Magnetic Resonance of Coupled Spins*

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The solution of the time-dependent wave equation describing the interaction of two coupled spins with a rotating magnetic field in the presence of a steady field, as in the usual magnetic resonance situation, has been reexamined. By extending the method previously developed by Salwen, an exact expression is derived for all components of the wave function describing a three-state system under magnetic-resonance conditions. This solution describes in analytical form all the single and multiple resonances of which the system is capable for fields of any intensity. It is shown that when z is the axis of quantization, the projection of the wave function on an eigenstate of F_x oscillates at twice the resonance frequency at exact double quantum resonance. An approximate form is derived for the transition probability near double quantum resonance, showing that our solution is consistent with Salwen's in the limit of well-separated single and double quantum resonances. The theory is applied to the uppermost three substates of the upper hyperfine multiplet of an alkali metal of arbitrary nuclear spin, a case of interest to the analysis of magnetic resonance in optically pumped vapors.

INTRODUCTION

MAGNETIC resonance frequently involves the interaction of two or more coupled spins with external magnetic fields. This interaction differs significantly from the corresponding interaction of single (uncoupled) spins, primarily because of the partial decoupling of the spins caused by the applied steady magnetic field. A characteristic aspect of the magnetic resonance of coupled spins is the occurrence of multiple quantum transitions.[1-4]

Transitions of this type have been investigated theoretically by other investigators,[5-8] and in particular in some detail by H. Salwen.[6] Salwen developed a method for finding an exact formal solution of the time-dependent wave equation describing the interaction of two or more coupled spins with the external fields used in magnetic resonance. This formal solution was then applied to an analysis of multiple quantum transitions with the aid of perturbation theory.

The object of the work reported here is to extend Salwen's theory so as to derive an exact analytical solution of the complete problem in certain cases, without the use of perturbation theory. Such a solution is of interest when perturbation theory will not provide a good approximation, as in the transition region between tightly coupled and slightly decoupled spins, that is, in the region of overlapping single and multiple quantum resonances. Furthermore, the analytical solution provides explicit expressions for all components of the wave function of the coupled spins, rather than just the amplitude of its z projection. The projections in a

transverse direction are important in the analysis of the modulation of a transverse beam of resonance radiation by an optically pumped vapor.[9,10]

When the various resonances are widely separated, the predictions of the exact analytical solution will be shown to be equivalent to those obtained by the use of perturbation theory, as will be demonstrated for the case of the Zeeman resonances of atomic hydrogen. This example will be contrasted with the Zeeman resonances in the uppermost three substates of the $F=I+\frac{1}{2}$ hyperfine multiplet of an alkali metal of nuclear spin $I>\frac{1}{2}$. In hydrogen, both the perturbation theory solution[6] and our solution predict a shift in the double quantum resonance-frequency proportional to the square of the rf field intensity; the shift is, however, practically unobservable in hydrogen. For the alkali metals, the corresponding shifts are large and should be easily observable, particularly in optically pumped vapors. A study of related shifts in an atomic beam of K^{39} has been reported by Kusch,[4] and analyzed by Salwen.[11]

The analytical solution assumes a particularly simple form at exact double quantum resonance. It will be of interest to demonstrate that under these conditions the x projection of the wave function oscillates at harmonics of the resonance frequency. This effect, which is related to the light beat experiments of Series,[12,13] should be observable in cross-beam light modulation experiments with optically pumped vapors.

FORMAL SOLUTION

The influence of an oscillating or rotating magnetic field on a spin system may be described by a time-dependent wave equation in which the Hamiltonian function is an explicit function of time. It is well known

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that a particularly simple formal solution of this equation can be obtained when two conditions are fulfilled, namely when the time-independent part of the spin Hamiltonian, $\mathfrak{IC}_0$, is invariant to a rotation about the axis of quantization (the z axis, the axis of the applied steady magnetic field), and when the time-dependent part of the Hamiltonian, $\mathfrak{IC}_1(t)$, is associated with a field rotating *about* the axis of quantization. In that case, the wave function may be reduced to a constant by two successive unitary transformations. The first of these transforms the system to a singly and the second one to a doubly rotating frame of reference.

As an example, let us consider two coupled spins, **K** and **J**, with coupling energy

$$a\mathbf{K}\cdot\mathbf{J}=a[(\tfrac{1}{2})(K_+J_-+K_-J_+)+K_zJ_z],\qquad(1)$$

where a is the interaction constant. The coupled spins are subjected to a steady field H_0 in the z direction and to an additional field H_1 rotating about the z axis with angular velocity ω. The time-independent part of the Hamiltonian, namely

$$\mathfrak{IC}_0=a[(\tfrac{1}{2})(K_+J_-+K_-J_+)+K_zJ_z]$$
$$+(\omega_{0j}J_z-\omega_{0k}K_z),\qquad(2)$$

commutes with $F_z=K_z+J_z$, which insures that $\mathfrak{IC}_0$ is invariant to a rotation about the z axis, or in other words, that $\mathfrak{IC}_0$ commutes with the operator $V=\exp[-(i/\hbar)F_z\omega t]$. Here we have set $\omega_{0j}=|\gamma_j|H_0=-\gamma_jH_0$, where γ_j is the (assumed negative) gyromagnetic ratio of the spin J, and $\omega_{0k}=\gamma_kH_0$, where γ_k is the (assumed positive) gyromagnetic ratio of the spin K.

The time-dependent part of the Hamiltonian associated with the rotating field in the x-y plane, namely

$$\mathfrak{IC}_1(t)=\tfrac{1}{2}(\omega_{1j}J_+-\omega_{1k}K_+)e^{-i\omega t}+\tfrac{1}{2}(\omega_{1j}J_--\omega_{1k}K_-)e^{i\omega t},\qquad(3)$$

where $\omega_{1j}=|\gamma_j|H_1=-\gamma_jH_1$ and $\omega_{1k}=\gamma_kH_1$, can be made time-independent by transforming to a frame of reference rotating about the z axis with the angular velocity ω of the rf field:

$$\mathfrak{IC}_1'=\exp[(i/\hbar)F_z\omega t]\mathfrak{IC}_1$$
$$\times\exp[-(i/\hbar)F_z\omega t]=\omega_{1j}J_x-\omega_{1k}K_x.\qquad(4)$$

A formal solution of the wave equation

$$(i/\hbar)(\partial\psi/\partial t)=(\mathfrak{IC}_0+\mathfrak{IC}_1)\psi$$

is then given by

$$\psi(t)=\exp[-(i/\hbar)F_z\omega t]$$
$$\times\exp[-(i/\hbar)(\mathfrak{IC}_0+\mathfrak{IC}_1'-\omega F_z)t]\psi(0).\qquad(5)$$

This result is well known.[7] In order to find explicit expressions for the components of the wave function at time t, it is necessary to derive the matrix elements of the exponential unitary operators on the right-hand side of (5). The operator $\exp[-(i/\hbar)F_z\omega t]$ is formed from the diagonal Hermitian operator $F_z=K_z+J_z$, and is, therefore, itself diagonal. In order to evaluate the matrix

elements of the second operator, $\exp[-(i/\hbar)(\mathfrak{IC}_0+\mathfrak{IC}_1'-\omega F_z)t]$, we make use of the following relation,[14] which holds for any time-independent Hermitian operator, O:

$$e^{-(i/\hbar)Ot}=S\{\exp[-(i/\hbar)S^{-1}OSt]\}S^{-1}.\qquad(6)$$

Here S is a time-independent unitary matrix such that $S^{-1}OS$ is diagonal. Therefore, the matrix $\exp[-(i/\hbar)S^{-1}OSt]$ is also diagonal, and the matrix elements of $\exp[-(i/\hbar)Ot]$ are known when S is known.

The relation (6) can be proved by expanding the exponential operator in a power series, as follows:

$$S\{\exp[-(i/\hbar)S^{-1}OSt]\}S^{-1}$$
$$=S\{1-(it/\hbar)S^{-1}OS+(1/2!)(it/\hbar)^2$$
$$\times(S^{-1}OSS^{-1}OS)-\cdots\}S^{-1}$$
$$=1-(it/\hbar)O+(1/2!)(it/\hbar)^2O^2-\cdots=e^{-(i/\hbar)Ot}.$$

For the case of the magnetic resonance of a single (uncoupled) spin, the matrix S considered as an operator is identical with the rotation operators defined by Wigner[15] and applied to the solution of magnetic resonance problems by Salwen[6] and Series.[12] For coupled spins, the interpretation of S is not so straightforward, but S can always be constructed from the eigenfunctions of the Hermitian operator O occurring in $\exp[-(i/\hbar)Ot]$. Thus, if ϕ_n is the eigenfunction of O associated with the eigenvalue λ_n, so that $O\phi_n=\lambda_n\phi_n$, then $S_{pn}=(\phi_n)_p$, where $(\phi_n)_p$ is the pth component of ϕ_n. The problem of finding the matrix elements of the exponential unitary operator (6) is thus reduced to the algebraic problem of finding the eigenvalues and eigenfunctions of the time-independent Hermitian operator O, that is, of $\mathfrak{IC}_0+\mathfrak{IC}_1'-\omega F_z$ in our case.

We can then restate the formal solution (5) of the wave equation for coupled spins under magnetic resonance conditions as follows:

$$\psi(t)=\exp[-(i/\hbar)F_z\omega t]S\{\exp[-(i/\hbar)t$$
$$\times S^{-1}(\mathfrak{IC}_0+\mathfrak{IC}_1'-\omega F_z)S]\}S^{-1}\psi(0).\qquad(7)$$

This equation is essentially identical with Eq. (20) of Salwen's paper.[6] Our subsequent procedure will differ from his, however, in that we shall find analytical expressions for the matrix elements of S by an algebraic solution of the secular equation associated with the eigenvalue problem mentioned above. This will then enable us to derive equations for the components of $\psi(t)$; the validity of these equations is not limited by the use of perturbation theory, as stated earlier.

ZEEMAN RESONANCES OF ATOMIC HYDROGEN

The simplest of all atomic systems involving two coupled spins K and J is the one for which $k=\tfrac{1}{2}$ and $j=\tfrac{1}{2}$, as in atomic hydrogen, where K now refers to the nuclear spin and J to the electron spin. It is convenient

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[15] E. Wigner, *Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren* (Edwards Bros. Inc., Ann Arbor, Michigan, 1944), Ch. 15.

to express the spin Hamiltonian to begin with in an uncoupled (kjm_km_j) representation. The representation, of dimensionality $(2k+1)(2j+1)=4$, is such that, for example,

$$K_zJ_z= (\hbar/2)\begin{pmatrix} J_z & 0 \\ 0 & -J_z \end{pmatrix}= (\hbar^2/4)\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}.$$

We shall assume that the symbols $\mathfrak{K}_0$ and $\mathfrak{K}_1$ refer to the components of the Hamiltonian in the coupled $(kjFm_F)$ representation, so that the Hamiltonian in the uncoupled representation is $U(\mathfrak{K}_0+\mathfrak{K}_1)U^{-1}$, where U is a unitary matrix which defines the transformation from the uncoupled to the coupled representation. It is then easily shown that

$$U(\mathfrak{K}_0+\mathfrak{K}_1)U^{-1}=\frac{\hbar}{2}\begin{bmatrix} \omega_{0j}-\omega_{0k}+\omega_F/2 & \omega_{1j}e^{-i\omega t} & -\omega_{1k}e^{-i\omega t} & 0 \\ \omega_{1j}e^{i\omega t} & -\omega_{0j}-\omega_{0k}-\omega_F/2 & \omega_F & -\omega_{1k}e^{-i\omega t} \\ -\omega_{1k}e^{i\omega t} & \omega_F & \omega_{0j}+\omega_{0k}-\omega_F/2 & \omega_{1j}e^{-i\omega t} \\ 0 & -\omega_{1k}e^{i\omega t} & \omega_{1j}e^{i\omega t} & -\omega_{0j}+\omega_{0k}+\omega_F/2 \end{bmatrix}.$$

Here ω_F is the hyperfine resonance frequency in zero field. The transformation to the coupled representation defined by U will diagonalize the time-independent part of the Hamiltonian. A second transformation to a singly rotating frame of reference then yields the expression

$$\mathfrak{K}_0+\mathfrak{K}_1'-\omega F_z=\hbar\begin{bmatrix} \lambda_1-\omega & A/2 & B/2 & 0 \\ A/2 & \lambda_2 & 0 & -C/2 \\ B/2 & 0 & \lambda_3 & D/2 \\ 0 & -C/2 & D/2 & \lambda_4+\omega \end{bmatrix}. \quad (8)$$

$\mathfrak{K}_1'$ is defined by (4), and the other symbols are defined as follows:

$$\lambda_1=\tfrac{1}{2}(\omega_{0j}-\omega_{0k}+\tfrac{1}{2}\omega_F),$$
$$\lambda_2=\tfrac{1}{2}[-(\omega_0^2+\omega_F^2)^{1/2}-\tfrac{1}{2}\omega_F],$$
$$\lambda_3=\tfrac{1}{2}[(\omega_0^2+\omega_F^2)^{1/2}-\tfrac{1}{2}\omega_F],$$
$$\lambda_4=\tfrac{1}{2}(-\omega_{0j}+\omega_{0k}+\tfrac{1}{2}\omega_F),$$
$$A=\omega_{1j}\cos(\tfrac{1}{2}\eta)+\omega_{1k}\sin(\tfrac{1}{2}\eta),$$
$$B=\omega_{1j}\sin(\tfrac{1}{2}\eta)-\omega_{1k}\cos(\tfrac{1}{2}\eta),$$
$$C=\omega_{1j}\sin(\tfrac{1}{2}\eta)+\omega_{1k}\cos(\tfrac{1}{2}\eta),$$
$$D=\omega_{1j}\cos(\tfrac{1}{2}\eta)-\omega_{1k}\sin(\tfrac{1}{2}\eta),$$
$$\omega_0=\omega_{0j}+\omega_{0k},$$
$$\cos\eta=\omega_0/(\omega_0^2+\omega_F^2)^{1/2}; \quad \sin\eta=\omega_F/(\omega_0^2+\omega_F^2)^{1/2}.$$

The energies $\hbar\lambda_1$, $\hbar\lambda_2$, $\hbar\lambda_3$, and $\hbar\lambda_4$ are the eigenvalues of the time-independent Hamiltonian (Breit-Rabi eigenstates). The ordering of the states is such that the subscripts 1, 3, 4 refer to the upper hyperfine multiplet $(F=1)$, with $m_F=1$, 0, -1, respectively, while the subscript 2 refers to the $F=0$, $m_F=0$ state.

Since our interest is directed toward the Zeeman resonances in the upper hyperfine multiplet $(F=1)$, we shall confine our attention to the submatrix of (8) which involves states 1, 3, and 4, namely,

$$\mathfrak{K}_0+\mathfrak{K}_1'-\omega F_z=\hbar\lambda_3\mathbf{1}+\hbar\begin{bmatrix} \delta+\Delta\omega & B/2 & 0 \\ B/2 & 0 & D/2 \\ 0 & D/2 & \delta-\Delta\omega \end{bmatrix}. \quad (9)$$

Here, $\delta=\omega_{13}-\tfrac{1}{2}\omega_{14}=(\lambda_1-\lambda_3)-\tfrac{1}{2}(\lambda_1-\lambda_4)$ measures the frequency separation of the single and double quantum resonances, and $\Delta\omega=\tfrac{1}{2}\omega_{14}-\omega$ measures the deviation of the frequency ω of the rf field from the double quantum resonance frequency $\tfrac{1}{2}\omega_{14}$. It is evident that single quantum resonances will occur when $\Delta\omega=\delta$ and $\Delta\omega=-\delta$, while a double quantum resonance corresponds to the condition $\Delta\omega=0$. The significance of δ is illustrated in Fig. 1.

The definitions of the frequencies B and D given above involve both the electron nutation frequency ω_{1j} and the nuclear nutation frequency ω_{1k}. For all practical purposes, ω_{1k} is completely negligible compared to ω_{1j}, so that B and D can be written $B=\omega_1\sin(\tfrac{1}{2}\eta)$ and $D=\omega_1\cos(\tfrac{1}{2}\eta)$, where $\cos\eta=\omega_0/(\omega_0^2+\omega_F^2)^{1/2}$, as above.

If the eigenvalues of $\mathfrak{K}_0+\mathfrak{K}_1'-\omega F_z$ are written $\hbar(\lambda_3+\sigma_i)$, where $i=1$, 3, or 4, then the frequencies σ_i are
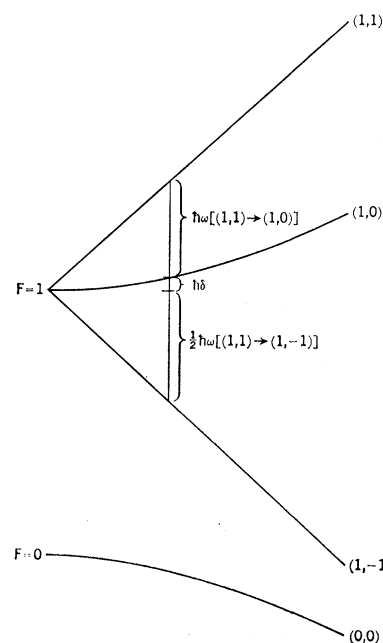

FIG. 1. Schematic diagram of the hyperfine multiplet of atomic hydrogen, illustrating the significance of the parameter δ. Energy is measured vertically and magnetic field intensity horizontally.

the three roots of the cubic equation

$$[\sigma-(\tfrac{2}{3})\delta]^3-[(\tfrac{1}{3})\delta^2+(\Delta\omega)^2+(\tfrac{1}{4})\omega_1^2][\sigma-(\tfrac{2}{3})\delta]$$
$$-(\tfrac{1}{3})\delta[2(\Delta\omega)^2-(2/9)\delta^2-(\tfrac{1}{4})\omega_1^2]$$
$$+\Delta\omega(\tfrac{1}{4})\omega_1^2\cos\eta=0. \quad (10)$$

These roots are given by

$$\sigma_1=(\tfrac{2}{3})\delta\{1-G\cos[(2\pi+\theta)/3]\},$$
$$\sigma_3=(\tfrac{2}{3})\delta\{1-G\cos(\tfrac{1}{3}\theta)\}, \quad (11)$$
$$\sigma_4=(\tfrac{2}{3})\delta\{1-G\cos[(4\pi+\theta)/3]\},$$

where

$$G=[1+3(\Delta\omega/\delta)^2+(\tfrac{3}{4})(\omega_1/\delta)^2]^{1/2}, \quad (11a)$$

$$\cos\theta=G^{-3}\{1+(9/8)(\omega_1/\delta)^2[1+(3\Delta\omega/\delta)\cos\eta]$$
$$-9(\Delta\omega/\delta)^2\}. \quad (11b)$$

If the eigenfunctions of $\mathfrak{K}_0+\mathfrak{K}_1'-\omega F_z$ belonging to the eigenvalues $\hbar(\lambda_3+\sigma_i)$ are written

$$\xi_i=\begin{bmatrix}\alpha_i\\\beta_i\\\gamma_i\end{bmatrix},$$

where $i=1$, 3, or 4, then the three simultaneous equations $(\mathfrak{K}_0+\mathfrak{K}_1'-\omega F_z)\xi_i=\hbar(\lambda_3+\sigma_i)\xi_i$ can be solved by inspection for the three components of the normalized eigenfunctions:

$$\alpha_i=\left[1+\frac{(\delta+\Delta\omega-\sigma_i)^2}{(\omega_1^2/8)(1-\cos\eta)}\right.$$
$$\left.+\left(\frac{1+\cos\eta}{1-\cos\eta}\right)\left(\frac{\delta+\Delta\omega-\sigma_i}{\delta-\Delta\omega-\sigma_i}\right)^2\right]^{-1/2},$$
$$(12)$$
$$\beta_i=-\left[\frac{\delta+\Delta\omega-\sigma_i}{(\sqrt{2}/4)\omega_1(1-\cos\eta)^{1/2}}\right]\alpha_i,$$

$$\gamma_i=\left(\frac{1+\cos\eta}{1-\cos\eta}\right)^{1/2}\left(\frac{\delta+\Delta\omega-\sigma_i}{\delta-\Delta\omega-\sigma_i}\right)\alpha_i.$$

Returning now to the complete (four-state) space, the

matrix S will be given by

$$S=\begin{bmatrix}\alpha_1 & 0 & \alpha_3 & \alpha_4\\0 & 1 & 0 & 0\\\beta_1 & 0 & \beta_3 & \beta_4\\\gamma_1 & 0 & \gamma_3 & \gamma_4\end{bmatrix},$$

and the matrix elements of
$\exp[-(i/\hbar)(\mathfrak{K}_0+\mathfrak{K}_1'-\omega F_z)t]$

$$=S\{\exp[-(i/\hbar)S^{-1}(\mathfrak{K}_0+\mathfrak{K}_1'-\omega F_z)St]\}S^{-1}$$

are known. Thus, if we write

$$\{\exp[-(i/\hbar)(\mathfrak{K}_0+\mathfrak{K}_1'-\omega F_z)t]\}_{np}=R_{np}$$

then, for example,

$$R_{11}=(|\alpha_1|^2e^{-i\sigma_1t}+|\alpha_3|^2e^{-i\sigma_3t}+|\alpha_4|^2e^{-i\sigma_4t})e^{-i\lambda_3t},$$
$$R_{31}=(\alpha_1^*\beta_1e^{-i\sigma_1t}+\alpha_3^*\beta_3e^{-i\sigma_3t}+\alpha_4^*\beta_4e^{-i\sigma_4t})e^{-i\lambda_3t}, \quad (13)$$
$$R_{41}=(\alpha_1^*\gamma_1e^{-i\sigma_1t}+\alpha_3^*\gamma_3e^{-i\sigma_3t}+\alpha_4^*\gamma_4e^{-i\sigma_4t})e^{-i\lambda_3t}.$$

Similar expressions hold for the other matrix elements.

If we assume that the system is in the $F=1$, $m_F=1$ state initially, so that

$$\psi(0)=\begin{bmatrix}1\\0\\0\\0\end{bmatrix},$$

then Eq. (5) gives for the wave function at time t,

$$\psi(t)=\begin{bmatrix}R_{11}e^{-i\omega t}\\0\\R_{31}\\R_{41}e^{i\omega t}\end{bmatrix}. \quad (14)$$

This is a complete solution of the problem from which all properties of the system can be inferred. As examples of the usefulness of this solution, it will be of interest to examine its application in two limiting cases.

TRANSVERSE PROJECTION AT DOUBLE QUANTUM RESONANCE

The wave function (14) is expressed in a representation in which the time-independent part of the spin Hamiltonian is diagonal. In this representation, the operator F_x, the x component of the total angular momentum, is defined by

$$F_x=\frac{\hbar}{2}\begin{bmatrix}0 & (1-\sin\eta)^{1/2} & (1+\sin\eta)^{1/2} & 0\\(1-\sin\eta)^{1/2} & 0 & 0 & (1-\sin\eta)^{1/2}\\(1+\sin\eta)^{1/2} & 0 & 0 & (1+\sin\eta)^{1/2}\\0 & (1-\sin\eta)^{1/2} & (1+\sin\eta)^{1/2} & 0\end{bmatrix}, \quad (15)$$

where $\cos\eta=\omega_0/(\omega_0^2+\omega_F^2)^{1/2}$, as before. The eigenfunction of this operator corresponding to the eigenvalue $+\hbar$ is

$$\Phi_+=\tfrac{1}{2}\begin{bmatrix}1\\(1-\sin\eta)^{1/2}\\(1+\sin\eta)^{1/2}\\1\end{bmatrix}, \quad (16)$$

and the projection of (14) on Φ_+ is given by

$$\tfrac{1}{2}[R_{11}e^{-i\omega t}+(1+\sin\eta)^{1/2}R_{31}+R_{41}e^{i\omega t}]\Phi_+.$$

The absolute square of the coefficient multiplying Φ_+ in this expression measures the probability of finding the

coupled spin system in the state Φ_+:

$$P(+\hbar) = \tfrac{1}{4}\{1 + \sin\eta |R_{31}|^2 + 2\Re(R_{11}^* R_{41} e^{2i\omega t})$$
$$+ 2(1+\sin\eta)^{1/2} R_{31}\,\mathcal{I}[(R_{11}^* - R_{41})e^{i\omega t}]\}. \quad (17)$$

Here $\Re$ denotes "real part of" and $\mathcal{I}$ denotes "imaginary part of."

The components $R_{11}(t)$, $R_{31}(t)$, and $R_{41}(t)$ of the wave function (14) satisfy the initial condition $R_{11}(0)=1$; $R_{31}(0)=R_{41}(0)=0$. $R_{41}(t)$ is always very small except when the frequency ω of the rf field approaches the double quantum resonance condition $\Delta\omega = \tfrac{1}{2}\omega_{14} - \omega = 0$. When this condition is satisfied, then $|R_{41}(t)|$ as well as $\tfrac{1}{2}\Re[R_{11}^*(t)R_{41}(t)e^{2i\omega t}]$ become large periodically. Therefore, the probability of finding the spin system in the eigenstate (16) of F_x oscillates at twice the resonance frequency ω near a double quantum resonance.

The explicit form of the term $\tfrac{1}{2}\Re[R_{11}^* R_{41} e^{2i\omega t}]$ at exact double quantum resonance can be inferred from Eqs. (11), (12), and (13) by setting $\Delta\omega = 0$. It follows then that $\sigma_1 = (\tfrac{1}{2}\delta)\{1 + [1+(\omega_1/\delta)^2]^{1/2}\}$, $\sigma_3 = (\tfrac{1}{2}\delta)\{1 - [1+(\omega_1/\delta)^2]^{1/2}\}$ and $\sigma_4 = \delta$, so that

$$R_{11} = \sin^2(\tfrac{1}{2}\eta)\{\cos^2(\tfrac{1}{2}\rho)\exp[-(\tfrac{1}{2}it)(\delta^2 + \omega_1^2)^{1/2}]$$
$$+ \sin^2(\tfrac{1}{2}\rho)\exp[(\tfrac{1}{2}it)(\delta^2 + \omega_1^2)^{1/2}]\}$$
$$+ \cos^2(\tfrac{1}{2}\eta)\exp[-(\tfrac{1}{2}i\delta t)],$$

$$R_{31} = -2i\sin(\tfrac{1}{2}\eta)\sin(\tfrac{1}{2}\rho)\cos(\tfrac{1}{2}\rho) \qquad (18)$$
$$\times \sin[\tfrac{1}{2}t(\delta^2 + \omega_1^2)^{1/2}],$$

$$R_{41} = \sin(\tfrac{1}{2}\eta)\cos(\tfrac{1}{2}\eta)\{\cos^2(\tfrac{1}{2}\rho)$$
$$\times \exp[-(\tfrac{1}{2}it)(\delta^2 + \omega_1^2)^{1/2}] + \sin^2(\tfrac{1}{2}\rho)$$
$$\times \exp[(\tfrac{1}{2}it)(\delta^2 + \omega_1^2)^{1/2}] - \exp[-(\tfrac{1}{2}i\delta t)]\},$$

where

$$\cos\rho = \frac{\delta}{(\delta^2 + \omega_1^2)^{1/2}}.$$

This holds without approximation. A particularly simple form of the term $\tfrac{1}{2}\Re(R_{11}^* R_{41} e^{2i\omega t})$ is obtained when the single and double quantum resonances are well separated, so that $(\omega_1/\delta) \ll 1$. Then

$$\left| \tfrac{1}{2}\Re(R_{11}^* R_{41} e^{2i\omega t}) \right|$$

$$\cong \tfrac{1}{4}\sin\eta\left\{\cos\eta - \cos\eta\cos\left[\frac{\omega_1 t}{4}\left(\frac{\omega_1}{\delta}\right)\right]\cos 2\omega t \right.$$

$$\left. + \sin\left[\frac{\omega_1 t}{4}\left(\frac{\omega_1}{\delta}\right)\right]\sin 2\omega t\right\}. \quad (19)$$

We shall see later that $\omega_1(\omega_1/\delta)$ is proportional to the nutation frequency at double quantum resonance. We may, therefore, regard Eq. (19) as describing an oscillation of a transverse component of the angular momentum at twice the resonance frequency modulated at the nutation frequency. (For simplicity, we have ignored the fact that the peak of the double quantum resonance

does not occur at $\omega = \tfrac{1}{2}\omega_{14}$, but is slightly shifted from this value, as discussed later.)

It is clear that $R_{11}^* R_{41} e^{2i\omega t}$ is an off-diagonal element of the density matrix of the coupled spin system. Any physical arrangement in which such off-diagonal matrix elements are probed, as in magnetic induction, or in the cross-beam light modulation experiments referred to earlier, should reveal the existence of the double frequency oscillation discussed above.

APPROXIMATE FORM OF TRANSITION PROBABILITY AT DOUBLE QUANTUM RESONANCE

To establish the correspondence between the exact solution of the Zeeman resonance problem for atomic hydrogen given by Eqs. (11)–(14), and Salwen's solution obtained by a different method,[6] it will be of interest to derive an approximate expression for the probability that the spin system has left its initial state, valid in the vicinity of a double quantum resonance in the limit of widely separated single and multiple quantum resonances. In this limit, characterized by the condition $(\omega_1/\delta) \ll 1$, the predictions of the two solutions should agree.

The probability that the system described by the wave function (14) has left its initial state is given by

$$1 - |R_{11}|^2 = 4\{|\alpha_1|^2|\alpha_3|^2 \sin^2[\tfrac{1}{2}t(\sigma_1 - \sigma_3)]$$
$$+ |\alpha_3|^2|\alpha_4|^2 \sin^2[\tfrac{1}{2}t(\sigma_3 - \sigma_4)]$$
$$+ |\alpha_4|^2|\alpha_1|^2 \sin^2[\tfrac{1}{2}t(\sigma_4 - \sigma_1)]\} \quad (20)$$

in accordance with (13). When $(\omega_1/\delta) \ll 1$, we can obtain a simpler form of this expression by expanding Eqs. (11a) and (11b), which define the parameters G and $\cos\theta$, in powers of (ω_1/δ) and $(\Delta\omega/\delta)$, keeping in mind that near a double quantum resonance $(\Delta\omega/\delta)$ is at most of order $(\omega_1/\delta)^2$:

$$\cos\theta \cong 1 - (27/2)M,$$

where

$$M = [(\Delta\omega/\delta) - \tfrac{1}{8}(\omega_1/\delta)^2 \cos\eta]^2 + [\tfrac{1}{8}(\omega_1/\delta)^2 \sin\eta]^2.$$

The angle θ is evidently very small near the double quantum resonance. We can, therefore, use the expansion of the cosine for small values of its argument to obtain the following approximate expressions for the roots (11) of the secular equation:

$$\sigma_1 \cong \delta[1 + \tfrac{1}{8}(\omega_1/\delta)^2 + M^{1/2}],$$

$$\sigma_3 \cong -\delta\{\tfrac{1}{4}(\omega_1/\delta)^2[1 + (\Delta\omega/\delta)\cos\eta] - \tfrac{1}{16}(\omega_1/\delta)^4\}, \quad (21)$$

$$\sigma_4 \cong \delta[1 + \tfrac{1}{8}(\omega_1/\delta)^2 - M^{1/2}].$$

These expressions are correct to order $(\Delta\omega/\delta)^2$, $(\Delta\omega/\delta)(\omega_1/\delta)^2$, and $(\omega_1/\delta)^4$. Evidently σ_3 is very small compared to σ_1 and σ_4 near $\Delta\omega = 0$. It follows that $|\alpha_3|^2$ is also very small, and the first two terms of (20) can be neglected in comparison with the last one:

$$1 - |R_{11}|^2 \cong 4|\alpha_1|^2|\alpha_4|^2 \sin^2[\tfrac{1}{2}t(\sigma_1 - \sigma_4)]. \quad (22)$$

In the expressions for $|\alpha_4|^2$ and $|\alpha_1|^2$ given by the first of Eqs. (12), the middle term in the brackets is also negligibly small compared to the first and last terms near the double quantum resonance, so that

$$|\alpha_1|^2 \cong \left[1+\left(\frac{1+\cos\eta}{1-\cos\eta}\right)\left(\frac{\delta+\Delta\omega-\sigma_1}{\delta-\Delta\omega-\sigma_1}\right)^2\right]^{-1}$$

$$= \left\{1+\cot^2\left(\frac{\eta}{2}\right)\left[\frac{\cos\phi-\tan(\eta/2)\sin\phi-1}{\cos\phi+\cot(\eta/2)\sin\phi+1}\right]^2\right\}^{-1}$$

$$= \cos^2\left(\frac{\phi}{2}\right), \qquad (23)$$

where we have set

$$\cos\phi = \left[\left(\frac{\Delta\omega}{\delta}\right)-\tfrac{1}{8}(\omega_1/\delta)^2\cos\eta\right]M^{-1/2}.$$

Similarly,

$$|\alpha_4|^2 \cong \left[1+\left(\frac{1+\cos\eta}{1-\cos\eta}\right)\left(\frac{\delta+\Delta\omega-\sigma_4}{\delta-\Delta\omega-\sigma_4}\right)^2\right]^{-1}$$

$$= \left\{1+\cot^2\left(\frac{\eta}{2}\right)\left[\frac{\cos\phi-\tan(\eta/2)\sin\phi+1}{\cos\phi+\cot(\eta/2)\sin\phi-1}\right]^2\right\}^{-1}$$

$$= \sin^2(\tfrac{1}{2}\phi). \qquad (24)$$

The probability that the system has left the initial state is, therefore,

$$1-|R_{11}|^2 = \sin^2\phi\cdot\sin^2[\tfrac{1}{2}t(\sigma_1-\sigma_4)]$$

$$= \frac{\Omega_1^2}{(\Delta\omega-\omega^*)^2+\Omega_1^2}$$

$$\times\sin^2\{t[(\Delta\omega-\omega^*)^2+\Omega_1^2]^{1/2}\}. \qquad (25)$$

Here,

$$\Omega_1 = (\tfrac{1}{8})\omega_1(\omega_1/\delta)\sin\eta = (\tfrac{1}{8})\omega_1(\omega_1/\delta)[1+(\omega_0/\omega_F)^2]^{-1/2} \quad (26)$$

is the nutation frequency at exact double quantum resonance, and

$$\omega^* = (\tfrac{1}{8})\omega_1(\omega_1/\delta)\cos\eta = (\tfrac{1}{8})\omega_1(\omega_1/\delta)[1+(\omega_F/\omega_0)^2]^{-1/2} \quad (27)$$

is the amount by which the peak of the double quantum resonance curve is shifted from the expected value $\Delta\omega = (\tfrac{1}{2})\omega_{14}-\omega=0$. These two features of the solution, as well as the absence of a factor of $\tfrac{1}{2}$ in the argument of the $\sin^2$ factor of the resonance formula (25), as compared to the usual Rabi formula[16] for single quantum transitions, agree exactly with the predictions of Salwen's perturbation theory solution.[6]

DOUBLE QUANTUM ZEEMAN RESONANCE IN ALKALI METAL VAPOR

In the discussion above, atomic hydrogen was chosen as the simplest of all coupled spin systems undergoing magnetic resonance. Next in complexity are monatomic vapors of elements that consist of one-electron atoms of nuclear spin k greater than $\tfrac{1}{2}$, as one of the alkalis. Multiple quantum transitions induced among the Zeeman levels of the hyperfine multiplets of such atoms have been studied by Kusch[2,4] and Kastler's group,[17] and analyzed by Salwen[11] and Winter.[8]

Nevertheless, it will be of interest to apply our method of analysis to a particular case of double quantum Zeeman resonance in such atoms. Such an analysis is justified first of all by the fact that the theory developed for atomic hydrogen may be applied directly to this case, with only minor modifications, and secondly by the importance of the example chosen to the analysis of events observed in optically pumped vapors.

The formulation of the problem proceeds exactly as in the case of atomic hydrogen. We shall assume again that the nuclear magnetic moment is positive and that the nuclear nutation frequency $\omega_{1_k}=\gamma_k H_1$ is negligibly small compared to the electron nutation frequency $\omega_{1_j}=|\gamma_j|H_1$. Recalling the definitions of $\mathcal{3C}_0$ and $\mathcal{3C}_1'$ given by (2) and (4), the operator $\mathcal{3C}_0+\mathcal{3C}_1'-\omega F_z$ in the coupled representation is defined by the following matrix of dimensionality $2(2k+1)$:

$$\mathcal{3C}_0+\mathcal{3C}_1'-\omega F_z = \hbar \begin{bmatrix} \lambda_1-\omega(k+\tfrac{1}{2}) & \tfrac{1}{2}a_1\omega_{1_j} & \tfrac{1}{2}b_1\omega_{1_j} & 0 & 0 & \cdots \\ \tfrac{1}{2}a_1\omega_{1_j} & \lambda_2-\omega(k-\tfrac{1}{2}) & 0 & -\tfrac{1}{2}b_1a_2\omega_{1_j} & -\tfrac{1}{2}b_1b_2\omega_{1_j} & \cdots \\ \tfrac{1}{2}b_1\omega_{1_j} & 0 & \lambda_3-\omega(k-\tfrac{1}{2}) & \tfrac{1}{2}a_1a_2\omega_{1_j} & \tfrac{1}{2}a_1b_2\omega_{1_j} & \cdots \\ 0 & -\tfrac{1}{2}b_1a_2\omega_{1_j} & \tfrac{1}{2}a_1a_2\omega_{1_j} & \lambda_4-\omega(k-\tfrac{3}{2}) & 0 & \cdots \\ 0 & -\tfrac{1}{2}b_1b_2\omega_{1_j} & \tfrac{1}{2}a_1b_2\omega_{1_j} & 0 & \lambda_5-\omega(k-\tfrac{3}{2}) & \cdots \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \end{bmatrix}. \qquad (28)$$

Here $\hbar\lambda_1$, $\hbar\lambda_3$, $\hbar\lambda_5$, $\cdots$ are the energies of the stationary states (Breit-Rabi eigenstates) in the $F=k+\tfrac{1}{2}$ hyperfine multiplet, listed in order of decreasing m_F, whereas $\hbar\lambda_2$, $\hbar\lambda_4$, $\cdots$ are the corresponding energies in the $F=k-\tfrac{1}{2}$ multiplet, also listed in order of decreasing m_F. The other symbols are defined as follows:

$$a_1 = \cos(\tfrac{1}{2}\eta_{k-1/2}),$$
$$b_1 = \sin(\tfrac{1}{2}\eta_{k-1/2}),$$
$$a_2 = \cos(\tfrac{1}{2}\eta_{k-3/2}),$$
$$b_2 = \sin(\tfrac{1}{2}\eta_{k-3/2}), \qquad (29)$$

[16] I. I. Rabi, Phys. Rev. 51, 652 (1937).
[17] A. Kastler, J. Opt. Soc. Am. 47, 460 (1957).

where

$$\cos\eta_m = \frac{\omega_0 + [2m/(2k+1)]\omega_F}{\{\omega_F^2 + [4m/(2k+1)]\omega_F\omega_0 + \omega_0^2\}^{1/2}}. \quad (30)$$

We now direct our attention to the Zeeman resonances among the uppermost three sublevels of the $F = k + \frac{1}{2}$ hyperfine multiplet in the low field limit, that is, in the limit where $\omega_0 = \omega_{0_j} + \omega_{0_k}$ can be neglected in comparison with the hyperfine resonance frequency ω_F in the expression (30) for $\cos\eta_m$. This is a situation comparable to the atomic hydrogen case, although in that case we had no restriction on the intensity of the steady field H_0. To this end, we select out from the matrix of $\mathcal{3C}_0 + \mathcal{3C}_1' - \omega F_z$ the submatrix which describes the interactions of these states, namely,

$$\mathcal{3C}_0 + \mathcal{3C}_1' - \omega F_z = \hbar \begin{bmatrix} \lambda_1 - \omega(k+\frac{1}{2}) & \omega_1/[2(2k+1)^{1/2}] & 0 \\ \omega_1/[2(2k+1)^{1/2}] & \lambda_3 - \omega(k-\frac{1}{2}) & \omega_1 k^{1/2}/(2k+1) \\ 0 & \omega_1 k^{1/2}/(2k+1) & \lambda_5 - \omega(k-\frac{3}{2}) \end{bmatrix}. \quad (31)$$

This can be written

$$\mathcal{3C}_0 + \mathcal{3C}_1' - \omega F_z = \hbar[\lambda_3 - \omega(k-\frac{1}{2})]\mathbf{1} + \hbar \begin{bmatrix} \delta + \Delta\omega & \omega_1/[2(2k+1)^{1/2}] & 0 \\ \omega_1/[2(2k+1)^{1/2}] & 0 & \omega_1 k^{1/2}/(2k+1) \\ 0 & \omega_1 k^{1/2}/(2k+1) & \delta - \Delta\omega \end{bmatrix}, \quad (32)$$

where, as in the atomic hydrogen case, $\delta = \omega_{13} - \frac{1}{2}\omega_{15} = (\lambda_1 - \lambda_3) - \frac{1}{2}(\lambda_1 - \lambda_5)$ is a measure of the frequency separation of the single and double quantum Zeeman resonances, and $\Delta\omega = \frac{1}{2}\omega_{15} - \omega$ measures the departure of the actual frequency ω of the rf field from the double quantum resonance frequency $\frac{1}{2}\omega_{15}$.

Equation (32) can be compared directly to Eq. (9) which describes the interaction of the three $F = 1$ Zeeman substates of atomic hydrogen. We can apply all the expressions derived for atomic hydrogen also to this case by replacing $\cos\eta$ used there by $(2k-1)/(6k+1)$, and ω_1 by $\Gamma_1 = [(6k+1)^{1/2}/(2k+1)]\omega_1$.

Let us assume that the system is initially in the state $F = k + \frac{1}{2}$, $m_F = k + \frac{1}{2}$ (state 1). Then at exact double quantum resonance, in accordance with (19), the probability of finding the coupled spins in the eigenstate of F_x belonging to the eigenvalue $+\hbar$ is given by

$$\frac{[k(2k+1)]^{1/2}}{6k+1} \left\{ \left(\frac{2k-1}{6k+1} \right) - \left(\frac{2k-1}{6k+1} \right) \cos\left[\frac{\Gamma_1 t}{4} \left(\frac{\Gamma_1}{\delta} \right) \right] \right. $$
$$\left. \times \cos 2\omega t + \sin\left[\frac{\Gamma_1 t}{4} \left(\frac{\Gamma_1}{\delta} \right) \right] \sin 2\omega t \right\}. \quad (33)$$

On the other hand, for small values of $\Delta\omega$ (vicinity of double quantum resonance), in analogy with (25) the probability that the system has left that state will be

$$\frac{\Omega^2}{(\Delta\omega - \omega^*)^2 + \Omega^2} \sin^2\{t[(\Delta\omega - \omega^*)^2 + \Omega^2]^{1/2}\}. \quad (34)$$

The nutation frequency at exact double quantum resonance is now given by

$$\Omega = [k^{1/2}/2(2k+1)^{3/2}]\omega_1(\omega_1/\delta), \quad (35)$$

and the peak of the double quantum resonance will be

shifted from the expected value $\Delta\omega = 0$ by an amount

$$\omega^* = [(2k-1)/8(2k+1)^2]\omega_1(\omega_1/\delta). \quad (36)$$

These expressions differ from the corresponding expressions for atomic hydrogen in that their validity is restricted to relatively moderate values of the intensity of the applied steady magnetic field H_0, that is, to values of H_0 such that $\omega_0 = (|\gamma_j| + \gamma_k)H_0 \ll \omega_F$, as stated earlier. It is precisely under these conditions, however, that double quantum resonances can be observed. In contrast, in the case of atomic hydrogen the shift in the double quantum resonance frequency given by (27) would be unobservably small when $\omega_0 \ll \omega_F$, so that $\cos\eta \ll 1$. Therefore, (33), (34), (35), and (36) describe a realistic physical situation.

Furthermore, it is of interest to note that optical pumping with circularly polarized resonance radiation containing a single D line[18] tends to produce an excess population of the substates with the largest values of m_F, that is, precisely of those states whose interaction has been considered above.

ACKNOWLEDGMENT

APPENDIX: MAGNETIC RESONANCE OF SPIN ONE PARTICLE

To illustrate the method of treating magnetic resonance problems presented here, it is of interest to apply it to a well-known case, the magnetic resonance of a spin one particle. The wave function at time t is related to the initial wave function by

$$\psi(t) = \exp[-(i/\hbar)J_z\omega t]$$
$$\times \exp[-(i/\hbar)(J_z\cos\zeta + J_x\sin\zeta)2\Omega t]\psi(0),$$

[18] W. Franzen and A. G. Emslie, Phys. Rev. 108, 1453 (1957).

where

$$\sin\zeta = \omega_1/2\Omega,$$

$$\cos\zeta = (\omega_0-\omega)/2\Omega,$$

$$2\Omega = [\omega_1{}^2 + (\omega_0-\omega)^2]^{1/2},$$

$$\omega_1 = |\gamma_j|H_1,$$

$$\omega_0 = |\gamma_j|H_0,$$

$$\mathbf{H} = (\hat{\mathbf{i}}\cos\omega t + \hat{\mathbf{j}}\sin\omega t)H_1 + \hat{\mathbf{k}}H_0.$$

Now in the J_z-diagonal representation

$$(1/\hbar)(J_z\cos\zeta + J_x\sin\zeta) = \begin{bmatrix} \cos\zeta & \sin\zeta/\sqrt{2} & 0 \\ \sin\zeta/\sqrt{2} & 0 & \sin\zeta/\sqrt{2} \\ 0 & \sin\zeta/\sqrt{2} & -\cos\zeta \end{bmatrix}.$$

The eigenvalues of this matrix are $m = +1, 0, -1$. The components of the corresponding eigenfunctions

$$\phi_m = \begin{bmatrix} \alpha_m \\ \beta_m \\ \gamma_m \end{bmatrix}$$

are then related to each other by

$$\alpha_m = \frac{\sin\zeta}{\sqrt{2}(m-\cos\zeta)}\beta_m,$$

$$\gamma_m = \frac{\sin\zeta}{\sqrt{2}(m+\cos\zeta)}\beta_m.$$

On normalization, these lead to the three eigenfunctions ϕ_m, with $m = +1, 0, -1$, which constitute the three columns of the matrix S:

$$S = \begin{bmatrix} (\tfrac{1}{2})(1+\cos\zeta) & -(\sqrt{2}/2)\sin\zeta & (\tfrac{1}{2})(1-\cos\zeta) \\ (\sqrt{2}/2)\sin\zeta & \cos\zeta & -(\sqrt{2}/2)\sin\zeta \\ (\tfrac{1}{2})(1-\cos\zeta) & (\sqrt{2}/2)\sin\zeta & (\tfrac{1}{2})(1+\cos\zeta) \end{bmatrix}.$$

We have chosen the arbitrary phases of the three eigenfunctions in such a way that for $\zeta = 0$, i.e., zero rf field intensity, they reduce to the forms

$$\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \quad \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \quad \text{and} \quad \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix},$$

respectively.

The matrix S so defined has the property that

$$S^{-1}(J_z\cos\zeta + J_x\sin\zeta)S = J_z.$$

In this form, S considered as an operator is identical with the rotation operator used by Series.[12] The corresponding matrix S which occurred in our analysis of the magnetic resonance of the $F=1$ hyperfine multiplet of atomic hydrogen reduces to precisely this form for $\delta = 0$, that is, for zero steady field (exact coincidence of single and multiple quantum resonances).

The solution of the magnetic resonance problem is then given by

$$\psi(t) = \exp[-(i/\hbar)J_z\omega t]S\{\exp[-(i/\hbar)J_z2\Omega t]\}S^{-1}\psi(0).$$

The matrix elements of both exponential operators are now known since they are formed from the diagonal operator J_z. Thus, for an initial state $\psi(0) = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}$,

$$\psi(t) = \begin{bmatrix} [\sin^2(\Omega t)\sin^2\zeta + \cos(2\Omega t) - i\sin(2\Omega t)\cos\zeta]e^{-i\omega t} \\ -\sqrt{2}\sin(\Omega t)\sin\zeta[\sin(\Omega t)\cos\zeta + i\cos(\Omega t)] \\ -[\sin^2(\Omega t)\sin^2\zeta]e^{i\omega t} \end{bmatrix}.$$

Then the probability of finding the spin in the state $\begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$ at time t is given by

$$\sin^4(\Omega t)\sin^4\zeta$$

$$= \frac{\omega_1{}^4}{[\omega_1{}^2 + (\omega_0-\omega)^2]^2}\sin^4\left\{\frac{t}{2}[\omega_1{}^2 + (\omega_0-\omega)^2]^{1/2}\right\},$$

and the probability of finding it in the eigenstate of F_x belonging to the eigenvalue $-\hbar$, that is, in the state

$$\tfrac{1}{2}\begin{bmatrix} -1 \\ \sqrt{2} \\ -1 \end{bmatrix}$$

will be given by

$$\{\tfrac{1}{2}[1 - \sin(\omega_0 t)\sin(\omega_1 t)]\}^2$$

$$= \tfrac{1}{16}\{5 - 8\sin(\omega_0 t)\sin(\omega_1 t) \\ - \cos(2\omega_0 t) - \cos(2\omega_1 t) + \cos(2\omega_0 t)\cos(2\omega_1 t)\}.$$

Again we note that the x projection oscillates at twice the resonance frequency.