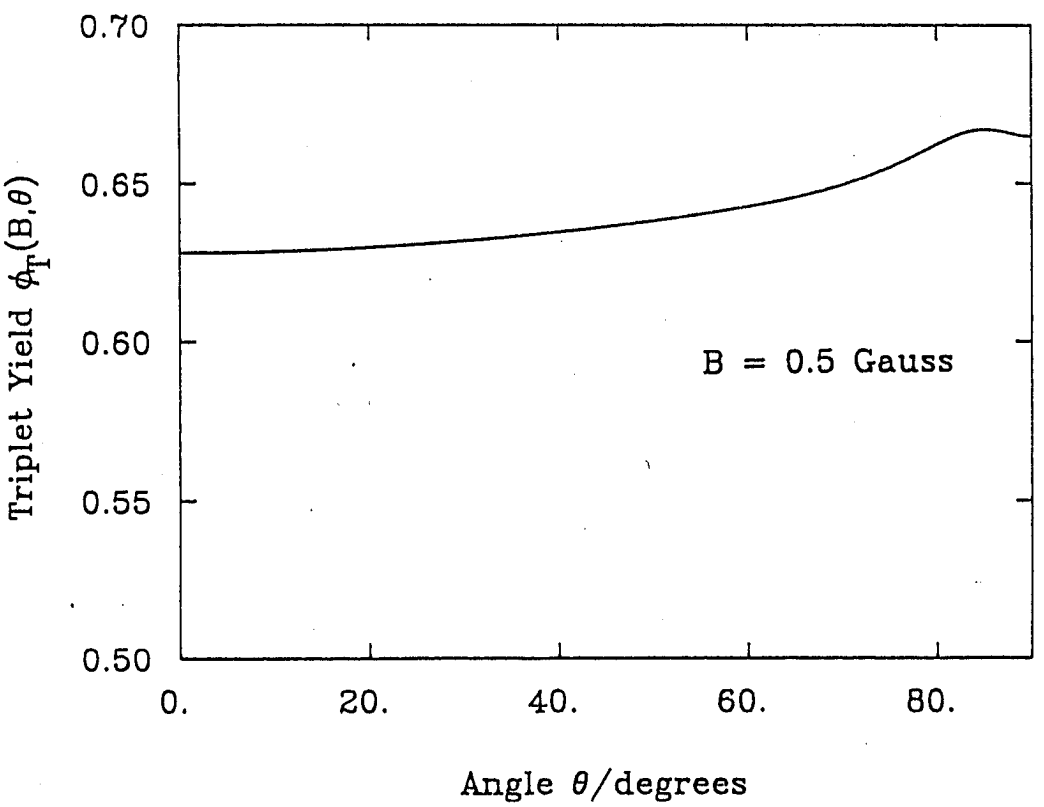

Figure 4a

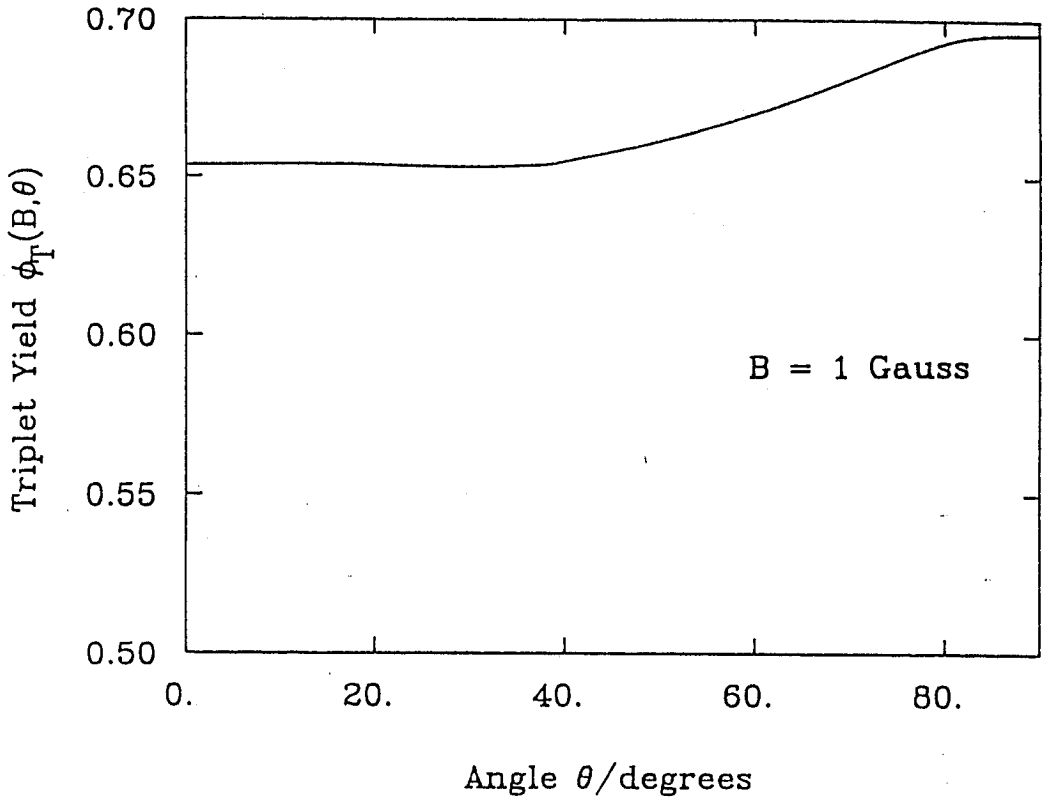

Figure 4b

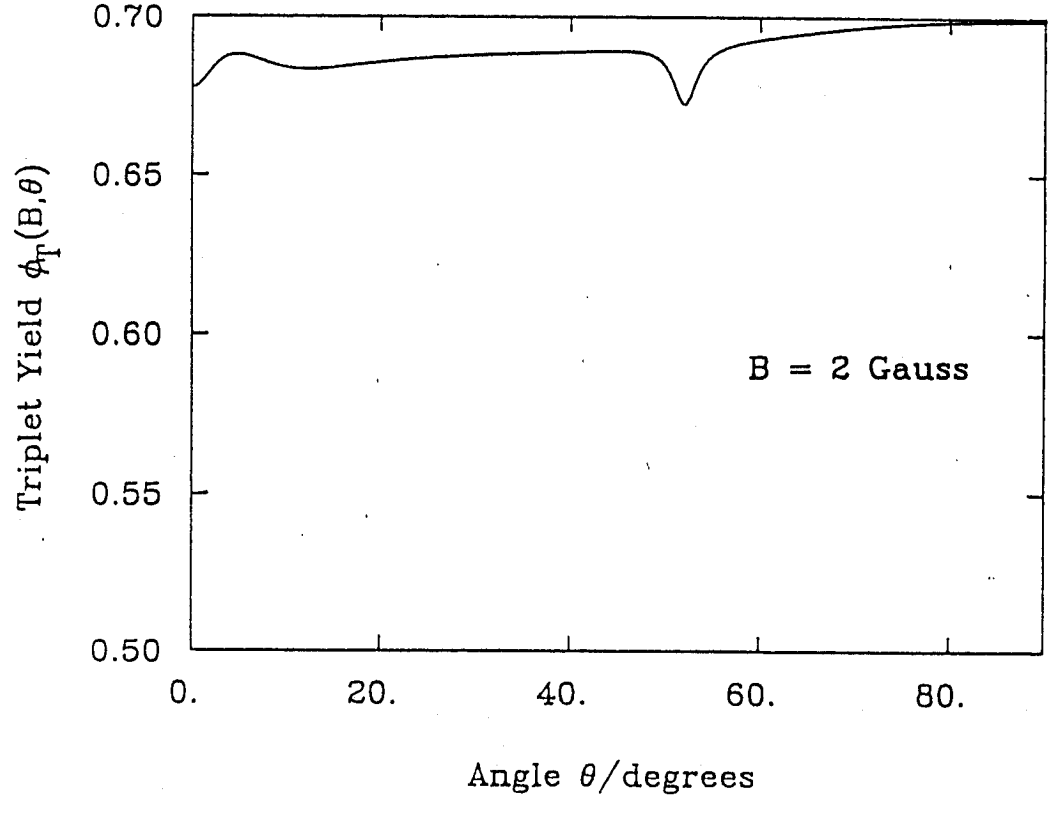

Figure 4c

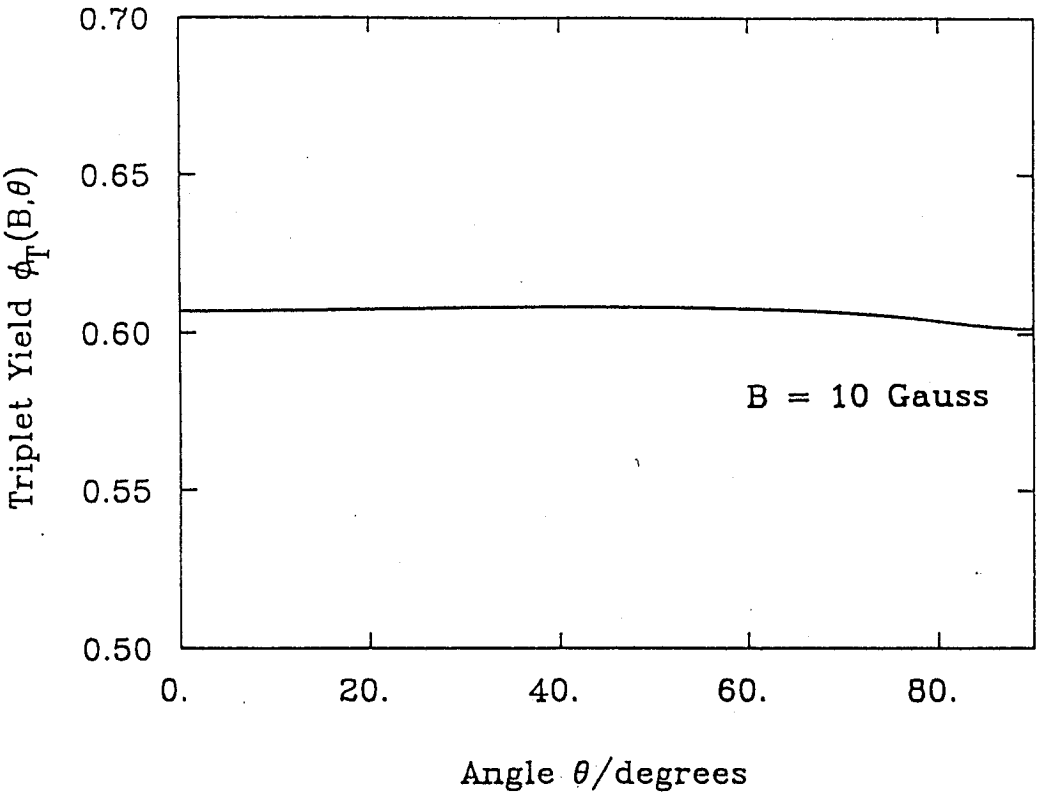
0.70
0.65
0.60
0.55
0.50
Triplet Yield $\phi_T(B,\theta)$
B = 10 Gauss
0.
20.
40.
60.
80.
Angle θ/degrees

Figure 4d