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COHERENCE IN MULTILEVEL SYSTEMS. II. DESCRIPTION OF A MULTILEVEL SYSTEM AS TWO LEVELS IN CONTACT WITH A POPULATION RESERVOIR.

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ABSTRACT

The effects of incoherent feeding and decay on a coherently driven two-level system are investigated using density matrix techniques. A closed form solution that includes the effects of relaxation and spontaneous emission between the two levels is obtained for cases in which the sample size is both small and large compared to the wavelength of the coherent driving field. The steady-state solutions reveal that under appropriate conditions a significant coherent component can be maintained by the combination of driving field and incoherent feeding, and should provide a useful method for the study of superradiance from excited states.

I. INTRODUCTION

The time evolution of an ensemble of two-state systems under the influence of a coherent radiation field is a problem of considerable importance and has been treated extensively for the case in which the ensemble is always composed of the same members. By this we mean that the identity of the individual members and the number of members in the ensemble is constant in time. Proton nuclear magnetic resonance is an example of this, where for a given sample size the number of protons is fixed, and the individual proton maintains its identity throughout an experiment. In many cases, such as double resonance,[1] optical pumping, chemically induced nuclear and electron spin polarization,[2,3] stark shift optical coherence,[4] and any process which involves excited states, the total population of the two-level ensemble is not constant in time. Although most of the processes mentioned above have been treated within their own context, little emphasis has been placed on how the creation and destruction of the states affect the properties of the ensemble in the presence of a coherent driving field. It is the aim of this paper to treat an idealized two-level system which is coherently coupled and at the same time is being *incoherently* fed and is spontaneously decaying. In such a case the number and identity of the individual members of the ensemble does not remain constant in time, since the ensemble of excited states will not only evolve under the influence of the coherent radiation field, but will also decay to the ground state by radiative and non-radiative processes. In these cases the trace of the density matrix describing the ensemble is not constant in time, but rather decays from an initial

$t = 0$ value to zero. An additional feature is apparent when the excitation source responsible for producing the excited states is left on after $t = 0$. Specifically, new excited states are continually created and also evolve under the influence of the coherent radiation field. The collection of excited state two-level systems is therefore not a time-independent collection, but rather an ensemble which constantly has members feeding into and decaying from it.

In addition to providing a basis for understanding the modifications which occur when coherent coupling experiments are performed on systems undergoing feeding and decay, the mathematical formulation developed in the body of the paper predicts that an important new effect may be observed. This effect is the production of long-term coherence in the ensemble of excited state two-level systems that results directly from incoherent feeding. We will term this "kinetic coherence" and show that it is possible to maintain a coherent superposition state in the ensemble for times greatly exceeding the lifetimes of the excited states. In fact it can remain as long as the radiation field remains coherent and population continues to be fed into the ensemble by incoherent pumping. The magnitude of the coherent component is controlled by the "effective field" angle, the incoherent pumping rate and the decay rate constants. This type of effect is also manifest in conventional magnetic resonance systems; however, it is very small owing to the inability of T_1 processes competing with the applied field to maintain a sizeable population difference. In a properly chosen system this is not a problem for the case we are considering because the intrinsic rate constants and the rate of incoherent pumping determine the population difference.

If the transition involved in producing the kinetic coherent state is an electric dipole transition in the optical region, the coherent component is a precessing macroscopic electric dipole, and the system will exhibit enhanced coherent spontaneous emission (superradiance).[5] Since previous experiments dealing with the superradiant state, such as the photon echo,[6] can measure the manifestations of coherence only for very short times, the kinetic coherent state should be valuable in probing the nature of superradiance because this state is not transitory. In principle one should be able to choose any "cooperation number" merely by changing the angle of the effective field.

An additional possibility exists if the kinetic coherent state can be maintained in the optical frequency region. Since the intensity of coherent light emitted by the kinetic coherent state is determined by the rate of *incoherent* pumping and the lifetimes of the states, in principle a carefully chosen system could exhibit gain, and therefore it could act as a coherent light amplifier. This amplifier is tunable over the spectral region in which gain occurs. Further, if a system is found which exhibits gain, the amplified emission could be fed back in phase into the superradiant amplifier and the applied coherent field removed. If the gain is great enough to overcome the losses in the feedback cavity, the superradiant amplifier would go into a self-sustaining continuous mode, emitting coherent light at the wavelength of the initial applied field.

In this paper we will present a mathematical development that treats coherent coupling in two-level systems which undergo feeding and decay. Three problems, transient nutation, spin lock and kinetic coherence, will be discussed in detail to illustrate the physical role that feeding

and decay play in the coherent coupling problem. Initially the problem is considered for the case in which the wavelength of the radiation field is large relative to the size of the sample. The equation of motion of the density matrix includes the Hamiltonian, a decay term which is analogous to adding decay to the Schrödinger equation, and a feeding term which is arranged to only affect the diagonal elements of the density matrix. T_1 and T_2 processes are not included at this point. The equation of motion for the density matrix, neglecting T_1 and T_2 processes, is solved exactly using matrix algebra techniques. The problem is then rewritten to include T_1 and T_2. It is shown that the qualitative results obtained in the absence of T_1 and T_2 are correct, provided that high power applied fields are used. Finally, the case in which the wavelength of the radiation field is small relative to the size of the sample (the optical case) is considered. It is shown that except for the usual directional properties associated with coherent optical problems, the results obtained for the long wavelength case also apply to the optical wavelength region.

II. DISCUSSION

In order to discuss the role that feeding and decay play in the excited state two-level coherent coupling problem, we must have a well-defined model for these processes. For this purpose, the entire experimental system is divided into two parts. The first part consists of the ensemble of excited two-level systems which are coupled by the field. The second part is taken to be an infinite reservoir that represents both a source and a sink for population to enter and leave the ensemble of two-level systems. At a given instant of time, the ensemble of two-level systems is evolving under the influence of the applied radiation field, it is also decaying into the reservoir at a rate which is characteristic of the lifetimes of the two excited states. Population is also constantly being transferred from the reservoir into the ensemble. We assume that only the states which are affected by the radiation field are included in the ensemble, and that the reservoir is taken to be unaffected by the field. As a consequence, population which is transferred incoherently from the reservoir to the ensemble enters the ensemble in <u>one</u> of its two eigenstates, and not in a coherent superposition state; however, once the population has entered the ensemble it may evolve into a coherent superposition state since it is now influenced by the radiation field. In terms of a density matrix description of the ensemble, this implies that feeding only occurs to the diagonal elements of the density matrix. Off-diagonal elements occur only due to the effect of the radiation field on the population which is already in the ensemble. Decay, however, affects both the diagonal and off-diagonal elements. Since the reservoir is

infinite in extent and unaffected by the two-level ensemble, the populating rate into the two eigenstates of the ensemble is taken to be constant. Thus, the model for feeding and decay processes contains the following features. (1) Feeding only occurs to the eigenstates of the ensemble of excited two-level systems and not to coherent superposition states. (2) The rates for feeding into the two eigenstates are constants, and are independent of the state of the ensemble. (3) Decay occurs from both the eigenstates and superposition states of the ensemble. (4) The rate of decay from the ensemble will depend on the state of the ensemble and therefore the total population of the ensemble need not be constant in time.

The above model for the feeding and decay processes is simple and well-defined, and closely approximates many physically realizable experimental situations. For example, consider ESR experiments performed on molecular excited triplet states in a molecular crystal.[7] An incoherent light source promotes molecules from their ground singlet state into excited singlet states, and some of the molecules in excited singlet states intersystem cross into the lowest lying excited triplet state. In this case two of the magnetic spin sublevels of the triplet state may be coherently[8] coupled by the application of a microwave field of the appropriate frequency, and molecules in the excited triplet state decay to the ground singlet state with lifetimes characteristic of the individual magnetic spin sublevels. At a given instant of time, those molecules which are found to be in the spin sublevels being perturbed by the applied microwave field are taken to compose the ensemble discussed above, and the rest of the molecules comprise the reservoir. If the number of

molecules in the excited triplet state is small compared to the number of molecules in the sample, which is generally the case, then the singlet population is independent of the triplet state population and the intersystem crossing rates into the triplet spin sublevels, i.e., the feeding rates discussed above, will be constant provided that the light source responsible for the excitation remains constant in intensity. Furthermore, the molecules which are in singlet states are unaffected by the applied microwave field, and thus when intersystem crossing occurs, it will populate the triplet eigenstates in a manner which is identical to the intersystem crossing process in the absence of a microwave field coupling the triplet spin sublevels. Once population has intersystem crossed, it will evolve under the influence of the applied microwave field until it decays to the ground state which again is part of the reservoir. Therefore, the situation encountered in the excited triplet state ESR experiment is completely analogous to the model we have established. We have a reservoir comprised of all the states of the sample except those two excited triplet spin sublevels which are coupled by the microwave field. The reservoir is unaffected by the field, there are constant feeding rates from the reservoir into the ensemble, and decay occurs from the ensemble into the reservoir.

A qualitative picture describing the examples to be discussed in the matehmatical development may be made in terms of a geometrical representation for the two-level system. The initial population difference between the two levels is represented by a vector that is aligned along the r_3 direction of the r-space of the well-known Feynman, Vernon and Hellwarth (FVH)[9] model. If a coherent radiation field with frequency

equal to the frequency separation of the two levels is turned on, the vector, viewed in a reference frame rotating at the frequency of the applied field, will begin to precess about the field, resulting in a transient nutation.[10] In an idealized case in which there are no T_1 or T_2 relaxation processes, and also
where the composition of the ensemble remains constant in time, the vector will continue to precess about the applied field indefinitely. However, if we are dealing with an ensemble of excited states, the population vector which began to precess when the radiation field was turned on will decay with the lifetimes associated with the excited states. Further , population which enters the ensemble of excited states at times after the radiation field has been turned on will also precess about the field. This feeding and decay process can be viewed in the geometrical model as a vector which suddenly appears along r_3, immediately starts precessing about the effective field, and shrinks in length as it precesses. These vectors have different phase than the initial population vector, and have a random phase relationship among themselves. In the NMR problem we merely had to follow the precession of a single vector, whereas in the excited state problem, we must follow the precession of the initial vector which is decaying in magnitude at a rate dependent upon its location in r-space, and in addition follow the precession of the entering vectors which also are decaying.

Another important experimental situation which demonstrates the necessity of including feeding and decay processes in the analysis of the experiment is spin locking.[11] In an NMR experiment where there is no feeding or decay, the initial population difference vector is made to precess about the applied radiation field, as in the transient nutation experiment discussed above. After it has precessed 90°, the applied radiation field is turned off. If nothing else were done at this point, the vector, which is now in the plane normal to the direction it was initially pointing, would rapidly vanish due to fanning in the rotating frame caused by the inhomogeneous nature of the line undergoing the transition. However, the field is immediately reapplied along the direction that the population vector is pointing in the rotating frame. The vector finds itself aligned along the rotating frame static field and the fanning does not occur. In such a case, the population is said to be spin-locked in a superposition state. The vector will remain spin-locked for a time corresponding to the $T_{1\rho}$ time in the rotating frame. If the analogous experiment is performed on the magnetic spin sublevels of an excited molecular triplet state, the spin-locked vector will vanish due to both $T_{1\rho}$ processes and relaxation to the ground state. Furthermore, new population is continually entering the ensemble of triplet states that are coupled by the radiation field. However, this additional population intersystem crosses into the triplet eigenstates, not into the spin-locked superposition state. We therefore encounter the situation in which the population that existed at time $t = 0$, which we will refer to as the $t = 0$ subensemble, is spin-locked,

whereas the entering population is not. The entering vectors are nonetheless driven by the applied radiation field and execute transient nutations in the plane normal to the spin-locked vector. In the NMR problem we had to deal only with the single initial population vector, whereas in the triplet state problem, both the $t = 0$ subensemble and the entering vectors must be considered. In addition, for excited states there is another path for the loss of the spin-locked vector due to radiative or non-radiative decay of the excited spin-locked states to the ground state.

As we will show, the kinetic coherent state is produced by essentially spin-locking a set of vectors along an off-resonance effective field. The initial population difference vector executes an off-resonance transient nutation about the effective field direction, and describes a cone around the effective field as illustrated in Figure 1. Owing either to field inhomogeneity or sample inhomogeneity, this inital vector will fan out around the conical path producing a thin cone of vectors precessing around the effective field. (Inhomogeneity is not required, for even with a homogeneous field and sample, the feeding process itself will cause a cone of vectors.) The cone of vectors has a net projection along the effective field direction which can be resolved into an r_3 component and an r_1 coherent component. The cone will

decay due to relaxation of the excited states to the ground state. However, as this initial population decays, additional population is fed into the system,continually forming a new cone with a colinear r_1 component. Thus, as the r_1 vector due to the first cone decays, it is replaced by the r_1 vector from succeeding cones through continual feeding. The cone, and therefore the coherent r_1 vector, is constantly replenished.

III. MATHEMATICAL DEVELOPMENT

We consider the situation depicted in Fig. 2 in which a two-level system, characterized by the states $|y\rangle$ and $|x\rangle$ is populated from the reservoir at a constant rate, decays back into the reservoir, and is also driven coherently by a sinusoidally oscillating field. In order to isolate and examine the effects of feeding and decay, we shall first consider the simplest case in which the wavelength of the radiation is much greater than the sample size, i.e., $\lambda^3 >> \text{vol}$. We shall also, at first, neglect all relaxation processes such as T_1, homogeneous and inhomogeneous T_2, and driving field inhomogeneities. These considerations complicate the development considerably but at the same time do not significantly alter many of the qualitative features of the problem, and are thus reserved for later sections of the discussion.

We shall use a semi-classical approach for the driving field Hamiltonian. Without loss of generality we assume that the driving field has real matrix elements and express the Hamiltonian as

$$\mathcal{H}' = \mathcal{H}_o + V(t) \tag{1a}$$

$$\mathcal{H}_o = \frac{\hbar\omega_o}{2}\,\sigma_3 \tag{1b}$$

$$V(t) = \hbar\omega_1\sigma_1 \cos\omega t \tag{1c}$$

$\mathcal{H}_o$ is the time-independent Hamiltonian with eigenstates $|y\rangle$ and $|x\rangle$, separated in energy by $\hbar\omega_o$, and σ_n are the Pauli spin matrices. Invoking the rotating field approximation we have

$$\mathcal{H}' = \frac{\hbar\omega_o}{2}\,\sigma_3 + \frac{\hbar\omega_1}{2}\, e^{\frac{-i\sigma_3\omega t}{2}}\,\sigma_1\, e^{\frac{i\sigma_3\omega t}{2}} \tag{2}$$

By performing a suitable transformation on the state vector $|t\rangle'$ we can obtain an equation of motion in which the Hamiltonian is time independent. Let

$$U = e^{\frac{i\sigma_3 \omega t}{2}} \tag{3}$$

and

$$|t\rangle = U|t\rangle' \tag{4}$$

From the Schrodinger equation

$$i\hbar \frac{d}{dt} |t\rangle' = \mathcal{H}'|t\rangle' \tag{5}$$

We substitute for $|t\rangle'$ in terms of $|t\rangle$ and obtain

$$i\hbar \frac{d}{dt} |t\rangle = \mathcal{H}|t\rangle \tag{6}$$

where

$$\mathcal{H} = \frac{\hbar}{2} (\omega_o - \omega) \sigma_3 + \frac{\hbar\omega_1}{2} \sigma_1 \tag{7}$$

The Hamiltonian in Eq. (7) is time independent for any value of the driving field frequency, ω, and reduces to the interaction representation for $\omega = \omega_o$. The use of the unitary matrix defined by Eq. (3) is equivalent to transforming to a rotating frame[12] in terms of the Feynman, Vernon, Hellwarth (FVH) geometrical representation.

By considering a model system consisting of a reservoir, details of the feeding and decay processes are not considered explicitly and thus allow the many-body problem to become tractable. The simplest way to include decay of a state is to assume that the amplitude for being in the state decays exponentially. For the two-level system we

have the state vector represented as a linear combination

$$|t\rangle = y|y\rangle + x|x\rangle \tag{8}$$

where y and x are the usual time-dependent coefficients.[13] We now let these amplitudes decay exponentially[14]

$$\dot{y} = -\frac{k_y}{2}\, y \tag{9a}$$

$$\dot{x} = -\frac{k_x}{2}\, x \tag{9b}$$

k_y and k_x are physically observable rate constants associated with the decay of the states $|y\rangle$ and $|x\rangle$, respectively.

As discussed earlier, the populating process occurs only to the eigenstates $|y\rangle$ and $|x\rangle$ and cannot appear in a superposition state; thus, the equations describing the feeding process must deal only with the <u>probabilities</u> yy^* and xx^* and cannot affect the terms which define the relative phase factor as given by xy^* or yx^*. The result of this is that the feeding cannot be added to the amplitudes y and x but only to the probabilities.

At this point there are two possible ways to treat the problem. First, one could solve the coupled differential equations formed by combining Eq. (6) and Eq. (9), take products of the solutions and form integral equations that include the feeding process.[15] Despite the fact that this method is exceedingly lengthy, it provides a certain

amount of physical insight to the problem since it is straightforward. The second approach is to use the density matrix formulation which effectively deals with the coefficient products from the beginning. The solutions are much simpler from the computational point of view, and the development is mathematically less clumsy. We shall use this method in the following development.

A. Density Matrix Solution

Equation (6) can be expressed in terms of the density matrix[16] as

$$i\hbar\dot{\rho} = [\mathcal{H},\rho] \tag{10}$$

The rotating frame Hamiltonian is the same as Eq. (7). The decay terms of Eq. (9) are incorporated into the equation of motion by constructing the imaginary operator K given in the y-x basis by

$$K = \frac{i\hbar}{2}\begin{pmatrix} k_y & 0 \\ 0 & k_x \end{pmatrix} \tag{11}$$

and the decay process is described by an anticommutator relation

$$i\hbar\dot{\rho} = -[K,\rho]_+ \tag{12}$$

The operator K must be imaginary in order to cause the density matrix to decay. Combining Eqs. (10) and (12) one obtains a description of a two-level system whose states can decay with or without an applied driving field.

$$i\hbar\dot{\rho} = [\mathcal{H},\rho] - [K,\rho]_+ \tag{13}$$

The differential equation can be solved by constructing an evolution operator, Q, defined by

$$Q = \exp\left\{i\,\frac{(\mathcal{H} + K)}{\hbar}\,t\right\} \tag{14}$$

Notice that since $\mathcal{H}$ is real and K imaginary the adjoint of Q is not the inverse

$$Q^{\dagger} = \exp\left\{-i\frac{(\mathcal{H} - K)}{\hbar}\,t\right\} \neq Q^{-1} \tag{15}$$

and thus Q is not unitary. Equation (16) is a solution to Eq. (13) as can be verified by differentiation

$$\rho(t) = Q^{\dagger}\rho(0)\,Q \tag{16}$$

The operations in Eq. (16) do not result in a similarity transformation. This is to be expected, however, since the decay process must cause the trace of $\rho(t)$ to vanish--a result which is not possible with a similarity transformation. Owing to the fact that the constant trace condition has been relaxed, one will need four, rather than the usual three, independent variables to describe the density matrix completely. This can be done easily by defining the components of the density matrix as follows:

$$\rho = \begin{pmatrix} r_y & \dfrac{r_1 - ir_2}{2} \\ \dfrac{r_x + ir_2}{2} & r_x \end{pmatrix} \tag{17}$$

These components have a geometrical significance which is only slightly different from the FVH model. r_y is represented by a vector which points "up" in a three dimensional r-space whereas r_x points "down". They both share the same "in-plane" components r_1 and r_2. The FVH vector

component r_3 is given by $r_y - r_x$. In terms of observables, r_y and r_x are proportional to the upper and lower level populations, respectively. The r_1 and r_2 components contain coherence information and are proportional to the expectation values of an induced or permanent electric or magnetic dipole depending on the explicit form of V(t). An explicit form for Q is obtained from Eq. (14) using Putzer's method.[17]

$$Q = e^{-\frac{k_A t}{2}} \begin{pmatrix} \cos\frac{\Omega t}{2} + \frac{k_D + i\Delta\omega}{\Omega}\sin\frac{\Omega t}{2} & \frac{i\omega_1}{\Omega}\sin\frac{\Omega t}{2} \\ \frac{i\omega_1}{\Omega}\sin\frac{\Omega t}{2} & \cos\frac{\Omega t}{2} - \frac{k_D + i\Delta\omega}{\Omega}\sin\frac{\Omega t}{2} \end{pmatrix} \tag{18}$$

Equation (18) incorporates the following definitions

$$k_A = \frac{k_x + k_y}{2} \tag{19a}$$

$$k_D = \frac{k_x - k_y}{2} \tag{19b}$$

$$\Delta\omega = \omega_o - \omega \tag{19c}$$

$$\Omega = (\omega_1^2 + (\Delta\omega - ik_D)^2)^{1/2} \tag{19d}$$

In accordance with earlier discussions, feeding is allowed only to the r_y and r_x components. This is expressed by a feeding matrix F given by

$$F = i\hbar \begin{pmatrix} F_y & 0 \\ 0 & F_x \end{pmatrix} \tag{20}$$

The total equation of motion which includes feeding, decay and a driving field is thus given by

$$i\hbar\dot{\rho} = [\mathcal{H},\rho] - [K,\rho]_+ + F \tag{21}$$

Before solving this equation it is worthwhile to write it explicitly in terms of the r-components

$$\dot{r}_1 = -\Delta\omega r_2 - k_A r_1 \tag{22a}$$

$$\dot{r}_2 = \Delta\omega r_1 - \omega_1(r_y - r_x) - k_A r_2 \tag{22b}$$

$$\dot{r}_y = \frac{\omega_1 r_2}{2} - k_y r_y + F_y \tag{22c}$$

$$\dot{r}_x = -\frac{\omega_1 r_2}{2} - k_x r_x + F_x \tag{22d}$$

By comparing Eqs. (22) to the rotating frame Bloch Equations,[18] one can see immediately that the average of the decay rate constants k_A will have the same effect as a T_2 process and the combination of feeding and decay will appear to be a T_1 process. This is quite reasonable from a physical point of view since the in-plane components involve a superposition state which can be viewed as being "undecided" from which eigenstate it will eventually decay, thus giving rise to k_A. Also, an incoherent T_1 process will have a similar effect as decay from $|y\rangle$ or $|x\rangle$ into the reservoir with subsequent incoherent feeding into $|x\rangle$ and $|y\rangle$. The important difference between T_1 and feeding and decay, however, is that the final population difference in the levels is determined by a Boltzmann distribution in the T_1 case, as opposed to the feeding and decay process in which practically any polarization is possible, depending on the ratios of the feeding and decay constants and on the conditions of the experiment.

We now return to the solution of Eq. (21). An equation of the form

$$\rho(t) = Q^{\dagger}(\rho(o) - A)\, Q + A \tag{23}$$

is indeed a solution if the undetermined time-independent matrix, A, can be found. Equation (23) is of the form

$$\rho(t) = B(t) + A \tag{24}$$

by differentiating Eq. (24)

$$i\hbar\dot{\rho} = [\mathcal{H},B] - [K,B]_{+} \tag{25}$$

and also substituting Eq. (24) into Eq. (21)

$$i\hbar\dot{\rho} = [\mathcal{H},B] - [K,B]_{+} + [\mathcal{H},A] - [K,A] + F \tag{26}$$

we see that A must satisfy the condition

$$[\mathcal{H},A] - [K,A]_{+} + F = 0 \tag{27}$$

At this point we note that since Q contains decay terms, some new steady-state value of the density matrix will exist at $t = \infty$. It is simple to solve for this matrix, ρ_s, by letting $\dot{\rho} = 0$. We obtain

$$[\mathcal{H},\rho_s] - [K,\rho_s]_{+} + F = 0 \tag{28}$$

which is identical to Eq. (27). Thus the matrix A is merely the steady-state value that the density matrix approaches for a given set of experimental conditions. Equation (28) is solved for ρ_s by performing the commutation operations using the explicit forms for $\mathcal{H}$ (Eq. (7)), K (Eq. (11)) and F (Eq. (20)) and representing ρ_s by

$$\rho_s = \begin{pmatrix} r_y^s & \frac{r_1^s - ir_2^s}{2} \\ \frac{r_1^s + ir_2^s}{2} & r_x^s \end{pmatrix} \tag{29}$$

The components are given by

$$r_1^s = \frac{\Delta\omega\omega_1}{k_A^2} (F_y k_x - F_x k_y)/D \tag{30a}$$

$$r_2^s = \frac{\omega_1}{k_A} (F_x k_y - F_y k_x)/D \tag{30b}$$

$$r_y^s = \left[F_y k_x \left(1 + \frac{\Delta\omega^2}{k_A^2}\right) + \frac{\omega_1^2}{k_A}\left(\frac{F_x + F_y}{2}\right)\right] /D \tag{30c}$$

$$r_x^s = \left[F_x k_y \left(1 + \frac{\Delta\omega^2}{k_A^2}\right) + \frac{\omega_1^2}{k_A}\left(\frac{F_x + F_y}{2}\right)\right] /D \tag{30d}$$

$$D = \omega_1^2 + k_x k_y \left(1 + \frac{\Delta\omega^2}{k_A^2}\right) \tag{30e}$$

In view of the similarity between the rotating frame Bloch equations and Eqs. (22), we cast Eqs. (30) into a more familiar form. First, noting that the steady-state populations in the absence of a driving field are given by ($\omega_1 = \Delta\omega = 0$),

$$r_y^\circ = \frac{F_y}{k_y} \tag{31a}$$

$$r_x^\circ = \frac{F_x}{k_x} \tag{31b}$$

and

$$r_3^0 = r_y^0 - r_x^0 \tag{31c}$$

and by defining <u>effective</u> relaxation terms,

$$t_2 = 1/k_A \tag{32a}$$

$$t_1 = \frac{k_A}{k_x k_y} \tag{32b}$$

we obtain

$$r_1^s = \frac{r_3^\circ \Delta\omega\omega_1 t_2^2}{1 + \Delta\omega^2 t_2^2 + \omega_1^2 t_2 t_1} \tag{33a}$$

$$r_2^s = \frac{-r_3^\circ \omega_1 t_2}{1 + \Delta\omega^2 t_2^2 + \omega_1^2 t_2 t_1} \tag{33b}$$

$$r_y^s = \frac{r_y^\circ\left(1 + \Delta\omega^2 t_2^2\right) + \omega_1^2 t_1 t_2^2 \left(\frac{F_x + F_y}{2}\right)}{1 + \Delta\omega^2 t_2^2 + \omega_1^2 t_2 t_1} \tag{33c}$$

$$r_x^s = \frac{r_x^\circ\left(1 + \Delta\omega^2 t_2^2\right) + \omega_1^2 t_2 t_1 \left(\frac{F_x + F_y}{2}\right)}{1 + \Delta\omega^2 t_2^2 + \omega_1^2 t_2 t_1} \tag{33d}$$

and

$$r_3^s = \frac{r_3^\circ(1 + \Delta\omega^2 t_2^2)}{1 + \Delta\omega^2 t_2^2 + \omega_1^2 t_2 t_1} \tag{34}$$

These are the familiar forms for continuous wave spectra in magnetic resonance. When the "power factor" $\omega_1^2 t_2 t_1$ is small, the components reduce to Lorentzian lineshapes. It is interesting that the effective "transverse" relaxation, t_2, is determined by the average of the decay

rate constants whereas the effective T_1 is determined by the average of the decay lifetimes. The final solution to Eq. (21) is thus

$$\rho(t) = Q^{\dagger}[\rho(0) - \rho_s]\, Q + \rho_s \tag{35}$$

where the components of ρ_s are given by Eqs. (33).

The expression for F in Eq. (20) could be generalized easily to situations in which the feeding occurs to a superposition state, such as when a triplet state is optically pumped in the presence of a high magnetic field, and also could be made time-dependent. The solution for ρ_s follows the same format.

If one wishes to monitor the effects of feeding and decay more explicitly, Eq. (35) may be broken up into two parts corresponding to the "zero time" subensemble mentioned in the discussion and the "fed" subensemble

$$\rho(t) = Q^{\dagger}\, \rho(0)\, Q + \rho_s - Q^{\dagger}\rho_s Q \tag{36}$$

The first term corresponds to the zero-time subensemble. Since feeding into $|y\rangle$ and $|x\rangle$ are independent processes, one could separate the last two terms of Eq. (36) into y-fed and x-fed subensembles by setting $F_x = 0$ and $F_y = 0$, respectively. This might prove useful if one wishes to determine only the effects of feeding on the system.

B. Transient Solutions: Special Cases

The simple form for Eq. (35) might lead one to think that it would be worthwhile to multiply the matrices explicitly and thereby obtain analytical expressions for the r-vector components. Unfortunately

the solutions are complicated enough to mask the physics contained within them so we shall restrict our attention to various special cases which give some insight into the effects of feeding and decay. First, we consider the trivial case of no driving field. Setting $\omega_1 = \Delta\omega = 0$, we have $\Omega = ik_D$, and Q has a very simple form:

$$Q = e^{-\frac{k_A t}{2}} \begin{bmatrix} e^{\frac{k_A t}{2}} & 0 \\ 0 & e^{\frac{-k_A t}{2}} \end{bmatrix} = e^{-\frac{Kt}{i\hbar}} = Q^{\dagger} \tag{37}$$

The solutions are, from Eq. (35)

$$r_1 = r_1(o)\, e^{-k_A t} \tag{38a}$$

$$r_2 = r_2(o)\, e^{-k_A t} \tag{38b}$$

$$r_y = \left(r_y(o) - \frac{F_y}{k_y}\right) e^{-k_y t} + \frac{F_y}{k_y} \tag{38c}$$

$$r_x = \left(r_x(o) - \frac{F_x}{k_x}\right) e^{-k_x t} + \frac{F_x}{k_x} \tag{38d}$$

Notice that r_1 and r_2 are not fed, but merely decay from whatever initial values they had at time t = 0. Equations (38) agree with simple rate equations that can be written by inspection from the two-level system pictured in Fig. (2).

We next consider an on-resonance transient nutation. In this case, $\Delta\omega = 0$, $\Omega = (\omega_1^2 - k_D^2)^{1/2}$. We assume initial random phases, i.e., $r_1(o) = 0$, $r_2(o) = 0$, and let the initial values of the diagonal

elements be steady-state values without the coherent driving field. $r_y(o) = r_y^\circ$, $r_x(o) = r_x^\circ$. We obtain from Eq. (35) and Eq. (33)

$$r_1 = 0 \tag{39a}$$

$$r_2 = \frac{e^{-k_A t}}{\Omega^2}\left[r_2^s\left(k_D^2 - \omega_1^2\cos\Omega t\right) - (r_3^\circ - r_3^s)\,\Omega\omega_1\sin\Omega t - (r_y^0 - r_y^s + r_x^0 - r_x^s)\,\omega_1 k_D(1 - \cos\Omega t)\right] + r_2^s \tag{39b}$$

$$r_y = \frac{e^{-k_A t}}{\Omega^2}\left[\left(r_y^\circ - r_y^s\right)\left(\Omega\cos\frac{\Omega t}{2} + k_D\sin\frac{\Omega t}{2}\right)^2 + \left(r_x^\circ - r_x^s\right)\omega_1^2\sin^2\frac{\Omega t}{2} - r_2^s\omega_1\sin\frac{\Omega t}{2}\left(\Omega\cos\frac{\Omega t}{2} + k_D\sin\frac{\Omega t}{2}\right)\right] + r_y^s \tag{39c}$$

$$r_x = \frac{e^{-k_A t}}{\Omega^2}\left[\left(r_x^\circ - r_x^s\right)\left(\Omega\cos\frac{\Omega t}{2} - k_D\sin\frac{\Omega t}{2}\right)^2 + \left(r_y^\circ - r_y^s\right)\omega_1^2\sin^2\frac{\Omega t}{2} + r_2^s\omega_1\sin\frac{\Omega t}{2}\left(\Omega\cos\frac{\Omega t}{2} - k_D\sin\frac{\Omega t}{2}\right)\right] + r_x^s \tag{39d}$$

despite the formidable appearance of these equations, the qualitative features are simple, since they are analogous to a damped harmonic oscillator. If $\Omega \leqslant k_A$ the curves will be dominated by the exponential term and will be highly damped. When $k_D > \omega_1$ the system behaves much like an overdamped oscillator. Any shifts in frequency or phase when $\omega_1 \gtrsim k_D$ will be masked by the exponential terms. When $\Omega \geqslant k_A$ it is also necessarily true that $\omega_1 \geqslant k_D$ and the observable oscillations will have nutation frequencies close to ω_1 in magnitude. If we allow the driving

field to become very large, i.e., $\omega_1^2/k_x k_y >> 1$, Eqs. (39) reduce to much simpler forms which are easier to relate to the geometrical model

$$r_1 = 0 \tag{40a}$$

$$r_2 \cong r_3^\circ \, e^{-k_A t} \left(\frac{1}{\omega_1 k_A} \cos\omega_1 t - \sin\omega_1 t \right) - \frac{r_3^\circ}{\omega_1 k_A} \tag{40b}$$

$$r_y \cong \frac{r_3^\circ}{2} \, e^{-k_A t} \left(\frac{k_D}{k_A} + \cos\omega_1 t \right) + \frac{F_y + F_x}{k_x + k_y} \tag{40c}$$

$$r_x \cong \frac{r_3^\circ}{2} \, e^{-k_A t} \left(\frac{k_D}{k_A} - \cos\omega_1 t \right) + \frac{F_y + F_x}{k_x + k_y} \tag{40d}$$

Notice that all the expressions contain the initial population polarization or alignment $r_3^0 = r_y^0 - r_x^0$. As expected from the geometrical model, the vectors precess only in the $r_2 - r_3$ plane. After the transient terms have died away the populations in the two levels are approximately equal and r_2 is very small. This is to be expected from the vector model, since the "disc" that is ultimately formed has a vector sum of zero. In the absence of feeding or decay, Eqs. (39) and (40) reduce to the standard nutation of the Torque Equation in the rotating frame. As is the case in NMR, we see that the ability to do well-defined pulse rotations of the r-vector depends upon the relationship between the applied field strength and the effective relaxation $k_A = 1/t_2$. For sufficiently high power, a $\pi/2$ pulse ($\omega_1 t = \pi/2$) gives from Eqs. (40):

$$r_2(\pi/2) \cong -r_3^\circ \tag{41a}$$

$$r_y(\pi/2) \cong r_x(\pi/2) \cong r_3^\circ \frac{k_D}{k_A} + \frac{F_y + F_x}{k_x + k_y} \tag{41b}$$

The effects of feeding and decay on a spin-locked superposition state can be investigated by using Eqs. (41) as initial conditions for a phase-shifted transient nutation. Shifting the phase by 90° is tantamount to setting $r_1(o) = -r_2(\pi/2) = r_3^\circ$ and $r_2(o) = 0$. r_y and r_x are unaffected by the phase shift. From These initial conditions, the expression for the spin-locked component is, from Eq. (35).

$$r_1 \cong r_1(o)\, e^{-k_A t} = r_3^\circ\, e^{-k_A t} \tag{42}$$

From the vector model one would predict that feeding subsequent to establishing the spin-locked component would contribute only a disc in the $r_2 - r_3$ plane and thus could not affect the spin-locked component. Equation (42) shows that the spin-locked signal is indeed independent of feeding, and decays with the average of the decay rate constants for the two levels.

C. Long Term or "Kinetic" Coherence

Equation (42) demonstrates that a coherent component can be made to last on the order of the lifetime of the levels. In this section we shall propose that this time is by no means an upper limit, and in fact it should be possible to maintain a significant coherent component for long periods of time, limited only by the coherence time of the driving field. In many ways this is similar to dynamic equilibrium in which the component parts of the long term coherence are continually feeding

and decaying, but a steady state value is reached. The coherence is maintained by the driving field and is not destroyed by incoherent feeding or decay.

The steady-state expressions in Eqs. (33) can be somewhat deceptive if one does not keep in mind the fact that the effective relaxation term t_1 was constructed only to show the analogy to T_1 and is not related to the actual thermalization of the two levels. The ratios of feeding and decay constants determine the initial polarization of the system and the population difference can thus be highly non-Boltzmann. With this in mind we re-examine Eq. (33a). The r_1 component represents the "dispersion spectrum" or the real part of the susceptibility in the language of NMR, and reaches a maximum "off resonance". Owing to the fact that r_3° can be significantly larger than a Boltzmann distribution of population, the steady-state coherent component can be orders of magnitude larger than the thermally populated case. From the vector model, one would expect the condition $\Delta\omega = \omega_1$ to give a maximum inplane component. The special form of Eq. (33a) suggests that the problem is identical to the one treated long ago by Bloch when he calculated the maximum nuclear induction signal in an NMR experiment.[18] The off-resonance value which corresponds to a maximum value of r_1^s is

$$\Delta\omega_{max} = \frac{1}{t_2}\left(1 + \omega_1^2 t_1 t_2\right)^{1/2} \tag{43}$$

giving a value for r_1^s

$$r_1^s(\max) = \frac{\omega_1 t_2\, r_3^\circ}{2\left(1 + \omega_1^2 t_1 t_2\right)^{1/2}} \tag{44}$$

and for sufficiently high power, i.e., $\omega_1^2 t_1 t_2 >> 1$,

$$r_1^s(\max) \cong \frac{r_3^\circ}{2}\sqrt{\frac{t_2}{t_1}} \tag{45}$$

The maximum value for r_2^s, on resonance, is equal in magnitude to the high power value for r_1^s given in Eq. (45):

$$r_2^s(\max) = \frac{-r_3^\circ}{2}\sqrt{\frac{t_2}{t_1}} \tag{46}$$

If the lifetimes of the two levels are equal, the long-term coherent component would be half the initial polarization and $\Delta\omega_{max} \cong \omega_1$. Since r_1 in Eq. (45) is linearly dependent on r_3°, the coherent component could be doubled by doubling the feeding rates, unless, of course, this results in a significant depletion of the "infinite" reservoir in which case the assumptions that lead to Eq. (45) are no longer valid.

Of course, the expected value for r_1^s in Eq. (45) is not realistic owing to omission of the effects of relaxation. These will be dealt with analytically at the end of the next section. However, the similarity of Eq. (45) to the Bloch equation solution allows one to speculate that if the field is strong enough to "overcome" relaxation effects, i.e., if one can observe a transient nutation, the long-term coherent component will be present and can approach the value given by Eq. (45).

D. Relaxation

At this point we shall investigate the effects of relaxation on the steady-state components of the r-vector. These terms may be obtained in a reasonably simple analytical form if we restrict ourselves to Bloch-type relaxation terms T_1 and T_2. The transient solutions will be dealt

with at the end of this section.

Relaxation is most easily incorporated into the problem by adding the appropriate terms to the differential forms given in Eq. (22). One obtains

$$\dot{r}_1 = -\Delta\omega r_2 - (k_A + 1/T_2)\, r_1 \tag{47a}$$

$$\dot{r}_2 = \Delta\omega r_1 - \omega_1(r_y - r_x) - (k_A + 1/T_2)\, r_2 \tag{47b}$$

$$\dot{r}_y = \frac{\omega_1 r_2}{2} - (k_y + 1/T_y)\, r_y + r_x/T_x + F_y \tag{47c}$$

$$\dot{r}_x = -\frac{\omega_1 r_2}{2} - (k_x + 1/T_x)\, r_x + r_y/T_y + F_x \tag{47d}$$

Here T_2 is the homogeneous relaxation time, T_x and T_y are related to the probability per unit time for a transition from $|x\rangle$ to $|y\rangle$ and from $|y\rangle$ to $|x\rangle$, respectively. Notice that this form allows for spontaneous emission from $|y\rangle$ to $|x\rangle$ in addition to "spin lattice relaxation" terms; specifically, we could break T_y into two terms,

$$1/T_y = 1/T_{ys} + 1/T_{1y} \tag{48}$$

in which T_{ys} is related to spontaneous emission from $|y\rangle$ to $|x\rangle$ and T_{1y} is related to the normal thermal probability for a transition from $|y\rangle$ to $|x\rangle$. If spontaneous emission is negligible, as is the case in a rf region of the applied field, we have the normal spin-lattice relaxation (SLR) time encountered in NMR.

$$1/T_1 = 1/T_x + 1/T_{1y} \tag{49}$$

T_x and T_{1y} are related by the Boltzmann factor

$$\frac{T_{1y}}{T_x} = e^{-\frac{\hbar\omega_o}{kT}} \tag{50}$$

If ω_o is in the region of optical frequencies, spontaneous emission could be much more important than SLR in which case $T_y \cong T_{ys}$. The steady-state solutions are readily solved by setting the time derivatives equal to zero and solving for the components. As was done earlier, we choose to define relaxation terms T and τ such that the functional forms for the components can be recognized as being similar to the NMR expressions.

$$r_1^s = \frac{r_3^\circ \omega_1 \Delta\omega T^2}{1 + \Delta\omega^2 T^2 + \omega_1^2 T\tau} \tag{51a}$$

$$r_2^s = \frac{-r_3^\circ \omega_1 T}{1 + \Delta\omega^2 T^2 + \omega_1^2 T\tau} \tag{51b}$$

$$r_y^s = \frac{r_y^\circ(1 + \Delta\omega^2 T^2) + \frac{\omega_1^2 T\tau}{k_A}\left(\frac{F_x + F_y}{2}\right)}{1 + \Delta\omega^2 T^2 + \omega_1^2 T\tau} \tag{51c}$$

$$r_x^s = \frac{r_x^\circ(1 + \Delta\omega^2 T^2) + \frac{\omega_1^2 T\tau}{k_A}\left(\frac{F_x + F_y}{2}\right)}{1 + \Delta\omega^2 T^2 + \omega_1^2 T\tau} \tag{51d}$$

We have used the definitions

$$1/T = k_A + 1/T_2 \tag{52a}$$

$$\tau = \frac{k_A}{k_x k_y + k_y/T_x + k_x/T_y} \tag{52b}$$

$$r_y^\circ = \frac{F_y(k_x + 1/T_x) + F_x(1/T_x)}{k_x k_y + k_y/T_x + k_x/T_y} \tag{52c}$$

$$r_x^\circ = \frac{F_x(k_y + 1/T_y) + F_y(1/T_y)}{k_x k_y + k_y/T_x + k_x/T_y} \tag{52d}$$

$$r_3^\circ = r_y^\circ - r_x^\circ \tag{52e}$$

Thus far only the homogeneous relaxation time, T_2, has been considered. The inhomogeneous relaxation time, T_2^*, can be included by assuming some lineshape distribution, usually Lorentzian or Gaussian, centered about some average Larmor frequency, $\bar{\omega}_o$. We treat here the case for a Lorentz distribution given by the normalized shape function

$$g(\omega_o) = \frac{T_2^*}{\pi} \frac{1}{1 + (\omega_o - \bar{\omega}_o)^2 \, T_2^{*2}} \tag{53a}$$

$$\int_{-\infty}^{\infty} g(\omega_o) \, d\omega_o = 1 \tag{53b}$$

integration of the coherent components over all Larmor frequencies, ω_o, yields

$$\overline{r_1^s} = \frac{r_3^\circ \omega_1 \overline{\Delta\omega}}{\overline{\Delta\omega}^2 + [1/T_2^* + 1/T(1 + \omega_1^2 T\tau)^{1/2}]^2} \tag{54a}$$

$$\overline{r_2^s} = \frac{-r_3^\circ \omega_1 \left(1/T + 1/T_2^* \left(\frac{1}{(1 + \omega_1^2 T\tau)^{1/2}}\right)\right)}{\overline{\Delta\omega}^2 + [1/T_2^* + 1/T(1 + \omega_1^2 T\tau)^{1/2}]^2} \tag{54b}$$

where $\overline{\Delta\omega} = \bar{\omega}_o - \omega$. We are now in a position to look again at the long-term coherent components. The off-resonance value that corresponds to a maximum value of $\overline{r_1^s}$ is

$$\Delta\omega_{max} = 1/T_2^* + 1/T(1 + \omega_1^2 T\tau)^{1/2} \tag{55}$$

yielding

$$\overline{r_1^s}(max) = \frac{r_3^\circ \omega_1}{2(1/T_2^* + 1/T(1 + \omega_1^2 T\tau)^{1/2}} \tag{56}$$

If one has sufficient driving field strength to "exceed the linewidth", i.e., $\omega_1 T_2^* >> 1$, $\omega_1 T >> 1$, and $\omega_1^2 T\tau >> 1$, Eq. (56) reduces to an expression similar to Eq. (45)

$$\overline{r_1^s}(max) \cong \frac{r_3^\circ}{2} \sqrt{\frac{T}{\tau}} \tag{57}$$

under the influence of inhomogeneous broadening the maximum value of $\overline{r_2^s}$ on resonance is <u>not</u> equal to the high power limit for $\overline{r_1^s}$ given in Eq. (57) in contrast to the cases treated in Eqs. (45) and (46) in which relaxation was neglected. To see this we rewrite Eq. (54b) for on resonance, $\Delta\omega = 0$

$$\overline{r_2^s} = \frac{-r_3^\circ \omega_1 T}{1 + \omega_1^2 T\tau + T/T_2^*(1 + \omega_1^2 T\tau)^{1/2}} \tag{58}$$

Notice that any nonzero value for $1/T_2^*$ will reduce the size of $\overline{r_2^s}$. Figure 3 gives the ratio of the maximum values of $\overline{r_2^s}$ and $\overline{r_1^s}$ as a function of the parameter T/T_2^*.

As is seen from Fig. 3, significant differences between the maximum values of $\overline{r_1^s}$ and $\overline{r_2^s}$ become observable when the inhomogeneous relaxation time is greater than or equal to the homogeneous relaxation time. This is what one would expect physically, since the high power conditions required to obtain Eq. (57) imply that all isochromats in the line behave identically, whereas the low-power conditions required to obtain a maximum for $\overline{r_2^s}$ imply that each isochromat in the inhomogeneous line will have a different effective field direction and the vector sum over the isochromats will necessarily be less.

An additional point can be made about Eq. (57). Bloch noted[18] that an excessively long T_1 time could be troublesome if one attempts to observe the coherent component. With feeding and decay this is not a problem, in fact one would like to have T_1 as long as possible, for then $\tau \cong t_1$, and the "recovery" of the system is due to feeding, decay and T_2 processes. If T is short and is unaffected by the high fields applied to the system, the long-term coherent component can be reduced considerably in size. However, in many cases, T_2 is field dependent and can become quite long if the driving field is on the order of the inhomogeneous linewidth.

For high-power driving fields in solids, Redfield suggested[19] an alternative form for the Bloch equations, separating T_2 into T_{2e}, a transverse spin-lattice relaxation time applied to the driving field direction, and T_2, the normal transverse relaxation time. This distinction becomes necessary, for example, in the spin lock experiment in which the decay of the spin locked vector is not an energy conserving process and thus cannot be due to "spin-spin" relaxation. Using this formalism we may write an expression replacing Eq. (47a):

$$\dot{r}_1 = -\Delta\omega r_2 - (k_A + 1/T_{2e})\, r_1 \tag{59}$$

Solving the coupled Eqs. (47) with this substitution results in the steady-state values for r_1 and r_2:

$$r_1^s = \frac{r_3^\circ \omega_1 \Delta\omega T T_e}{1 + \Delta\omega^2 T T_e + \omega_1^2 T\tau} \tag{60a}$$

$$r_2^s = \frac{-r_3^\circ \omega_1 T}{1 + \Delta\omega^2 T T_e + \omega_1^2 T\tau} \tag{60b}$$

We have defined T_e by

$$1/T_e = k_A + 1/T_{2e} \tag{61}$$

Expressions for the maximum values of these components are readily obtained for high power and on resonance, respectively

$$r_1(\max) \cong \frac{r_3^\circ}{2}\sqrt{\frac{T_{2e}}{\tau}} \tag{62a}$$

$$r_2(\max) = \frac{-r_3^\circ}{2}\sqrt{\frac{T}{\tau}} \tag{62b}$$

Notice that the value for r_2 is unchanged from the value it would have without the modified Bloch equations. Conversely, r_1 can be significantly larger than r_2 owing to the fact that $T_{2e} \cong \tau$ for sufficiently high fields. The arguments concerning inhomogeneous broadening apply in the same fashion and Eq. (62a) may thus be assumed to be an upper limit for the size of a long term coherent component including the effects of feeding, decay and relaxation.

It should thus be possible to find systems that, under the proper conditions, satisfy Eq. (62a) and a large coherent component (compared to the initial polarization) can be maintained. Such a system has been found in the microwave region of applied field and an experimental report will follow in a future publication.

A solution for the transient behavior of the density matrix including relaxation is not simple from an operational point of view. One concise representation is in the form of the Liouville operator.[20] In this case we treat the elements of the 2×2 density matrix as being the components of a four-vector. Equation (10) is then written as

$$i\hbar\dot{\rho} = \hbar L\rho \tag{63}$$

where the Liouville operator is defined by a 4×4 matrix with elements

$$\hbar L_{mn,m'n'} = \mathcal{H}_{mm'}\delta_{nn'} - \delta_{mm'}\mathcal{H}_{n'n} \tag{64}$$

Relaxation and decay are easily incorporated into the L matrix, owing to the fact that terms which multiply only the off-diagonal or diagonal elements of ρ can be inserted by inspection whereas it is clumsy to perform this operation in the matrix representation of the density matrix. Explicitly, the L matrix corresponding to Eqs. (47) and (59) is given by

$$L = \begin{bmatrix} -i(k_y + 1/T_y) & -\omega_1/2 & \omega_1/2 & i/T_x \\ -\omega_1/2 & \Delta\omega - \frac{i}{2}\left[\left(\frac{1}{T_{2e}} + \frac{1}{T_2}\right) + 2k_A\right] & -\frac{i}{2}\left(\frac{1}{T_{2e}} - \frac{1}{T_2}\right) & \omega_1/2 \\ \omega_1/2 & -\frac{i}{2}\left(\frac{1}{T_{2e}} - \frac{1}{T_2}\right) & -\Delta\omega - \frac{i}{2}\left[\left(\frac{1}{T_{2e}} + \frac{1}{T_2}\right) + 2k_A\right] & -\omega_1/2 \\ i/T_y & \omega_1/2 & -\omega_1/2 & -i(k_x + 1/T_x) \end{bmatrix} \tag{65}$$

and the equation of motion corresponding to Eq. (21) becomes

$$i\hbar\dot{\rho} = \hbar L\rho + i\hbar F \tag{66}$$

F is a feeding vector which in this case has two non-zero elements, F_y and F_x. The solution to Eq. (66) is straightforward:

$$\rho(t) = \exp(-iLt)(\rho(0) + iL^{-1}F) - iL^{-1}F \tag{67}$$

Arguments used earlier can be used to show that the solution can be written in terms of a steady-state density matrix ρ_s.

$$\rho(t) = \exp(-iLt)(\rho(0) - \rho_s) + \rho_s \tag{68}$$

The exponential operator can be calculated in matrix form using Putzer's method,[15] and a closed form solution may be obtained. It might be noted that the characteristic equation for L yields a quartic polynomial with real coefficients. A strict algorithm for calculating the eigenvalues and the resulting exponential matrix can be made, and one may avoid iterative methods that generally restrict calculations to time regions that lie relatively close to t = 0.

E. Case in Which $\lambda^3 << VOL$

When the wavelength of the driving field becomes much smaller than the sample size, the phase of the radiation field is no longer constant throughout the sample, and, therefore, the jth molecule within the sample which is at a position $\vec{r}_j$ will experience an interaction Hamiltonian $V_j(t)$ given by

$$V_j(t) = \hbar\omega_1 \cos(\omega t - \vec{k} \cdot \vec{r}_j) \tag{68}$$

where $\vec{k}$ is the wavevector of the radiation with frequency ω. Under the rotating field approximation, the Hamiltonian for the jth molecule is

$$\mathcal{H}'_j = \frac{\hbar\omega_o}{2}\sigma_3 + \frac{\hbar\omega_1}{2} e^{-i\sigma_3 \frac{\omega t - k\cdot r^j}{2}} \sigma_1 e^{i\sigma_3 \frac{\omega t - k\cdot r^j}{2}} \tag{69}$$

which is similar to Eq. (2). For the same reasons that prompted a rotating frame transformation, we may perform a suitable unitary transformation on the density matrix which will remove the explicit time and space dependence from the Hamiltonian. Defining

$$U_{k,j} = e^{i\sigma_3 \frac{\omega t - k\cdot r^j}{2}} \tag{70}$$

we transform the laboratory frame density matrix for the jth molecule

$$\rho_j(t) = U_{k,j}\, \rho'_j(t)\, U^{-1}_{k,j} \tag{71}$$

This leads to an equation of motion

$$i\hbar\dot{\rho}_j = [\mathcal{H},\rho_j] \tag{72}$$

where the Hamiltonian $\mathcal{H}$ is identical to the rotating frame Hamiltonian in Eq. (7). If we assume that we have a sample of identical, non interacting systems, the form of $\mathcal{H}$, which is both time and space independent, renders the j index in Eq. (72) superfluous. The equation of motion is thus identical to Eq. (10) and the development follows the same lines. Note, however, that the unitary transformation carries the implicit dependence on j, r, k and ω, and the laboratory frame behavior of the system can be obtained by an inverse transformation. The spatial transformation is not as trivial as the rotating frame transformation and will depend strongly on the shape of the sample, how it is driven by the applied field, and how it is observed. This type of effect is well known theoretically and experimentally. In the photon echo experiment,[6] for example, light is emitted from the sample in a direction which is determined by the wavevectors of the coherent exciting radiation. Explicitly, if the second pulse in the two-pulse sequence enters at an angle α from the first pulse, the superradiant echo emission is observed at an angle 2α. In the special case of a small sample which is observed at a large distance, the observed behavior of the system will be the sum of the molecular density matricies

$$\rho_{obs} = \sum_j \rho_j \tag{73}$$

If we include the spatial dependence explicitly by an inverse transformation,we have, assuming a quasi-continuous distribution of molecules,

$$\rho_{obs} = \int_{-\infty}^{\infty} G(r)\, e^{-i\sigma_3 \frac{k\cdot r}{2}}\, \rho\, e^{-i\sigma_3 \frac{k\cdot r}{2}}\, d^3r \tag{74}$$

where G(r) is the function that describes the shape of the sample. The form of Eq. (74) results in a three dimensional spatial Fourier transform of G(r) for the off-diagonal elements. The diagonal elements yield simply an integration over the normalized shape function G(r).

We have shown above that the position-dependent phase factor introduced into the Hamiltonian for the short wavelength case in essence does not alter the development of the previous sections, and, in particular, does not hinder the production of a long term coherent state. Through the use of a spatially-dependent unitary transformation one can relate the optical case to the simple and highly useful geometrical picture. It must be noted, however, that for optical frequency energy separations, the long term coherent component will manifest itself as a precessing macroscopic electric dipole and, therefore, the sample itself will produce a coherent radiation field, i.e., coherent enhanced spontaneous emission. If this field becomes comparable to the driving field, it must be included in the Hamiltonian. This problem and other considerations inherent in a practical optical case such as specific spatial effects, noise due to on-resonance spontaneous emission, non-linear effects, and specific relaxation mechanisms are too involved to treat in general, and it is beyond the scope or intent of this paper to deal with these points in detail; however, a few aspects of the induced field will be discussed qualitatively.

The radiation field emitted by the sample will be at the same frequency as the driving field, since this is the rotating frame frequency and, therefore, the frequency of the dipole precession. If the magnitude of the coherent component is small due to either the intrinsic rate constants of the system or the rate of incoherent excitation, and if the coherent driving field is reasonably large, a small volume element of the sample will emit a negligible amount of radiation relative to the magnitude of the applied fields and, therefore, the emitted field may be disregarded. For this case the development of the previous sections is quite adequate to treat the optical region.

However, if the field emitted by a small volume element of the sample is not negligible, two cases must be distinguished. (1) If the long term coherent component is produced along the $\vec{r}_2$ axis by the on-resonance method, the precessing dipole and therefore the emitted E_1 field will be 90° out of phase with the driving $\vec{E}$ field applied along the $\vec{r}_1$ axis. This will cause position dependent phase and amplitude shifts of the vector resultant $\vec{E}$ field throughout the sample. Depending upon sample details, this effect could hinder the emission of coherent radiation from the sample. This is probably not a serious problem since T_2 processes will most likely inhibit the production of a sizable coherent component along $\vec{r}_2$ in any case. (2) If the long term coherent component is produced along the r_1 axis by the off resonance method, the emitted and applied field will be in phase. Thus the sample will not experience a phase shift problem but the amplitude of the resultant $\vec{E}$ field will still vary with position in the sample.

This does not present a problem for either the production of a long term coherent component or the emission of radiation from the sample. Regardless of the magnitude of the $\vec{E}$ field, i.e., the magnitude of ω_1, in a given volume element of the sample, a coherent component will still be produced which is colinear with the coherent components produced in other parts of the sample. The magnitude of ω_1 will simply determine the size of the coherent component developed in that volume element. Furthermore, since the maximum coherent component occurs for

$$\omega_1 \cong \Delta\omega \sqrt{\frac{T_e}{\tau}} \tag{75}$$

and since the coherent component becomes smaller for values of ω_1 greater than this,

the E field will not continue to grow

and in a sense the system will self-regulate the magnitude of ω_1 inside the sample. Thus, we have the <u>possibility</u> that with an appropriate set of rate constants and for high values of incoherent excitation, the sample will emit a radiation field which is at the same frequency and in-phase with the coherent driving field. If the amplitude of the driving field is such that ω_1 is less than the value in Eq. (75),

the superradiant emission of the sample itself may amplify the applied field to the point where ω_1, in the sample and emitted the sample, will

build up to the value given in Eq. (75). In this sense, production of long term coherence in optical systems may be useful as a tunable coherent light amplifier.

III. SUMMARY

We have presented a discussion of coherence in an ensemble of excited state two-level systems for the case in which population is being fed into the ensemble at a constant rate and decay is occurring from the ensemble at a rate dependent upon the state of the ensemble. The problem was initially treated in the absence of conventional T_1 and T_2 processes and an exact solution was obtained using the density matrix formalism. Several examples were treated to illustrate modifications which must be considered when a coherent coupling experiment is performed on an excited ensemble.

We have shown that it is possible to produce and maintain a coherent state in the excited ensemble for times which are only limited by the coherence time of the driving field despite the fact that this time may greatly exceed the lifetimes of the excited states. Conventional T_1 and T_2 processes were added to the development and exact solutions were obtained for the steady-state case which is important when examining the possibility of producing long term or kinetic coherence. It was demonstrated that if the modified Bloch equations are applicable, T_1 and T_2 processes do not modify the qualitative results obtained in their absence. Furthermore, even when rapid T_2 processes occur under low power conditions, it was shown that for high power in some instances sizable long term coherent components may nonetheless be maintained since the coherent component is effectively "spin locked" along the rotating frame static field.

Finally, it was shown that the development applies to the short wavelength optical case in addition to the long wavelength case. It was pointed out that the long term coherent component in optical systems will exhibit long term superradiant emission, i.e., continuous enhanced

coherent spontaneous emission, and that it may be possible to employ this effect as a coherent light amplifier. By choosing the proper system, the development of Section A should prove useful in interpreting experimental results.

Experimental verfication of long term kinetic coherence has been established for phosphorescent excited triplet states in zero field and will be presented in a forthcoming publication.

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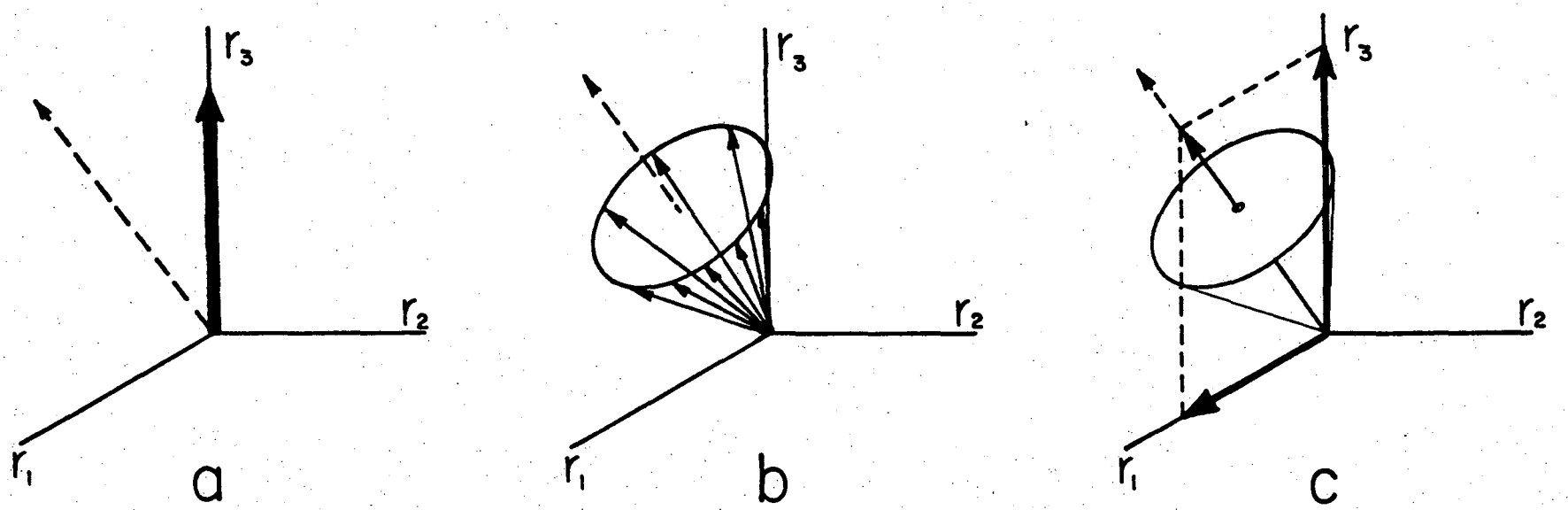
FIGURE CAPTIONS

Figure 1: (a) Initial population difference vector (heavy arrow) will precess about the effective field direction (dashed arrow in r_1-r_3 plane). (b) Feeding and dephasing processes produce a cone of vectors about the effective field direction. (c) Vector sum of the cone yields a vector aligned along the effective field direction and having a coherent component.

Figure 2: Pictorial description of the model system presented in the discussion. F_y and F_x are constant feeding rates, whereas k_y and k_x are decay rate constants.

Figure 3: Comparison of the two in-plane coherent components under the influence of inhomogeneous decay. The maximum value of the r_1 component is obtained under conditions of high power applied field and is thus independent of inhomogeneous decay. The maximum value of r_2 is obtained for relatively low power and is strongly affected when the homogeneous and inhomogeneous relaxation times become comparable.



XBL 751-5624

Fig. 1

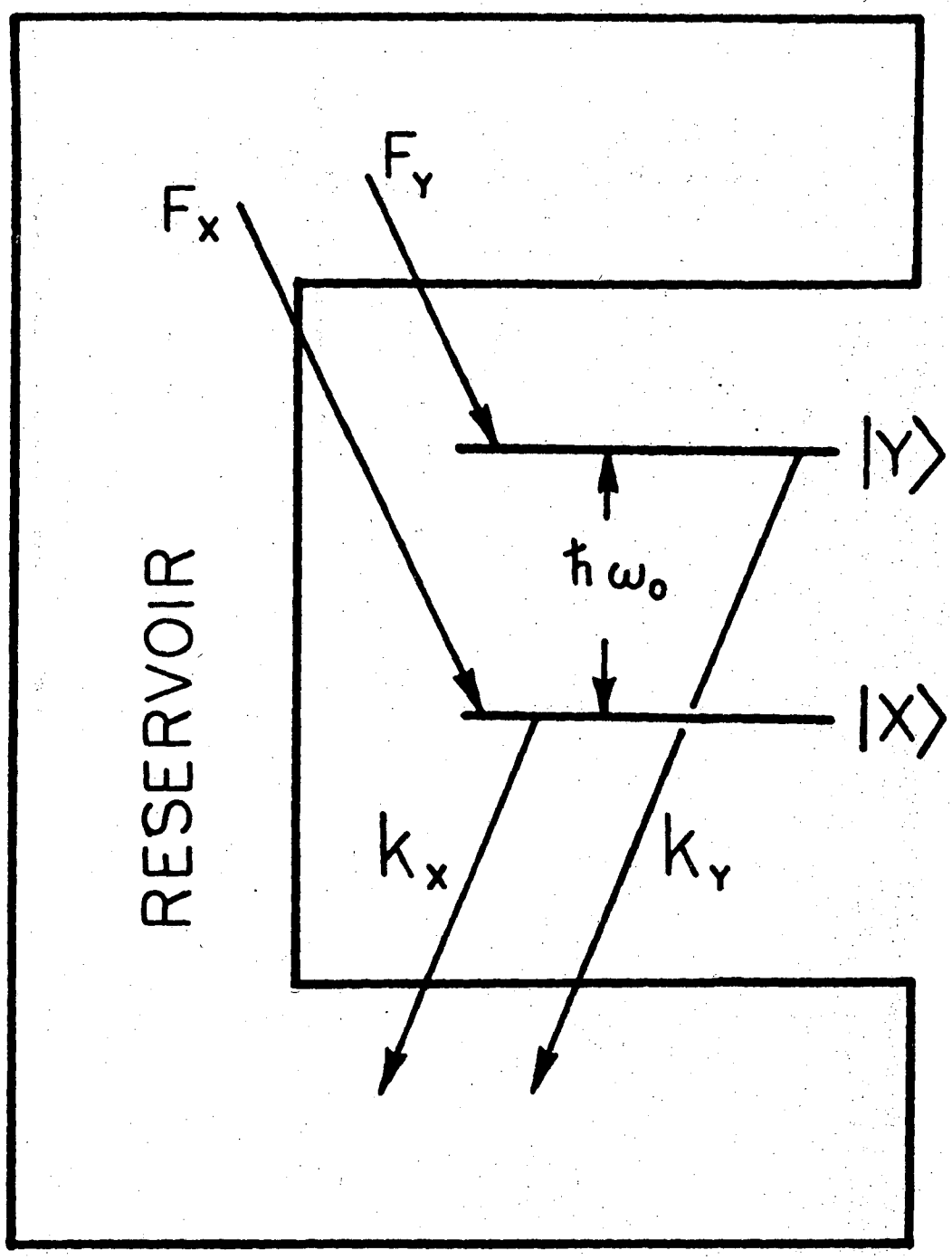


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Fig. 2

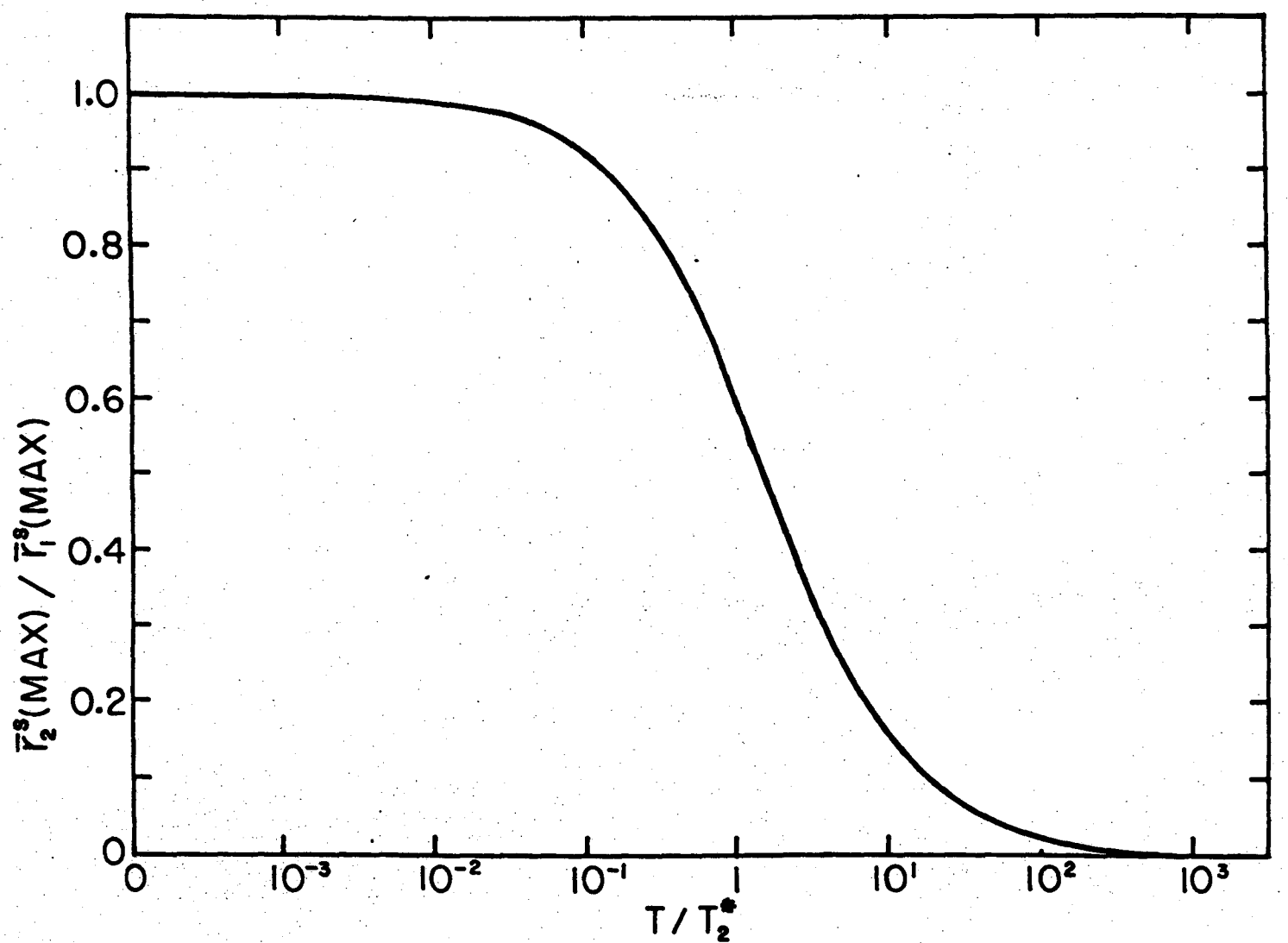
1.0
0.8
0.6
0.4
0.2
0
$\bar{r}_2^s(MAX) / \bar{r}_1^s(MAX)$
0
10^{-3}
10^{-2}
10^{-1}
1
10^{1}
10^{2}
10^{3}
T / T_2^*

Fig. 3

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