Theory of Adiabatic Rapid Passage for Three Equally Spaced Levels*

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In experiments reported elsewhere, adiabatic rapid passage (ARP) has been performed on multilevel electron-paramagnetic crystals having three equally spaced energy levels separated by $\hbar\omega_0$. All transitions among the three levels are allowed due to crystalline electric-field mixing of the pure spin states. Simultaneous ARP inversion of the two coincident transitions at ω_0 produces a negative temperature simultaneously on all three transitions, at ω_0 and $2\omega_0$. The present paper explains these results through an analysis of adiabatic rapid passage in a spin system having an arbitrary spin-Hamiltonian with three equally spaced energy levels. Previous treatments of ARP have been limited either to the multilevel case with pure spin states or to the two-level case with mixed states. In the present analysis, the 3×3 density matrix is transformed to an equivalent matrix whose equation of motion contains a Hamiltonian which is real and constant, even with the rf perturbation applied. The transformed matrix is expanded in terms of nine orthonormal Hermitian basis matrices. Three of the expansion coefficients are directly related to state populations. The time variation of the expansion coefficients is calculated for ARP conditions. The transition probabilities of the two ω_0 transitions are not required to be equal. The final values of the three relevant expansion coefficients indicate negative temperatures on all three transitions.

INTRODUCTION

MOST experimental work on adiabatic rapid passage (ARP) in electron-paramagnetic solids has been concerned with magnetic resonance either in two-level systems[1–4] or in two-level transitions of multilevel systems.[5–7] This work has been conceptually based on the motion of the macroscopic magnetization vector as described by the Bloch equations.[8] Strictly speaking, the Bloch equations are applicable only to solids for which the crystalline electric field does not appear as a term in the spin Hamiltonian. For such cases the undamped portions of the Bloch equations,

$$(d/dt)\langle\mathbf{M}\rangle=\gamma\langle\mathbf{M}\rangle\times\mathbf{H}, \tag{1}$$

are equivalent to the time-dependent Schrödinger equation which describes the motion of the pure spin states in the presence of the external magnetic field. Equations (1) then lead to ARP inversion of $\langle M_z\rangle$ for both the two-level and the multilevel cases.

However, when a crystalline term appears, the expectation components $\langle M_x\rangle$,$\langle M_y\rangle$, and $\langle M_z\rangle$ of the magnetization vector no longer obey Eqs. (1) unless the operator for the crystalline term commutes with the vector spin operator.[9] For this reason, Eqs. (1) are not usually valid for solids. When they are not, the Schrödinger equation can still be cast in a form identical to Eqs. (1) as long as the rf fields induce transitions between only two states.[10] The two-state motion is given by

$$(d/dt)\mathbf{r}=\boldsymbol{\omega}\times\mathbf{r}. \tag{2}$$

Components of the vector $\mathbf{r}$ are appropriate combinations of the state coefficients which describe the time development of the complete quantum state for the two levels involved, when that state is expanded in terms of the two corresponding stationary eigenstates of the stationary spin Hamiltonian. This description has allowed the Bloch equations to be conceptually used by workers who have performed ARP experiments on isolated pairs of energy levels in multilevel crystals.

A notable exception is an experiment of Wagner, Castle, and Chester[11,12] which was performed at a point in the paramagnetic spectrum where the crystalline and Zeeman terms were comparable, and where three successive energy levels (E_1,E_2,E_3) were equally spaced. An adiabatic rapid passage was simultaneously performed on the 1-2 and 2-3 transitions. Before passage, the system was in equilibrium with a thermal bath, but after passage, each of the three transitions (1-2, 2-3, and 1-3) achieved a negative spin temperature. The author has continued this work,[13] and has found, under the experimental condition $(E_3-E_2)=(E_2-E_1)\lesssim kT_{\text{bath}}$, that the negative spin temperatures are approximately equal. Since both experiments were performed under conditions where the crystalline and Zeeman terms were comparable, and where transitions were simultaneously

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[11] P. E. Wagner, J. G. Castle, Jr., and P. F. Chester, in *Quantum Electronics*, edited by C. H. Townes (Columbia University Press, New York, 1960), p. 509.

[12] P. E. Wagner, J. G. Castle, Jr., and P. F. Chester, J. Appl. Phys. **31**, 1498 (1960).

[13] R. J. Morris, see Ref. 9, Chap. V.

induced between more than two spin states, neither Eqs. (1) nor Eqs. (2) are applicable. The experiments therefore pose a new problem in magnetic resonance.

Wagner, Castle, and Chester[11] postulated an explanation of the simultaneous ARP inversion phenomenon. They assumed, following Redfield,[14] that spin temperatures can be defined for the 1-2 and 2-3 transitions in the rotating frame, even in the presence of the large rf field required for ARP. They further assumed that spin-spin coupling between the superposed lines holds them at the same spin temperature throughout the passage, and thereby concluded that if either transition is inverted by ARP, the other will be inverted by spin-spin coupling to the first. No theoretical analysis has been presented in support of their argument.

The author questions the validity of their approach in cases where a crystalline term appears, for the following reasons. Redfield's spin Hamiltonian contains Zeeman and spin-spin terms but does not contain crystalline-electric terms. He was therefore able to remove the rf time dependence in the Hamiltonian by transforming the problem to a frame which rotates with the circularly-polarized rf field. Had crystalline terms been present, the rotating-frame transformation would not have removed the time dependence. Instead, it would have introduced additional rf variations due to the static-Zeeman or static-electric terms, or both, depending on the choice of rotation axis. Therefore, Redfield's calculation does not directly apply to the simultaneous ARP experiments, and the assumption that a rotating-frame spin temperature can be defined for these experiments is unsupported if the transformation is to be performed in real space. Some other transformation which suppresses the time dependence might possibly lead to the definition of a spin temperature for large rf fields, but it would be closely linked with the three-state dynamics of the system of noninteracting spins, which is the subject of this paper.

In the following analysis we treat the ARP behavior of a triplet of spin states having equally-spaced energy levels. The system is driven by a weak, sinusoidally time-dependent perturbation of angular frequency $\omega \approx \omega_0$, where $\hbar\omega_0$ is the energy spacing between adjacent levels. An adiabatic passage is simulated by slowly sweeping ω through ω_0, with ω_0 fixed, such that $\Delta\omega = \omega_0 - \omega$ adiabatically passes through zero. The rapid condition of ARP is satisfied by assuming that the total passage time is much smaller than all relevant spin-lattice relaxation times. The three-state analysis is not restricted to a simple triplet. If no other transition frequencies are near ω_0, it is equally applicable to three simultaneously resonant levels in a general $(2S+1)$-state multiplet for which $S>1$.[15]

The approach taken in this paper is essentially an extension of Eq. (2) to three equally spaced levels. Density matrix formalism is used, the matrix representation of operators being that for which the static spin Hamiltonian is diagonal. Use of this representation implies that the eigenstates of the static spin Hamiltonian are basic to the subsequent calculation of perturbations induced by a weak rf field. The chosen form of the static spin Hamiltonian is arbitrary in order that both Zeeman and crystalline electric terms be included in a general fashion. Solutions for the energy levels and rf perturbation matrix elements of particular paramagnetic crystals are presumably available elsewhere in the literature.

The first half of the paper is devoted to obtaining an equation of motion analogous to Eq. (2), and the second half to its ARP solutions. In our treatment the three-dimensional vector $\mathbf{r}$ of Eq. (2) is replaced by a nine-dimensional vector $\boldsymbol{\varrho}$. The components ρ_j of $\boldsymbol{\varrho}$ are appropriate combinations of the density-matrix elements. Both the equation of motion for $\boldsymbol{\varrho}$, Eq. (33), and the one for $\mathbf{r}$, Eq. (2), define orthogonal transformations in their respective vector spaces. They both possess time-dependent solutions which are precessions around their steady-state solutions. As a result, the ARP motion of $\boldsymbol{\varrho}$ will be similar to that of $\mathbf{r}$.

The components of $\boldsymbol{\varrho}$ are defined such that three of them (ρ_0, ρ_3, and ρ_4) collectively specify the three-state populations. Solutions are obtained for these components at the end of an adiabatic passage in terms of their initial values. The predicted final-state populations agree with existing experimental observations. Because of this agreement, it appears that the phenomenon of simultaneous ARP inversion is a property to be associated with the dynamics of individual three-level static-field spin systems and that it does not depend on extraneous spin-relaxation processes.[11]

QUANTUM-MECHANICAL MODEL

We consider an ensemble of identical paramagnetic ions of effective spin $S=1$ situated in a crystalline solid and subjected to a uniform static magnetic field, identical static crystalline electric fields, and a uniform rf magnetic field. The Hamiltonian operator consists of two parts[16]:

$$H^{\mathrm{op}}(t) = H_0{}^{\mathrm{op}} + V^{\mathrm{op}}(t). \tag{3}$$

The operator $H_0{}^{\mathrm{op}}$ is the static spin Hamiltonian which includes the effects of crystalline electric fields as well as the static Zeeman energy. The operator V^{op} accounts for the Zeeman energy of the spins when they are subjected to a rf magnetic field. Since both terms in H^{op} correspond to physical observables, H^{op} is a Hermitian operator.

We assume that $H_0{}^{\mathrm{op}}$ has three eigenstates $|\psi_j\rangle$ with energy eigenvalues E_j, such that

$$H_0{}^{\mathrm{op}}|\psi_j\rangle = E_j|\psi_j\rangle, \tag{4}$$

[14] A. G. Redfield, Phys. Rev. 98, 1787 (1955).

[15] R. J. Morris, see Ref. 9, Chap. III.

[16] We designate an operator by A^{op} and the corresponding matrix by A.

where $j=p, q, r$. We assume that the three-energy eigenvalues E_p, E_q, E_r, are equally spaced with

$$E_r=\hbar\omega_0, \tag{5a}$$

$$E_q=0, \tag{5b}$$

$$E_p=-\hbar\omega_0. \tag{5c}$$

The arbitrary zero reference level of the energy scale has been chosen such that $E_q=0$.

The rf magnetic field produces a time-dependent interaction $V^{\rm op}(t)$ which is assumed to be weak compared to $H_0{}^{\rm op}$ and sinusoidally varying at an angular frequency $\omega\approx\omega_0$. We assume that the rf magnetic field is linearly polarized and is given by $\mathbf{H}_1\cos\omega t$. The rf Zeeman energy operator of each ion is then

$$V^{\rm op}(t)=g\beta\mathbf{H}_1\cdot\mathbf{S}^{\rm op}\cos\omega t, \tag{6}$$

where g is the effective gyromagnetic ratio, β the Bohr magneton, and $\mathbf{S}^{\rm op}$ the effective spin operator.

The analysis ignores the various interactions between the paramagnetic spins and the crystal lattice, and between the spins themselves. The present calculations apply to *any* assembly of identical quantum systems, each of which has a number of energy levels, three and only three of which are equally spaced with spacing $\hbar\omega_0$, where the quantum systems are subjected to a weak sinusoidal perturbation of frequency $\omega\approx\omega_0$.

DENSITY MATRIX AND EQUATIONS OF MOTION

The quantum dynamics are calculated by means of the density-matrix formalism.[17,18] This method includes a statistical average over the assembly of expectation values for the individual ions and thereby yields information about observable macroscopic quantities. The formalism greatly simplifies the calculations since it allows one to handle a large number of dynamical variables in a systematic fashion. The physical significance of the individual density-matrix elements depends on the representation in which the matrix is calculated. We use the representation in which H_0 is diagonal. The elements of the density matrix are, by definition,

$$\rho_{jk}=\langle\psi_j|\,\rho^{\rm op}\,|\psi_k\rangle, \tag{7}$$

where $\rho^{\rm op}$ is the density operator.[16] In this representation, the diagonal elements ρ_{ii} are the ensemble-averaged occupation probabilities for the states $|\psi_i\rangle$. If N is the total number of ions in the ensemble (i.e., in the crystal sample), the population n_j of a particular state $|\psi_j\rangle$ is

$$n_j=N\rho_{jj}. \tag{8}$$

The off-diagonal elements ρ_{jk} give information about the ensemble-averaged phases of the quantum states. The matrix ρ is Hermitian.

We are principally interested in the behavior of the diagonal elements. However, since the motion of these elements is closely coupled to that of the off-diagonal elements, we must deal with the matrix as a whole. For our case ρ is a Hermitian matrix with three rows and columns, and contains nine real variables which are in general distinct. Only eight of these variables are independent since the sum of the diagonal elements must be unity in order to conserve probability. If the spin system is in thermal equilibrium, with $V^{\rm op}(t)\equiv0$, the density matrix is diagonal in our representation and

$$\rho_{jj}=\exp(-E_j/kT).$$

The time variation of ρ is obtained directly from the time-dependent Schrödinger equation:

$$\frac{d\rho}{dt}=\frac{1}{i\hbar}(H\rho-\rho H). \tag{9}$$

Here H is the matrix of $H^{\rm op}(t)$ when calculated with respect to the eigenstates of $H_0{}^{\rm op}$. Since ρ and H are Hermitian matrices containing three rows and columns, Eq. (9) is equivalent to a system of nine coupled differential equations in nine real variables, eight of which are in general independent.

The elements of H are

$$H_{jk}(t)=\langle\psi_j|\,H^{\rm op}(t)\,|\psi_k\rangle=H_{0jk}+V_{jk}(t). \tag{10}$$

The matrix H_0 is diagonal with real diagonal elements E_j, and V contains elements most of which are complex and all of which are in general nonzero. The elements of V are:

$$V_{jk}(t)=g\beta\langle\psi_j|\,\mathbf{H}_1\cdot\mathbf{S}^{\rm op}\,|\psi_k\rangle\cos\omega t=g\beta H_1\mu_{jk}\cos\omega t, \tag{11}$$

where $H_1=|\mathbf{H}_1|$, and μ_{jk} is the magnetic dipole-matrix element calculated between states $|\psi_j\rangle$ and $|\psi_k\rangle$ for an rf field of unit amplitude. The complex quantities μ_{jk} have magnitudes of order unity or less, and are dependent upon the particular transition j-k, upon the direction of $\mathbf{H}_1$, and upon the point in the paramagnetic spectrum for which they are calculated. We further write:

$$V_{jk}(t)=\hbar\omega_1\mu_{jk}(e^{i\omega t}+e^{-i\omega t}), \tag{12}$$

where $\omega_1=(1/2\hbar)g\beta H_1$.

TRANSFORMATION OF EQUATIONS OF MOTION

Solution of Eq. (9) will be simplified if we introduce the following transformation:

$$\rho'(t)=e^{iA\omega t}\rho(t)e^{-iA\omega t}, \tag{13a}$$

$$V'(t)=e^{iA\omega t}V(t)e^{-iA\omega t}, \tag{13b}$$

where

$$A\equiv\frac{H_0}{\hbar\omega_0}=\begin{bmatrix}-1&0&0\\0&0&0\\0&0&1\end{bmatrix}. \tag{13c}$$

[17] U. Fano, Rev. Mod. Phys. **29**, 74 (1957).
[18] D. ter Haar, Rept. Prog. Phys. **24**, 304 (1961).

Computation of the derivative of ρ' leads to

$$d\rho'/dt=(1/i\hbar)[(\hbar\Delta\omega A+V')\rho'-\rho'(\hbar\Delta\omega A+V')]. \quad (14)$$

The parameter $\Delta\omega=\omega_0-\omega$ specifies the extent to which the driving frequency ω differs from the magnetic resonance frequency ω_0 of the p-q and q-r transitions. We shall assume that ω is close enough to ω_0 that $\Delta\omega$ is much smaller than either ω or ω_0.

Except for the factor $\Delta\omega$, the transformation has accomplished the removal of the unperturbed Hamiltonian H_0 from the equations. We shall also see that it has removed the time dependence from some of the terms in the perturbation matrix V. This transformation is analogous to the rotating-frame transformation that is commonly used in magnetic resonance problems where the spin Hamiltonian contains only Zeeman terms. The advantage of the formulation is that the equations of motion explicitly contain the parameter $\Delta\omega$. By solving for the motion of ρ' assuming that $\Delta\omega$ is arbitrary and fixed, and then by considering the behavior of ρ' as $\Delta\omega$ slowly passes through a succession of quasifixed values, we will be able to obtain the occupation probabilities of the states p, q, and r at the end of an adiabatic passage in terms of their initial values. The transformed matrix ρ' will be sufficient for this purpose because its diagonal elements are identical with those of the original matrix ρ:

$$\rho_{jk}'=\rho_{jk}e^{i\omega(A_{jj}-A_{kk})t}, \quad (15a)$$

$$\rho_{jj}'=\rho_{jj}. \quad (15b)$$

The matrix equation (14) is a system of coupled differential equations with time-varying coefficients. The elements ρ_{jk}' may be regarded as coordinates in an oscillatory system with nine degrees of freedom. In this picture the transformed unperturbed Hamiltonian $\hbar\Delta\omega A$ determines the natural oscillations of the system, and the perturbation V' drives the oscillations via a set of sinusoidally time-varying coefficients in the equations of motion.

The natural frequencies of Eq. (14) can be identified by setting $V'=0$. Computation of the commutator $(A\rho'-\rho'A)$ leads to the following motion:

$$\dot\rho_{11}'=\dot\rho_{22}'=\dot\rho_{33}'=0, \quad (16a)$$

$$\rho_{12}'(t)=\rho_{12}'(0)e^{i\Delta\omega t}, \quad (16b)$$

$$\rho_{23}'(t)=\rho_{23}'(0)e^{i\Delta\omega t}, \quad (16c)$$

$$\rho_{13}'(t)=\rho_{13}'(0)e^{i2\Delta\omega t}. \quad (16d)$$

The natural frequencies are $\Delta\omega$ and $2\Delta\omega$ which are both very small compared to ω and ω_0.

We also determine the driving frequencies of V'. From Eq. (13b), we have

$$V_{jk}'=V_{jk}e^{i\omega(A_{jj}-A_{kk})t}.$$

Using Eq. (12) this becomes

$$V_{jk}'=\hbar\omega_1\mu_{jk}[e^{i\omega(A_{jj}-A_{kk}+1)t}+e^{i\omega(A_{jj}-A_{kk}-1)t}]. \quad (17)$$

If we denote the driving frequencies by

$$\nu_{jk\pm}=\omega(A_{jj}-A_{kk}\pm1), \quad (18)$$

and note that $A_{pp}=-1$, $A_{qq}=0$, and $A_{rr}=1$, we find that ν_{pq+}, ν_{qp-}, ν_{qr+}, and ν_{rq-} are zero, and that the other frequencies present are $\pm\omega$, $\pm2\omega$, and $\pm3\omega$.

We shall retain only the zero-frequency terms of V' since the other terms have frequencies which are substantially different from the natural oscillation frequencies and will, therefore, have a negligible effect on the motion, provided the perturbation is small. Discarding the high-frequency terms is analogous to neglecting the counter-rotating component of a linearly polarized transverse driving field in a simple magnetic resonance problem. For our case the procedure may be rigorously justified to first order in the perturbation by a method from the theory of nonlinear oscillations.

Suppose the matrix elements ρ_{jk}' are the components x_i of a vector $\mathbf{x}$ in a nine-dimensional vector space. When $|\Delta\omega|\lesssim\omega_1\ll\omega$, Eqs. (14) have the form:

$$d\mathbf{x}/dt=\omega_1\sum_s e^{i\nu_s t}\mathbf{X}_s(\mathbf{x}). \quad (19)$$

Here ω_1 is assumed to be small and the components of the vector $\mathbf{X}_s(\mathbf{x})$ do not explicitly depend on time. The quantities ν_s are the different values taken by the frequencies $\nu_{jk\pm}$. One of these is zero while all the others have magnitudes much greater than ω_1. Equation (19) is the standard form discussed at length by Bogoliubov and Mitropolsky.[19] These authors show that the approximate solution to Eq. (19) is, to first order in ω_1, the same as the solution of

$$d\mathbf{x}/dt=\omega_1\mathbf{X}_0(\mathbf{x}), \quad (20)$$

where $\mathbf{X}_0(\mathbf{x})$ is the vector coefficient of the zero-frequency term in the summation of Eq. (19).

We may therefore replace the time-dependent matrix $V'(t)$ by a constant matrix V'' in which all elements are zero except those that correspond to the constant terms in $V'(t)$. The new matrix is

$$V''=\hbar\omega_1\begin{bmatrix}0&\mu_{pq}&0\\ \mu_{qp}&0&\mu_{qr}\\ 0&\mu_{rq}&0\end{bmatrix}. \quad (21)$$

In general, the elements in V'' are all complex, but we need not work with a complex driving matrix. We write the complex elements of V'' in terms of their magnitudes and phases:

$$V_{pq}''=\hbar\omega_1\mu_{pq}=\hbar\omega_1M_{pq}e^{i\phi_{pq}}, \quad (22a)$$

$$V_{qp}''=\hbar\omega_1\mu_{qp}=\hbar\omega_1M_{pq}e^{-i\phi_{pq}}, \quad (22b)$$

$$V_{qr}''=\hbar\omega_1\mu_{qr}=\hbar\omega_1M_{qr}e^{i\phi_{qr}}, \quad (22c)$$

$$V_{rq}''=\hbar\omega_1\mu_{rq}=\hbar\omega_1M_{qr}e^{-i\phi_{qr}}. \quad (22d)$$

[19] N. N. Bogoliubov and Y. A. Mitropolsky, *Asymptotic Methods in the Theory of Non-Linear Oscillations*, translated from Russian (Hindustan Publishing Corporation, Delhi, India, 1961), Chap. 5.

In these equations, M_{pq} and M_{qr} are real numbers. We define a 3×3 diagonal matrix C whose only nonzero elements are $C_{pp}=+\phi_{pq}$ and $C_{rr}=-\phi_{qr}$,

$$C_{jl}=\delta_{jl}(\delta_{jp}\phi_{pq}-\delta_{jr}\phi_{qr}). \tag{23}$$

We define a new transformation as follows:

$$\rho^e=e^{-iC}\rho' e^{+iC}, \tag{24a}$$

$$V^e=e^{-iC}V'' e^{+iC}. \tag{24b}$$

Because of the definition of ρ', the diagonal elements of ρ^e are $\rho_{jj}{}^e=\rho_{jj}$ for $j=p,\ q,\ r$. They are the average occupation probabilities for the states $|\psi_p\rangle$, $|\psi_q\rangle$, and $|\psi_r\rangle$, respectively. The matrix elements of V^e may be obtained by using Eqs. (22), (23), and (24b), which gives

$$V^e=\hbar\omega_1\begin{bmatrix}0 & M_{pq} & 0\\ M_{pq} & 0 & M_{qr}\\ 0 & M_{qr} & 0\end{bmatrix}.$$

We take the time derivative of Eq. (24a), use Eq. (14) with V' replaced by V'', and define a new matrix $H_0{}^e=\hbar\Delta\omega A$. The resulting equation of motion for ρ^e is

$$\frac{d\rho^e}{dt}=\frac{1}{i\hbar}(H^e\rho^e-\rho^e H^e), \tag{25}$$

where $H^e=H_0{}^e+V^e$ is a real, constant matrix. The matrices ρ^e and H^e may be regarded as the effective density matrix and the effective Hamiltonian. Equations (25), which relate them, are sufficiently reduced for our problem. The remainder of this paper is devoted to their solution.

EXPANSION IN BASIS MATRICES

A powerful method exists for solving problems of density matrix dynamics.[17] One expands the matrix as a series in a complete set of orthonormal Hermitian basis matrices U_i. The coefficients of expansion are real numbers, and their time variation reflects the motion of the original matrix. If the basis matrices are judiciously chosen, one or more of the expansion coefficients will have a physical significance useful for a particular problem. The basis matrices are orthonormal in the sense that

$$\mathrm{Tr}(U_iU_j)=\delta_{ij}. \tag{26}$$

If the series expansion is to be a complete description of the original matrix, there must be as many different expansion coefficients as there are independent real parameters in the original matrix. For an arbitrary $l\times l$ Hermitian matrix, the set of basis matrices is a complete set (for purposes of expansion) when it contains l^2 orthogonal matrices. For describing the motion of the 3×3 effective density matrix ρ^e, we need a set of nine 3×3 orthonormal Hermitian basis matrices. Such a set is given below. The first four matrices are the identity matrix and the three Pauli-spin matrices. The remaining five have been devised by the author such that they are each orthogonal to the first four and to each other.

$$U_0=\frac{1}{\sqrt{3}}\begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}, \tag{27a}$$

$$U_1=\frac{1}{2}\begin{bmatrix}0 & 1 & 0\\ 1 & 0 & 1\\ 0 & 1 & 0\end{bmatrix}=\frac{1}{\sqrt{2}}S_x, \tag{27b}$$

$$U_2=\frac{i}{2}\begin{bmatrix}0 & -1 & 0\\ 1 & 0 & -1\\ 0 & 1 & 0\end{bmatrix}=\frac{1}{\sqrt{2}}S_y, \tag{27c}$$

$$U_3=\frac{1}{\sqrt{2}}\begin{bmatrix}1 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & -1\end{bmatrix}=\frac{1}{\sqrt{2}}S_z, \tag{27d}$$

$$U_4=\frac{1}{\sqrt{6}}\begin{bmatrix}1 & 0 & 0\\ 0 & -2 & 0\\ 0 & 0 & 1\end{bmatrix}, \tag{27e}$$

$$U_5=\frac{1}{2}\begin{bmatrix}0 & 1 & 0\\ 1 & 0 & -1\\ 0 & -1 & 0\end{bmatrix}, \tag{27f}$$

$$U_6=\frac{i}{2}\begin{bmatrix}0 & 1 & 0\\ -1 & 0 & -1\\ 0 & 1 & 0\end{bmatrix}, \tag{27g}$$

$$U_7=\frac{1}{\sqrt{2}}\begin{bmatrix}0 & 0 & 1\\ 0 & 0 & 0\\ 1 & 0 & 0\end{bmatrix}, \tag{27h}$$

$$U_8=\frac{i}{\sqrt{2}}\begin{bmatrix}0 & 0 & 1\\ 0 & 0 & 0\\ -1 & 0 & 0\end{bmatrix}. \tag{27i}$$

We expand the effective density matrix ρ^e in a series of the matrices U_k.

$$\rho^e=\sum_k \rho_k U_k. \tag{28}$$

The quantities ρ_k are real numbers, not matrices.

$$\rho_i=\mathrm{Trace}(\rho^e U_i). \tag{29}$$

The coefficients ρ_i are the projections of the effective density matrix ρ^e onto the various orthogonal basis matrices U_i.

Three of the basis matrices are diagonal, namely U_0, U_3, U_4. The corresponding expansion coefficients (ρ_0,ρ_3,ρ_4) have direct physical significance. The first coefficient is

$$\rho_0=(1/\sqrt{3})(\rho_{pp}+\rho_{qq}+\rho_{rr}). \tag{30a}$$

This quantity is a measure of the total number of spins in states $|\psi_p\rangle$, $|\psi_q\rangle$, and $|\psi_r\rangle$, and will prove to be independent of time. The other two coefficients are

$$\rho_3=(1/\sqrt{2})(\rho_{pp}-\rho_{rr}), \tag{30b}$$

$$\rho_4=6^{-1/2}(\rho_{pp}-2\rho_{qq}+\rho_{rr})$$
$$=6^{-1/2}[(\rho_{pp}-\rho_{qq})-(\rho_{qq}-\rho_{rr})]. \tag{30c}$$

These two quantities are measures of population differences and can be directly observed in magnetic resonance experiments. The first of these (ρ_3) is the population difference for the outside pair of levels. We shall see that the equations of motion predict that ρ_3 is inverted under conditions of simultaneous adiabatic rapid passage.

MOTION OF EXPANSION COEFFICIENTS

The time dependence of ρ^e can be converted into motion of the set of expansion coefficients ρ_i. To do so, we insert Eq. (28) into Eq. (25) and define a new, antisymmetric, real matrix Ω as follows:

$$\Omega_{jk}=-\frac{1}{i\hbar}\,\mathrm{Trace}[H^e(U_jU_k-U_kU_j)]. \tag{31}$$

The equations of motion for the expansion coefficients of Eq. (28) then become

$$\dot{\rho}_j=\sum_k \Omega_{jk}\rho_k. \tag{32}$$

Suppose we define the coefficients ρ_i to be the components of a column vector ϱ in a nine-dimensional vector space. The equation of motion for ϱ is

$$\begin{aligned} d\varrho/dt&=\Omega\varrho,\\ (\varrho+d\varrho)&=(1+\Omega dt)\varrho. \end{aligned} \tag{33}$$

Since Ω is antisymmetric and real, $(1+\Omega dt)$ is an infinitesimal orthogonal transformation on ϱ.[20] An orthogonal transformation leaves scalar products unchanged. Therefore, in the nine-dimensional space, lengths of vectors and angles between them are constant as the vectors move in the space, provided that they satisfy Eq. (33). If ϱ^c is a solution of Eq. (33) which is constant in time, and if ϱ is any time-dependent solution, the length of ϱ and the angle between ϱ and ϱ^c are both constants of the motion. We may therefore view all time-dependent solutions ϱ as precessions about the steady-state solution ϱ^c.

[20] H. Goldstein, *Classical Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1959), pp. 124–127.

	1	2	3	4	5	6	7	8
1	0	$\Delta\omega$	0	0	0	0	0	V_2
2	$-\Delta\omega$	0	$-V_1$	$-\sqrt{3}V_2$	0	0	V_2	0
3	0	V_1	0	0	0	$-V_2$	0	0
4	0	$\sqrt{3}V_2$	0	0	0	$-\sqrt{3}V_1$	0	0
5	0	0	0	0	0	$-\Delta\omega$	0	$-V_1$
6	0	0	V_2	$\sqrt{3}V_1$	$\Delta\omega$	0	V_1	0
7	0	$-V_2$	0	0	0	$-V_1$	0	$-2\Delta\omega$
8	$-V_2$	0	0	0	V_1	0	$2\Delta\omega$	0

FIG. 1. The matrix Ω.

To evaluate Ω, we expand the effective Hamiltonian in a series of the matrices U_k

$$H^e=\sum_k h_kU_k, \tag{34}$$

where $h_k=\mathrm{Trace}(H^eU_k)$. The two terms of H^e have the simple expansions

$$H_0{}^e=h_3U_3=-\sqrt{2}\hbar\Delta\omega U_3, \tag{35a}$$

$$V^e=h_1U_1+h_5U_5=\sqrt{2}\hbar V_1U_1+\sqrt{2}\hbar V_2U_5. \tag{35b}$$

We have here defined two new quantities, V_1 and V_2.

$$V_1=(\omega_1/\sqrt{2})(M_{pq}+M_{qr}), \tag{36a}$$

$$V_2=(\omega_1/\sqrt{2})(M_{pq}-M_{qr}). \tag{36b}$$

The various elements in Ω are obtained by evaluating the traces in Eq. (31). To do this, we use the values of the commutators $(U_jU_k-U_kU_j)$ which are presented in the Appendix. The commutators are all either zero or a constant multiple of some one basis matrix, except in two cases where they are a linear combination of two basis matrices. Because H^e is composed of only three of the basis matrices many of the commutators are orthogonal to H^e.

Using the expansion

$$H^e=h_1U_1+h_3U_3+h_5U_5,$$

and the commutation relationships, we obtain the matrix elements of Ω shown in Fig. 1. The row and column containing elements Ω_{j0} and Ω_{0k} have been omitted because all of these elements are zero. Since all elements Ω_{0k} are zero, $\dot{\rho}_0=0$, which means that the total occupation probability for the states $|\psi_p\rangle$, $|\psi_q\rangle$, $|\psi_r\rangle$ is a constant of the motion. Only the coefficients ρ_1, ρ_2, $\cdots$, ρ_8 are dependent on time. Thus it is sufficient to work with an 8×8 matrix Ω and the corresponding system of eight coupled differential equations.

Neglecting the trivial equation $\dot{\rho}_0=0$, Eqs. (32) become

$$\dot{\rho}_1=\Delta\omega\rho_2+V_2\rho_8, \tag{37a}$$

$$\dot{\rho}_2=-\Delta\omega\rho_1-V_1\rho_3-\sqrt{3}V_2\rho_4+V_2\rho_7, \tag{37b}$$

$$\dot{\rho}_3=V_1\rho_2-V_2\rho_6, \tag{37c}$$

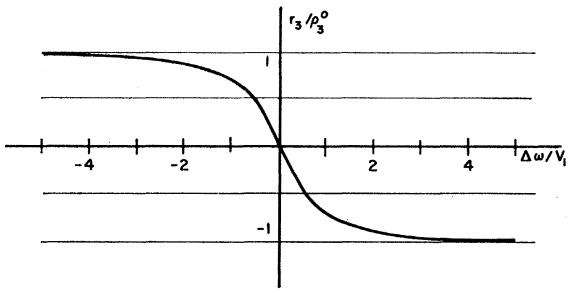

FIG. 2. Adiabatic passage inversion in the first space for $M_{pq}=M_{qr}$.

$$\dot{\rho}_4=\sqrt{3}V_2\rho_2-\sqrt{3}V_1\rho_6, \tag{37d}$$

$$\dot{\rho}_5=-\Delta\omega\rho_6-V_1\rho_8, \tag{37e}$$

$$\dot{\rho}_6=V_2\rho_3+\sqrt{3}V_1\rho_4+\Delta\omega\rho_5+V_1\rho_7, \tag{37f}$$

$$\dot{\rho}_7=-V_2\rho_2-V_1\rho_6-2\Delta\omega\rho_8, \tag{37g}$$

$$\dot{\rho}_8=-V_2\rho_1+V_1\rho_5+2\Delta\omega\rho_7. \tag{37h}$$

These equations determine the dynamical behavior of the system. We investigate their solution under some special conditions.

SOLUTION FOR EQUAL PERTURBATION MATRIX ELEMENTS

When the matrix elements M_{pq} and M_{qr} are equal, V_2 is zero, and Eqs. (37) break into two uncoupled sets. The problem in an eight-dimensional space reduces to two independent problems in smaller spaces.

First space:

$$\dot{\rho}_1=\Delta\omega\rho_2, \tag{38a}$$

$$\dot{\rho}_2=-\Delta\omega\rho_1-V_1\rho_3, \tag{38b}$$

$$\dot{\rho}_3=V_1\rho_2. \tag{38c}$$

Second space:

$$\dot{\rho}_4=-\sqrt{3}V_1\rho_6, \tag{39a}$$

$$\dot{\rho}_5=-\Delta\omega\rho_6-V_1\rho_8, \tag{39b}$$

$$\dot{\rho}_6=\sqrt{3}V_1\rho_4+\Delta\omega\rho_5+V_1\rho_7, \tag{39c}$$

$$\dot{\rho}_7=-V_1\rho_6-2\Delta\omega\rho_8, \tag{39d}$$

$$\dot{\rho}_8=V_1\rho_5+2\Delta\omega\rho_7. \tag{39e}$$

We consider the motion in the first space. Equations (38) have the form of Eq. (33), where ϱ is now a three-element column vector (ρ_1,ρ_2,ρ_3). Since the matrix Ω, which corresponds to Eqs. (38), is antisymmetric and real, the quantity

$$|\varrho|^2=\rho_1^2+\rho_2^2+\rho_3^2$$

is a constant of the motion. Also, all time-dependent solutions of Eqs. (38) are precessions about the steady-state solution. The general solution to Eqs. (38) is

$$\rho_1=(\Delta\omega/W)C_2\sin Wt+(\Delta\omega/V_1)C_3\cos Wt-(V_1/\Delta\omega)r_3, \tag{40a}$$

$$\rho_2=C_2\cos Wt-(W/V_1)C_3\sin Wt, \tag{40b}$$

$$\rho_3=C_3\cos Wt+(V_1/W)C_2\sin Wt+r_3. \tag{40c}$$

Here, $W=[V_1^2+(\Delta\omega)^2]^{1/2}$ and C_2, C_3, and r_3 are three arbitrary constants which are determined by initial conditions.

We consider ARP inversion in the three levels, still under the equal-matrix element or $V_2=0$ condition. We assume that the system is initially in a state which is characterized by a diagonal density matrix, and an rf magnetic field is applied whose frequency is off resonance such that $(\Delta\omega)^2\gg V_1^2$. At $t=0$, ρ_1 and ρ_2 are zero, and ρ_3 has a particular initial value ρ_3^0, which leads to the following initial constants:

$$r_3=[(V_1/\Delta\omega)^2+1]^{-1}\rho_3^0, \tag{41a}$$

$$C_2=0, \tag{41b}$$

$$C_3=(V_1/\Delta\omega)^2r_3. \tag{41c}$$

For $(V_1/\Delta\omega)^2\ll 1$, $r_3\approx\rho_3^0$, and consequently $C_3\ll\rho_3^0$. Since C_2 is zero and C_3 is effectively zero, application of the off-resonance driving field does not appreciably excite the oscillatory solutions. Equations (40) show that ρ_1 and ρ_2 are negligibly small for $t>0$, provided $(\Delta\omega)^2\gg V_1^2$ and therefore the quantity $|\varrho|$ is essentially equal to the initial population difference ρ_3^0.

Now, suppose we slowly sweep the driving frequency through the magnetic resonance frequency, or vice versa, so that $\Delta\omega$ passes through zero. If the sweep is slow enough, the exact motion is very nearly given by the steady-state solution when that solution is used for each value of $\Delta\omega$ in the sweep. The steady-state solution is

$$\rho_1=-(V_1/\Delta\omega)r_3, \tag{42a}$$

$$\rho_2=0, \tag{42b}$$

$$\rho_3=r_3. \tag{42c}$$

When $\Delta\omega$ is slowly swept, we replace the steady-state solution, which is exact for fixed $\Delta\omega$, by a quasisteady-state solution. We know that $|\varrho|$ remains constant throughout such a sweep. Assuming C_2 and C_3 are zero for all values of $\Delta\omega$, the quantity $|\varrho|^2$ is given by

$$|\varrho|^2=\left[\frac{V_1^2+(\Delta\omega)^2}{(\Delta\omega)^2}\right]r_3^2. \tag{43}$$

Using the quasisteady-state solution and the condition $|\varrho|=$constant, we calculate the component r_3 of ϱ for each value of $\Delta\omega$, assuming that the sweep takes $\Delta\omega$ from one side of resonance to the other, and that both the initial and final values of $\Delta\omega$ are sufficiently far off resonance that each satisfies the inequality $(\Delta\omega)^2\gg V_1^2$.

Applying the initial condition $|\varrho|=\rho_3^0$ to Eq. (43), we obtain

$$r_3=\frac{\pm(\Delta\omega/V_1)}{[1+(\Delta\omega/V_1)^2]^{1/2}}\rho_3^0. \tag{44}$$

This relation is plotted in Fig. 2. The choice of sign depends on whether $\Delta\omega$ is initially negative or positive. Since initially $r_3=\rho_3^0$, we take the negative sign if $\Delta\omega$ is initially negative and the positive sign if $\Delta\omega$ is initially positive. In particular, when $\Delta\omega$ is initially a large negative value and is slowly swept through resonance, r_3 approaches the final value $-\rho_3^0$, and the p-r population-difference inverts.

Use of the quasisteady-state solution is justified by the assumption that the passage through resonance is an adiabatic one. That is to say, the passage is assumed to be slow enough that the quasisteady-state solution is a good approximation to the exact behavior. It can be shown[15] that the adiabatic condition on the passage rate $d(\Delta\omega)/dt$ is the following:

$$|d(\Delta\omega)/dt|\ll[V_1^2+(\Delta\omega)^2]. \tag{45}$$

We turn to the second space: Eqs. (39). The general solution, which is given elsewhere,[15] consists of a complex precessional motion superimposed on a steady-state solution. We expect the precession to be negligible in an adiabatic passage with appropriate initial conditions; the steady-state solution should be sufficient. We will denote the steady-state solution by $\rho_i=r_i(i=4 \text{ to } 8)$. The components r_6 and r_8 are zero, and the nonzero components r_4, r_5, r_7 are related thus:

$$r_5=\frac{2\sqrt{3}(\Delta\omega)V_1}{[V_1^2-2(\Delta\omega)^2]}r_4, \tag{46a}$$

$$r_7=\frac{-\sqrt{3}V_1^2}{[V_1^2-2(\Delta\omega)^2]}r_4. \tag{46b}$$

In the absence of precession, the quantity

$$|\varrho|^2=\sum_4^8 \rho_i^2$$

is simply $(r_4^2+r_5^2+r_7^2)$

$$|\varrho|^2=\frac{4[V_1^2+(\Delta\omega)^2]^2}{[V_1^2-2(\Delta\omega)^2]^2}r_4^2.$$

We denote the initial value of ρ_4 by a quantity ρ_4^0, corresponding to $(\Delta\omega)^2\gg V_1^2$, and obtain

$$r_4=\frac{2(\Delta\omega/V_1)^2-1}{2[(\Delta\omega/V_1)^2+1]}\rho_4^0. \tag{47}$$

The negative sign is taken in the square root, because the expression multiplying ρ_4^0 is an even function of $\Delta\omega$. Equation (47) is plotted in Fig. 3. Note that r_4 halfway inverts midway through passage, but reinverts as the passage is completed. There is no net inversion of ρ_4 in a complete adiabatic passage when $V_2=0$.

Having solved for the expansion coefficients ρ_i within the two spaces in an adiabatic passage, the state populations after passage can be obtained directly. We denote

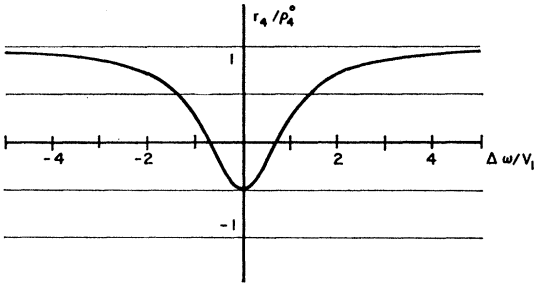

FIG. 3. Adiabatic passage in the second space for $M_{pq}=M_{qr}$.

the values of the expansion coefficients before and after passage by ρ_j^0 and ρ_j^f, respectively. From the above discussion, we have

$$\rho_0^f=\rho_0^0, \tag{48a}$$

$$\rho_3^f=-\rho_3^0, \tag{48b}$$

$$\rho_4^f=+\rho_4^0. \tag{48c}$$

These expansion coefficients are given in terms of the diagonal density matrix elements by Eqs. (30), which are in turn related to the state populations by Eq. (8). If the populations before and after an adiabatic passage are denoted by n_j^0 and n_j^f, respectively, Eqs. (48) lead to the result

$$n_p^f=n_r^0, \tag{49a}$$

$$n_q^f=n_q^0, \tag{49b}$$

$$n_r^f=n_p^0. \tag{49c}$$

The populations of states p and r interchange, and the population of state q remains the same.

SOLUTION FOR ONE-PERTURBATION MATRIX-ELEMENT ZERO

We assume that the element M_{qr} is zero and that M_{pq} is nonzero. Then $V_2=V_1$, and Eqs. (37) become

$$\dot\rho_1=\Delta\omega\rho_2+V_1\rho_8, \tag{50a}$$

$$\dot\rho_2=-\Delta\omega\rho_1-V_1\rho_3-\sqrt{3}V_1\rho_4+V_1\rho_7, \tag{50b}$$

$$\dot\rho_3=V_1\rho_2-V_1\rho_6, \tag{50c}$$

$$\dot\rho_4=\sqrt{3}V_1\rho_2-\sqrt{3}V_1\rho_6, \tag{50d}$$

$$\dot\rho_5=-\Delta\omega\rho_6-V_1\rho_8, \tag{50e}$$

$$\dot\rho_6=V_1\rho_3+\sqrt{3}V_1\rho_4+\Delta\omega\rho_5+V_1\rho_7, \tag{50f}$$

$$\dot\rho_7=-V_1\rho_2-V_1\rho_6-2\Delta\omega\rho_8, \tag{50g}$$

$$\dot\rho_8=-V_1\rho_1+V_1\rho_5+2\Delta\omega\rho_7. \tag{50h}$$

It is useful to define three quantities ρ_1', ρ_2', and ρ_3' as follows:

$$\rho_1'=(1/\sqrt{2})(\rho_1+\rho_5), \tag{51a}$$

$$\rho_2'=(1/\sqrt{2})(\rho_2-\rho_6), \tag{51b}$$

$$\rho_3'=\tfrac{1}{2}(\rho_3+\sqrt{3}\rho_4). \tag{51c}$$

From Eqs. (30b) and (30c), we see that $\rho_3'=(1/\sqrt{2})\times(\rho_{pp}-\rho_{qq})$ and is therefore a measure of the population difference for the p-q transition. By adding the proper pairs of Eqs. (50), we can cast the dynamical equations in the form

$$\dot{\rho}_1'=\Delta\omega\rho_2', \tag{52a}$$

$$\dot{\rho}_2'=-\Delta\omega\rho_1'-2\sqrt{2}V_1\rho_3', \tag{52b}$$

$$\dot{\rho}_3'=2\sqrt{2}V_1\rho_2'. \tag{52c}$$

These equations are precisely the same as Eqs. (38), provided we make the following notational replacements: $\rho_1\rightarrow\rho_1'$, $\rho_2\rightarrow\rho_2'$, $\rho_3\rightarrow\rho_3'$, and $V_1\rightarrow 2\sqrt{2}V_1$. Therefore, ρ_3' inverts in an adiabatic passage, which implies that the population difference (n_p-n_q) inverts. The population of state r is not affected by the passage if $M_{qr}=0$. Therefore, the populations of states p and q interchange, and the population of state r remains the same.

The other case ($M_{pq}=0$) is treated in a similar fashion. When $M_{pq}=0$, we define three appropriate quantities:

$$\rho_1''=(1/\sqrt{2})(\rho_1-\rho_5),$$
$$\rho_2''=(1/\sqrt{2})(\rho_2+\rho_6),$$
$$\rho_3''=\tfrac{1}{2}(\rho_3-\sqrt{3}\rho_4).$$

One can show that ρ_3'' inverts in an adiabatic passage, and thus the populations of states q and r interchange while the population of state p remains the same.

The foregoing two-level dynamics are to be expected, because when either M_{pq} or M_{qr} is zero, the whole problem can be solved on a two-level basis.[10]

SOLUTION FOR THE GENERAL CASE

We assume that M_{pq} and M_{qr} are unequal and are both nonzero. We use the general Eqs. (37). Although there are eight equations, only six of these are linearly independent. The dependent relations are Eqs. (37c) and (37d). One can readily verify the following dependence relations:

$$\dot{\rho}_3=\frac{V_1}{\Delta\omega}\dot{\rho}_1+\frac{V_2}{\Delta\omega}\dot{\rho}_5, \tag{53}$$

$$\dot{\rho}_4=\frac{2\sqrt{3}V_2[(\Delta\omega)^2-V_1^2]}{\Delta\omega[2(\Delta\omega)^2-(V_1^2+V_2^2)]}\dot{\rho}_1 + \frac{2\sqrt{3}V_1[(\Delta\omega)^2-V_2^2]}{\Delta\omega[2(\Delta\omega)^2-(V_1^2+V_2^2)]}\dot{\rho}_5 + \frac{\sqrt{3}(\Delta\omega)(V_2^2-V_1^2)}{\Delta\omega[2(\Delta\omega)^2-(V_1^2+V_2^2)]}\dot{\rho}_7. \tag{54}$$

Consider possible steady-state solutions for which there is no precession. Let $(r_1, r_2, \cdots, r_8)$ be the values of $(\rho_1, \rho_2, \cdots, \rho_8)$ which satisfy Eqs. (37) when the time derivatives are zero. Then we have

$$\Delta\omega r_2+V_2r_3=0, \tag{55a}$$

$$\Delta\omega r_1+V_1r_3+\sqrt{3}V_2r_4-V_2r_7=0, \tag{55b}$$

$$V_1r_2-V_2r_6=0, \tag{55c}$$

$$\sqrt{3}V_2r_2-\sqrt{3}V_1r_6=0, \tag{55d}$$

$$\Delta\omega r_6+V_1r_8=0, \tag{55e}$$

$$V_2r_3+\sqrt{3}V_1r_4+\Delta\omega r_5+V_1r_7=0, \tag{55f}$$

$$V_2r_2+V_1r_6+2\Delta\omega r_8=0, \tag{55g}$$

$$V_2r_1-V_1r_5-2\Delta\omega r_7=0. \tag{55h}$$

The above set is a system of linear homogeneous algebraic equations which has a nontrivial solution only if the determinant of the coefficient matrix is zero. The determinant is obviously zero, because two rows are linear combinations of other rows. Since there are two dependent rows, the largest nonzero determinant, which is contained in this matrix, must be of order six or less. The order is six, because direct evaluation shows that none of the sixth-order determinants vanish, provided V_2 is not equal to zero or $\pm V_1$. Therefore, the rank of the coefficient matrix is six. A system of 8 linear homogeneous algebraic equations in 8 unknowns, with a coefficient matrix of rank 6, has 2 and only 2 linearly independent solutions. Each solution contains an arbitrary constant. We let the two constants be r_3 and r_4. The first solution is obtained by setting $r_4=0$ in Eqs. (55), and the second by setting $r_3=0$.

Solution for $r_4=0$:

$$r_1=-(V_1/\Delta\omega)r_3, \tag{56a}$$

$$r_5=-(V_2/\Delta\omega)r_3, \tag{56b}$$

$$r_2=r_6=r_7=r_8=0. \tag{56c}$$

Solution for $r_3=0$:

$$r_1=\frac{2\sqrt{3}V_2[(\Delta\omega)^2-V_1^2]}{\Delta\omega[V_1^2+V_2^2-2(\Delta\omega)^2]}r_4, \tag{57a}$$

$$r_5=\frac{2\sqrt{3}V_1[(\Delta\omega)^2-V_2^2]}{\Delta\omega[V_1^2+V_2^2-2(\Delta\omega)^2]}r_4, \tag{57b}$$

$$r_7=\frac{\sqrt{3}(\Delta\omega)(V_2^2-V_1^2)}{\Delta\omega[V_1^2+V_2^2-2(\Delta\omega)^2]}r_4, \tag{57c}$$

$$r_2=r_6=r_8=0. \tag{57d}$$

We look for adiabatic-passage inversion in each of the above solutions. Our approach directly follows the nonprecessional $V_2=0$ case.

Adiabatic passage for $r_4=0$:

$$|\varrho|^2=\left[\left(\frac{V_1}{\Delta\omega}\right)^2+\left(\frac{V_2}{\Delta\omega}\right)^2+1\right]r_3^2=\left[\frac{V_1^2+V_2^2+(\Delta\omega)^2}{(\Delta\omega)^2}\right]r_3^2.$$

When $(\Delta\omega)^2 \gg (V_1^2+V_2^2)$, $|\varrho| = r_3$. Therefore, we set $|\varrho| = \rho_3^0$ and obtain

$$r_3 = \frac{\pm\Delta\omega}{[V_1^2+V_2^2+(\Delta\omega)^2]^{1/2}}\rho_3^0. \tag{58}$$

This result is identical with Eq. (44), which applies to the case $V_2=0$, except that V_1^2 is replaced by $(V_1^2+V_2^2)$. Therefore, ρ_3 inverts in an adiabatic passage when $V_2 \neq 0$ or $\pm V_1$, provided that ρ_4 is initially zero and remains zero throughout the passage.

Adiabatic passage for $r_3=0$.

$$|\varrho|^2 = \left\{\frac{12V_2^2[(\Delta\omega)^2-V_1^2]^2+12V_1^2[(\Delta\omega)^2-V_2^2]^2+3(\Delta\omega)^2(V_2^2-V_1^2)^2}{(\Delta\omega)^2[V_1^2+V_2^2-2(\Delta\omega)^2]^2}+1\right\}r_4^2.$$

When $(\Delta\omega)^2 \gg (V_1^2+V_2^2)$, we have $|\varrho| = r_4$. Therefore, we set $|\varrho| = \rho_4^0$, and obtain

$$r_4 = \frac{\pm\Delta\omega[V_1^2+V_2^2-2(\Delta\omega)^2]\rho_4^0}{\{12V_2^2[(\Delta\omega)^2-V_1^2]^2+12V_1^2[(\Delta\omega)^2-V_2^2]^2+3(\Delta\omega)^2(V_2^2-V_1^2)^2+(\Delta\omega)^2[V_1^2+V_2^2-2(\Delta\omega)^2]^2\}^{1/2}}. \tag{59}$$

Because the expression which multiplies ρ_4^0 in the above equation is an odd function of $\Delta\omega$, ρ_4 inverts in an adiabatic passage for $V_2 \neq 0$ or $\pm V_1$, provided that ρ_3 is initially zero and remains zero throughout the passage.

If ρ_3 and ρ_4 both have nonzero values before the passage, the steady-state solution is a linear combination of the two independent solutions in Eqs. (56) and (57). Unfortunately, the quasi-steady-state method used in the $r_4=0$ and $r_3=0$ cases does not lead to an adiabatic-passage solution when r_3 and r_4 are both nonzero. One can take an arbitrary linear combination of the solutions in Eqs. (56) and (57) and add the squares of the components of the resulting general $\mathbf{r}$ vector to get $|\varrho|^2$. However, this sum will involve terms in r_3^2, r_3r_4, and r_4^2, and it will not yield separate expressions for r_3 and r_4 in terms of ρ_3^0 and ρ_4^0. If we use the quasisteady-state approach we must be satisfied with either the $r_4=0$ or the $r_3=0$ solutions.

The $r_4=0$ solution has the greatest practical significance. In order that ρ_4 be initially zero, the initial population distribution must be a linear function of the energy for the states p, q, r. This is approximately true in thermal equilibrium if $\hbar\omega_0$ is small compared to kT, because the exponential Boltzmann distribution is nearly linear over the energies E_p, E_q, and E_r. We may reasonably assume that if ρ_4 is zero before passage, it will remain so throughout. This is expected, because ρ_2 and ρ_6 are zero during the passage, and therefore at all points we have from Eq. (37d)

$$\dot{\rho}_4 = \sqrt{3}V_2\rho_2 - \sqrt{3}V_1\rho_6 = 0.$$

Thus, if ρ_4 is zero before the passage is started, then to the extent that the passage is adiabatic, ρ_4 remains zero, and we obtain inversion of ρ_3. As in the $M_{pq}=M_{qr}$ case, inversion of ρ_3 means that the p-q, q-r, and p-r transitions are simultaneously inverted. When $0 \neq M_{pq} \neq M_{qr} \neq 0$, and $\hbar\omega_0 \ll kT$, our dynamics have shown that the populations after passage are related to the populations before by Eqs. (49).

We can summarize all of the three-level calculations in one statement: Except for the isolated cases $M_{pq}=0$ and $M_{qr}=0$, the dynamical equations predict simultaneous ARP inversion of the three transitions for all combinations of the driving matrix elements, provided $\hbar\omega_0 \ll kT$ when $M_{pq} \neq M_{qr}$.

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APPENDIX

A complete set of orthonormal Hermitian 3×3 basis matrices U_j is presented in Eqs. (27). The commutators $[U_j,U_k]=U_jU_k-U_kU_j$ are given here.

$$[U_j,U_0]=0 \quad \text{for} \quad j=1, 2, \cdots, 8$$
$$[U_1,U_2]=(i/\sqrt{2})U_3$$
$$[U_2,U_3]=(i/\sqrt{2})U_1$$
$$[U_3,U_1]=(i/\sqrt{2})U_2$$
$$[U_2,U_6]=(i/\sqrt{2})U_8$$
$$[U_6,U_8]=(i/\sqrt{2})U_2$$
$$[U_8,U_2]=(i/\sqrt{2})U_6$$
$$[U_1,U_5]=(i/\sqrt{2})U_8$$
$$[U_5,U_8]=(i/\sqrt{2})U_1$$
$$[U_8,U_1]=(i/\sqrt{2})U_5$$
$$[U_1,U_4]=(i/\sqrt{2})\sqrt{3}U_6$$
$$[U_4,U_6]=(i/\sqrt{2})\sqrt{3}U_1$$
$$[U_6,U_1]=(i/\sqrt{2})(\sqrt{3}U_4+U_7)$$
$$[U_1,U_7]=(i/\sqrt{2})U_6$$
$$[U_7,U_6]=(i/\sqrt{2})U_1$$

$$[U_5,U_3]=(i/\sqrt{2})U_6 \qquad [U_8,U_7]=(i/\sqrt{2})2U_3$$
$$[U_3,U_6]=(i/\sqrt{2})U_5 \qquad [U_7,U_3]=(i/\sqrt{2})2U_8$$
$$[U_6,U_5]=(i/\sqrt{2})U_3 \qquad [U_4,U_5]=(i/\sqrt{2})\sqrt{3}U_2$$
$$[U_4,U_3]=0 \qquad [U_2,U_4]=(i/\sqrt{2})\sqrt{3}U_5$$
$$[U_4,U_7]=0 \qquad [U_5,U_2]=(i/\sqrt{2})(\sqrt{3}U_4-U_7)$$
$$[U_4,U_8]=0 \qquad [U_5,U_7]=(i/\sqrt{2})U_2$$
$$[U_3,U_8]=(i/\sqrt{2})2U_7 \qquad [U_7,U_2]=(i/\sqrt{2})U_5.$$

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Resonance Scattering of Phonons by Molecular Impurity Centers*

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The scattering of phonons at polyatomic (molecular) impurity centers cannot be handled by the regular Lifshitz method because of the additional degrees of freedom. A method is presented which makes it possible to eliminate the molecular coordinates by means of a molecular Green's function. This Green's function defines an effective disturbance in the lattice system with singular poles at the molecular frequencies. Thus the low rank t matrix of the scattering formalism, defining the scattering amplitude, has sharp resonances near the molecular frequencies. The abstract scattering formalism is applied to a simple example which exhibits the influence of librational modes of a molecule with strong internal bindings on phonon scattering. The t matrix for the chosen model is diagonalized by complete group theoretical reduction and reveals the structure of the molecular resonances explicitly. It is found that the resonance is very sharp if the molecular frequency is much smaller than the Debye frequency, and decreases for higher frequencies.

INTRODUCTION

RECENTLY, the problem of phonon resonance scattering at impurity centers has attracted much interest, mainly because these resonances give rise to indentations in the curves of thermal conductivity versus temperature. This was shown by Pohl[1] for the system KCl:KNO_2, and by Walker and Pohl[2] for systems like KCl:KI, KCl:NaCl, etc. In the first case we have a molecular impurity center, in the second a monatomic one, and both experiments can be explained rather well by a quasiphenomenological theory given by the author in a previous paper.[3] But as this theory still contains adjustable parameters, so it is desirable to investigate the underlying scattering process in full detail.

There is no difficulty in handling the monatomic impurities, because the number of degrees of freedom in the lattice is unchanged in this case and the application of the Lifshitz[4] method is straightforward. Very recent calculations by Krumhansl,[5] Klein,[6] and Takeno[7] have shown that there are, under certain conditions, resonances in the phonon scattering at monatomic centers due to the alterations in mass and force constants. These resonances can be said to be more or less "accidental"; they correspond to quasilocalized modes within the phonon bands which dissipate slowly into the surrounding lattice if the substitutional mass is very large,[8] or if the force constants are weakened drastically near the impurity center, e.g., for U centers or F centers.[5]

In contrast to that, there are, in general, more pronounced resonances in the case of molecular impurities. This problem, however, seems to be much more complicated because of the new degrees of freedom brought in by the molecular nuclei. The author[9] has shown how, in principle, the additional coordinates can be excluded by means of a molecular Green's function and the Lifshitz method is then easily applied to the remaining unchanged number of lattice coordinates. But there is now an additional effective disturbance which has poles at the molecular frequencies via the molecular Green's function. These poles will produce new sharp resonances if they lie within the phonon bands.

The abstract formalism for the general problem is outlined in Secs. I–III. In the remaining sections we will choose a particularly simple model of a molecule exhibit-

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