TABLE I. A comparison of our results for the x-ray incoherent scattering function s_0^2 with the numerical results (s_0^2 is a function of w.)

w	0	0.025	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.8	∞
x_0	∞	16.499	9.955	5.851	3.282	2.275	1.705	1.349	1.099	0.7780	0
$s_0^2(w)$	0	0.198	0.308	0.459	0.646	0.761	0.839	0.893	0.931	0.977	1
$s_0^2(w)$	0	0.199	0.319	0.486	0.674	0.776	0.839	0.880	0.909	0.944	1

for all known approximate solutions for the sake of the character of this note will be given in a forthcoming paper, in which the intensity for coherent and incoherent scattering of x-rays will be calculated.

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Multiple-Quantum Transitions in Nuclear Magnetic Resonance*

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The theory of Bloch and Wangsness for nuclear magnetic resonance signals is applied to multiple-quantum transitions. In most of the NMR experiments, the energy level schemes are only slightly different from an equally spaced Zeeman pattern, so that a simultaneous absorption of several radiation quanta with the same frequency can take place. It is found that the multiplicity, or the number of quanta absorbed in the transition, is most easily determined through the specific dependence of the multiple quantum signals on the rf field amplitude. The dependence of the signals on various relaxation parameters is developed and is found to provide information about relaxation processes which is not derivable from ordinary single-quantum transitions.

A method of enhancing multiple transitions by audio-modulating the radio-frequency field is described. This is helpful in cases where the frequency deviations from an equally spaced Zeeman pattern are so large that a direct multiple transition is too weak to be observed.

INTRODUCTION

THE detection of nuclear magnetic resonance signals corresponding to a transition with a change of magnetic quantum number by more than unity has recently been reported.[1,2] It had been predicted by Hughes and Geiger[3] that the energy level schemes usually encountered in NMR experiments are particularly suitable for the observation of multipole quantum transitions. The relatively late discovery of these apparently "forbidden" transitions is due to the stringent conditions required for their observation. Physically, such transitions are associated with an elementary act of simultaneous absorption of several radiation quanta and a case of special importance is is that in which all the quanta have the same energy. Mathematically, the transition probability is obtained by applying a high-order perturbation calculation to the interaction of the radio-frequency (rf) field with the nuclear spin system. In this respect, the particular nature of the spin system is unimportant. Similar transitions may occur, in principle, in any quantum-mechanical system interacting with a radiation field.[4] Most of the experimental and theoretical work recently published on these transitions is associated with experiments in atomic and molecular beams,[5,6] or with the optical methods of Kastler and De Brossel.[7,8] In both methods the systems interacting with the applied radiation are practically isolated.

Consequently, most of the information about these transitions is obtained by calculating the transition probabilities of a representative single system interacting only with the rf field.

The present work, in contrast, was undertaken in an effort to describe multiple-quantum transitions (m.q.t.) in nonisolated spin systems, i.e., in systems which interact also with the random fluctuating fields of the

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molecular surroundings. Such systems are typical in nuclear magnetic resonance experiments where the phenomenon of relaxation plays an important role, and conditions are particularly favorable for the observation of m.q.t. with quanta of the same energy. This may be seen by considering the most important condition needed to make such transitions relatively probable. In a specific n-quantum transition between the levels a and b, let the interval $a-b$ be subdivided into n equal parts. The intensity of the transition will be seen to depend upon the positions of the intermediate levels with respect to the $n-1$ equally-spaced points in the interval and, in particular, to fall off as the deviations of these levels from the nearby spacing points increase. On the other hand, a coincidence or a near-coincidence of intermediate levels with any of the spacing points introduces the ambiguity of another m.q.t. with the same frequency but a different number of quanta and is, therefore, ruled out from the treatment. It is consequently evident that a rather exceptional set of "almost" equally-spaced levels is desirable. While such a set is rarely found in optical or nuclear spectroscopy, it is rather common in nuclear magnetic resonance where the uniform spacing of the energy levels in the presence of a strong external magnetic field is slightly modified by small internal perturbations.

The statistical nature of the relaxation processes has been treated in papers by Wangsness and Bloch,[9] who derived the Boltzmann transport equation for the distribution matrix σ (defined in I). This matrix is a function only of the spin variables and of the time, and is used to obtain the statistical expectation value of any operator Q that depends on the same variables. In the present work we adhere closely to the technique and notation developed in these papers. A similar approach has been undertaken by Meiboom and Kaplan,[2] who calculated the properties of double-quantum transitions and compared them with the results of their experiments with the molecule ethyl alcohol. They were also able to detect traces of higher multiple transitions in the same molecule.

I. THE BOLTZMANN EQUATIONS

Nuclear magnetic resonance signals are proportional to the transverse components of the nuclear polarization, which are obtained from the solution of the Boltzmann equation for the distribution matrix σ. This equation forms a generalization of the usual set of equations for the rate of change of populations in the various energy levels and contains terms which arise from relaxation processes.

Following I, the entire Hamiltonian of the system consists of three parts; the energy of the "molecular" system $\hbar F$, the energy of the spin system $\hbar E$, and the interaction energy $\hbar G$ of the spin system with the molecular surroundings, where the latter is to be considered as a small perturbation.

The spin system is assumed to consist of a group of nuclear moments of the same species which is typically found in molecules of a liquid or gaseous substance. The nuclei are exposed to a strong and constant magnetic field H_0 and to an rf field whose frequency is in the vicinity of the Larmor frequencies of the magnetic moments. It will further be assumed that there exist chemical shifts[10] which have the same value for certain subgroups of equivalent moments and that two such groups s and t are coupled to each other by an interaction energy proportional to the scalar product of their total spin vectors $\mathbf{I}_s$ and $\mathbf{I}_t$, respectively.[11] The contribution to the energy, as well as that due to chemical shifts and to the applied rf field, is considered to be small, compared to the Zeeman energy of the spin system in the strong field H_0.

A suitable form of the Boltzmann equation for the distribution matrix σ is found in Eq. (2.52) in III,

$$d\sigma/dt=-i[E+\Delta+\Gamma,\sigma]+\Gamma(\sigma), \tag{1.1}$$

Δ and Γ are defined in Eqs. (2.26) and (2.54) in III, respectively. They represent the first- and second-order approximations in the perturbing energy $\hbar G$. An appreciable contribution to Δ and Γ is due to the interaction of the surrounding electrons in the molecule, which may be considered as part of the molecular surroundings. This contribution gives rise to the chemical shift, as well as to the spin-spin coupling, and may be combined with the term E of Eq. (1.1). Retaining the letter E to denote the resulting enlarged quantity and splitting this term according to the time dependence of its constituents, one obtains, thus,

$$d\sigma/dt+i[E,\sigma]=\Gamma(\sigma), \tag{1.2}$$

with

$$E=E_0+E_1, \tag{1.3}$$

$$E_0=-\textstyle\sum_s I_s{}^0\omega_s+\sum_{s>t} J_{st}(\mathbf{I}_s\cdot\mathbf{I}_t), \tag{1.4}$$

$$E_1=-\mathfrak{D}(e^{i\omega t}I^1+e^{-i\omega t}I^{-1}). \tag{1.5}$$

Here ω_s is the chemically-shifted frequency of subgroup s, and J_{st} is a coupling constant of the scalar spin-spin interaction. The superscripts 0, 1, and -1 in (1.4) and (1.5) have the same significance as in III, so that $I_s{}^0=I_{sz}$ is the z component of the spin vector I_s of subgroup s and $I^{\pm1}=I_x\pm I_y$, where I_x and I_y are the x and y components of the total spin vector $\mathbf{I}$ of the system. In addition,

$$\mathfrak{D}=\gamma H_1/2, \tag{1.6}$$

where H_1 is the amplitude of the rf field and γ is the gyromagnetic ratio of the nuclear species involved. The fact that nuclei of other species may also be contained in the molecule does not materially modify the results derived in this paper. The frequency ω of the rf field is

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assumed to be close to the Larmor frequencies, so that

$$\Delta_s=\omega-\omega_s \tag{1.7}$$

satisfies the condition

$$\Delta_s\ll\omega. \tag{1.8}$$

$\Gamma(\sigma)$, in Eqs. (1.1) and (1.2) represents the dissipative part of the interaction energy of the nuclear spins with the molecular system. It has the form[12]

$$\Gamma(\sigma)=\pi\sum_{pq}e^{i\omega_{pq}t}[e^{-\beta\omega_p}\{G_{-p}\sigma G_{-q}\}^{\omega_p}-\sigma\{G_{-p}G_{-q}\}^{\omega_p}+e^{\beta\omega_q}\{G_{-p}\sigma G_{-q}\}^{-\omega_q}-\{G_{-p}G_{-q}\}^{-\omega_q}\sigma. \tag{1.9}$$

Equation (1.2) assumes a more convenient form by the familiar transformation to a frame of reference which rotates in phase with the applied rf field represented by the term E_1 of Eq. (1.5).

The actual transformation is carried out in Appendix I and leads to the following equations for the transformed distribution matrix σ_S:

$$d\sigma_S/dt+i[E_S,\sigma_S]=\Gamma(\sigma_S), \tag{1.10}$$

with

$$E_S=E_{0S}+E_{1S}, \tag{1.11}$$

$$E_{0S}=\sum_s\Delta_sI_s^0+\sum_{s>t}J_{st}(\mathbf{I}_s\cdot\mathbf{I}_t), \tag{1.12}$$

$$E_{1S}=\mathfrak{D}(I^1+I^{-1}), \tag{1.13}$$

$$\Gamma(\sigma_S)=\pi\sum_\tau[2e^{\beta\tau}\{G^\tau\sigma_SG^{-\tau}\}^{-\tau\omega}-\sigma_S\{G^\tau G^{-\tau}\}^{-\tau\omega}-\{G^\tau G^{-\tau}\}^{-\tau\omega}\sigma_S]. \tag{1.14}$$

The magnetic resonance signal is obtained by substituting the solution of Eq. (1.10) in Eq. (4.22) in II. In the rotating frame, this expression takes the form

$$\mathcal{S}=N\hbar\gamma\frac{d}{dt}\operatorname{Tr}(I_S^1\sigma_S). \tag{1.15}$$

Here, use has been made of the invariance of the trace to any canonical transformation by means of an operator S. N stands for the number of nuclei with gyromagnetic ratio γ in the sample. Further,

$$I_S^1=S_0I^1S_0^{-1}, \tag{1.16}$$

where

$$S_0=\exp(-i\omega I^0t) \tag{1.17}$$

is the required operator for the transformation to the rotating frame. Using the commutation rule $[I^0,I^{\pm1}]=\pm I^{\pm1}$, it can be shown that

$$I_S^{\pm1}=e^{\pm i\omega t}I^{\pm1}. \tag{1.18}$$

Thus, the signal becomes

$$\mathcal{S}=N\hbar\gamma(d/dt)[\operatorname{Tr}(I^1\sigma_S)e^{-i\omega t}]. \tag{1.19}$$

It should be noted that in the absence of an external rf field, i.e., if E_S in (1.10) is replaced by E_{0S}, the distribution

$$\sigma_0=\zeta\exp(\beta\omega I^0), \tag{1.20}$$

with

$$\zeta^{-1}=\operatorname{Tr}\exp(\beta\omega I^0), \tag{1.21}$$

represents a stationary solution of Eq. (1.10). One verifies this by noting that $[E_0,\sigma_0]=0$ and $\Gamma(\sigma_0)=0$. The first relation results from the commutation of E_0 and I^0 and the second relation follows from the properties of G^τ which is defined to have nonvanishing matrix elements $(\epsilon|G^\tau|\epsilon')$ only between spin states whose magnetic quantum numbers satisfy

$$m'-m=\tau. \tag{1.22}$$

This leads to the relations

$$\begin{aligned}\exp(\beta\omega I^0)G^\tau\exp(-\beta\omega I^0)&=e^{\beta\omega\tau}G^\tau,\\ \exp(-\beta\omega I^0)G^{-\tau}\exp(\beta\omega I^0)&=e^{\beta\omega\tau}G^{-\tau}.\end{aligned} \tag{1.23}$$

The vanishing of $\Gamma(\sigma_0)$ follows then by substitution of expression (1.23) into Eq. (1.10). Actually, in the absence of an rf field, i.e., for $E_1=0$, Eq. (1.2) and, hence, also Eq. (1.10) has the rigorous solution $\sigma\sim e^{\beta E_0}$. The form (1.20) arises from the assumption $(J,\Delta_s)\ll(\omega,1/\beta,\omega_s)$, which is used in Appendix I to arrive at the simplified expression (1.14) for $\Gamma(\sigma_S)$.

Let us now choose

$$\sigma_S=\sigma_0+\chi=\zeta\exp(\beta\omega I^0)+\chi, \tag{1.24}$$

where χ represents the deviation of σ_S from its static value σ_0. Substituting this in (1.10) and using the properties of σ_0, one obtains

$$d\chi/dt+i[E_S,\chi]-\Gamma(\chi)=i\zeta\mathfrak{D}[I^1+I^{-1},\exp(\beta\omega I^0)], \tag{1.25}$$

with the understanding that $\Gamma(\chi)$ is obtained from $\Gamma(\sigma_S)$ in (1.14), and replacing σ_S by χ. A solution of Eq. (1.25) will be obtained in the following section and will be used to obtain the signal $\mathcal{S}$ by means of Eqs. (1.19) and (1.24).

II. SOLUTION OF THE BOLTZMANN EQUATIONS FOR A TRANSITION INVOLVING n EQUAL QUANTA

A. Preliminary Assumptions and Simplifications

A more detailed discussion of Eq. (1.25) requires its representation in a matrix form. The choice of a representation is irrelevant as far as the signal $\mathcal{S}$ is concerned, since it does not affect the value of the trace which appears in Eq. (1.19). It is most convenient, however, to work in a representation where the two commuting operators E_{0S} and I^0 are simultaneously diagonal.

Assuming no degeneracy, each state can then be uniquely characterized by an eigenvalue ϵ of E_{0S} and by an eigenvalue m of I^0.

[12] Equation (2.52) of III. The significance of the various symbols in this equation are likewise found in III.

Using this representation, it is possible to write the quantity χ of Eq. (1.24), as a sum of the form

$$\chi=\sum_p \chi^p, \tag{2.1}$$

where the matrix elements of a particular term χ^p in this sum are required to satisfy the condition

$$(\epsilon|\chi^p|\epsilon')=0, \quad \text{unless} \quad m_\epsilon-m_{\epsilon'}=p. \tag{2.2}$$

In this notation, the superscript p has the same significance in relation to the matrix elements χ^p as the superscripts τ, 1, 0, and -1, to the matrix elements of G^τ, I^1, I^0, and I^{-1}, respectively.

The Hermiticity of χ implies

$$(\epsilon|\chi^p|\epsilon')^*=(\epsilon'|\chi^{-p}|\epsilon), \tag{2.3}$$

and one has further for two states ϵ and ϵ' with $m_\epsilon-m_{\epsilon'}=p$,

$$(\epsilon|\Gamma(\chi)|\epsilon')=(\epsilon|\Gamma(\chi^p)|\epsilon'). \tag{2.4}$$

This result follows from the general understanding of the superscripts mentioned above, by which an operator Q^λ is meant to have nonvanishing matrix elements $(\epsilon|G^\lambda|\epsilon')$ only if $m_\epsilon-m_{\epsilon'}=\lambda$. Consider now a product,

$$\prod_s Q_s^{\lambda_s}=Q^\lambda, \tag{2.5}$$

of such operators $Q_s^{\lambda_s}$. It follows from the rules of matrix multiplication that the selection rules of the product, indicated by the superscript λ, are expressed in terms of those of the factors by the equation

$$\sum_s \lambda_s=\lambda. \tag{2.6}$$

Such products occur when the quantity σ_s of Eq. (1.14) is replaced by the expression (2.1).

It is to be noted, in particular, that a product of G^τ, $G^{-\tau}$, and χ^p, in any order, has nonvanishing matrix elements between the states ϵ and ϵ', only if $m_\epsilon-m_{\epsilon'}=p$; conversely, if $m_\epsilon-m_{\epsilon'}=p$, only terms with χ^p in $\Gamma(\chi)$ contribute to these matrix elements, and this is indeed the result expressed in Eq. (2.4).

Using this result, together with the properties of $I^{\pm1}$, one obtains from Eq. (1.25),

$$\begin{aligned}-id\chi^p/dt+[E_0 s,\chi^p]-\mathfrak{D}([I^1,\chi^{p-1}]+[I^{-1},\chi^{p-1}])\\ +i\Gamma(\chi^p)=\mathfrak{D}\zeta\{[I^1,\exp(\beta\omega I^0)]\delta_{p1}\\ +[I^{-1},\exp(\beta\omega I^0)]\delta_{p-1}\}.\end{aligned} \tag{2.7}$$

Equations (1.20), (1.24), and (2.1) lead to a modification of the expression (1.19) for the signal:

$$\mathcal{S}=N\hbar\gamma\frac{d}{dt}[\mathrm{Tr}(I^1\chi^{-1})e^{-i\omega t}]. \tag{2.8}$$

To verify this result, it should be noted that the trace of any operator of the type Q^λ vanishes unless $\lambda=0$. With σ_0 depending only upon I^0, the product $I^1\sigma_0$ is an operator of the type Q^1 and, therefore, does not contribute to the trace in Eq. (1.19). Further, only the term χ^{-1} of the sum (2.1), which leads in the product $1^1\chi$ to an operator of the type Q^0, gives a finite contribution to $\mathcal{S}$. On the other hand, matrix elements of χ^p with $p\neq1$ are coupled to the elements of χ^{-1} through Eq. (2.7), so that they appear indirectly in the signal. It will be seen later that the resonance character of an n-quantum transition is reflected in the form of a specific matrix element of χ^{-n}, so that the last remark anticipates the manner in which this resonance behavior shows up in the expression for the signal.

Before beginning the actual solution of the Boltzmann equations, the following remark is added in an attempt to elucidate the physical background of the preceding results.

The diagonal form of the distribution matrix σ_0 in the energy representation and in the absence of a rf field represents the incoherence of the relative phases of probability amplitudes belonging to different spin states. The presence of a rf field with the proper frequency induces a correlation between the phases of states whose energy difference is equal to some multiple of the rf frequency.

This correlation, in turn, is responsible for the nonvanishing of the matrix element of σ connecting the two states. However, the nature of the interaction of the rf field with the spin system is such that, in first order approximation, only the phases of states with adjacent magnetic quantum numbers are correlated. Hence, any correlation between states with nonadjacent quantum numbers is due to a higher-order perturbation calculation of this interaction. Considering the form of the resulting higher-order approximation,[4] one realizes that the correlation between levels with $\Delta m>1$ takes place through a stepwise correlation between the phases of a series of intermediate levels with $\Delta m=1$. Therefore, a resonance increase in the magnitude of a nondiagonal resonance matrix element between any pair of states is associated with the simultaneous increase in the magnitude of matrix elements connecting the intermediate levels.

The following discussion is concerned only with the stationary solutions of Eqs. (2.7). There exist also transient solutions decaying exponentially with time constants of the order of $1/|\Gamma|$ which will be disregarded in the present treatment.

The matrix elements of χ^p in the stationary solutions do not depend on the time. Hence, omitting the time derivative and rewriting Eqs. (2.7) in a matrix form, one obtains

$$\begin{aligned}(\epsilon-\epsilon')(\epsilon|\chi^p|\epsilon')-\mathfrak{D}(\epsilon|[I^1,\chi^{p-1}]\\ +[I^{-1},\chi^{p-1}]|\epsilon')+i(\epsilon|\Gamma(\chi^p)|\epsilon')\\ =\mathfrak{D}(\epsilon|I^1+I^{-1}|\epsilon')[\sigma_0(\epsilon')-\sigma_0(\epsilon)],\end{aligned} \tag{2.9}$$

with the abbreviations

$$\sigma_0(\epsilon)=e^{\beta\omega m_\epsilon}, \tag{2.10}$$

$$\begin{aligned}(\epsilon|\Gamma(\chi^p)|\epsilon')\\ =-\sum_{\epsilon''\epsilon'''}(\epsilon\epsilon''|\Gamma^p|\epsilon'''\epsilon')(\epsilon''|\chi^p|\epsilon'''),\end{aligned} \tag{2.11}$$

where

$$(\epsilon\epsilon''|\Gamma^p|\epsilon'''\epsilon')=\sum_{\nu\tau}[\Gamma^\tau(\epsilon'''\epsilon^\nu\epsilon^\nu\epsilon')+\Gamma^\tau(\epsilon\epsilon^\nu\epsilon^\nu\epsilon'')-2e^{\beta\omega\tau}\Gamma^\tau(\epsilon\epsilon''\epsilon'''\epsilon')], \quad (2.12)$$

$$\Gamma^\tau(\epsilon\epsilon''\epsilon'''\epsilon')=\{(\epsilon|G^\tau|\epsilon'')(\epsilon'''|G^{-\tau}|\epsilon')\}^{-\tau\omega}. \quad (2.13)$$

In the last relation the notation of (2.28) in III is used. The right-hand side of Eq. (2.9) vanishes unless p is equal to ±1, as is evident from the properties of $I^{\pm1}$. It will be shown later that the element $(\epsilon|\chi^p|\epsilon')$, for which $\epsilon-\epsilon'$ nearly vanishes, is particularly important since its magnitude increases considerably as $\epsilon-\epsilon'$ approaches zero. Let us denote the eigenvalues of the operator E_0 in Eq. (1.4) by ϵ_0. ϵ_0 is then related to the eigenvalues ϵ of the operator E_{0S} in Eq. (1.12) by

$$\epsilon=\epsilon_0+m_\epsilon\omega. \quad (2.14)$$

Thus, for two corresponding pairs (ϵ_0,ϵ_0') and (ϵ,ϵ'), the relation

$$\epsilon-\epsilon'=\epsilon_0-\epsilon_0'+(m_\epsilon-m_{\epsilon'})\omega=\epsilon_0-\epsilon_0'+p\omega \quad (2.15)$$

holds, so that for $\epsilon-\epsilon'\approx0$,[13] and $p\neq0$,

$$\omega\approx(\epsilon_0'-\epsilon_0)/p. \quad (2.16)$$

This means that the energy difference $\epsilon_0-\epsilon_0'$ is nearly equal to the energy sum of p equal radiation quanta. One notes that for systems with only one nuclear ingredient the energy splitting of the levels in the rotating frame corresponds to the deviation of the actual energy levels from the nearest value $m\omega$. But since $(J,\Delta_s)\ll\omega$, this is far smaller than the Zeeman splitting itself. Henceforth, a matrix element $(\epsilon|\chi^p|\epsilon')$ for which $\epsilon-\epsilon'\approx0$ and the corresponding Eq. (2.9) will be referred to as the resonance element and resonance equation, respectively.

To be more specific, let us assume that $\epsilon=a$ and $\epsilon'=b$ and that the condition

$$a-b\approx0, \quad (2.17)$$

with $m_a=m+n$, $m_b=m$, is satisfied. Denoting the eigenvalues of E_0 corresponding to a and b by a_0 and b_0, then following Eq. (2.16), the frequency defined by $a-b=0$ satisfies the condition

$$\omega=(b_0-a_0)/n, \quad (2.18)$$

where it is assumed that $n>0$ and $b_0>a_0$. We assume further that for any pair of energy values ϵ, ϵ' of which at least one is different from a or b,

$$\epsilon-\epsilon'\gg|\Gamma|, \quad (2.19)$$

where $|\Gamma|$ is of the order of the natural line width.[14] The condition (2.19) expresses an assumption, stated in the introduction, that the frequency difference between a specific multiple-quantum transition frequency and any other single- or multiple-quantum transition frequency is much larger than the natural line width and is amply satisfied in many actual cases. In the special case of $n=1$ it is permissible, in view of (2.19), to neglect all nondiagonal matrix elements except the resonance one. The ordinary single-quantum transition signal is then obtained by solving for the resonance element and its complex conjugate, as was done in Sec. 3 of II. For cases with $n>1$ the set of Eqs. (2.9) becomes more difficult to solve. Nevertheless, a considerable simplification leading to an approximate solution may be carried out if one uses the properties and relative magnitudes of the operators in (2.9).

For instance, considering the coefficients of the different nondiagonal matrix elements in Eq. (2.9), one notes that since for nonresonance elements $(\epsilon''|\chi^p|\epsilon''')$, the energy values ϵ'' and ϵ''' satisfy the relation $|\epsilon''-\epsilon'''|\gg|\Gamma|$ there is a considerable disparity with regard to the relative magnitude of terms of the form $(\epsilon\epsilon''|\Gamma^p|\epsilon'''\epsilon')(\epsilon''|\chi^p|\epsilon''')$, as compared with the term $(aa|\Gamma^n|bb)$ in the resonance equation or the terms $(\epsilon\epsilon'|\Gamma^p|\epsilon'\epsilon)$ in the equations for the matrix elements of χ^0. In fact, one can prove that neglecting all the terms in $(\epsilon|\Gamma(\chi^p)|\epsilon')$, except the ones just mentioned, involves an error of the order of magnitude of $|\Gamma/\Delta|^2$, where $|\Delta|$ denotes the order of magnitude of the nonresonance energy differences $\epsilon-\epsilon'$. This may be verified if one notes that in any of the nonresonance Eqs. (2.9), the coefficient of the main matrix element of χ^p is roughly $|\Delta|+i|\Gamma|$. The coefficients of all the other matrix elements of χ^p in the same equation are $i|\Gamma|$. It is possible to solve these equations for the unknown matrix elements of χ^p in terms of the elements of χ^{p+1} and χ^{p-1} that appear in them, if then χ^p, χ^{p+1} and χ^{p-1} symbolically stand for their corresponding matrix elements, and if $|\Delta|$, $|\Gamma|$, and $|\mathfrak{D}|$ represent symbolically the actual quantities with the corresponding orders of magnitude, one can prove that the solution of these equations has the form:

$$\chi^p=|\mathfrak{D}/\Delta|[1+O(|\Gamma/\Delta|^2)](\chi^{p+1}+\chi^{p-1}).$$

If this result is substituted back into the original equations, it is seen that an error of the order of $|\Gamma/\Delta|^2$ is made in neglecting the terms with coefficients $|\Gamma|$.

An error of the same order of magnitude is made in neglecting the nondiagonal matrix elements of χ^0. This can be shown in a manner similar to that used for the preceding case.

A further simplification of Eqs. (2.9), which is permissible in the light of subsequent results, can be carried out if one assumes that

$$|\mathfrak{D}/\Delta|\ll1. \quad (2.20)$$

This justifies the omission of the matrix elements of χ^p and their corresponding equations whenever $p>n+1$.

[13] The relation $\epsilon-\epsilon'\approx0$ here and in the rest of the paper means that the energy interval $\epsilon-\epsilon'$ is comparable to or smaller than the natural line width Γ.

[14] The quantity $|\Gamma|$ in Eq. (2.19) as well as $|\Delta|$ in the following discussion are not to be confused with Γ and Δ in Eq. (1.1). The meaning of the notation implied in the present section is retained throughout the rest of the present work.

The error committed in this omission is of the order of $|\mathfrak{D}/\Delta|^2$. To verify this, one notes that in any finite spin system the superscript of χ^p cannot exceed a certain maximum value M assumed to be different from n. The equation for χ^M has the symbolic form

$$\Delta\chi^M+\mathfrak{D}\chi^{M-1}=0.$$

The equations for the matrix elements of χ^{M-1} have the symbolic form

$$\Delta\chi^{M-1}+\mathfrak{D}\chi^M+\mathfrak{D}\chi^{M-2}=0.$$

Eliminating χ^M from the two sets of equations leads to

$$(\Delta-\mathfrak{D}^2/\Delta)\chi^{M-1}+\mathfrak{D}\chi^{M-2}=0.$$

The same holds for the successive eliminations of χ^{M-1}, χ^{M-2} and so on, down to χ^{n+2}. As a result the equations for the elements of χ^{n+1} take the form

$$\Delta[1+O(|\mathfrak{D}/\Delta|^2)]\chi^{n-1}-\mathfrak{D}\chi^n=0.$$

Hence, retaining the equations with $p>n-1$ amounts to a change of the order of $|\mathfrak{D}/\Delta|^2$ in the coefficient of χ^{n-1}. Similar arguments hold for the omission of matrix elements $(\epsilon|\chi^p|\epsilon')$ with $p\leq n-1$, when the corresponding eigenvalues ϵ_0 and ϵ_0' of E_0 are not included in the interval a_0-b_0.

B. The Explicit Solution

With the simplifying assumptions introduced in the preceding section, and under the condition (2.17) and (2.19), one is led to the following set of equations for the various matrix elements of χ.

$$(\epsilon-\epsilon')(\epsilon|\chi^{n+1}|\epsilon')-\mathfrak{D}(\epsilon|[I^1,\chi^n]|\epsilon')=0, \quad (2.21)$$

$$(\theta'-i\Gamma_{ab})(a|\chi^n|b)-\mathfrak{D}(a|[I^1,\chi^{n-1}]+[I^{-1},\chi^{n+1}]|b)=0, \quad (2.22)$$

$$(\epsilon-\epsilon')(\epsilon|\chi^p|\epsilon')-\mathfrak{D}(\epsilon|[I^1,\chi^{p-1}]+[I^{+1},\chi^{p-1}]|\epsilon')=0, \quad (2.23)$$

for $n>p>1$,

$$(\epsilon-\epsilon')(\epsilon|\chi^1|\epsilon')-\mathfrak{D}(\epsilon|I^1|\epsilon')[\chi^0(\epsilon')-\chi^0(\epsilon)+\sigma_0(\epsilon')-\sigma_0(\epsilon)]-\mathfrak{D}(\epsilon|[I^{-1},\chi^2]|\epsilon')=0, \quad (2.24)$$

$$\textstyle\sum_{\epsilon''}[V(\epsilon'')-V(\epsilon)]/R_{\epsilon\epsilon''}=\mathfrak{D}\ \mathrm{Im}(\epsilon|[I^{-1},\chi^1]|\epsilon), \quad (2.25)$$

$$\theta'=a-b\approx 0, \quad (2.26)$$

$$\Gamma_{ab}=(aa|\Gamma^n|bb), \quad (2.27)$$

$$\chi(\epsilon)=(\epsilon|\chi^0|\epsilon), \quad (2.28)$$

$$V(\epsilon)=\chi(\epsilon)\exp(\beta m_\epsilon\omega), \quad (2.29)$$

$$R_{\epsilon\epsilon''}=\exp(\beta m_\epsilon\omega)/\Gamma^r(\epsilon\epsilon''\epsilon''\epsilon). \quad (2.30)$$

An approximate solution of these equations can be carried out by the following procedure. The value of the matrix elements of χ^{n+1} and χ^{n-1} from Eqs. (2.21) and (2.23), respectively, are substituted in the resonance Eq. (2.22). This leads to

$$(\theta-i\Gamma_{ab})(a|\chi^n|b)-\mathfrak{D}^2\sum_\epsilon\left\{\frac{(a|I^1|\epsilon)(\epsilon|[I^1,\chi^{n-2}]|b)}{\epsilon-b}-\frac{(a|[I^1,\chi^{n-2}]|\epsilon)(\epsilon|I^1|b)}{a-\epsilon}\right\}=0, \quad (2.31)$$

where

$$\theta=\theta'-d, \quad (2.32)$$

$$d=\mathfrak{D}^2\sum_\epsilon{}'\left[\frac{|(a|I^1+I^{-1}|\epsilon)|^2-|(\epsilon|I^1+I^{-1}|b)|^2}{\epsilon-b}\right]. \quad (2.33)$$

The prime on the summation sign in Eq. (2.22) indicates that energy states with m_ϵ equal to m or $m+n$ should be excluded from the summation. Such states have the same magnetic quantum numbers as the states a or b and they do not appear in formula (2.33) unless $n=1$, that is, in single quantum transitions. This exclusion is related to the unique structure of Eq. (2.25) for the matrix elements of χ^0, a uniqueness which in the case of $n=1$, prevents the substitution of the matrix elements of $\chi^{n-1}=\chi^0$ in a way that led to (2.31).

The significance of the last relation, indicating a frequency shift proportional to the square of the rf field amplitude, will be discussed later.

Eliminating the matrix elements of χ^{n-1} between Eqs. (2.23) for $p=n-1$ and $p=n-2$, one is left with relations between matrix elements of χ^{n-2}, χ^{n-3} and the resonance element $(a|\chi^n|b)$. These may be solved for the unknown matrix elements of χ^{n-2} in terms of those of χ^{n-3} and $(a|\chi^n|b)$. The solution is then expanded in powers of $|\mathfrak{D}/\Delta|^2$ retaining only the zeroth order term. The error committed by neglecting all higher powers is of the order of $|\mathfrak{D}/\Delta|^2$ and is small according to (2.20).

The same procedure of elimination and expansion is then repeated successively with the matrix elements of χ^{n-2}, χ^{n-3}, $\cdots$ down to χ^2. The elimination of these matrix elements from the resonance equation introduces higher-order frequency shifts, that are negligible compared with the one given in (2.33).

In any intermediate step, the following set of equations for $n-p>0$ is obtained:

$$(\theta-i\Gamma_{ab})(a|\chi^n|b)-\mathfrak{D}^{p+1}\sum_{\nu=1}^{p+1}\delta_{\alpha\epsilon_1}\delta_{\epsilon_{p+2}b}\sum_{\epsilon_1\cdots\epsilon_{p+2}}(\epsilon_\nu-\epsilon_{\nu+1})$$
$$\times\frac{(\epsilon_1|I^1|\epsilon_2)\cdots(\epsilon_{\nu-1}|I^1|\epsilon_\nu)(\epsilon_\nu|\chi^{n-p}|\epsilon_{\nu+1})(\epsilon_{\nu-1}|I^1|\epsilon_{\nu-2})\cdots(\epsilon_{p+1}|I^1|\epsilon_{p+2})}{(\epsilon_2-b)\cdots\qquad\qquad\cdots(\epsilon_{p+1}-b)}$$
$$=\zeta\mathfrak{D}(a|[I^1,\exp(\beta\omega I^0)+\chi^0]|b)\delta_{n1},\quad(2.34)$$

$$(\epsilon|\chi^{n-p}|\epsilon')-\mathfrak{D}(\epsilon-\epsilon')^{-1}(\epsilon|[I^1,\chi^{n-p-1}]|\epsilon')-\mathfrak{D}^p\sum_{\epsilon_1\cdots\epsilon_{p-2}}$$
$$\times\frac{(\epsilon|I^{-1}|\epsilon_1)\cdots(\epsilon_\nu|I^{-1}|a)(a|\chi^n|b)(b|I^{-1}|\epsilon_{\nu+1})\cdots(\epsilon_{p-2}|I^{-1}|\epsilon')}{(\epsilon-b)(\epsilon_1-b)\cdots(\epsilon_\nu-b)(\epsilon_{\nu-1}-b)\cdots(\epsilon_{p-2}-b)(\epsilon'-b)}=\zeta\frac{\mathfrak{D}(\epsilon|[I^1,\exp(\beta\omega I^0)]|\epsilon')}{\epsilon-\epsilon'}\delta_{n-p,1}.\quad(2.35)$$

The right-hand terms in both equations are self-explanatory and have been incorporated for the case of single-quantum transitions ($n=1$), and for the last stages of reduction $n-p=1$, respectively. The detailed derivation of the remaining parts in these equations is found in Appendix II. For $p=n-1$, Eqs. (2.34) and (2.35) express relations between $(a|\chi^n|b)$ and the matrix elements of χ^1 and χ^0. Let us substitute the values of the matrix elements of χ^1 from Eq. (2.35) ($p=n-1$) into the right-hand side of Eq. (2.25). It can be shown that only the third term on the left side of (2.35) gives a nonzero contribution. Equation (2.25) then assumes the form:

$$\sum_{\epsilon''}\frac{[V(\epsilon'')-V(\epsilon)]}{R_{\epsilon''\epsilon}}=-I\delta_{\epsilon a}=I\delta_{\epsilon b},\quad(2.36)$$

where I stands for

$$I=\mathrm{Im}\{K^*(a|\chi^n|b)\},\quad(2.37)$$

and K is defined as

$$K=\mathfrak{D}^n\sum_{\epsilon_1\cdots\epsilon_{n-1}}\frac{(a|I^1|\epsilon_1)\cdots(\epsilon_{n-1}|I^1|b)}{(\epsilon_1-b)\cdots(\epsilon_{n-1}-b)}.\quad(2.38)$$

In analogy to the discussion presented in Sec. 3 of III, Eqs. (2.36) can be interpreted as a set of relations between the voltages $V(\epsilon)$, the resistances $R_{\epsilon''\epsilon}$, and the current I. In the present case an external emf is applied across the terminals a and b, and a total current I flows from a to b. Following the arguments in Sec. 3 of II, Eqs. (2.36) have a finite solution in spite of the fact that they do not form an independent set.

The solution of these equations has the form

$$\chi(\epsilon'')-\chi(\epsilon)=T_{\epsilon''\epsilon}I=T_{\epsilon''\epsilon}\,\mathrm{Im}\{K^*(a|\chi^n|b)\}.\quad(2.39)$$

The quantities $R_{\epsilon''\epsilon}$ are positive in view of the definitions (2.30) and (2.13), and of the Hermitian character of G. Comparing (2.39) with (2.36), one sees that T_{ab} is positive. Equations (2.35) for the case of $p=n-1$, have the form

$$(\epsilon|\chi^1|\epsilon')-\mathfrak{D}(\epsilon-\epsilon')^{-1}(\epsilon|I^1|\epsilon')[\chi(\epsilon')-\chi(\epsilon)+\sigma_0(\epsilon')-\sigma_0(\epsilon)]$$
$$-\mathfrak{D}^{n-1}\sum_{\epsilon_1\cdots\epsilon_{n-3}}\frac{(\epsilon|I^{-1}|\epsilon_1)\cdots(\epsilon_\nu|I^{-1}|a)(a|\chi^n|b)(b|I^{-1}|\epsilon_{\nu+1})\cdots(\epsilon_{n-3}|I^{-1}|\epsilon')}{(\epsilon-b)(\epsilon_1-b)\cdots(\epsilon_\nu-b)(\epsilon_{\nu-1}-b)\cdots(\epsilon_{n-3}-b)(\epsilon'-b)}=0.\quad(2.40)$$

Eliminating the matrix elements $(\epsilon|\chi^1|\epsilon')$ between Eqs. (2.40) and (2.34) for $p=n-1$, one obtains

$$(\theta-i\Gamma_{ab})(a|\chi^n|b)$$
$$-K[\chi(b)-\chi(a)+\sigma_0(b)-\sigma_0(a)]=0.\quad(2.41)$$

Substituting for $\chi(b)-\chi(a)$ their values from (2.39) that $T_{ab}=-T_{ba}$, one obtains

$$(\theta-i\Gamma_{ab})(a|\chi^n|b)+K[T_{ab}\,\mathrm{Im}\{K^*(a|\chi^n|b)\}$$
$$+\sigma_0(a)-\sigma_0(b)]=0.\quad(2.42)$$

The solution of this equation for the matrix element $(a|\chi^n|b)$ has the form:

$$(a|\chi^n|b)=\frac{[\sigma_0(b)-\sigma_0(a)]K(\theta+i\Gamma_{ab})}{\theta^2+\Gamma_{ab}^2+\Gamma_{ab}T_{ab}|K|^2}.\quad(2.43)$$

Except for the fact that it refers to stationary, rather than to rotating coordinates, Eq. (3.19) of II represents a special case of Eq. (2.42), above, for the particular choice $n=1$. To obtain the signal $\mathcal{S}$, according to Eq. (2.8), one can use the relation (2.3) for $p=1$ to obtain

$$\mathrm{Tr}(I^1\chi^{-1})=\sum_{\epsilon\epsilon'}(\epsilon|I^1|\epsilon')(\epsilon'|\chi^{-1}|\epsilon)$$
$$=\sum_{\epsilon\epsilon'}(\epsilon|I^1|\epsilon')(\epsilon|\chi^1|\epsilon')^*.\quad(2.44)$$

The summation over ϵ and ϵ' covers all the energy states of the spin system. Some of the matrix elements $(\epsilon|\chi^1|\epsilon')$ are related to the matrix element $(a|\chi^n|b)$ by Eq. (2.40); others connect energy states which are outside the interval a_0-b_0 in the nonrotating frame and, therefore, have different relations to $(a|\chi^n|b)$.

It can be shown that the corresponding equation for

the latter type of elements have the form:

$$(\epsilon|\chi^1|\epsilon')-\mathfrak{D}(\epsilon-\epsilon')^{-1}(\epsilon|I^1|\epsilon') \times[\chi(\epsilon')-\chi(\epsilon)-\sigma_0(\epsilon')-\sigma_0(\epsilon)]-B(a|\chi^n|b)=0, \quad (2.45)$$

where the quantity B is smaller than the coefficient of $(a|\chi^n|b)$ in Eq. (2.40) by a factor of $|\mathfrak{D}/\Delta|$ at least. Consequently, when the values of the matrix elements $(\epsilon|\chi^1|\epsilon')$ derived from Eqs. (2.40) and (2.45) are substituted in Eq. (2.44), the contribution of the third term in Eq. (2.45) can be neglected in comparison with that of the corresponding term in Eq. (2.40). When this substitution is carried out and use is made of the relation (2.39), the following expression for the signal is obtained:

$$\mathcal{S}=-iN\hbar\omega\gamma\sum_{\epsilon\epsilon'}\Bigg[\mathfrak{D}\frac{|(\epsilon|I^1|\epsilon')|^2}{\epsilon-\epsilon'} \times\Bigg\{\sigma_0(\epsilon')-\sigma_0(\epsilon)+\frac{|K|^2T_{\epsilon'\epsilon}[\sigma_0(b)-\sigma_0(a)]\Gamma_{ab}}{\theta^2+\Gamma_{ab}{}^2+\Gamma_{ab}T_{ab}|K|^2}\Bigg\} +\frac{n|K|^2(\theta-i\Gamma_{ab})[\zeta(b)-\zeta(a)]}{\mathfrak{D}(\theta^2+\Gamma_{ab}{}^2+\Gamma_{ab}T_{ab}|K|^2)}\Bigg]e^{-i\omega t}. \quad (2.46)$$

Using this result and denoting the two components of $\mathcal{S}$ which are in and out of phase with the driving rf field by $\mathcal{S}_a$ and $\mathcal{S}_d$, respectively, one obtains

$$\mathcal{S}_a=\frac{N\hbar\omega\gamma|K|^2[\sigma_0(a)-\sigma_0(b)]\Gamma_{ab}n}{\mathfrak{D}(\theta^2+\Gamma_{ab}{}^2+\Gamma_{ab}T_{ab}|K|^2)}e^{-i\omega t} \quad (2.47)$$

for the part of the signal which corresponds to the absorption, and

$$\mathcal{S}_d=iN\hbar\omega\gamma\Bigg[\sum_{\epsilon\epsilon'}\frac{\mathfrak{D}|(\epsilon|I^1|\epsilon')|^2}{\epsilon-\epsilon'}\Bigg\{\sigma_0(\epsilon')-\sigma_0(\epsilon) +\frac{\Gamma_{ab}T_{\epsilon'\epsilon}|K|^2[\sigma_0(b)-\sigma_0(a)]n}{\theta^2+\Gamma_{ab}{}^2+\Gamma_{ab}T_{ab}|K|^2}\Bigg\} +\frac{|K|^2[\sigma_0(a)-\sigma_0(b)]n\theta}{\mathfrak{D}(\theta^2+\Gamma_{ab}{}^2+\Gamma_{ab}T_{ab}|K|^2)}\Bigg]e^{-i\omega t} \quad (2.48)$$

for that which corresponds to the dispersion.

DISCUSSION

A. Single-Quantum Transitions ($n=1$)

The general expressions for the n-quantum transition signals given above are also valid for $n=1$. However, upon comparison of these expressions for $p=1$ with the corresponding expression, Eq. (5.4) of II, it is found that there is a slight difference between them. Written in the notation of the present paper, Eq. (5.4) of II has the form

$$\mathcal{S}=\frac{iN\hbar\omega\gamma\mathfrak{D}|(a|I^1|b)|^2|\theta-i\Gamma_{ab}|[\sigma_0(a)-\sigma_0(b)]}{\theta'^2+\Gamma_{ab}{}^2+\Gamma_{ab}T_{ab}\mathfrak{D}^2|(a|I^1|b)|^2}e^{-i\omega t}. \quad (2.49)$$

It follows from the definition (2.26) and the relation (2.18) that θ' measures the deviation of the frequency ω from the single quantum resonance frequency b_0-a_0, whereas θ in Eq. (2.46) includes also the frequency shift d defined in Eq. (2.33). Further, one finds in the dispersion signal in Eq. (2.48) the first term which is absent from the dispersive component of the signal (2.49). This term represents a contribution due to the "tails" of the dispersion components of all other possible single-quantum transitions. The quantity in the curly brackets in this term represents an effective Boltzmann population difference between the levels ϵ and ϵ' and will be discussed in more detail following Eq. (2.60).

It is seen that the absolute magnitude of the original Boltzmann population difference $\sigma_0(\epsilon')-\sigma_0(\epsilon)$ is reduced by an amount proportional to the resonance absorption signal between a and b. The coefficient $T_{\epsilon\epsilon'}$ measures the effectiveness of the relaxation processes to maintain a population difference between the levels ϵ and ϵ', when a resonance transition from a to b takes place. The differences between expressions (2.46) and (2.49) arise because expression (2.49), derived in II, is rigorously valid for systems with only two levels, whereas the frequency shift, as well as the additional term in Eq. (2.48), appears only in systems with more than two levels.

B. Multiple-Quantum Transition Signals with $n>1$

Considering the signal (2.46) as a function of the rf field amplitude, it is instructive to discuss separately two regions. These regions are conveniently specified by the quantity K which is related to the rf field amplitude through the definitions (2.38) and (1.6).

1. *The* m.q.t. *is Unsaturated*

This is expressed by the inequality $\Gamma_{ab}T_{ab}|K|^2\ll\Gamma_{ab}{}^2$, which characterizes the region where the m.q.t. is unsaturated, and the observed line-width is determined by the quantity Γ_{ab}. It should be noted, however, that in spite of the formal similarity of the expressions (2.47) for different values of n, the observed line-width has a different relation to Γ_{ab} for different values of n.

Following Eqs. (2.17), (2.18), and (2.26), the quantity θ in the absorption signal (2.47) satisfies the relation

$$\theta=n\omega-(b_0-a_0)-d. \quad (2.50)$$

The frequency shift d can be neglected in this region

of low rf field, so that

$$\theta \approx n\left(\omega - \frac{b_0 - a_0}{n}\right) = n\Delta\omega, \tag{2.51}$$

where $\Delta\omega$ is the actual deviation of the applied frequency ω from the exact resonance frequency of the multiple transition.

Dividing the numerator and denominator of Eq. (2.47) by n and introducing the notation $\Gamma_{ab}' = \Gamma_{ab}/n$, $T_{ab}^1 = T_{ab}/n$, one obtains the absorption signal:

$$\mathcal{S}_a = \frac{N\hbar\omega\gamma |K|^2 \Gamma_{ab}'[\sigma_0(a) - \sigma(b)]}{\mathfrak{D}(\Delta\omega^2 + (\Gamma_{ab}')^2 + \Gamma_{ab}' T_{ab}' |K|^2)} e^{-i\omega t}. \tag{2.52}$$

The quantity Γ_{ab} which corresponds to $1/T_2$ in Bloch's phenomenological treatment[9] can be considered to have the same order of magnitude for different values of n since the two main contributions to the line-width, i.e., the low-frequency fluctuation of the local magnetic field and the broadening of the energy levels, due to the shortening of their lifetimes by the relaxation, lead to quantities of the same order of magnitude for transitions with different orders of multiplicities n. Consequently, for low-rf fields it follows that the observed reduced line width $\Gamma_{ab}' = \Gamma_{ab}/n$ is roughly n times as narrow as the corresponding line width for $n=1$. This relative narrowness of m.q.t. signals compared with that of single transitions had been realized before and was confirmed experimentally.[4] A second distinction between the absorption signals for different values of n lies in their dependence on the rf field amplitude. Since, according to Eq. (2.38), the quantity K defined in Eq. (2.47) is proportional to the nth power of the rf field amplitude H_1, the observed absorption signal grows as H_1^{2n-1} before saturation begins. These two aspects of m.q.t. signals for $n>1$, i.e., their relative narrowness and their specific dependence on the strength of the rf field, provide the best means of determining experimentally the order of the multiplicity. In fact, the slope of a log-log plot of the signal strength *versus* the rf field amplitude gives the multiplicity n of the transition directly.

2. *Saturation of the* m.q.t.

This is the region where the signal strength and shape are appreciably influenced by the saturation of the transitions. From the experimental point of view the most interesting part of this region is where the signal attains its maximum value. In many cases this is the only region where the signal can be observed at all. The value $\mathfrak{D} = H_1/2$ which corresponds to the maximum signal can be conveniently obtained with the help of symbolic notation. By this, it is meant that the quantities appearing in Eq. (2.52) will be replaced by symbols indicating their corresponding order of magnitude. For instance, $\epsilon - b \sim \Delta$, $K \sim \mathfrak{D}^n \Delta^{1-n}$, $n\Gamma_{ab}' \sim \Gamma$, $nT_{ab}' \sim T$.

For exact resonance ($\Delta\omega = 0$) the symbolic expression for the absorption signal becomes:

$$\mathcal{S}_a \simeq \frac{\mathfrak{D}^{2n-1}\Delta^{2-2n}[\sigma_0(a) - \sigma_0(b)]n}{\Gamma + T\mathfrak{D}^{2n}\Delta^{2-2n}}. \tag{2.53}$$

This expression attains its maximum value when

$$\mathfrak{D} = \mathfrak{D}_M = [(2n-1)\Gamma T^{-1}\Delta^{2n-2}]^{1/2n}. \tag{2.54}$$

For $n=1$, $\mathfrak{D}_M^2 \sim \Gamma T^{-1}$, which is a well-known result for single quantum transitions. Equation (2.54) indicates that $\mathfrak{D}_M$ grows with n and approaches the value Δ for very large values of n. This implies that the higher the multiplicity n of the transition, the stronger the rf field required for attaining the maximum signal. Eventually, for large values of n, the assumption $|\mathfrak{D}/\Delta| \ll 1$ involved in the derivation of Eq. (2.46) will cease to be valid in the interesting region of maximum signal.

In the case of an alcohol molecule, for example, Δ is of the order of 100 cycle/sec and Γ is of the order of 1 cycle-sec.[15] Consequently, $\mathfrak{D}_M$ remains appreciably smaller than Δ only for $n \leq 3$ and, therefore, $n=3$ represents the maximum multiplicity that would usually be detected in such a case. Substituting the values of $\mathfrak{D}_M$ from Eq. (2.54) into Eq. (2.53) leads to

$$\mathcal{S}_{aM} \sim n\Gamma^{-1-1/2n} T^{1/2n-1} \Delta^{(1/n)-1}[\sigma_0(a) - \sigma_0(b)]. \tag{2.55}$$

It is instructive to compare the value of the maximum signal for different values of n. For this purpose one should note that for temperatures ordinarily used in the experiments there is an additional factor of n describing the ratio of the Boltzmann population differences of an n-quantum to a single quantum case. Taking this into account, the ratio r of the maximum signal with $n>1$ to that of a single quantum transition is approximately

$$r \sim n^2 \Gamma^{\frac{1}{2}-1/2n} T^{1/2n-\frac{1}{2}} \Delta^{(1/n)-1}. \tag{2.56}$$

Assuming that $T \sim 1/\Gamma$ as is approximately true in non-viscous liquids, this becomes $r \sim n^2(\Gamma/\Delta)^{1-1/n}$ which for small values of $n>1$ are small compared to unity according to the assumptions (2.19) and the definition of Δ. This indicates that the n-multiple transition signals are weak compared with single transitions. It is sometimes desirable to compare the absorption signal of a multiple transition with the off-resonance value of single-quantum absorption signals at the frequency of the m.q.t. This is particularly important for the understanding of the enhancement technique that will be described in Sec. IV. To do this one has to compare the expression (2.55) for with the off-resonance values of the single transitions obtained from Eq. (2.49). However, the comparison is meaningful only if the single quantum absorption signal is also evaluated with the rf amplitude given in Eq. (2.54).

Thus, the off-resonance value of the single transition

[15] J. Arnold, Phys. Rev. **102**, 136 (1955).

expressed in order-of-magnitude symbols become

$$\mathcal{S}(\text{off-resonance}) \sim \frac{\Gamma[(2n-1)\Gamma T^{-1}\Delta^{2n-2}]^{1/2n}[\sigma(a)-\sigma(b)]}{\Delta^2+\Gamma T[(2n-1)\Gamma T^{-1}\Delta^{2n-2}]^{1/n}}. \quad (2.57)$$

In nonviscous liquids where $\Gamma\sim T^{-1}$, and for not too large values of n, the second term in the denominator can be neglected in comparison with the first. Using this and the ratio of the Boltzmann differences in Eqs. (2.55) and (2.57), the approximate ratio r' of the m.q.t. maximum absorption signal to a "tail" of a single quantum signal becomes

$$r'\sim n^2(\Delta/\Gamma)^{2/n}. \quad (2.58)$$

In spite of the crudeness of this result it shows that with an optimum rf field, the m.q.t. signals are well above the level of the "tails" of the single transitions. But, even in cases where the ratio is not large enough, the narrowness of the m.q.t. signals compared to the flat background of the "tails" will facilitate their detection.

Considering the expression (2.55) for the maximum signal, it is seen that for $n>1$ the signals' strength grows as Δ decreases. This property suggested a method of enhancing m.q.t. signals by an artificial reduction of Δ. The gist of this method which is described in Sec. 4. lies in the fact that it is possible to induce multiple transitions by a radiation field consisting of several different frequencies. The sum of the absorbed frequencies should be equal to the frequency difference of the multiple transition interval. In that case it can be shown that with a proper choice of these frequencies one can reduce the effective value of Δ in Eq. (2.55) and thus enhance the signals' strength.

In the rough calculations of this section, the frequency shift d, defined in Eqs. (2.32) and (2.33) has been neglected. The corresponding shift d' which ought to be incorporated in the reduced Eq. (2.52) is equal to $d^1\sim d/n$ and this is of the order of magnitude of $\mathfrak{D}^2/n\Delta$. Substituting for $\mathfrak{D}$, the value of $\mathfrak{D}_M$ from (2.54), leads to

$$d_M'\sim n^{-1}\Gamma(\Gamma/\Delta)^{(2/n)-1}, \quad (2.59)$$

where, in the last step, T was replaced by Γ^{-1}. For $n=1$, the frequency shift amounts to only a small fraction of the natural line width. For $n=2$, it is comparable to the line width, and for $n=3$, it is larger than the line width.

It should be added that although m.q.t. with different multiplicities n differ in their rf dependence in the vicinity of the signal maximum or below, they all decrease in the same way when the rf amplitude H_1 becomes very large.

The time T_{ab} in Eqs. (2.46), (2.47), and (2.48) has the same physical significance as the relaxation time T_1 in Bloch's phenomenological equation.[16] It measures, according to (2.39), the competence of the relaxation processes to preserve the Boltzmann population differences of the levels a and b against the equalizing action of the rf field. The time $T_{\epsilon\epsilon'}$ measures a similar property with respect to the intermediate levels ϵ and ϵ'. It is important to note, however, that the time $T_{\epsilon\epsilon'}$ for an intermediate interval is different from a quantity with the same form calculated when the interval $\epsilon-\epsilon'$ becomes a resonance interval for another multiple transition. In the terminology of circuit theory and in conformity with Eqs. (2.36) and (2.39), the quantity $T_{\epsilon\epsilon'}$ plays the role of an input impedance when $\epsilon_0-\epsilon_0'$ is a resonance interval and is a transfer impedance when $\epsilon_0-\epsilon_0'$ is an intermediate interval for a second multiple transition.

According to the definitions (1.20), (1.24), and (2.39), and by virtue of the expression (2.43) for $(a|\chi^n|b)$

$$\sigma(\epsilon)-\sigma(\epsilon')=\sigma_0(\epsilon)-\sigma_0(\epsilon') + \frac{T_{\epsilon\epsilon'}|K|^2\Gamma_{ab}[\sigma_0(b)-\sigma_0(a)]}{\theta^2+\Gamma_{ab}{}^2-\Gamma_{ab}T_{ab}|K|^2}. \quad (2.60)$$

This represents the population difference of the levels ϵ and ϵ' as a function of $|K|^2$. $\sigma(\epsilon)$ stands for the diagonal elements of the distribution matrix σ_S. In particular, for saturating rf fields, K satisfies the condition $\Gamma_{ab}T_{ab}|K|^2\gg\Gamma_{ab}{}^2+\theta^2$ from which it follows that for $\epsilon=a$ and $\epsilon'=b$, $\sigma(a)\approx\sigma(b)$. In principle, the Overhauser effect[17] described by Eq. (2.60) can be used to find all the quantities T_a experimentally. This is done by first saturating the n-quantum transition between a and b and then measuring the weak rf transition signals between the levels ϵ and ϵ' where $\epsilon_0-\epsilon'$ is a subinterval of the interval a_0-b_0 in the nonrotating frame. The relative change in strength of these transitions is easily shown to be

$$\left(\frac{\sigma_0(b)-\sigma_0(a)}{\sigma_0(\epsilon)-\sigma_0(\epsilon')}\right)\frac{T_{\epsilon\epsilon'}}{T_{ab}}.$$

In practice, such an experiment may be quite difficult to perform because the detection of a signal change in the subinterval should take place when the saturating radiation between a and b is tuned off. Otherwise, the simultaneous application of radiation fields with two different frequencies enables a new multiple transition to take place, in which quanta with both frequencies are absorbed, and this complicates the interpretation of the proposed experiment. It can be carried out, however, if the various relaxation times are long enough so that the instantaneous population at the end of the saturating period does not change appreciably during the time of switching from one frequency to the other.

[16] F. Bloch, Phys. Rev. **70**, 460 (1946).
[17] A. W. Overhauser, Phys. Rev. **92**, 411 (1953).

3. *Applications to Special Cases*

a. Two nonequivalent nuclei of spins 1/2.—The simplest example for which the general results of the preceding sections apply consists of a system of two nonequivalent nuclei of spin 1/2 in a molecule in liquid solution. For single quantum transitions this system was treated in Sec. 5 of II. One can also find there the energy levels at the Hamiltonian E_0 in (1.4) and the values of the matrix elements of the operators $I^{\mp 1}$ between the different levels. The possible m values for the system are -1, 0, and 1, so that the only possible m.q.t. is a double quantum transition from the levels with $m_a=1$ to that with $m_b=-1$. The corresponding energy levels in the rotating frame are found to be.

$$\begin{aligned} a&=\omega-\tfrac{1}{2}(\omega_s+\omega_t)+\tfrac{1}{4}J, \qquad \epsilon=\tfrac{1}{2}(\delta^2+J^2)^{\frac{1}{2}}-\tfrac{1}{4}J, \\ b&=-\omega+\tfrac{1}{2}(\omega_s+\omega_t)+\tfrac{1}{4}, \quad \epsilon'=-\tfrac{1}{2}(\delta^2+J^2)^{\frac{1}{2}}-\tfrac{1}{4}J, \end{aligned} \tag{3.1}$$

ω_s and ω_t are the resonance frequencies of the two spins considered "uncoupled," and $\delta=\omega_s-\omega_t$ is the chemical shift.

The double quantum resonance occurs when

$$a-b=2\omega-(\omega_s+\omega_t)=0, \tag{3.2}$$

$$\omega=(\omega_s+\omega_t)/2. \tag{3.3}$$

The deviation of this frequency from the corresponding resonance frequencies of the single transitions are then

$$\begin{aligned} a-\epsilon&=b-\epsilon=\tfrac{1}{2}[J+(\delta^2+J^2)^{\frac{1}{2}}], \\ a-\epsilon'&=b-\epsilon'=\tfrac{1}{2}[\delta+(\delta^2+J^2)^{\frac{1}{2}}]. \end{aligned} \tag{3.4}$$

Similarly, from Eq. (5.47) in II,

$$\begin{aligned} (a|I^1|\epsilon)&=(\epsilon|I^1|b)=u^{\frac{1}{2}}+v^{\frac{1}{2}}, \\ (a|I^1|\epsilon')&=(\epsilon'|I^1|b)=u^{\frac{1}{2}}-v^{\frac{1}{2}}, \end{aligned} \tag{3.5}$$

with

$$u=1-v=\tfrac{1}{2}[1-\delta^2(\delta^2+J^2)^{-\frac{1}{2}}]. \tag{3.6}$$

In applying these values to the general expressions (2.46), (2.47), and (2.48), for the m.q.t. signals, it should be noted that the condition (2.19), involved in their derivation, restricts the range of variation of J and δ. In fact, the condition (2.19) is satisfied only if the inequality

$$\delta^2/J\gg\Gamma \tag{3.7}$$

holds. Assuming that this relation is satisfied, one can substitute the values of the differences (3.4) and matrix elements (3.5) into expression (2.38) for K and (2.47) for the absorption signal. One then obtains

$$S_a=\frac{16N\hbar\omega\gamma^4J^2\delta^{-4}H_1^3[\sigma_0(a)-\sigma_0(b)]\Gamma_{ab}}{\theta^2+\Gamma_{ab}^2+4\Gamma_{ab}T_{ab}(\gamma H_1)^4J^2\delta^{-4}}e^{-i\omega t}. \tag{3.8}$$

This signal vanishes for $J=0$ as expected, since then the two spins behave as two independent systems.

It follows from (3.4), for values of δ/J small compared to unity, but still consistent with the inequality (3.7), that $a-\epsilon'\gg a-\epsilon$. Furthermore, $|(a|I^1|\epsilon)|\gg|(a|I^1|\epsilon')|$, which implies that only the level ϵ contributes appreciably to the quantity K in Eq. (3.8). Thus, the simplest possible system for double quantum transitions, consisting of essentially three levels only, is realized. This system was treated theoretically by Meiboom and Kaplan.[2] It is to be noted, however, that δ cannot be too small if the relation (3.7) is to remain valid.

TABLE I. The resonance frequencies and relative intensities of double quantum transitions involving simultaneous spin flips of the methyl and the methylene groups.

Initial state								
I_A	I_B	M_A	M_B	Frequency[a]	Degeneracy	Relative intensity	Grouping of unresolved lines	
3/2	1	−3/2	−1	$\frac{1}{2}(\omega_A+\omega_B)-\frac{3}{4}J+\rho$	1	3	3	α_1
3/2	1	−3/2	0	$\frac{1}{2}(\omega_A+\omega_B)-\frac{1}{4}J+\rho$	1	3		
3/2	1	−1/2	−1	$\frac{1}{2}(\omega_A+\omega_B)-\frac{1}{4}J+2\rho$	1	4	9	α_2
1/2	1	−1/2	−1	$\frac{1}{2}(\omega_A+\omega_B)-\frac{1}{4}J-\rho$	2	2		
3/2	1	1/2	−1	$\frac{1}{2}(\omega_A+\omega_B)+\frac{1}{4}J+\rho$	1	3		
3/2	1	−1/2	0	$\frac{1}{2}(\omega_A+\omega_B)+\frac{1}{4}J+2\rho$	1	4	9	α_3
1/2	1	−1/2	0	$\frac{1}{2}(\omega_A+\omega_B)+\frac{1}{4}J-\rho$	2	2		
3/2	1	1/2	0	$\frac{1}{2}(\omega_A+\omega_B)+\frac{3}{4}J+\rho$	1	3	3	α_4

[a] $\rho=J^2/[4(\omega_B-\omega_A)]$.

The quantity Γ_{ab} in (3.9) can be evaluated, assuming a specific relaxation process. This was done for the case where the relaxation is due to a fluctuating magnetic field at the nuclear sites. This field is assumed to act incoherently on the two spins. The result of the calculation is

$$\Gamma_{ab}=\tfrac{1}{2}(1/T_{2s}+1/T_{2t}), \tag{3.9}$$

where T_{2s} and T_{2t} represent the transverse relaxation times of the two spins considered as independent of each other. Unlike the ordinary single-quantum transitions in the same system, no contribution from the longitudinal relaxation times T_{1s} and T_{1t} appears in the expression for the width of the double-quantum signal.

b. Double-quantum transitions in impure ethyl alcohol.—The observation of double quantum transitions in this molecule was reported by Kaplan and Meiboom.[2] In this case the ratio of J/δ reported by Arnold[15] is of the order of 0.1, so that to a good approximation the total spin wave function may be considered as a product to the individual spin functions of each of the chemically identical groups in the molecule. The only clear multiple-quantum transitions that have been observed thus far are those involving simultaneous changes in the magnetic quantum numbers of the methyl and methylene groups. The frequencies associated with these transitions are calculated to the second order in J/δ from formulas given by Anderson.[18]

$$\begin{aligned} \omega&=\frac{1}{2\hbar}[E(m_A,m_B)-E(m_A+1,m_B+1)] \\ &=\tfrac{1}{2}(\omega_A+\omega_B)+\tfrac{1}{2}(m_A+m_B+1)J+[J^2/4(\omega_B-\omega_A)] \\ &\quad\times\{m_A-m_B-[I_B(I_B+1)-(m_B+1)^2] \\ &\qquad -[I_A(I_A+1)-(m_A+1)^2]\}, \end{aligned} \tag{3.10}$$

[18] W. Anderson, Phys. Rev. **102**, 151 (1955).

where I_A, m_A, and I_B, m_B refer to the spin variables of the methyl and methylene groups, respectively, and where $J=J_{AB}$. The frequencies of all possible transitions are given in Table I. Thus, eight different signals may appear. Actually, only four signals have been observed and these correspond to the four different frequencies in the first-order approximation designated by α_1, α_2, α_3, and α_4 in Table I. The intensity ratio expected for the different transitions can be calculated with the help of expression (2.47) for the absorption component of the signals. This calculation is based on the assumption that the natural line-widths Γ_{ab} are equal for all the transitions in Table I. Expanding the expressions for the intensities in powers of the ratio J/δ and neglecting powers higher than the first, one obtains the results in the last column of Table I for the relative intensities of the different lines. Actually, since the second-order contribution to the energy splitting is not resolved experimentally, the intensities of the observed four lines which are resolved should be compared with the calculated intensities of the lines with the same energy in first order. The calculated intensity ratios are 1:3:3:1.[19]

4. *Enhancement of the Double-Quantum Transitions by Audiomodulating the Amplitude of the rf Field*

It was mentioned previously that a possible method of enhancing a multiple-transition signal is based on the use of an appropriate multiple-frequency field. This is illustrated in the case of a double-quantum transition when the multifrequency field is generated by audiomodulating a monochromatic rf field. It is well known that an rf field with frequency ω which is amplitude-modulated by an audio-frequency is equivalent to a superposition of three monochromatic fields with frequencies ω and $\omega\pm\omega_a$. This particular combination is found to be suitable for enhancing m.q.t. signals of the kind described in the preceding sections where the deviations of the energy intervals from a strictly equally-spaced Zeeman pattern are small, amounting to several hundred cycles per second at most. The interaction energy of the radiation field with the spin system has the form

$$E_1=-(\mathfrak{D}_0 I^1 e^{i\omega t}+\mathfrak{D}_0{}^* I^{-1}e^{-i\omega t}) -2\cos\omega_0 t(\mathfrak{D}_1 I^1 e^{i\omega t}+\mathfrak{D}_1{}^* I^{-1}e^{-i\omega t}), \quad (4.1)$$

or, in a shorter notation,

$$E_1=-\sum_{\mu=-1,0,1}(\mathfrak{D}_\mu e^{i(\omega+\mu\omega_a)t}I^1+\mathfrak{D}_\mu{}^* e^{-i(\omega+\mu\omega_a)t}I^{-1}), \quad (4.2)$$

where

$$\mathfrak{D}_\mu=\mathfrak{D}_{-\mu}{}^*=\tfrac{1}{2}\gamma H_\mu\exp(i\varphi_\mu), \quad (4.3)$$

and $H_1e^{\pm i\varphi_1}$ and $H_0e^{i\varphi_0}$ are the complex amplitudes of the rf fields with frequencies $\omega\pm\omega_a$ and ω, respectively.

[19] This result is different from that obtained by Meiboom and Kaplan[2] on a basis of counting the possible three level combinations giving rise to a specific double-quantum line. Their result is 1:4:4:1 for the same ratios.

Using the properties of $I^{\pm1}$ described in Eq. (1.18), one can transform E_1 into a rotating frame by applying the transformation

$$S_0=\exp(-i\omega I^0 t). \quad (4.4)$$

This leads to

$$E_{1S}=S_0E_1S_0{}^{-1} =-\sum_{\mu=0,\pm1}(\mathfrak{D}_\mu e^{i\mu\omega_a t}I^1+\mathfrak{D}_\mu{}^* e^{-i\mu\omega_a t}I^{-1}). \quad (4.5)$$

Unlike the case of a single rf frequency, the rf field in the present case has components that are time dependent even in the rotating frame. Consequently, the stationary solutions of the Boltzmann equations in the rotating frame contains non-negligible time-dependent constituents. Anticipating the form of this dependence, we assume that the part of the density matrix χ, defined in Eq. (1.24) has the following form.

$$\chi=\sum_p\sum_{\mu=-p}^{p}\chi_\mu{}^p e^{i\mu\omega_a t}. \quad (4.6)$$

Thus, each of the χ^p defined in (2.1) is split into $2\mu+1$ components $\chi_\mu{}^p e^{i\mu\omega_a t}$. The meaning of the index p implied in the definition (2.1) is retained, and the range of variation of the running index μ $(p\geqslant\mu\geqslant-p)$ is related to the maximum number of quanta of frequency $\omega\pm\omega_a$ or ω that can be associated with a p-multiple quantum transition.

From the Hermiticity of χ one infers that

$$(\epsilon|\chi_\mu{}^p|\epsilon'|{}^*=(\epsilon'|\chi_{-\mu}{}^{-p}|\epsilon). \quad (4.7)$$

Following the procedure involved in the derivation of Eq. (2.9), with E_{1S} of (4.5), and χ of (4.6) and replacing the corresponding quantities defined in Eqs. (1.13) and (2.1), respectively, one arrives at

$$\begin{aligned}&(\mu\omega_a+\epsilon-\epsilon')(\epsilon|\chi_\mu{}^p|\epsilon')\\ &-\textstyle\sum_\nu\{\mathfrak{D}_{\mu-\nu}(\epsilon|[I^1,\chi_\nu{}^{p-1}]|\epsilon')\\ &-\mathfrak{D}_{\nu-\mu}{}^*(\epsilon|[I^{-1},\chi_\nu{}^{p+1}]|\epsilon')\}+(\epsilon|\Gamma(\chi_\mu{}^p)|\epsilon')\\ &=[\mathfrak{D}_\mu(\epsilon|I^1|\epsilon')-\mathfrak{D}_{-\mu}{}^*(\epsilon|I^{-1}|\epsilon')]\\ &\qquad\times[\sigma_0(\epsilon')-\sigma_0(\epsilon)]. \quad (4.8)\end{aligned}$$

The resonance character of a matrix element $(\epsilon|\chi_\mu{}^p|\epsilon')$ is determined by the vanishing of $(\mu\omega_a+\epsilon-\epsilon')$. Following relation (2.14), this can be expressed in terms of the applied frequency ω and the corresponding energy levels ϵ_0 and $\epsilon_0{}'$ in the nonrotating frame by the relation

$$\mu\omega_a+\epsilon-\epsilon'=\mu\omega_a+\epsilon_0-\epsilon_0{}'+(m_\epsilon-m_{\epsilon'})\omega=0. \quad (4.9)$$

Hence, for any two energy levels ϵ and ϵ' with $m_\epsilon-m_{\epsilon'}=p\neq0$ there exist $2p+1$ different resonance frequencies ω, determined by the $2p+1$ values of μ.

Physically, the various resonance frequencies are related to the different possible combinations of p quanta with frequencies ω and $\omega\pm\omega_a$, where the sum of frequencies is equal to $\epsilon_0{}'-\epsilon_0$. Although an rf field of the form (4.1) can be used to enhance any n-multiple

transition, it does not represent the best choice of multifrequency field for $n>2$. We therefore illustrate the method of enhancing in the case of double quantum transition for which the radiation field defined in (4.2), is particularly effective.

Solution of the Boltzmann Equations for Double Quantum Transitions

Let us specify again $a-b$ as the resonance interval with $m_b=m$, and $m_a=m+2$. Condition (4.9) for the resonance assumes the form:

$$\mu\omega_a+2\omega+(a_0-b_0)=0, \tag{4.10}$$

where a_0 and b_0 are again the energy levels corresponding to a and b in the nonrotating frame. μ in Eq. (4.10) can assume the values ±2, ±1, and 0. The values -2 and 2 are not interesting, since they represent absorptions of two *equal* quanta with frequencies $\omega-\omega_a$ and $\omega+\omega_a$, respectively, and the expressions for the signals involve only the amplitude of the specific frequency which is being absorbed. Such transitions have already been treated in the preceding sections and have nothing to do with the enhancement technique. In each of the other three possibilities, a simultaneous absorption of two unequal quanta takes place. Let us consider the case of $\mu=0$; a similar treatment applies to the cases of $\mu=\pm1$.

Following the assumption (2.19) for the single-frequency multiple transitions, it is also assumed here that any pair of values ϵ and ϵ', of which at least one is different from a or b, satisfy the inequality

$$|(\mu\omega_a+\epsilon-\epsilon')|\gg|\Gamma| \tag{4.11}$$

for any value of $|\mu|<|m_\epsilon-m_{\epsilon'}|$. The Boltzmann equations (4.8) for this specific case assume the form

$$(\mu\omega_a+\epsilon-\epsilon')(\epsilon|\chi_\mu{}^3|\epsilon')-\mathfrak{D}_\mu(\epsilon|[I^1,\chi_0{}^2]|\epsilon')=0, \tag{4.12}$$

$$(\theta'-i\Gamma_{ab})(a|\chi_0{}^2|b)-\sum_{\mu=-1}^{1}\{\mathfrak{D}_\mu(a|[I^1,\chi_{-\mu}{}^1]|b)+\mathfrak{D}_\mu{}^*(a|[I^{-1}\chi_\mu{}^3]|b)\}=0, \tag{4.13}$$

$$(\mu\omega_a+\epsilon-\epsilon')(\epsilon|\chi_\mu{}^1|\epsilon')-\mathfrak{D}_\mu(\epsilon|I^1|\epsilon')[\chi^0(\epsilon')-\chi^0(\epsilon)+\sigma_0(\epsilon')-\sigma(\epsilon)]-\mathfrak{D}_{-\mu}{}^*(\epsilon|[I^{-1}\chi_0{}^2]|\epsilon')=0, \tag{4.14}$$

$$\sum_{\epsilon''}[V(\epsilon'')-V(\epsilon)]\Gamma_{\epsilon''\epsilon}=\mathrm{Im}\{\textstyle\sum_\mu \mathfrak{D}_\mu{}^*(\epsilon|[I^{-1},\chi_\mu{}^1]|\epsilon). \tag{4.15}$$

Here, the same notation has been used as in Eqs. (2.21) to (2.30). The solution of these equations is carried out in Appendix III. To obtain the expression for the signal from this solution, one first has to substitute Eq. (4.6) into Eq. (2.8). This leads to

$$\mathcal{S}=-N\hbar\gamma\frac{d}{dt}\{\sum_{\mu=-1}^{1}\mathrm{Tr}(I^1\chi_\mu{}^{-1})e^{-i(\omega-\mu\omega_a)t}\}. \tag{4.16}$$

But, according to the relations (4.7)

$$\mathrm{Tr}(I^1\chi_\mu{}^{-1})=\sum_{\epsilon\epsilon'}(\epsilon|I^1|\epsilon')(\epsilon'|\chi_\mu{}^{-1}|\epsilon)=\sum_{\epsilon\epsilon'}(\epsilon|I^1|\epsilon')(\epsilon|\chi_{-\mu}{}^1|\epsilon')^*. \tag{4.17}$$

Substituting for the matrix elements $(\epsilon|\chi_{-\mu}{}^1|\epsilon')$ their value derived from Eq. (4.14) and using the results of Eqs. (6) and (8) of Appendix III, one arrives at

$$\mathcal{S}=-i\hbar N\gamma\sum_\mu\Bigg\{\sum_{\epsilon\epsilon'}\frac{\mathfrak{D}_\mu{}^*(\omega+\mu\omega_a)|(\epsilon|I^1(\epsilon')|^2}{\mu\omega_a+\epsilon-\epsilon'}\Bigg[\sigma_0(\epsilon')-\sigma_0(\epsilon)+\frac{T_{\epsilon\epsilon'}|K|^2\Gamma_{ab}[\sigma_0(b)-\sigma_0(a)]}{\theta^2+\Gamma_{ab}+\Gamma_{ab}T_{ab}|K|^2}\Bigg]+\sum_\epsilon\mathfrak{D}_{-\mu}\frac{2(\omega+\mu\omega_a)(\epsilon-b)(a|I^1|\epsilon)(\epsilon|I^1|b)[\sigma_0(b)-\sigma_0(a)]K^*(\theta-i\Gamma_{ab})}{[(\epsilon-b)^2-(\mu\omega_a)^2][\theta^2+\Gamma_{ab}{}^2+\Gamma_{ab}T_{ab}|K|^2]}\Bigg\}e^{-i(\omega+\mu\omega_a)t}, \tag{4.18}$$

where K has now the form

$$K=\sum_{\mu=0,1}\sum_\epsilon\frac{2|\mathfrak{D}_\mu|^2(a|I^1|\epsilon)(\epsilon|I^1|b)(\epsilon-b)}{(\epsilon-b)^2-(\mu\omega_a)^2}.$$

The absorption components of this signal can be divided into three parts

$$\mathcal{S}_a=\mathcal{S}_{-1}+\mathcal{S}_0+\mathcal{S}_1,$$

where

$$\mathcal{S}_{-1}=\sum_\epsilon 2\mathfrak{D}_1(\omega-\omega_a)\frac{(a|I^1|\epsilon)(\epsilon|I^1|b)(\epsilon-b)}{(\epsilon-b)^2-\omega_a{}^2}R\times e^{-i(\omega-\omega_a)t}, \tag{4.19}$$

$$\mathcal{S}_0=\sum_\epsilon 2\mathfrak{D}_0\omega\frac{(a|I^1|\epsilon)(\epsilon|I^1|b)}{\epsilon-b}Re^{-i\omega t}, \tag{4.20}$$

$$\mathcal{S}_1=\sum_\epsilon 2\mathfrak{D}_{-1}(\omega+\omega_a)\frac{(a|I^1|\epsilon)(\epsilon|I^1|b)(\epsilon-b)}{(\epsilon-b)^2-\omega_a{}^2}R\times e^{-i(\omega+\omega_a)t}, \tag{4.21}$$

and

$$R=\frac{[\sigma_0(a)-\sigma_0(b)]K^*\Gamma_{ab}}{\theta^2+\Gamma_{ab}{}^2+\Gamma_{ab}T_{ab}|K|^2}. \tag{4.22}$$

It is interesting to note that each of the three signals depends on the amplitude of the fields in the other two frequencies. In each of the expressions for $\mathcal{S}_{-1}$, $\mathcal{S}_0$, and

$\mathcal{S}_1$ there are terms with a denominator $(\epsilon-b)^2-\omega_a^2$. The increase in the magnitude of these terms as the frequency ω_a approaches the interval $\epsilon-b$ explains the principle of the enhancement method. In fact, following the arguments involved in the derivation of expression (2.55) for the maximum of the multiple transition signals, it can be shown that the maximum value of the signals $\mathcal{S}_{-1}$ and $\mathcal{S}_1$ increases as $|\epsilon-b-\omega_a|^{-\frac{1}{2}}$, which plays the role of $\Delta^{-\frac{1}{2}}$ in the double quantum signals described in Eq. (2.55). Evidently, the derivation of the expression (4.19), (4.20), and (4.21) was based on the assumption (4.11) which does not permit the difference $|\epsilon-b-\mu\omega_a|$ to become too small. This restriction implies more than a mere computational convenience, since in the excluded region of $|\epsilon-b-\mu\omega_a|\sim\Gamma$ single-quantum transitions induced by the frequencies $\omega+\omega_a$, would become more important and thus complicate the interpretation of the observed results. Unfortunately, it can be shown that the contribution of the pure double quantum transition to the signal, considered as a function of the modulation frequency ω_a does not attain any extremum for values of ω_a satisfying the condition $|\epsilon-b-\omega_a|>\Gamma$. This contribution is the part of the signal that is proportional to the third power of the rf field amplitude for low amplitudes. Consequently, it is advisable in performing the enhancement process, to confirm at certain stages whether the signal still possesses the main features of a double-quantum transition. The behavior of the signals when the sideband frequencies $\omega\pm\omega_a$ coincides with the resonance frequencies of some single-quantum transitions will be treated in a forthcoming paper.

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APPENDIX I

Referring to Eq. (2.53) and (2.3) in III, the quantities in (1.9) are defined as

$$G_-{}^{p,q}=SG^{p,q}S^{-1}, \tag{1}$$

where S satisfies

$$dS/dt=iSE. \tag{2}$$

The operator G is a function of the operators $I_s{}^0$, $I_s{}^{\pm1}$ and can be decomposed into

$$G=\sum_\tau G^\tau, \tag{3}$$

where each of the G^τ has nonvanishing matrix elements $(\epsilon|G^\tau|\epsilon')$ only between spin states with $m-m'=\tau$, m being the eigenvalue of I^0. The transformation S imposed on $G_-{}^{p,q}$ a time variation with frequencies which are mainly determined by the dominant part $-\omega I^0$ in E. Consequently, it is convenient to assume that

$$S=S_1S_0, \tag{4}$$

$$S_0=\exp(-iI^0\omega t), \tag{5}$$

where S_1 is a relatively slowly varying operator. This may be verified by substituting the expression for S in (4) and (5) into Eq. (2), with the result

$$\left(\frac{dS_1}{dt}-iS_1\omega I^0\right)\exp(-iI^0\omega t)=iS_1E\exp(-iI^0\omega t). \tag{6}$$

Multiplying on the right by $S_0{}^{-1}$ and noting that E_0 commutes with I^0, one arrives at

$$dS_1/dt=iS_1[\omega I^0+E_0+S_0E_1S_0{}^{-1}]. \tag{7}$$

It can further be shown that

$$S_0I^{\pm1}S_0{}^{-1}=e^{\mp i\omega t} \tag{8}$$

by taking the time derivative of the left-hand side and using the commutation relations $[I^0,I^{\pm1}]=\pm I^{\pm1}$. Equation (7) can thus be rewritten in a form

$$dS_1/dt=iS_1E_0, \tag{9}$$

with

$$E_S=\sum_s\Delta_sI_s{}^0+\sum_{s<t}(\mathbf{I}_s\cdot\mathbf{I}_t)-\mathfrak{D}(I^1+I^{-1}). \tag{10}$$

Considering now that $(J,\mathfrak{D},\Delta_s)\ll\omega$, it is seen that (11)

$$E_S\ll E_0. \tag{12}$$

Let now

$$S_1G^\tau S_1{}^{-1}=\sum_\lambda G_\lambda{}^\tau\exp(i\omega_{\tau\lambda}t), \tag{13}$$

where the operators $G_\lambda{}^\tau$ are time independent. This leads to

$$SGS^{-1}=\sum_{\tau,\lambda}G_\lambda{}^\tau\exp[i(-\tau\omega+\omega_{\tau\lambda})t], \tag{14}$$

$$\omega_{\tau\lambda}\ll(\omega,\beta^{-1},\omega^*), \tag{15}$$

from (11) and Eq. (2.41) in III.

By characterizing any of the indices p or q with a double-symbol (τ,λ), the frequencies $\omega_{p,q}$ of Eq. (1.9) appear in the form

$$\omega_p=\omega_{\tau,\lambda}=-\tau\omega+\omega_{\tau\lambda}, \tag{16}$$

$$SGS^{-1}=\sum_p e^{i\omega_pt}G^p=\sum_{\tau,\lambda}G_\lambda{}^\tau\exp[i(-\tau\omega+\omega_{\tau\lambda})t]. \tag{17}$$

Introducing this expression into (1.9) and neglecting all high-frequency terms in conformity with the assumption $|E_0|\gg\Gamma$, one arrives at

$$\begin{aligned}\Gamma(\sigma)=\pi\sum_{\tau\lambda\mu}&\exp[i(\omega_{\tau\lambda}+\omega_{-\tau\mu})t]\\&\times[e^{\beta\tau\omega}\{G_{\lambda-}{}^\tau\sigma G_{\mu-}{}^{-\tau}\}^{-\tau\omega}-\sigma\{G_{\lambda-}{}^\tau G_{\mu-}{}^{-\tau}\}^{-\tau\omega}\\&+e^{\beta\tau\omega}\{G_{\lambda-}{}^\tau\sigma G_{\mu-}{}^{-\tau}\}^{-\tau\omega}-\{G_{\lambda-}{}^\tau G_{\mu-}{}^{-\tau}\}^{-\tau\omega}\sigma].\end{aligned} \tag{18}$$

In the last expression the quantity $\beta\omega_{\tau\lambda}$, which according to (15) is small compared with $\beta\omega$, has been neglected and the approximation

$$\{G_{\lambda-}{}^\tau OG_{\mu-}{}^{-\tau}\}^{-\tau\omega}\approx\{G_{\lambda-}{}^\tau OG_{\mu-}{}^{-\tau}\}^{-\tau\omega+\omega\tau\lambda}$$

is based on Eq. (2.46) of III and on the relation (15).

But

$$\sum_\lambda \exp(i\omega_{\tau\lambda}t)G_{\lambda-}{}^{\tau}=S^{-1}S_1G^{\tau}S_1^{-1}S=e^{i\tau\omega t}G^{\tau},$$

and similarly

$$\sum_\mu \exp(i\omega_{-\tau\mu}t)G_{\mu-}{}^{-\tau}=S_0^{-1}G^{-\tau}S_0=e^{-i\tau\omega t}G^{-\tau}.$$

Consequently,

$$\Gamma(\sigma)\approx\pi\sum_\tau[2e^{\beta\tau\omega}\{G^{\tau}\sigma G^{-\tau}\}^{-\tau\omega} -\sigma\{G^{\tau}G^{-\tau}\}^{-\tau\omega}-\{G^{\tau}G^{-\tau}\}^{-\tau\omega}\sigma]. \quad (19)$$

With this simplified form, it is convenient to apply the transformation $S_0=\exp(-iI^0\omega t)$ to Eq. (1.2). Making use of the fact that

$$S_0G^{\tau}S_0^{-1}\sigma_S S_0G^{-\tau}S_0^{-1}=G^{\tau}\sigma_S G^{-\tau}, \quad (20)$$

which results from relations (12), one obtains

$$d\sigma_S/dt+i[E_S,\sigma_S]=\pi\sum_\tau[2e^{\beta\tau\omega}\{G^{\tau}\sigma_S G^{-\tau}\}^{-\tau\omega} -\sigma_S\{G^{\tau}G^{-\tau}\}^{-\tau\omega}-(G^{\tau}G^{-\tau}\}^{-\tau\omega}\sigma_S]=\Gamma(\sigma_S) \quad (21)$$

in agreement with Eqs. (1.9) and (1.14) of the text.

APPENDIX II

A. Proof of Equations (2.35)

The relation (2.35) is true for $p=1$, as is evident by comparison with Eq. (2.23) for $p=n-1$.

Assuming that Eqs. (2.35) are true for all matrix elements of χ^{n-p+1}, one can show that they hold also for the matrix elements of χ^{n-p}.

Consider the relation

$$(\epsilon|\chi^{n-p}|\epsilon')=\frac{\mathfrak{D}}{\epsilon-\epsilon'}(\epsilon|[I^1,\chi^{n-p-1}]|\epsilon') +\frac{\mathfrak{D}}{\epsilon-\epsilon'}(\epsilon|[I^{-1},\chi^{n-p+1}]|\epsilon'),$$

which hold for $n-p>1$.

Introducing for the matrix elements of χ^{n-p+1} their value given by Eq. (2.35), one finds

$$\begin{aligned}(\epsilon|\chi^{n-p}|\epsilon')&=\frac{\mathfrak{D}}{\epsilon-\epsilon'}(\epsilon|[I^1,\chi^{n-p-1}](\epsilon')\\ &+\frac{\mathfrak{D}^p}{\epsilon-\epsilon'}\sum_{\epsilon_1\cdots\epsilon_\nu\epsilon_{\nu+1}\cdots\epsilon_p}(\epsilon|I^{-1}|\epsilon)\cdots\\ &\times(\epsilon_\nu|I^{-1}|a)(a|\chi^n|b)(b|I^{-1}|\epsilon_{\nu-1})\cdots\\ &\times(\epsilon_{p-2}|I^{-1}|\epsilon')\left[\frac{1}{(\epsilon_1-b)\cdots(\epsilon_{p-2}-b)(\epsilon'-b)}\right.\\ &\left.-\frac{1}{(\epsilon-b)(\epsilon_1-b)\cdots(\epsilon_{p-2}-b)}\right].\end{aligned}$$

In arriving at this result, the fact that $a\approx b$ has been used, and corrections of the order of magnitude of $|\mathfrak{D}/\Delta|^2$ have been neglected. Combining the two terms in the square brackets, one obtains

$$(\epsilon|\chi^{n-p}|\epsilon')=\frac{\mathfrak{D}(\epsilon|[I^1,\chi^{n-p-1}]|\epsilon')}{\epsilon-\epsilon'}-\mathfrak{D}^p\sum_{\epsilon_1\cdots\epsilon_{p-2}}\frac{(\epsilon|I^{-1}|\epsilon_1)\cdots(\epsilon_\nu|I^{-1}|a)(a|\chi^n|b)(b|I^{-1}|\epsilon_{\nu+1})\cdots(\epsilon_{p-2}|I^{-1}|\epsilon')}{(\epsilon-b)(\epsilon_1-b)\cdots(\epsilon_\nu-b)(\epsilon_{\nu+1}-b)\cdots(\epsilon_{p-2}-b)(\epsilon'-b)}=0.$$

This proves Eq. (2.35) for $n-p>1$. The additional term on the right-hand side in the case of $n-p=1$ is a consequence of the specific form of Eq. (2.24) for the matrix elements of χ^1.

B. Proof of Equation (2.34)

A similar procedure of mathematical induction leads to the proof of relation (2.34).

It can be easily verified that the equation is true for the case of $p=1$. Assuming that the relation (2.34) holds for a certain value $p=p'-1$, we show that it holds also for $p=p'$. Indeed, replacing in Eq. (2.34), p by $p-1$ and with $n-p+1>1$, one has

$$(\theta-i\Gamma_{ab})(a|\chi^n|b)=\mathfrak{D}^p\sum_{\nu=1}^{p}\delta_{a\epsilon_1}\delta_{\epsilon_{p+1}b}\sum_{\epsilon_1\cdots\epsilon_{p+1}}(\epsilon_\nu-\epsilon_{\nu+1}) \times\frac{(\epsilon_1|I^1|\epsilon_2)\cdots(\epsilon_{\nu-1}|I^1|\epsilon_\nu)(\epsilon_\nu|\chi^{n-p+1}|\epsilon_{\nu+1})(\epsilon_{\nu+1}|I^1|\epsilon_{\nu+2})\cdots(\epsilon_p|I^1|\epsilon_{p+1})}{(\epsilon_2-b)\cdots(\epsilon_p-b)}. \quad (1)$$

The quantity $(\epsilon_\nu|\chi^{n-p+1}|\epsilon_{\nu+1})$ can be replaced, according to the preceding section by

$$[\mathfrak{D}/(\epsilon_\nu-\epsilon_{\nu+1})](\epsilon_\nu|[I^1,\chi^{n-p}]|\epsilon_{\nu+1})+A(a|\chi^n|b),$$

where A is of the order of magnitude of $(\mathfrak{D}/\Delta)^{p-1}$. Substituting this expression in (1) one can see that the term $A(a|\chi^n|b)$ introduces a frequency shift which for $p=1$ was already incorporated in θ and for higher values of p

is negligibly small. Omitting this term and expressing $(\epsilon_\nu|[I^1,\chi^{n-p}]|\epsilon_{\nu+1})$ explicitly, one obtains

$$(\theta-i\Gamma_{ab})(a|\chi^n|b)=\mathfrak{D}^{p+1}\sum_{\nu=1}^{p+1}\delta_{a\epsilon_1}\delta_{\epsilon_{p+2}b}\sum_{\epsilon_1\cdots\epsilon_{p+2}}$$

$$\times\frac{(\epsilon_1|I^1|\epsilon_2)\cdots(\epsilon_{\nu-1}|I^1|\epsilon_\nu)[(\epsilon_\nu|I^1|\epsilon_{\nu+1})(\epsilon_{\nu+1}|\chi^{n-p}|\epsilon_{\nu+2})-(\epsilon_\nu|\chi^{n-p}|\epsilon_{\nu+1})(\epsilon_{\nu+1}|I^1|\epsilon_{\nu+2})]\times(\epsilon_{\nu+2}|I^1|\epsilon_{\nu+3})\cdots(\epsilon_{p+1}|I^1|\epsilon_{p+2})}{(\epsilon_2-b)\cdots(\epsilon_\nu-b)(\epsilon_{\nu+2}-b)\cdots(\epsilon_{p+1}-b)}.$$

The right-hand side can also be written in the form:

$$\mathfrak{D}^{p+1}\Bigg[\sum_{\nu=2}^{p+1}\delta_{a\epsilon_1}\delta_{\epsilon_{p+2}b}\sum_{\epsilon_1\cdots\epsilon_{p+2}}\frac{(\epsilon_1|I^1|\epsilon_2)\cdots(\epsilon_{\nu-1}|I^1|\epsilon_\nu)(\epsilon_\nu|\chi^{n-p}|\epsilon_{\nu+1})(\epsilon_{\nu+1}|I^1|\epsilon_{\nu+2})\cdots(\epsilon_{\nu+1}|I^1|\epsilon_{p+2})}{(\epsilon_2-b)\cdots(\epsilon_{\nu-1}-b)(\epsilon_{\nu+1}-b)\cdots(\epsilon_{p+1}-b)}$$

$$-\sum_{\nu=1}^{p+1}\delta_{a\epsilon_1}\delta_{\epsilon_{p+2}b}\sum_{\epsilon_1\cdots\epsilon_{p+2}}\frac{(\epsilon_1|I^1|\epsilon_2)\cdots(\epsilon_{\nu-1}|I^1|\epsilon_\nu)(\epsilon_\nu|\chi^{n-p}|\epsilon_{\nu+1})(\epsilon_{\nu+1}|I^1|\epsilon_{\nu+2})\cdots(\epsilon_{p+1}|I^1|\epsilon_{p+2})}{(\epsilon_2-b)\cdots(\epsilon_\nu-b)(\epsilon_{\nu+2}-b)\cdots(\epsilon_{p+1}-b)}\Bigg],$$

which if combined leads to

$$(\theta-i\Gamma_{ab})(a|\chi^n|b)-\mathfrak{D}^{p+1}\sum_{\nu=1}^{p+1}\delta_{a\epsilon_1}\delta_{\epsilon_{p+2}b}\sum_{\epsilon_1\cdots\epsilon_{p+2}}(\epsilon_\nu-\epsilon_{\nu+1})$$

$$\times\frac{(\epsilon_1|I^1|\epsilon_2)\cdots(\epsilon_{\nu-1}|I^1|\epsilon_\nu)(\epsilon_\nu|\chi^{n-p}|\epsilon_{\nu+1})(\epsilon_{\nu+1}|I^1|\epsilon_{\nu+2})\cdots(\epsilon_{p+1}|I^1|\epsilon_{p+2})}{(\epsilon_2-b)\cdots(\epsilon_{p+1}-b)}=0,$$

with the asserted form of Eq. (2.34) for $n>1$.

APPENDIX III

In order to solve Eqs. (4.12) and (4.15) one eliminates first the matrix elements of χ_μ^3 and χ_μ^1 between Eqs. (4.12), (4.14) and (4.13). Equation (4.13) becomes

$$(\theta-i\Gamma_{ab})(a|\chi_0^2|b)-K[\chi(b)-\chi(a)+\sigma_0(b)-\sigma_0(a)]=0, \tag{1}$$

with

$$\theta=\theta'-\sum_\epsilon\sum_{\mu=0,1}\frac{2\mathfrak{D}_\mu\mathfrak{D}_\mu^*[|(a|I^1+I^{-1}|\epsilon)|^2-|(\epsilon|I^1+I^{-1}|b)|^2]}{(\epsilon-b)^2-(\mu\omega_a)^2}, \tag{2}$$

and

$$K=\sum_{\mu=0,1}\sum_\epsilon\frac{2|\mathfrak{D}_\mu|^2(a|I^1|\epsilon)(\epsilon|I^1|b)(\epsilon-b)}{(\epsilon-b)^2-(\mu\omega_a)^2}. \tag{3}$$

The second term on the right-hand side of Eq. (2) describes a frequency shift. It is assumed that this shift is always small compared to the line width Γ_{ab}. In deriving expressions (2) and (3), the relation (4.3) has been used.

Elimination of the matrix elements of χ_μ^1 between (4.14) and (4.15) leads to

$$\sum_{\epsilon''}[V(\epsilon'')-V(\epsilon)]/R_{\epsilon''\epsilon}=-I\delta_{\epsilon a}=I\delta_{\epsilon b}, \tag{4}$$

where I stands for

$$I=\mathrm{Im}\{K^*(a|\chi_0^2|b)\}. \tag{5}$$

Again, we assume that Eqs. (4.15) have a solution

$$\chi(\epsilon'')-\chi(\epsilon)=T_{\epsilon''\epsilon}I=T_{\epsilon''\epsilon}\,\mathrm{Im}\{K^*(a|\chi_0^2|b)\}. \tag{6}$$

Substituting this result in Eq. (1) leads to

$$(\theta-i\Gamma_{ab})(a|\chi_0^2|b)+K[T_{ab}\,\mathrm{Im}\{K^*(a|\chi^n|b)\}+\sigma_0(a)-\sigma_0(b)]=0, \tag{7}$$

and its solution is

$$(a|\chi_0^2|b)=\frac{[\sigma_0(b)-\sigma_0(a)]K(\theta+i\Gamma_{ab})}{\theta^2+\Gamma_{ab}{}^2+\Gamma_{ab}T_{ab}|K|^2}. \tag{8}$$

This result is used in Eq. (4.18) of the text.