steady-state current. Rosenkrantz[11] has also observed a similar behavior.

(3) The current remained steady for several seconds and then rose steadily an order of magnitude in 10 or 15 sec when it suddenly dropped to its original value and the process then repeated itself.

The noise was neither field-dependent nor wavelength-dependent in the sense that the same percent noise was observed for virtually all wavelengths in the visible and near ultraviolet, and for all fields from about 500 V/cm (highest field used) to below 20 V/cm. Aside from the possibility of charging and subsequent breakdown in the sample, no explanation can be offered here for this phenomenon.

---

[11] D. Rosenkrantz (private communication).

PHYSICAL REVIEW VOLUME 137, NUMBER 2A 18 JANUARY 1965

Relaxation Effects in Nuclear Magnetic Double Resonance

B. D. Nageswara Rao
Department of Chemistry, Harvard University, Cambridge, Massachusetts

(Received 7 August 1964)

A general method, based on the density-matrix formalism of magnetic resonance given by Bloch and using the notational simplicity of Redfield, has been described for analyzing relaxation and coherence effects in nuclear magnetic double resonance. The method consists of transforming the equation of motion of the spin density matrix to a coordinate system rotating at the angular frequency of the strong irradiating field. The effect of the strong field is then calculated in the absence of the observing field. The effect of the observing field is calculated by obtaining a steady-state solution of the equation of motion. The method is briefly illustrated for the case of a single nucleus of spin $\frac{1}{2}$.

1. INTRODUCTION

A STRAIGHTFORWARD effect of the second radio-frequency field $\mathbf{H}_2$ on the resonance spectrum in a nuclear magnetic double-resonance experiment is to cause additional transitions by mixing the various unperturbed eigenstates of the spin Hamiltonian. Such features have been analyzed, in considerable detail and under various conditions[1–4] by transforming the spin Hamiltonian to a coordinate system rotating at the angular frequency of the strong irradiating field and treating the weak observing field by first-order time-dependent perturbation theory. However, in addition to this effect, the irradiating field introduces a strong coherence in the motion of the spins; it also provides a significant new factor in the dynamics of the magnetic polarization of the sample, which is otherwise determined by the interaction within the spin system and by the interaction of the spin system with the molecular surroundings and the static external field. Depending on the strength of the irradiating field relative to the relaxation processes, a variety of intensity and linewidth changes can occur in the spectrum.[5–8] A knowledge of the different relaxation mechanisms in the system and their relative importance allows a prediction of these effects on the double-resonance spectrum, or conversely, the analysis of these effects on the spectrum may furnish significant information on the relaxation mechanisms in the system. Density-matrix techniques provide a convenient method for describing these features.

Bloch[9] has given a general density-matrix formalism of nuclear induction and illustrated it for a variety of general situations. Redfield[10] has given a theory of relaxation processes with significant simplification in notation. In his calculation of the double-resonance problem, Bloch[9] used the approximation that off-diagonal matrix elements of the stationary part of the spin density matrix are negligible in the rotating frame in a representation in which the stationary part of the spin Hamiltonian is diagonal. This approximation requires that the separation of any two eigenvalues of the spin Hamiltonian in the rotating frame should be large compared with the corresponding off-diagonal matrix element of the relaxation Hamiltonian. Using the general formalism of Bloch, and with the notational simplicity of Redfield, Baldeschwieler[11] calculated the double-resonance spectrum for a single spin $\frac{1}{2}$ and applied this analysis to the description of double resonance experiments on the proton in $CHCl_3$. It was suggested from the results that when the frequency of the irradiating field is nearly equal to some single-

---

[1] A. L. Bloom and J. N. Shoolery, Phys. Rev. **97**, 1261 (1955).
[2] R. Freeman and D. Whiffen, Proc. Phys. Soc. (London) **79**, 794 (1962).
[3] W. A. Anderson and R. Freeman, J. Chem. Phys. **37**, 85 (1962).
[4] B. D. Nageswara Rao and J. D. Baldeschwieler, J. Chem. Phys. **37**, 2473 (1962).
[5] A. W. Overhauser, Phys. Rev. **92**, 411 (1953).
[6] K. Kuhlmann and J. D. Baldeschwieler, J. Am. Chem. Soc. **85**, 1010 (1963).
[7] L. H. Piette, J. D. Ray, and R. A. Ogg, J. Mol. Spectry. **2**, 66 (1958).
[8] G. W. Flynn and J. D. Baldeschwieler, J. Chem. Phys. **37**, 2907 (1962).
[9] F. Bloch, Phys. Rev. **102**, 104 (1956).
[10] A. G. Redfield, IBM J. Res. Develop. **1**, 19 (1957).
[11] J. D. Baldeschwieler, J. Chem. Phys. **40**, 459 (1964).

resonance frequencies, the approximation proposed by Bloch is not valid. The procedure given by Baldeschwieler for obtaining the complete density matrix involves two steps: The deviation caused by the irradiating field, in the absence of the observing field, on the density matrix is first determined in the laboratory frame of reference and the resulting matrix is transformed into the rotating frame; the effect of the observing field on the transformed density matrix is then calculated in the rotating frame of reference. In the first step of this method, it is assumed that the only important off-diagonal matrix element of the deviation density matrix occurs between states with their difference in energies close to the frequency of the irradiating field. This assumption is valid only for small amplitudes of irradiating field and large separations between different single resonance transitions such that other states of the system are not appreciably perturbed, and thus precludes application of this method to a number of cases of high-resolution NMR spectra.

A method for analyzing the relaxation effects applicable to most high-resolution nuclear magnetic double resonance experiments is described in this paper. It is also shown that the approximation proposed by Bloch is valid, for systems with weak relaxation, over a wide range of conditions usually obtained in these experiments, even when irradiation is done very close to single-resonance transitions. The density-matrix formalism of Bloch[9] forms the basis of this work, and the notation of Redfield[10] is used for the relaxation matrix. The general notation of the paper is similar to that given by Baldeschwieler.[11]

2. EQUATION OF MOTION OF SPIN DENSITY MATRIX IN THE ROTATING FRAME

The development of the equation of motion for the spin density matrix[9,12] is briefly described here for the sake of completeness. The Hamiltonian $\mathcal{H}$, in angular frequency units, of the complete system is given by

$$\mathcal{H}=\mathcal{H}(t)+F+\mathcal{H}', \tag{1}$$

where $\mathcal{H}(t)$, F, and $\mathcal{H}'$, respectively, represent the Hamiltonian of the spin system, which in our case is time-dependent, the lattice and their mutual interaction. The equation of motion of the density matrix ρ of the system in Schrödinger representation is

$$d\rho/dt=-i[\mathcal{H},\rho]. \tag{2}$$

Introducing operators in interaction representation

$$\mathcal{H}'^{I}(t)=U(t)e^{iFt}\mathcal{H}'e^{-iFt}U^{-1}(t), \tag{3}$$

$$\rho^{I}(t)=U(t)e^{iFt}\rho e^{-iFt}U^{-1}(t), \tag{4}$$

where $U(t)=U(t,0)$ obeys the differential equation

$$dU(t)/dt=iU\mathcal{H}(t), \tag{5}$$

with

$$U(t_0,t_0)=1 \quad\text{and}\quad U(t-\tau)=U(t)U(t-\tau,t), \tag{6}$$

leads to the equation of motion for ρ^I:

$$d\rho^I/dt=-i[\mathcal{H}'^{I},\rho^{I}]. \tag{7}$$

Integrating Eq. (7) in two successive approximations and neglecting higher-order terms, and replacing $\rho^I(0)$ by $\rho^I(t)$ in the integrand by assuming that the correlation time is short, gives

$$\frac{d\rho^I}{dt}=-i[\mathcal{H}'^{I}(t),\rho^{I}(0)] -\int_0^t [\mathcal{H}'^{I}(t),[\mathcal{H}'^{I}(t-\tau),\rho^{I}]]d\tau. \tag{8}$$

The spin density matrix σ is defined through the equations

$$\sigma(t)=\mathrm{Tr}_f\{\rho(t)\} \quad\text{and}\quad \sigma^I(t)=\mathrm{Tr}_f\{\rho^I(t)\}, \tag{9}$$

with

$$\sigma^I(t)=U(t)\sigma(t)U^{-1}(t),$$

which, under the assumption that the lattice remains always in thermal equilibrium because of its very large heat capacity, lead to

$$\rho(t)=P(F)\sigma(t), \tag{10}$$

where

$$P(F)=e^{-\hbar F/kT}/\mathrm{Tr}\{e^{-\hbar F/kT}\}.$$

Taking an ensemble average on both sides of Eq. (8) gives zero for the first term, if $\mathcal{H}'(t)$ is assumed to be a random operator uncorrelated with $\sigma(0)$ and yields the result

$$d\sigma^I/dt= -\mathrm{Tr}_f\left\langle\int_0^t [\mathcal{H}'^{I}(t),[\mathcal{H}'^{I}(t-\tau),P(F)\sigma^{I}(t)]]d\tau\right\rangle_{\mathrm{av}}, \tag{11}$$

with the understanding that σ hereinafter represents an average density matrix. The angular brackets in Eq. (11) denote the ensemble average.

We assume "extreme narrowing" or $|\mathcal{H}_0\tau_c|\ll 1$, where $\mathcal{H}_0$ is the stationary part of the spin Hamiltonian and τ_c is the correlation time. This assumption is likely to hold for most high-resolution NMR spectra in liquids, and would allow us to write $U(t-\tau,t)\approx 1$ and extend the upper limit of integration Eq. (11) to ∞.[13] Assuming further that $\hbar\mathcal{H}_0/kT\ll 1$ in taking the trace over f,[14] and that

$$\langle\mathcal{H}'(t)\mathcal{H}'(t-\tau)\rangle_{\mathrm{av}}=\langle|\mathcal{H}'(t)|^2\rangle_{\mathrm{av}}e^{-|\tau|/\tau_c} \tag{12}$$

---

[12] A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, London, 1961). The development of the equation of motion of the density matrix described here [until Eq. (15)] is similar to that given in Sec. D, Chap. VIII and Sec. A, Chap. XII of Abragam's book. Therefore, no attempt is made to reconstruct all the arguments except mentioning some relevent assumptions and introducing the notation.

[13] A. Abragam, Ref. 12, p. 516.

[14] A. Abragam, Ref. 12, p. 288.

leads, at first, to

$$d\sigma^I/dt = -\frac{1}{2}\left\langle\int_{-\infty}^{\infty}[\mathcal{H}'^I(t),[\mathcal{H}'^I(t-\tau),\sigma^I-\sigma_0]]d\tau\right\rangle_{\mathrm{av}}, \quad (13)$$

with

$$\sigma_0=\frac{1}{N}\left[1-\frac{\hbar\mathcal{H}_0}{kT}\right]=\frac{1}{N}-q\mathcal{H}_0, \quad (14)$$

where N is the number of eigenvalues of $\mathcal{H}_0$ and $q=\hbar/NkT$. Transforming back to Schrödinger representation and using the above-mentioned assumptions gives

$$d\sigma/dt=-i[\mathcal{H}(t),\sigma]-\langle\tau_c[\mathcal{H}'(t),[\mathcal{H}'(t),\sigma(t)-\sigma_0]]\rangle_{\mathrm{av}}. \quad (15)$$

In the double-resonance problem with a static magnetic field $\mathbf{H}_0=H_0\mathbf{k}$, and radio-frequency fields $\mathbf{H}_1=H_1\cos\omega_1t\mathbf{i}-H_1\sin\omega_1t\mathbf{j}$ and $\mathbf{H}_2=H_2\cos\omega_2t\mathbf{i}-H_2\sin\omega_2t\mathbf{j}$ used for observing and irradiating purposes, respectively, the spin Hamiltonian $\mathcal{H}(t)$ takes the form

$$\mathcal{H}(t)=\mathcal{H}_0+\mathcal{H}_1(t)+\mathcal{H}_2(t), \quad (16)$$

with

$$\mathcal{H}_0=2\pi\{\sum_i \nu_{0i}I_z(i)+\sum_{i<j}J_{ij}\mathbf{I}(i)\cdot\mathbf{I}(j)\}, \quad (17)$$

$$\mathcal{H}_k(t)=D_{k+}\exp(i\omega_kt)+D_{k-}\exp(-i\omega_kt), \quad k=1, 2, \quad (18)$$

$$\nu_{ki}=-\gamma_iH_k/2\pi, \quad k=0, 1, 2, \quad (19)$$

and

$$D_{k\pm}=\pi\sum_i \nu_{ki}I_\pm(i), \quad k=1, 2, \quad (20)$$

where $\mathbf{I}(i)$ and γ_i are the spin and gyromagnetic ratio including the chemical shift of the ith nucleus and J_{ij} is its spin-spin coupling constant with nucleus j. The quantities J_{ij} and ν_{ki} ($k=0, 1, 2$) are expressed in cycles per second. In the present calculation, only the steady-state solution of the spin density matrix is required. The deviations caused in the unperturbed spin density matrix σ_0, in the steady state, by the two radio-frequency fields are introduced explicitly by writing

$$\sigma(t)=\sigma_0+\chi(t)+\eta(t), \quad (21)$$

where $\chi(t)$ is the effect of $\mathbf{H}_2$ on the unperturbed system in the absence of $\mathbf{H}_1$ and $\eta(t)$ is the effect of $\mathbf{H}_1$ on the resulting system.

It is convenient, at this point, to introduce a transformation to a coordinate system rotating at the angular frequency $-\omega_2\mathbf{k}$ of $\mathbf{H}_2$ through the operator

$$T=\exp(-i\omega_2k_zt), \quad (22)$$

where $k_z=\sum_i I_z(i)$. Designating all operators in the rotating frame by putting a tilde ($\sim$) on top, Eq. (15) becomes

$$\frac{d\tilde{\sigma}}{dt}=-i[\mathcal{H}_0+\omega_2k_z+\tilde{\mathcal{H}}_2+\tilde{\mathcal{H}}_1(t),\tilde{\sigma}] -\tau_c\langle[\tilde{\mathcal{H}}'(t),[\tilde{\mathcal{H}}'(t),\tilde{\sigma}(t)-\sigma_0]]\rangle_{\mathrm{av}}, \quad (23)$$

since it can be seen from Eq. (17) that $\tilde{\mathcal{H}}_0=T\mathcal{H}_0T^{-1}=\mathcal{H}_0$ and from Eq. (14) that $\tilde{\sigma}_0=T\sigma_0T^{-1}=\sigma_0$. Furthermore,

$$\tilde{\mathcal{H}}_2=T\mathcal{H}_2T^{-1}=D_{2+}+D_{2-}, \quad (24)$$

$$\tilde{\mathcal{H}}_1=T\mathcal{H}_1T^{-1}=D_{1+}\exp(i\omega't)+D_{1-}\exp(-i\omega't), \quad (25)$$

where

$$\omega'=\omega_1-\omega_2,$$

so that $\tilde{\mathcal{H}}_2$ is stationary. The stationary part of the spin Hamiltonian in the rotating frame is given by

$$\mathcal{H}_0{}^R=\mathcal{H}_0+\omega_2k_z+\tilde{\mathcal{H}}_2 =2\pi\{\sum_i A_iI_z(i)+\sum_{i<j}J_{ij}\mathbf{I}(i)\cdot\mathbf{I}(j)\} +(D_{2+}+D_{2-}), \quad (26)$$

where

$$A_i=\nu_{0i}+(\omega_2/2\pi).$$

Equation (23) may then be rewritten as

$$d\tilde{\sigma}/dt=-i[\mathcal{H}_0{}^R+\tilde{\mathcal{H}}_1(t),\,\tilde{\sigma}] -\langle\tau_c[\tilde{\mathcal{H}}'(t),[\tilde{\mathcal{H}}'(t),\,\tilde{\sigma}(t)-\sigma_0]]\rangle_{\mathrm{av}}. \quad (27)$$

The explicit form of $\mathcal{H}'(t)$ depends on the relaxation mechanism. For convenience $\mathcal{H}'(t)$ may be written as

$$\mathcal{H}'(t)=\sum_q F^{(q)}A^{(q)}, \quad (28)$$

where $F^{(q)}$ are random functions of the lattice operators and $A^{(q)}$ are spin operators expressed in irreducible form. The functions $F^{(q)}$ are, in general, complex and the operators $A^{(q)}$ are, in general, non-Hermitian. The Hermiticity of $\mathcal{H}'$ is obtained by requiring that

$$\begin{aligned} F^{(q)*}&=F^{(-q)},\\ A^{(q)\dagger}&=A^{(-q)}. \end{aligned} \quad (29)$$

The correlation functions, with this form for $\mathcal{H}'(t)$, simplify through the relation

$$\langle F^{(q)*}(t)F^{(q')}(t)\rangle_{\mathrm{av}}=\delta_{qq'}\langle|F^{(q)}(t)|^2\rangle_{\mathrm{av}} \quad (30)$$

for most of the relaxation mechanisms or combinations of them. With the requirements of Eqs. (28), (29), (30) and using Eq. (22) it can be shown that the ensemble average of the double commutator in Eq. (27) is unchanged by replacing $\tilde{\mathcal{H}}'(t)$ by $\mathcal{H}'(t)$, resulting in the equation

$$d\tilde{\sigma}/dt=-i[\mathcal{H}_0{}^R+\tilde{\mathcal{H}}_1(t),\,\tilde{\sigma}] -\langle\tau_c[\mathcal{H}'(t),[\mathcal{H}'(t),\,\tilde{\sigma}(t)-\sigma_0]]\rangle_{\mathrm{av}}. \quad (31)$$

Taking matrix elements in a basis $|\alpha\rangle$, $|\alpha'\rangle$, $|\beta\rangle$, $|\beta'\rangle,\cdots$, etc., in which $\mathcal{H}_0{}^R$ is diagonal, such that $\mathcal{H}_0{}^R|\alpha\rangle=E_\alpha|\alpha\rangle$, and using the notation developed by Redfield,[10,15] Eq. (31) may be rewritten as

$$d\tilde{\sigma}/dt=-i[\mathcal{H}_0{}^R+\tilde{\mathcal{H}}_1(t),\,\tilde{\sigma}]-\Gamma(\tilde{\sigma}-\sigma_0)\,,\tag{32}$$

where

$$\Gamma_{\alpha\alpha'}(\tilde{\sigma}-\sigma_0)=-\sum_{\beta\beta'}R_{\alpha\alpha'\beta\beta'}(\tilde{\sigma}-\sigma_0)_{\beta\beta'}\,,\tag{33}$$

with

$$R_{\alpha\alpha'\beta\beta'}=J_{\alpha\beta\alpha'\beta'}-\delta_{\alpha'\beta'}\sum_{\gamma}\tfrac{1}{2}J_{\gamma\beta\gamma\alpha}-\delta_{\alpha\beta}\sum_{\gamma}\tfrac{1}{2}J_{\gamma\alpha'\gamma\beta'}\tag{34}$$

and

$$J_{\alpha\beta\alpha'\beta'}=\langle\langle\alpha|\mathcal{H}'(t)|\beta\rangle\langle\alpha'|\mathcal{H}'(t)|\beta'\rangle^*\rangle_{\text{av}}2\tau_c\,.\tag{35}$$

Substituting from Eq. (28), and using Eqs. (29) and (30) and the fact that the matrix elements of $A^{(q)}$ are all real, Eq. (35) becomes

$$J_{\alpha\beta\alpha'\beta'}=2\tau_c\sum_{q}\langle|F^{(q)}|^2\rangle_{\text{av}}\langle\alpha|A^{(q)}|\beta\rangle\langle\alpha'|A^{(q)}|\beta'\rangle\,.\tag{36}$$

This form of $J_{\alpha\beta\alpha'\beta'}$ readily yields the equalities[16]

$$J_{\alpha\beta\alpha'\beta'}=J_{\alpha'\beta'\alpha\beta}=J_{\beta\alpha\beta'\alpha'}=J_{\beta'\alpha'\beta\alpha}\,;\tag{37}$$

and substituting Eq. (37) in Eq. (34) gives the extremely useful relations

$$R_{\alpha\alpha'\beta\beta'}=R_{\beta\beta'\alpha\alpha'}=R_{\alpha'\alpha\beta'\beta}=R_{\beta'\beta\alpha'\alpha}\tag{38}$$

and

$$\sum_{\beta}R_{\alpha\alpha'\beta\beta}=0\,.\tag{39}$$

Equations (32) through (39) form the basis for the equations derived in the rest of this paper.

3. EFFECT OF STRONG IRRADIATING FIELD H_2

The calculation of the spin density matrix describing double-resonance experiments is best accomplished in two steps, by determining separately the deviations caused by the strong irradiating field and the weak observing field on the unperturbed system. The effects of the irradiating and observing fields are given, respectively, by $\chi(t)$ and $\eta(t)$ defined in Eq. (21). In the rotating frame

$$\tilde{\sigma}(t)=\sigma_0+\tilde{\chi}+\tilde{\eta}(t)\,,\tag{40}$$

where $\tilde{\chi}$ is time-independent because when $\mathcal{H}_1(t)=0$, $\eta(t)=0$; the Hamiltonian in the rotating frame is time-independent, and a steady-state solution of the equation of motion is likewise independent of time. When $\mathcal{H}_1(t)=0$ and $\eta(t)=0$, Eq. (32) becomes

$$[\mathcal{H}_0{}^R,\,\tilde{\chi}+\sigma_0]-i\Gamma(\tilde{\chi})=0\,.\tag{41}$$

Substituting for $\mathcal{H}_0{}^R$ from Eq. (26) and for σ_0 from Eq. (14) gives

$$[\mathcal{H}_0{}^R,\tilde{\chi}]-i\Gamma(\tilde{\chi})=q[D_{2+}+D_{2-},\,\mathcal{H}_0]\,.\tag{42}$$

Substituting further for D_{2+} and D_{2-} from Eq. (20) and for $\mathcal{H}_0$ from Eq. (17) and making the assumption that the Larmor frequencies of the irradiated nuclei are much larger than the chemical shifts and spin-spin coupling constants between them, an assumption which is amply justified under the conditions in which double resonance experiments are usually performed, Eq. (42) becomes

$$[\mathcal{H}_0{}^R,\tilde{\chi}]-i\Gamma(\tilde{\chi})=-(2\pi q v_0)(\pi v_2)\sum_{j}[I_+(j)-I_-(j)]\,,\tag{43}$$

where the summation is taken over all the irradiated nuclei. Taking the matrix elements of Eq. (43) in the α, α', $\cdots$ basis gives

$$\begin{aligned}(E_\alpha-E_{\alpha'})\tilde{\chi}_{\alpha\alpha'}&+i\sum_{\beta\beta'}R_{\alpha\alpha'\beta\beta'}\tilde{\chi}_{\beta\beta'}\\&=-(2\pi q v_0)(\pi v_2)\sum_{j}[I_+(i)-I_-(j)]_{\alpha\alpha'}\,.\end{aligned}\tag{44}$$

Since $\tilde{\chi}$ is Hermitian,

$$\begin{aligned}\text{Re}(\tilde{\chi}_{\alpha\alpha'})&=\text{Re}(\tilde{\chi}_{\alpha'\alpha})\,,\\\text{Im}(\tilde{\chi}_{\alpha\alpha'})&=-\text{Im}(\tilde{\chi}_{\alpha'\alpha})\,,\end{aligned}\tag{45}$$

and the diagonal matrix elements $\tilde{\chi}_{\alpha\alpha}$ are real. Further, it may easily be verified that the right-hand side of Eq. (43) is a real and skew-symmetric matrix. Using Eqs. (45) and (38) to separate the real and imaginary parts of Eq. (44), the following equations are readily obtained:

$$\begin{aligned}(E_\alpha-E_{\alpha'})\,\text{Re}(\tilde{\chi}_{\alpha\alpha'})&-\sum_{\beta<\beta'}(R_{\alpha\alpha'\beta\beta'}-R_{\alpha\alpha'\beta'\beta})\,\text{Im}(\tilde{\chi}_{\beta\beta'})\\&=-(2\pi q v_0)(\pi v_2)\sum_{j}[I_+(j)-I_-(j)]_{\alpha\alpha'}\,,\end{aligned}\tag{46}$$

$$\begin{aligned}(E_\alpha-E_{\alpha'})\,\text{Im}(\tilde{\chi}_{\alpha\alpha'})&+\sum_{\beta<\beta'}(R_{\alpha\alpha'\beta\beta'}+R_{\alpha\alpha'\beta'\beta})\,\text{Re}(\tilde{\chi}_{\beta\beta'})\\&+\sum_{\beta}R_{\alpha\alpha'\beta\beta}\tilde{\chi}_{\beta\beta}=0\,,\end{aligned}\tag{47}$$

with $\alpha<\alpha'$, and when $\alpha=\alpha'$

$$2\sum_{\beta<\beta'}R_{\alpha\alpha\beta\beta'}\,\text{Re}(\tilde{\chi}_{\beta\beta'})+\sum_{\beta}R_{\alpha\alpha\beta\beta}\tilde{\chi}_{\beta\beta}=0\,.\tag{48}$$

Equations (46) and (47) each represent a set of $N(N-1)/2$ equations, and Eq. (48) represents N equations, forming in all a set of N^2 homogeneous linear simultaneous equations in the matrix elements of $\tilde{\chi}$. But it can be easily shown that the N equations given by Eq. (48) are linearly dependent by virtue of Eqs. (38) and (39). A nontrivial solution for $\tilde{\chi}$ can be obtained by replacing one of the Eqs. (48) by the relation

$$\sum_{\beta}\tilde{\chi}_{\beta\beta}=0\,,\tag{49}$$

which obtains from the condition

$$\text{Tr}\tilde{\sigma}=\text{Tr}\sigma_0=1\,.$$

Baldeschwieler[11] suggested a method of calculation of $\chi(t)$ in the laboratory frame of reference in the repre-

---

[15] See also J. M. Anderson, thesis, Harvard University, Cambridge, Massachusetts, 1963 (unpublished).

[16] J. M. Anderson, Mol. Phys. (to be published).

sentation a, a', $\cdots$, in which $\mathcal{H}_0$ is diagonal, so that $\mathcal{H}_0|a\rangle = a|a\rangle$. The set of equations (2.30) in that reference were obtained under the assumption that $\chi_{aa'}$ is the only important off-diagonal element of $\chi(t)$ when irradiation is done near the transition $a \rightarrow a'$. It should also be noted that this assumption is implicit in the derivation of Eq. (2.21) in that paper, though it enters there indirectly through the truncation of the expression for $\Gamma_{aa'}(\sigma-\sigma_0)$ in Eq. (2.14).[17] The assumption that $\chi_{aa'}$ is the only important off-diagonal element of $\chi(t)$ is based on the argument that, in the absence of degeneracies, $\chi_{aa'}$ is large only when the denominator in Eq. (2.22) (Ref. 11) is small, that is, when the irradiation is done close to the transition $a \rightarrow a'$. But it should be noted that the numerator in that expression is of the order of the strength of the irradiating field γH_2, which is commonly of the order of 5–10 cps. Thus all the transitions which are in the vicinity of the irradiated transition separated by a frequency of the order of γH_2 will be affected, and therefore the assumption that only a single off-diagonal element of $\chi(t)$ is significant at one time does not hold for many cases of high-resolution spectra even in the absence of coincident transitions. All the elements of χ are, in general, interrelated, and the set of simultaneous equations (46) through (49) afford an exact solution of $\tilde{\chi}$ matrix. It should be noted, however, that the assumption that only one off-diagonal element of $\chi(t)$ is important does not affect the calculations on the single spin-$\frac{1}{2}$ case, as there is only one off-diagonal matrix element for that particular case.[11]

If the spin system has a first-order single-resonance spectrum, a simplification in the calculation may be realized. For such systems it is well known[3,9,15] that $\mathcal{H}_0^R$ can be brought into a form diagonal in the spin-product representation by a transformation of the type

$$s = \exp[i\theta \sum_j I_y(j)], \tag{50}$$

where j represents the irradiated nuclei. In such cases, it may be simpler to transform Eq. (32) using this operator which gives

$$d\tilde{\sigma}_s/dt = -i[\mathcal{H}_0^s + \tilde{\mathcal{H}}_1^s(t), \tilde{\sigma}_s] - \Gamma_s(\tilde{\sigma}_s - \sigma_{0s}), \tag{51}$$

where s is added as a superscript or subscript to denote the operators transformed using Eq. (50), and then calculate $\tilde{\chi}_s$ and $\tilde{\eta}_s$. It is then possible to work entirely in the spin product representation in which $\mathcal{H}_0^s$ is diagonal. It is also worth noting that in the calculation of $\tilde{\chi}_s$ for which the basic equation is obtained by transforming Eq. (43), using the operator s, the right-hand side of the equation remains invariant and therefore retains the simple form it has in the spin-product representation. The relaxation matrix, however, becomes considerably different, and use can be made of the well-known properties of irreducible tensors under rotation-like transformations[18] to evaluate the transformed relaxation matrix.

4. EFFECT OF THE OBSERVING FIELD H₁

The deviation in the spin density matrix $(\tilde{\chi}+\sigma_0)$ due to the observing field $\mathbf{H}_1$ is given by $\tilde{\eta}(t)$. When $\mathcal{H}_1(t) \neq 0$ it can easily be shown from Eqs. (32), (40), and (41) that

$$d\tilde{\eta}/dt = -i[\mathcal{H}_0^R, \tilde{\eta}(t)] - i[\tilde{\mathcal{H}}_1(t), \tilde{\chi}+\tilde{\eta}(t)+\sigma_0] - \Gamma(\tilde{\eta}). \tag{52}$$

Substituting for $\tilde{\mathcal{H}}_1(t)$ from Eq. (25) gives

$$(d\tilde{\eta}/dt) + i[\mathcal{H}_0^R, \tilde{\eta}] + i[D_{1+}, \tilde{\eta}]e^{i\omega' t} + i[D_{1-}, \tilde{\eta}]e^{-i\omega' t} + \Gamma(\tilde{\eta}) = -i[D_{1+}, \tilde{\chi}+\sigma_0]e^{i\omega' t} - i[D_{1-}, \tilde{\chi}+\sigma_0]e^{-i\omega' t}. \tag{53}$$

A steady-state solution for the $\tilde{\eta}$ matrix may be obtained by assuming that the diagonal elements of $\tilde{\eta}(Y_{\alpha\alpha})$ are constant in time and the off-diagonal elements vary with time as

$$\tilde{\eta}_{\alpha\alpha'} = Y_{\alpha\alpha'}{}^{+} e^{i\omega' t} + Y_{\alpha\alpha'}{}^{-} e^{-i\omega' t}. \tag{54}$$

Since $\tilde{\eta}$ is Hermitian,

$$Y_{\alpha\alpha'}{}^{+} = (Y_{\alpha'\alpha}{}^{-})^*. \tag{55}$$

Taking matrix elements of Eq. (53) in the α, α', $\cdots$ basis, by using Eq. (54) and collecting the terms varying as $e^{i\omega' t}$, $e^{-i\omega' t}$, and terms constant in time, and dividing the resulting equations into real and imaginary parts leads to the following sets of simultaneous equations:

$$(\omega' + E_\alpha - E_{\alpha'})\,\mathrm{Re}(Y_{\alpha\alpha'}{}^{+}) + (Y_{\alpha'\alpha'} - Y_{\alpha\alpha})D_{1+\alpha\alpha'} + \sum_{\beta\beta', \beta\neq\beta'} R_{\alpha\alpha'\beta\beta'}\,\mathrm{Im}(Y_{\beta\beta'}{}^{+}) = -[D_{1+}, (\mathrm{Re}\tilde{\chi}+\sigma_0)]_{\alpha\alpha'}, \tag{56}$$

$$(\omega' + E_\alpha - E_{\alpha'})\,\mathrm{Im}(Y_{\alpha\alpha'}{}^{+}) - \sum_{\beta\beta', \beta\neq\beta'} R_{\alpha\alpha'\beta\beta'}\,\mathrm{Re}(Y_{\beta\beta'}{}^{+}) = -[D_{1+}, \mathrm{Im}\tilde{\chi}]_{\alpha\alpha'}, \tag{57}$$

$$(-\omega' + E_\alpha - E_{\alpha'})\,\mathrm{Re}(Y_{\alpha\alpha'}{}^{-}) + (Y_{\alpha'\alpha'} - Y_{\alpha\alpha})D_{1-\alpha\alpha'} + \sum_{\beta\beta', \beta\neq\beta'} R_{\alpha\alpha'\beta\beta'}\,\mathrm{Im}(Y_{\beta\beta'}{}^{-}) = -[D_{1-}, (\mathrm{Re}\tilde{\chi}+\sigma_0)]_{\alpha\alpha'}, \tag{58}$$

$$(-\omega' + E_\alpha - E_{\alpha'})\,\mathrm{Im}(Y_{\alpha\alpha'}{}^{-}) - \sum_{\beta\beta', \beta\neq\beta'} R_{\alpha\alpha'\beta\beta'}\,\mathrm{Re}(Y_{\beta\beta'}{}^{-}) = -[D_{1-}, \mathrm{Im}\tilde{\chi}]_{\alpha\alpha'}, \tag{59}$$

$$2\sum_{\alpha'\neq\alpha} D_{1+\alpha\alpha'}\,\mathrm{Im}(Y_{\alpha\alpha'}{}^{+}) + 2\sum_{\alpha'\neq\alpha} D_{1-\alpha\alpha'}\,\mathrm{Im}(Y_{\alpha\alpha'}{}^{-}) + \sum_{\beta} R_{\alpha\alpha\beta\beta} Y_{\beta\beta} = 0, \tag{60}$$

where

$$D_{1\pm\alpha\alpha'} = \langle\alpha|D_{1\pm}|\alpha'\rangle = \langle\alpha'|D_{1\mp}|\alpha\rangle.$$

It is possible to obtain a complete solution for the $\tilde{\eta}$ matrix by solving these simultaneous equations with

---

[17] This fact has been discussed in some detail by M. Barfield and J. D. Baldeschwieler, J. Chem. Phys. (to be published).

[18] For example, M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), Chap. V.

the additional condition

$$\sum_{\beta} Y_{\beta\beta}=0. \tag{61}$$

This condition should be used in place of the set of Eqs. (60) to avoid linear dependence, analogous to the determination of $\tilde{\chi}$.

A general solution of the type given by Eqs. (56) through (61) is usually quite cumbersome. Considerable simplification may, however, be obtained by restricting the strength of the observing field. For small values of H_1, it can be seen from Eqs. (56) through (59) that $\mathrm{Re}(Y_{\alpha\alpha'}{}^{+})$ and $\mathrm{Im}(Y_{\alpha\alpha'}{}^{+})$ are large only when $(\omega'+E_\alpha-E_{\alpha'})$ is small, and $\mathrm{Re}(Y_{\alpha\alpha'}{}^{-})$ and $\mathrm{Im}(Y_{\alpha\alpha'}{}^{-})$ are large only when $(-\omega'+E_\alpha-E_{\alpha'})$ is small. Thus both $Y_{\alpha\alpha'}{}^{+}$ and $Y_{\alpha\alpha'}{}^{-}$ can be simultaneously significant only if $(E_\alpha-E_{\alpha'})$ is very small. This can happen for vanishingly small strengths of irradiating field H_2 applied very near a single-resonance transition and when the observing field is also introduced very close to the same frequency. The immediate vicinity of the irradiating frequency is usually covered by a beat pattern[11] in a frequency sweep double-resonance spectrum and does not provide any useful information. Thus the equations for $Y_{\alpha\alpha'}{}^{+}$ (or $Y_{\alpha'\alpha}{}^{-}$) and $Y_{\alpha\alpha'}{}^{-}$ (or $Y_{\alpha'\alpha}{}^{+}$) can be made independent of each other by rewriting Eqs. (56) through (60) as

$$(\pm\omega'+E_\alpha-E_{\alpha'})\,\mathrm{Re}(Y_{\alpha\alpha'}{}^{\pm})+(Y_{\alpha'\alpha'}-Y_{\alpha\alpha})D_{1\pm\alpha\alpha'}$$

$$+\sum_{\beta<\beta'} R_{\alpha\alpha'\beta\beta'}\,\mathrm{Im}(Y_{\beta\beta'}{}^{\pm})=-[D_{1\pm},(\mathrm{Re}\tilde{\chi}+\sigma_0)]_{\alpha\alpha'}, \tag{62}$$

$$(\pm\omega'+E_\alpha-E_{\alpha'})\,\mathrm{Im}(Y_{\alpha\alpha'}{}^{\pm})-\sum_{\beta<\beta'} R_{\alpha\alpha'\beta\beta'}\,\mathrm{Re}(Y_{\beta\beta'}{}^{\pm})$$

$$=-[D_{1\pm},\,\mathrm{Im}\tilde{\chi}]_{\alpha\alpha'}, \tag{63}$$

$$2\sum_{\alpha<\alpha'} D_{1\pm\alpha\alpha'}\,\mathrm{Im}(Y_{\alpha\alpha'}{}^{\pm})+\sum_{\beta} R_{\alpha\alpha\beta\beta}Y_{\beta\beta}=0, \tag{64}$$

with the understanding that equations with positive sign are important when $(+\omega+E_\alpha-E_{\alpha'})$ is small and those with the minus sign are important when $(-\omega'+E_\alpha-E_{\alpha'})$ is small. It may be noted that this simplification in equations for $\tilde{\eta}$ obtains for moderately small values of H_1, even though these values are large enough to cause appreciable saturation and to make off-diagonal elements of $\tilde{\eta}$ between all pairs of energy levels simultaneously significant. It is therefore appropriate to solve the set of Eqs. (62) through (64) along with (61) if saturation effects due to the observing field are required. A calculation of saturation effects was performed by Barfield and Baldeschwieler,[17] with the implication that, when the value of the observing field is large enough to cause saturation, the diagonal elements of $\tilde{\eta}$ become significantly different from zero, but only the off-diagonal element corresponding to the transition being observed is important. When the value of H_1 is made large, not only the diagonal elements are significant, but also the other off-diagonal matrix elements become nonzero, particularly when there are transitions close to the one being observed. Whether the effect is large on the diagonal elements or off-diagonal elements or comparable for both depends on the characteristics of the particular spectrum and the strength of relaxation. It should be pointed out further that the frequency of the observing field is usually swept in the double resonance experiment and, if the strength of this field is large, the steady-state solution may not give a correct description of the spectrum obtained by sweeping the frequency ω_1. In a normal double-resonance experiment, it is important to determine that the observing field is small enough not to cause any saturation effects. Under these conditions, and if there are no coincident transitions in the double-resonance spectrum, Eqs. (62) and (63) become

$$(\pm\omega'+E_\alpha-E_{\alpha'})\,\mathrm{Re}(Y_{\alpha\alpha'}{}^{\pm})+R_{\alpha\alpha'\alpha\alpha'}\,\mathrm{Im}(Y_{\alpha\alpha'}{}^{\pm})$$

$$=-[D_{1\pm},\,(\mathrm{Re}\tilde{\chi}+\sigma_0)]_{\alpha\alpha'}, \tag{65}$$

$$(\pm\omega'+E_\alpha-E_{\alpha'})\,\mathrm{Im}(Y_{\alpha\alpha'}{}^{\pm})-R_{\alpha\alpha'\alpha\alpha'}\,\mathrm{Re}(Y_{\alpha\alpha'}{}^{\pm})$$

$$=-[D_{1\pm},\,\mathrm{Im}\tilde{\chi}]_{\alpha\alpha'}, \tag{66}$$

leading to the solution

$$\mathrm{Re}(Y_{\alpha\alpha'}{}^{\pm})=\frac{-(\pm\omega'+E_\alpha-E_{\alpha'})[D_{1\pm},(\mathrm{Re}\tilde{\chi}+\sigma_0)]_{\alpha\alpha'}+R_{\alpha\alpha'\alpha\alpha'}[D_{1\pm},\,\mathrm{Im}\tilde{\chi}]_{\alpha\alpha'}}{(\pm\omega'+E_\alpha-E_{\alpha'})^2+R_{\alpha\alpha'\alpha\alpha'}{}^2}, \tag{67}$$

$$\mathrm{Im}(Y_{\alpha\alpha'}{}^{\pm})=\frac{-R_{\alpha\alpha'\alpha\alpha'}[D_{1\pm},(\mathrm{Re}\tilde{\chi}+\sigma_0)]_{\alpha\alpha'}-(\pm\omega'+E_\alpha-E_{\alpha'})[D_{1\pm},\,\mathrm{Im}\tilde{\chi}]_{\alpha\alpha'}}{(\pm\omega'+E_\alpha-E_{\alpha'})^2+R_{\alpha\alpha'\alpha\alpha'}{}^2}. \tag{68}$$

When there are coincident transitions present in the double-resonance spectrum, more than one off-diagonal element is important at one time and a set of simultaneous equations should be solved to determine the matrix elements of $\tilde{\eta}$.

5. SIGNAL INTENSITY

The intensity of the nuclear induction signal observed in a double-resonance experiment may be calculated in a manner similar to that given by Bloch[9] and Baldeschwieler.[11] The signal intensity S is defined as

$$S=-K\frac{d}{dt}\sum_i \gamma_i\langle I_y(i)\rangle$$

$$=-\frac{K}{2i}\frac{d}{dt}\sum_i \gamma_i\,\mathrm{Tr}[I_+(i)\sigma-I_-(i)\sigma], \tag{69}$$

where K is a proportionality constant. Since the trace is invariant under a unitary transformation, using the operator T defined in Eq. (22), one obtains

$$S=-\frac{K}{2i}\frac{d}{dt}\sum_i \gamma_i \operatorname{Tr}[TI_+(i)T^{-1}T\sigma T^{-1} - TI_-(i)T^{-1}T\sigma T^{-1}]$$

$$=-\frac{K}{2i}\frac{d}{dt}\sum_i \gamma_i \operatorname{Tr}[I_+(i)e^{-i\omega_2 t}\tilde{\sigma} - I_-(i)e^{i\omega_2 t}\tilde{\sigma}]. \tag{70}$$

The time-independent part of $\tilde{\sigma}$ contributes to a signal intensity at frequency ω_2 and the time-dependent part of $\tilde{\sigma}$, which is the off-diagonal part of $\tilde{\eta}(t)$, gives signals at frequencies $(\pm\omega'+\omega_2)$ or ω_1, and $2\omega_2-\omega_1$. If $\tilde{\eta}_{\alpha\alpha'}$ and $\tilde{\eta}_{\alpha'\alpha}$ are the only important off-diagonal elements of $\tilde{\eta}(t)$, Eq. (70) may be simplified readily to obtain the absorption-mode signal intensity, at the frequency $\omega'+\omega_2=\omega_1$, as

$$S_{\alpha\alpha'}{}^{\pm}=\mp K\omega_1 \sum_i \gamma_i I_{\mp}(i)_{\alpha'\alpha} \operatorname{Im}(Y_{\alpha\alpha'}{}^{\pm}) \sin\omega_1 t, \tag{71}$$

where the two alternative signs refer to the two situations $(\pm\omega'+E_\alpha-E_{\alpha'})\approx 0$. Thus a nonvanishing signal intensity is obtained at two places in the spectrum for a pair of energy levels α and α'. The two signals are, in general, 180° out of phase so that one is "inverted" with respect to the other. Such transitions were observed in systems with single spin-$\frac{1}{2}$ nucleus by Anderson[19] and Baldeschwieler.[11] The occurance of significant signal intensity of the two places $(\pm\omega'+E_\alpha-E_{\alpha'})\approx 0$ results from the existence of rather large off-diagonal elements of $\tilde{\eta}$, which describe the coherent perturbation by the radiofrequency field, in the vicinity of these two points. The integrated intensity of the signal may be obtained by substituting for $\operatorname{Im}(Y_{\alpha\alpha'}{}^{\pm})$ in Eq. (71) from Eq. (68) and integrating over $\Delta\omega=(\pm\omega'+E_\alpha-E_{\alpha'})$.

6. BLOCH'S APPROXIMATION

In the original calculation of Bloch,[9] the application of the density-matrix method for double resonance was illustrated for systems with weak relaxation, with the approximation that $(\tilde{\chi}+\sigma_0)$ is diagonal in a basis set in which $\mathcal{H}_0{}^R$ is diagonal. This approximation obtains as a result of the condition

$$|E_\alpha-E_{\alpha'}|\gg|\langle\alpha|\Gamma(\tilde{\chi})|\alpha'\rangle| \tag{72}$$

for all $\alpha\neq\alpha'$. It can be seen from Eq. (41) that this condition leads to very small values for the off-diagonal matrix elements of $(\tilde{\chi}+\sigma_0)$, so that it may be assumed to be diagonal. Baldeschwieler[11] pointed out that this approximation may easily be violated when the frequency of the irradiating field ω_2 is set close to a single-resonance transition, since some of the $(E_\alpha-E_{\alpha'})$ in that case become very small and may be zero when ω_2 coincides with the single-resonance frequency. It is important to note that even though $(E_\alpha-E_{\alpha'})$ does become small when α and α' correspond to the single-resonance transition being irradiated, it will never be zero, even when ω_2 is exactly equal to the particular single-resonance frequency. When ω_2 is varied, E_α and $E_{\alpha'}$ change. The behavior of contours of these eigenvalues as functions of the irradiating frequency has been discussed before.[4] It has been shown that any crossing of a pair of contours, occuring in the absence of the irradiating field, becomes forbidden when the perturbation is introduced, so that it connects the two eigenfunctions representing the particular contours. The smallest value that $(E_\alpha-E_{\alpha'})$ reaches is of the order of v_2, the strength of the irradiating field. Thus, for values of v_2 sufficiently large compared with the matrix elements of $\Gamma(\tilde{\chi})$, which are of the order of the linewidths involved in the spectrum, Bloch's approximation is still applicable, since the condition in Eq. (72) obtains even when ω_2 is made to coincide with a transition frequency in the single-resonance spectrum. This is shown to be the case in the analysis of the double-resonance spectrum of an AB system 2-bromo-5-chlorothiophene.[20] When the value of v_2 approaches the order of linewidths in the spectrum, the condition in Eq. (72) is not satisfied if the irradiating frequency is close to a single-resonance frequency. In many high-resolution NMR spectra, where the relaxation is weak and the linewidths are small, the strength of irradiation required to violate the requirement of Eq. (72) may be too feeble to be interesting. It may thus be possible to apply the density-matrix method for a variety of interesting cases of double resonance spectra using the approximation proposed by Bloch. The validity of the approximation should, however, be tested for individual cases. When the approximation is not valid, the procedure given in Secs. 3 and 4 provides a complete solution for the density matrix.

It is important to note, further, that $\tilde{\chi}$ and σ_0 are not usually diagonal in the α, α', $\cdots$ basis set, but $(\tilde{\chi}+\sigma_0)$ is diagonal with the above approximation. If an exact solution of $\tilde{\chi}$ is attempted using Eqs. (46) through (49) for systems with weak relaxation one usually finds

$$\operatorname{Re}(\tilde{\chi}_{\alpha\alpha'})\gg\operatorname{Im}(\tilde{\chi}_{\alpha\alpha'}) \tag{73}$$

for all α and α'. From Eq. (46) it can then be seen that

$$\operatorname{Re}(\tilde{\chi}_{\alpha\alpha'})=\frac{-(2\pi q v_0)(\pi v_2)\sum_j [I_+(j)-I_-(j)]_{\alpha\alpha'}}{(E_\alpha-E_\alpha{}')}, \tag{74}$$

or the off-diagonal matrix elements of $\tilde{\chi}$ are independent of the relaxation matrix. This situation is similar to

---

[19] W. A. Anderson, Phys. Rev. **102**, 151 (1956).

[20] B. D. Nageswara Rao, J. D. Baldeschwieler, and J. M. Anderson (to be published).

Bloch's approximation and leads to the condition

$$(\tilde{\chi}+\sigma_0)_{\alpha\alpha'}=0 \quad \text{for} \quad \alpha\neq\alpha'. \tag{75}$$

Thus Eq. (73) may also be taken as a criterion for using Bloch's approximation. The use of this approximation provides considerable simplification in the problem of solving for the density matrix because the number of R elements required is reduced. Furthermore, even in cases where the approximation is found not to be applicable, the conditions represented by Eqs. (72) and (73) are likely to be satisfied for most pairs of energy levels, except those affected most by irradiation. In such cases, all $\chi_{\alpha\alpha'}$ that satisfy the condition in Eq. (73) may be written down readily using Eq. (74), thereby reducing the number of simultaneous equations and R elements required for a complete solution.

7. SINGLE SPIN-$\frac{1}{2}$ PROBLEM

The double-resonance problem for a single nucleus of spin-$\frac{1}{2}$ can be solved in closed form without making any restrictive assumptions. Most of the assumptions cited in the calculation of $\tilde{\chi}$ and $\tilde{\eta}(t)$ become either superfluous or unnecessary for this case. This problem has been solved earlier by both Bloch[9] and Baldeschwieler.[11] The results presented in the following mainly serve as an illustration of the present method and essentially reproduce the results of the earlier calculations. The spin Hamiltonian for this case is of the form

$$\mathcal{H}_0=2\pi v_0 I_z, \tag{76}$$

$$\mathcal{H}_k(t)=\pi v_k[I_+\exp(i\omega_k t)+I_-\exp(-i\omega_k t)],\ k=1,\,2; \tag{77}$$

and if the relaxation is assumed to be through an isotropic random field, $\mathcal{H}'(t)$ is of the form

$$\mathcal{H}'(t)=F_z(t)I_z+\tfrac{1}{2}[F_+(t)I_-+F_-(t)I_+], \tag{78}$$

with

$$\langle|F_z(t)|^2\rangle_{\text{av}}=\tfrac{1}{2}\langle|F_+(t)|\rangle_{\text{av}}{}^2=\tfrac{1}{2}\langle|F_-(t)|\rangle_{\text{av}}{}^2=f. \tag{79}$$

Transforming to the rotating coordinate system, $\mathcal{H}_0{}^R$ of Eq. (26) becomes

$$\mathcal{H}_0{}^R=2\pi(AI_z+v_2I_x). \tag{80}$$

Starting with the eigenfunctions of I_z denoted by $|\frac{1}{2}\rangle$ and $|-\frac{1}{2}\rangle$, $\mathcal{H}_0{}^R$ can be readily diagonalized by a rotation transformation through an angle θ leading to eigenfunctions

$$\begin{aligned}|1\rangle&=\cos\theta|\tfrac{1}{2}\rangle+\sin\theta|-\tfrac{1}{2}\rangle,\\ |2\rangle&=-\sin\theta|\tfrac{1}{2}\rangle+\cos\theta|-\tfrac{1}{2}\rangle,\end{aligned} \tag{81}$$

and eigenvalues

$$\begin{aligned}E_1&=\pi(A^2+v_2{}^2)^{1/2},\\ E_2&=-\pi(A^2+v_2{}^2)^{1/2},\end{aligned} \tag{82}$$

where

$$\tan 2\theta=v_2/A. \tag{83}$$

The elements of the relaxation matrix R can easily be calculated using Eqs. (78) and (79) for $\mathcal{H}'(t)$ and the definitions in Eq. (34) and (35). It can be shown that the rotation represented by Eq. (81) leaves invariant the values of R calculated in the $|\frac{1}{2}\rangle$, $|-\frac{1}{2}\rangle$ basis. This property can be derived for this case by considering properties of irreducible tensors in Eq. (78) under rotations.[18] For the present case, the only nonvanishing elements R, out of a total of sixteen, are given by

$$\begin{aligned}R_{1111}&=R_{2222}=-f\tau_c,\\ R_{1122}&=R_{2211}=f\tau_c,\\ R_{1212}&=R_{2121}=-1/T_2=-2f\tau_c.\end{aligned} \tag{84}$$

The simultaneous equations (46) through (49) for determination of $\tilde{\chi}$, for this case, are

$$\begin{aligned}(E_1-E_2)\ \text{Re}(\tilde{\chi}_{12})+(1/T_2)\ \text{Im}(\tilde{\chi}_{12})&=-(\pi v_2)(2\pi q v_0),\\ (E_1-E_2)\ \text{Im}(\tilde{\chi}_{12})-(1/T_2)\ \text{Re}(\tilde{\chi}_{12})&=0,\\ -\tilde{\chi}_{11}+\tilde{\chi}_{22}&=0,\\ \tilde{\chi}_{11}+\tilde{\chi}_{22}&=0,\end{aligned} \tag{85}$$

which can be readily solved to give

$$\begin{aligned}&\tilde{\chi}_{11}=\tilde{\chi}_{22}=0,\\ &\text{Re}(\tilde{\chi}_{12})/2\pi q v_0\\ &\quad=-(\pi v_2)T_2{}^2(E_1-E_2)/[1+T_2{}^2(E_1-E_2)^2],\\ &\text{Im}(\tilde{\chi}_{12})/2\pi q v_0=-(\pi v_2)T_2/[1+T_2{}^2(E_1-E_2)^2].\end{aligned} \tag{86}$$

These expressions can be shown to be equivalent to the solution of $\chi(t)$ given by Baldeschwieler in a different basis set and in a slightly different notation, by appropriate substitutions and simplifications. The σ_0 matrix in the $|1\rangle$, $|2\rangle$ basis is given by

$$\frac{\sigma_0}{2\pi q v_0}=\frac{1}{4\pi q v_0}\,\frac{\pi}{E_1-E_2}\begin{bmatrix}A & -v_2\\ -v_2 & -A\end{bmatrix}. \tag{87}$$

It can be seen from Eq. (86) that if $|E_1-E_2|\gg1/|T_2|$, then

$$\text{Re}(\tilde{\chi}_{12})\gg\text{Im}(\tilde{\chi}_{12}), \tag{88}$$

and further,

$$\text{Re}(\tilde{\chi}_{12})/2\pi q v_0=-\pi v_2/(E_1-E_2), \tag{89}$$

which makes the $(\text{Re}(\tilde{\chi})+\sigma_0)$ diagonal in this basis set. This is exactly the approximation proposed by Bloch.[9]

The simultaneous equations for the calculation of $\tilde{\eta}$ can now be set up, and they are

$$\begin{aligned}&(\pm\omega'+E_1-E_2)\ \text{Re}Y_{12}{}^{\pm}+(Y_{22}-Y_{11})D_{1\pm12}\\ &\qquad+R_{1212}\ \text{Im}Y_{12}{}^{\pm}=-[D_{1\pm},(\text{Re}\tilde{\chi}+\sigma_0)]_{12},\\ &(\pm\omega'+E_1-E_2)\ \text{Im}Y_{12}{}^{\pm}-R_{1212}\ \text{Re}Y_{12}{}^{\pm}\\ &\qquad\qquad=-[D_{1\pm},\text{Im}\tilde{\chi}]_{12},\\ &\quad 2D_{1\pm12}\ \text{Im}Y_{12}{}^{\pm}+R_{1111}Y_{11}+R_{1122}Y_{22}=0,\\ &\qquad Y_{11}+Y_{22}=0,\end{aligned} \tag{90}$$

which leads to the solution

$$\operatorname{Re}Y_{12}^{\pm}=-\frac{(\pm\omega'+E_1-E_2)[D_{1\pm},\operatorname{Re}\tilde{\chi}+\sigma_0]_{12}+(2/f\tau_c)(f^2\tau_c^2+D_{1\pm12}^2)[D_{1\pm},\operatorname{Im}\tilde{\chi}]_{12}}{(\pm\omega'+E_1-E_2)^2+4(f^2\tau_c^2+D_{1\pm12}^2)},$$

$$\operatorname{Im}Y_{12}^{\pm}=\frac{2f\tau_c[D_{1\pm},(\operatorname{Re}\tilde{\chi}+\sigma_0)]_{12}-(\pm\omega'+E_1-E_2)[D_{1\pm},\operatorname{Im}\tilde{\chi}]_{12}}{(\pm\omega'+E_1-E_2)^2+4(f^2\tau_c^2+D_{1\pm12}^2)},\tag{91}$$

$$Y_{22}=-Y_{11}=-D_{1\pm12}\operatorname{Im}Y_{12}^{\pm}/f\tau_c.$$

The relative intensity of the two signals observed in a double-resonance experiment near $(\pm\omega'+E_\alpha-E_{\alpha'})=0$ is given by

$$S_{12}^{+}/S_{12}^{-}=-I_{-21}\operatorname{Im}Y_{12}^{+}/I_{+21}\operatorname{Im}Y_{12}^{-}.\tag{92}$$

Substituting in this equation the values of $\operatorname{Im}Y_{12}^{\pm}$, when $(\pm\omega'+E_\alpha-E_{\alpha'})=0$, leads to

$$\frac{S_{12}^{+}}{S_{12}^{-}}=\frac{1+\cos2\theta}{1-\cos2\theta}\,\frac{D_{1+12}[(\operatorname{Re}\tilde{\chi}+\sigma_0)_{22}-(\operatorname{Re}\tilde{\chi}+\sigma_0)_{11}]+(\operatorname{Re}\tilde{\chi}+\sigma_0)_{12}(D_{1+11}-D_{1+22})}{D_{1-12}[(\operatorname{Re}\tilde{\chi}+\sigma_0)_{22}-(\operatorname{Re}\tilde{\chi}+\sigma_0)_{11}]+(\operatorname{Re}\tilde{\chi}+\sigma_0)_{12}(D_{1-11}-D_{1-22})}\,\frac{f^2\tau_c^2+D_{1-12}^2}{f^2\tau_c^2+D_{1+12}^2}$$

$$=-\frac{(1+\cos2\theta)^2}{(1-\cos2\theta)^2}\left\{1-\frac{2}{1-\cos2\theta T_2^2(E_1-E_2)^2}\right\}\left\{\frac{1+4D_{1-12}^2T_2^2}{1+4D_{1+12}^2T_2^2}\right\}.\tag{93}$$

If there is no saturation due to H_1, the last term becomes unity and a result equivalent to that given by Baldeschwieler[11] is obtained. If, further, the relaxation is weak enough to provide the condition $|E_1-E_2|\gg1/|T_2|$, the second term also becomes unity and the result given by Bloch[9] is obtained.

8. CONCLUSION

The density-matrix method can be used with considerable advantage to analyze relaxation and coherence effects observed in nuclear magnetic double resonance. A method for obtaining a steady-state solution of the complete density matrix, similar in part to the one given earlier by Baldeschwieler[11] but applicable more generally to a variety of high-resolution NMR spectra is described. It involves transforming the equation of motion of the density matrix to a coordinate system rotating at the angular frequency ω_2. The effect of the strong irradiating field is calculated in the absence of the observing field, and then the effect of the weak observing field is considered. It is shown, further, that an approximation proposed by Bloch[9] is generally valid for systems with weak relaxation, if the strength of irraidation is large compared to the linewidths in the spectrum, even when the irradiation frequency coincides with any of the single-resonance frequencies. The present method, without this approximation, gives a considerably more complex set of equations than those given by Baldeschwieler,[11] but with the approximation becomes simple and straightforward. It should be possible to apply this method not only to steady-state conditions but also to transient experiments,[21,22] by appropriate modification. The validity of Bloch's approximation depends more on the strength of irradiation and relaxation than on the irradiating frequency. It appears to be considerably more advantageous, therefore, in describing the variety of high-resolution nuclear magnetic double-resonance experiments in systems with weak relaxation, to use the approximation to simplify the calculations than not to use it and achieve simplicity by making other restrictive assumptions which may not, in fact, have as wide a range of applicability as Bloch's approximation has for these systems.

ACKNOWLEDGMENTS

Sincere thanks are due to Dr. John D. Baldeschwieler for his kind interest and encouragement. The financial support of Sloan Foundation is gratefully achnowledged.

---

[21] K. Kuhlmann and J. D. Baldeschwieler (to be published).

[22] J. H. Noggle, thesis, Harvard University, Cambridge, Massachusetts, 1964 (unpublished).