EESTI NSV TEADUSTE AKADEEMIA TOIMETISED. XVI KÖIDE
FÜÜSIKA * MATEMAATIKA. 1967, NR. 4

ИЗВЕСТИЯ АКАДЕМИИ НАУК ЭСТОНСКОЙ ССР. ТОМ XVI
ФИЗИКА * МАТЕМАТИКА. 1967, № 4

V. SINIVEE

THEORY OF NUCLEAR MAGNETIC TRIPLE RESONANCE SPECTRA IN THE CASE OF WEAK RADIO-FREQUENCY FIELDS. I

Signals observable at frequencies different from the frequencies of the external magnetic field are well known in the high resolution NMR spectroscopy. The modulation of the static magnetic field [1–3] or of the frequency of a strong rotating magnetic field [4, 5] gives rise to those signals. Another type of signals caused by strong *rf* fields is predicted by Bloch [6] and indicated by Anders and Baldeschwieler [7]. In general, the steady state solution of the density matrix equation describing the multiresonance experiment includes terms altering in time with frequencies that are combinations of the frequencies of external magnetic fields. Thus, the question of observable signals at these frequencies arises. A previous investigation of the double resonance problem [8] has shown that two weak *rf* fields are, in general, insufficient to cause signals at combined frequencies with an appreciable value. It is the special purpose of this work to show that signals at combined frequencies must exist in the case of triple resonance. In order to do that, the theory of triple resonance spectra is presented.

The following presumptions are assumed to be fulfilled below. 1) The system of nuclear spins of the representative molecule (the spin system) consists of identical spins with a positive magnetogyric ratio γ. 2) The time-independent part of the Hamiltonian of the spin system has no degenerate eigenvalues and equal differences of eigenvalues. 3) The three *rf* fields and the relaxation may be considered as weak [6].

1. Steady-state Equations for Triple Resonance

Definitions

Signals observed in a nuclear magnetic resonance experiment can be calculated on the basis of classical electrodynamics if the time dependence of the nuclear magnetic polarization vector

$$\vec{M} = \mathrm{Tr}(\sigma \vec{\mathbf{M}}) \tag{1.1}$$

of the liquid under investigation is known. The operator of the nuclear magnetic polarization vector $\vec{\mathbf{M}}$ of a solution with N molecules of actual interest per unit volume is given by

$$\vec{\mathbf{M}} = N\gamma\hbar\vec{\mathbf{F}}, \tag{1.2}$$

where $\hbar\vec{\mathbf{F}}$ denotes the summary spin of the spin system. The calculation of $\vec{M}$ requires, therefore, a knowledge of the density matrix

$$\sigma(t) = \sigma_0 + \chi(t); \quad \mathrm{Tr}\sigma = 1 \tag{1.3}$$

describing the average behaviour of a statistical ensemble of identical spin systems interacting with external magnetic field

$$\vec{H} = H_0\vec{k} + \vec{i}\sum_{\lambda=1}^{3} 2H_\lambda \cos\omega_\lambda t \tag{1.4}$$

and with molecular surroundings. If the ensemble placed in a static magnetic field H_0 is in thermal equilibrium, the density matrix σ_0 can be calculated on the basis of the equilibrium statistical mechanics [9]. At a not very low temperature T the Boltzmann distribution is given by

$$\sigma_0 = \mathbf{1} - q\mathbf{H}_0; \quad q = \frac{\hbar}{ZkT}. \tag{1.5}$$

In this investigation it is assumed that the time-independent part of the Hamiltonian of the spin system

$$\hbar\mathbf{H}_0 = -\hbar\sum_j \omega_j \mathbf{I}_z^j + \hbar\sum_{j<k} J_{jk}(\vec{\mathbf{I}}^j \cdot \vec{\mathbf{I}}^k), \tag{1.6}$$

has Z nondegenerate eigenstates given by the equation

$$\mathbf{H}_0 \mid p> = p \mid p>. \tag{1.7}$$

We further assume that equal differences of eigenvalues p do not exist.

In the presence of radio-frequency magnetic fields (1.4) the ensemble does not remain in thermal equilibrium and the density matrix (1.3) is time-dependent. Equations describing the time-dependence of the density matrix (1.3) in the case of an isotropic and nonviscous liquid are given by many authors [6,10–15]. In our case where $H_0 \gg H_\lambda$ and the *rf* fields H_λ and the relaxation are assumed to be weak [6], these equations take the simpler form

$$\frac{d\chi}{dt} + i[\mathbf{H}_0 + \mathbf{H}(t), \chi] = \Gamma(\chi) + iq[\mathbf{H}(t), \mathbf{H}_0]. \tag{1.8}$$

In the equation (1.8) the interaction of the spin system with *rf* fields is given by

$$\hbar\mathbf{H}(t) = \hbar\sum_{\lambda=1}^{3} \mathbf{D}_{+\lambda} e^{i\omega_\lambda t} + \mathbf{D}_{-\lambda} e^{-i\omega_\lambda t}, \tag{1.9}$$

where

$$\mathbf{D}_{\pm\lambda} = -\frac{1}{2}\gamma H_\lambda \mathbf{F}_\pm; \quad \mathbf{F}_\pm = \mathbf{F}_x \pm i\mathbf{F}_y. \tag{1.10}$$

The interaction of the spin system with molecular surroundings is taken into account by the relaxational term $\Gamma(\chi)$. In the representation defined by the equation (1.7), the relaxational term in the Redfield notation [11]

$$<p \mid \Gamma(\chi) \mid r> = \sum_s \sum_t R_{prst} <s \mid \chi \mid t> \tag{1.11}$$

contains only terms satisfying the relation $r-p=t-s$. This is the consequence of the weak *rf* fields and weak relaxation conditions

$$|(r-p)-(t-s)| \gg \gamma H_\lambda, R_{prst}. \tag{1.12}$$

In particular, in the case of a nondegenerate spin system

$$-<p|\Gamma(\chi)|r>=\frac{1}{T_{pr2}}=\sum_s \frac{1}{2}(W_{ps}+W_{rs})-J_{pprr}(0), \tag{1.13}$$

$$<p|\Gamma(\chi)|p>=\sum_s W_{ps}\{<s|\chi|s>-<p|\chi|p>\}, \tag{1.14}$$

where the relaxation coefficients are given by

$$W_{ps}=R_{ppss}=J_{psps}(p-s), \tag{1.15}$$

$$J_{psps}(\omega)=\int_{-\infty}^{+\infty}<<p|\mathbf{G}(t)|s><p|\mathbf{G}(t-\tau)|s>^*>e^{i\omega\tau}d\tau.$$

In the equation (1.15) it is assumed that the molecular surroundings are described classically and their interaction with the spin system is given by the stationary stochastic operator $\mathbf{G}(t)$.

It is useful to transform the equation (1.8) into a frame rotating with angular frequency $-\omega_1\vec{k}$. Then any operator $\mathbf{L}$ will transform according to the equation

$$\tilde{\mathbf{L}}=\mathbf{TLT}^{-1};\ \mathbf{T}=e^{-i\omega_1\mathbf{F}_z t}. \tag{1.16}$$

Considering the equation (1.8) as a matrix equation given in the representation (1.7), one obtains from (1.8) by transformation (1.6) the equation

$$\frac{d\tilde{\chi}}{dt}+i[\mathbf{H}_0+\omega_1\mathbf{F}_z+\tilde{\mathbf{H}}(t),\tilde{\chi}]=\Gamma(\tilde{\chi})+iq[\tilde{\mathbf{H}}(t),\mathbf{H}_0], \tag{1.17}$$

where the notations

$$\tilde{\mathbf{H}}(t)=\sum_{\lambda=1}^{3}\mathbf{D}_{+\lambda}e^{i\Omega_\lambda t}+\mathbf{D}_{-\lambda}e^{-i\Omega_\lambda t},$$

$$\Omega_\lambda=\omega_\lambda-\omega_1, \tag{1.18}$$

have been used.

On the Steady-state Solution

The steady-state solution of the equation (1.17) can be obtained in the form of a double trigonometric series

$$\tilde{\chi}(t)=\sum_n\sum_m\tilde{\chi}_{nm}e^{i(n\Omega_2+m\Omega_3)t}. \tag{1.19}$$

In the further treatment the time-independent matrix $\tilde{\chi}_{nm}$ is referred to as the *nm*-th harmonic of the deviation matrix $\tilde{\chi}(t)$.

Since $\tilde{\chi}(t)$ is Hermitian

$$<r|\tilde{\chi}_{-n,-m}|p>=<p|\tilde{\chi}_{nm}|r>^*. \tag{1.20}$$

The normalisation condition is satisfied if $\mathrm{Tr}(\tilde{\chi}_{nm})=0$.

Inserting (1.19) into the equation (1.17) one obtains a set of coupled algebraic equations

$$i[\mathbf{H}_0+\omega_1\mathbf{F}_z,\tilde{\chi}_{nm}]+i(n\Omega_2+m\Omega_3)\tilde{\chi}_{nm}+$$
$$+i\sum_{\lambda=1}^{3}\{[\mathbf{D}_{+\lambda},\tilde{\chi}_{n'm'}]+[\mathbf{D}_{-\lambda},\tilde{\chi}_{n''m''}]\}=\Gamma(\tilde{\chi}_{nm})+iq\sum_{\lambda=1}^{3}\delta_{n'0}\delta_{m'0}[\mathbf{D}_{+\lambda},\mathbf{H}_0]+ \tag{1.21}$$
$$+iq\sum_{\lambda=1}^{3}\delta_{n''0}\delta_{m''0}[\mathbf{D}_{-\lambda},\mathbf{H}_0].$$

In order to make the equation (1.21) more compact the following convention of indices has been used

$$\begin{array}{llll} n'=n''=n, & m'=m''=m, & & \text{if } \lambda=1;\\ n'=n-1, & n''=n+1, & m'=m''=m, & \text{if } \lambda=2;\\ n'=n''=n, & m'=m-1, & m''=m+1, & \text{if } \lambda=3. \end{array}$$

As further shown the resonance property expressed by first two terms of equation (1.21) enables to greatly simplify this system of equations. As the conditions (1.12) are being fulfilled, the series (1.19) converges rapidly and only some harmonics will have matrix elements with appreciable value. Then in a first approximation one obtains from (1.21) a finite set of equations determining matrix elements of the harmonics as a function of the parameters characterizing spin system and molecular surroundings and of ω_λ, H_λ.

Inserting (1.19) into (1.1) one obtains the following expression for the y-component of the nuclear magnetic polarization vector

$$M_y(t)=-\sum_n\sum_m v_{nm}\cos(\omega_1+n\Omega_2+m\Omega_3)t+$$
$$+u_{nm}\sin(\omega_1+n\Omega_2+m\Omega_3)t, \tag{1.22}$$

where

$$\mathbf{M}_-=\mathbf{M}_x-i\mathbf{M}_y,$$
$$v_{nm}=\sum_{p<r}\sum\mathrm{Im}\{<p|\tilde{\chi}_{nm}|r><r|\mathbf{M}_-|p|>\}, \tag{1.23}$$
$$u_{nm}=\sum_{p<r}\sum\mathrm{Re}\{<p|\tilde{\chi}_{nm}|r><r|\mathbf{M}_-|p>\}.$$

Since the nuclear magnetic resonance signal induced in the receiver coil is proportional to $-\frac{dM_y}{dt}$ [16], the expressions of v_{nm} and u_{nm} represent absorption and dispersion signals detected by a lock-in detector at frequency $\omega_1+n\Omega_2+m\Omega_3$. Usually signals at one of the frequencies ω_λ are observed. According to (1.23) only the harmonics $\tilde{\chi}_{00}$, $\tilde{\chi}_{10}$, $\tilde{\chi}_{01}$ will contribute to those signals. It is then the special purpose of this work to determine conditions of existence of harmonics $\tilde{\chi}_{nm}$ contributing to signals at frequencies different from ω_λ. In order to do this, let us first write down the equation (1.21) in matrix elements.

Equations of Diagonal Matrix Elements

Using the formula (1.14) and taking into account the fact that $\mathbf{F}_z$ commutes with $\mathbf{H}_0$ one obtains from (1.21) in the case of a diagonal element

$$\sum_s W_{ps}\{<s|\tilde{\chi}_{nm}|s>-<p|\tilde{\chi}_{nm}|p>\}=i(n\Omega_2+ \\ +m\Omega_3)<p|\tilde{\chi}_{nm}|p>+i\sum_{\lambda=1}^{3}<p|[\mathbf{D}_{+\lambda},\tilde{\chi}_{n'm'}]|p>+ \\ +<p|[\mathbf{D}_{-\lambda},\tilde{\chi}_{n''m''}]|p>. \tag{1.24}$$

It is seen from equation (1.24) : if

$$\Omega_2, \Omega_3 \gg W_{ps}, \gamma H_\lambda \tag{1.25}$$

only the harmonic $\tilde{\chi}_{00}$ will have diagonal elements of appreciable value. Neglecting further diagonal elements of other harmonics, the abbreviation

$$<p|\tilde{\chi}_{00}|p>=\chi_p \tag{1.26}$$

will be used below. In the case of elements (1.26) the equations (1.24) can now be written in the form

$$\sum_s W_{ps}(\chi_s-\chi_p)=\sum_{\lambda=1}^{3}\{\sum_{r>p} I_\lambda^{pr}-\sum_{r<p} I_\lambda^{rp}\}, \tag{1.27}$$

where

$$I_1^{pr}=2\,\mathrm{Im}\{<p|\tilde{\chi}_{00}|r><r|\mathbf{D}_{-1}|p>\}, \\ I_2^{pr}=2\,\mathrm{Im}\{<p|\tilde{\chi}_{10}|r><r|\mathbf{D}_{-2}|p>\}, \\ I_3^{pr}=2\,\mathrm{Im}\{<p|\tilde{\chi}_{01}|r><r|\mathbf{D}_{-3}|p>\}, \tag{1.28}$$

and use has been made of the relation (1.20).

The equations (1.27) can be represented in a more convenient form by introducing the following row-vectors

$$\vec{\chi}=\{\chi_a, \chi_b, \dots\}$$

$$\vec{W}_p=\{W_{pa}, W_{pb}, \dots\};\ W_{pp}=-\sum_{s\neq p} W_{ps}. \tag{1.29}$$

With these notations the equations (1.27) are given by

$$\vec{W}_p\cdot\vec{\chi}=\sum_{\lambda=1}^{3}\{\sum_{r>p} I_\lambda^{pr}-\sum_{r<p} I_\lambda^{rp}\}. \tag{1.30}$$

To this equation the normalisation condition

$$\sum_s \chi_s=0 \tag{1.31}$$

is to be added.

Let now the row-vector $\vec{\chi}_\lambda^{pr}$ denote the solution of the system of equations

$$\begin{aligned}
&\vec{W}_p \cdot \vec{\chi}_\lambda^{pr} = I_\lambda^{pr} \\
&\vec{W}_r \cdot \vec{\chi}_\lambda^{pr} = -I_\lambda^{pr} \\
&\vec{W}_s \cdot \vec{\chi}_\lambda^{pr} = 0, \text{ if } s \neq p, r \\
&\sum_s \chi_{\lambda s}^{pr} = 0.
\end{aligned} \tag{1.32}$$

One can then be convinced that the solution of equations (1.30), (1.31) is given by the superposition

$$\vec{\chi} = \sum_{\lambda=1}^{3} \sum_{p<r} \sum \vec{\chi}_\lambda^{pr}. \tag{1.33}$$

The system of $Z+1$ equations (1.32) is in fact a system of equations of diagonal elements that is received by considering the monoresonance problem [6]. Bloch has shown [6] that the solution of equations (1.32) can be expressed as

$$\vec{\chi}_\lambda^{pr} = I_\lambda^{pr} \vec{T}^{pr}, \tag{1.34}$$

where the row-vector

$$\vec{T}^{pr} = \{T_a^{pr}, T_b^{pr}, \dots\} \tag{1.35}$$

is the solution of equations

$$\begin{aligned}
&\vec{W}_p \cdot \vec{T}^{pr} = 1, \\
&\vec{W}_r \cdot \vec{T}^{pr} = -1, \\
&\vec{W}_s \cdot \vec{T}^{pr} = 0, \text{ if } s \neq p, r \\
&\sum_s T_s^{pr} = 0.
\end{aligned} \tag{1.36}$$

The components of the row-vector (1.35) depend, therefore, upon the values of relaxation coefficients (1.15) and upon the position of the transition pr on the energy level diagram, but they do not depend upon ω_λ, H_λ.

Inserting now (1.34) into (1.33) one obtains

$$\vec{\chi} = \sum_{\lambda=1}^{3} \sum_{p<r} \sum I_\lambda^{pr} \vec{T}^{pr}. \tag{1.37}$$

It follows from (1.29) and (1.37) that

$$\chi_p - \chi_r = \sum_{s<t} \sum \sum_{\lambda=1}^{3} I_\lambda^{st} T_{pr1}^{st}, \tag{1.38}$$

where

$$T_{pr1}^{st} = T_p^{st} - T_r^{st}. \tag{1.39}$$

The population differences are, thus, given by

$$P_{pr} = q(r-p) + (\chi_p - \chi_r) = q(r-p) + \sum_{s<t} \sum \sum_{\lambda=1}^{3} I_\lambda^{st} \; T_{pr1}^{st}. \tag{1.40}$$

Inserting (1.40) into (1.21) one obtains a system of equations consisting only of the off-diagonal elements of the harmonics (in particular of those appearing in the signal formula (1.23)). The quantities (1.39) can be calculated by solving the system of equations (1.36) with the use of direct current electrical analogue [6] or analytically as in [17].

Equations of Off-diagonal Matrix Elements

To bring out the importance of the selection rules of the matrix elements of the operators $\mathbf{D}_{\pm\lambda}$ in the representation (1.7), we introduce a new upper index denoting the order of off-diagonal elements

$$< p \mid \tilde{\chi}_{nm} \mid r > = < p \mid \tilde{\chi}_{nm}^{(k)} \mid r >, \text{ if } M_p - M_r = k, \tag{1.41}$$

and M_p denotes the eigenvalue of the operator $\mathbf{F}_z$ in the state $\mid p >$. With the notation (1.41) the relation (1.20) is now to be written in the form

$$< r \mid \tilde{\chi}_{-n,-m}^{(-k)} \mid p > = < p \mid \tilde{\chi}_{nm}^{(k)} \mid r >^*. \tag{1.42}$$

It is further to be noted, that only the matrix elements of the order $k = 1$ are included in the equations (1.23), (1.28).

By taking into account the above-mentioned selection rules, one concludes that the following formula holds

$$< p \mid [\mathbf{D}_{\pm\lambda}, \tilde{\chi}_{nm}] \mid r > = < p \mid [\mathbf{D}_{\pm\lambda}, \tilde{\chi}_{nm}^{(k \mp 1)}] \mid r > \tag{1.43}$$

if $M_p - M_r = k$.

In the case of $k = \pm 1$ and $n = m = 0$, the expression (1.43) includes also diagonal elements (1.26). These elements will be excluded and further it is to be understood that expressions like (1.43) do not contain diagonal elements.

With the use of these conventions the equation (1.21) in the case of an off-diagonal element is given by

$$\Delta_{pr} < p \mid \tilde{\chi}_{nm}^{(k)} \mid r > + i \sum_{\lambda=1}^{3} < p \mid [\mathbf{D}_{+\lambda}, \tilde{\chi}_{n'm'}^{(k-1)}] \mid r > +$$

$$+ i \sum_{\lambda=1}^{3} < p \mid [\mathbf{D}_{-\lambda}, \tilde{\chi}_{n''m''}^{(k+1)}] \mid r > = \tag{1.44}$$

$$= i \sum_{\lambda=1}^{3} \{ \delta_{k1} \delta_{n'0} \delta_{m'0} < p \mid \mathbf{D}_{+\lambda} \mid r > + \delta_{k,-1} \delta_{n''0} \delta_{m''0} < p \mid \mathbf{D}_{-\lambda} \mid r > \} P_{pr},$$

where

$$\Delta_{pr} = \frac{1}{T_{pr2}} + i(p - r + k\omega_1 + n\Omega_2 + m\Omega_3). \tag{1.45}$$

The system of equations (1.44), (1.40) forms the basis for the further discussion of the triple resonance spectra.

2. Weak *rf* Field and Weak Relaxation Approximation

The Resonance Property

Below the equation (1.44) will be referred to as the equation of the matrix element $<p|\tilde{\chi}^{(k)}_{nm}|r>$. This matrix element is termed to be in resonance if

$$|\Delta\omega| = |(k\omega_1 + n\Omega_2 + m\Omega_3) - (r-p)| \lesssim \frac{1}{T_{pr2}}. \tag{2.1}$$

If $<p|\tilde{\chi}^{(k)}_{nm}|r>$ is in resonance, the conjugate element will also be in resonance. The matrix element $<p|\tilde{\chi}^{(k)}_{nm}|r>$ (and the corresponding conjugate element) is termed to be off-resonance if

$$|\Delta\omega| \gg \frac{1}{T_{pr2}}, \gamma H_\lambda. \tag{2.2}$$

Dividing the equation (1.44) by the term (1.45) one can represent (1.44) in the form

$$x_1 + \varepsilon a_{12}x_2 + \varepsilon a_{13}x_3 + \ldots = \varepsilon b_1 q\omega_0, \tag{2.3}$$

where $x_1, x_2 \ldots$ denote the off-diagonal elements of the harmonics, and

$$\varepsilon = \frac{\gamma H_\lambda T_{pr2}}{\sqrt{1+(\Delta\omega T_{pr2})^2}}. \tag{2.4}$$

The parameter ε expresses the order of magnitude of the absolute value of terms as $\frac{|<p|\mathbf{D}_{+\lambda}|s>|}{\Delta_{pr}}$. The terms $a_{12}, a_{13} \ldots$ consist of matrix elements of the type $<p|\mathbf{F}_+|s>$ and of phase factors. The term $q\omega_0 \approx |q(r-p)|$ (ω_0 denotes the Larmor frequency) has its origin in (1.40) and determines the order of magnitude of the absolute value of elements of $\tilde{\chi}(t)$.

The function $\varepsilon(\Delta\omega)$ has a sharp maximum at exact resonance ($\Delta\omega = 0$). If the matrix element x_1 in (2.3) is off-resonance, it follows from (2.4), (2.2) that

$$\varepsilon \approx \frac{\gamma H_\lambda}{\Delta\omega} \ll 1. \tag{2.5}$$

In this case ε may be considered as a small parameter and in the first approximation $x_1 = 0$. If, on the other hand, the matrix element x_1 is in resonance, $\varepsilon \approx \gamma H_\lambda T_{pr2} \gtrsim 1$ and in the first approximation $x_1 \neq 0$.

The conditions (1.12) enable us (at fixed frequencies ω_λ) to distribute all off-diagonal elements of the matrix $\tilde{\chi}(t)$ to those being in resonance and to those being off-resonance. In the above-mentioned first approximation the system (1.44) includes only the matrix elements being simultaneously in resonance.

In the case of the equation of the harmonic $\tilde{\chi}^{(1)}_{00}$, $\tilde{\chi}^{(1)}_{10}$ or $\tilde{\chi}^{(1)}_{01}$ the right hand side of (1.44) includes terms with off-diagonal elements. These matrix elements are to be included in the left-hand side of the equation (2.3). As a consequence of this the quantity T_{pr2} in (2.4) and in (2.2) is to be replaced by an effective quantity

$$T^{*}_{pr2} = \frac{T_{pr2}}{1 + |<p|\mathbf{D}_{+\lambda}|r>|^2 T^{pr}_{rp1} T_{pr2}}. \tag{2.6}$$

Thus, the width of the resonance region will increase by increasing the *rf* field strength. Nevertheless, the weak *rf* field strength condition (1.12) enables to neglect the off-resonance matrix elements if in addition to (1.12)

$$\gamma H_\lambda |\gamma H_\lambda T^{st}_{rp1}| \ll |(r-p)-(t-s)|. \tag{2.7}$$

Further it will be shown: if the matrix element $<s|\tilde{\chi}^{(l)}_{ij}|t>$ occurs in the equation of the matrix element $<p|\tilde{\chi}^{(k)}_{nm}|r>$ then the later matrix element occurs also in the equation of the former matrix element. Both matrix elements and their equations are referred to as being coupled. Thus, the system of equations (1.44) in the above-mentioned first approximation (in the weak *rf* field and weak relaxation approximation) consists of equations of matrix elements being simultaneously in resonance.

The system of equations can, in general, fall into subsystems of coupled equations. In order to have a nontrivial solution, the subsystem must have an absolute term. Thus, at least the equation of one of the matrix elements of the harmonics $\tilde{\chi}^{(1)}_{00}$, $\tilde{\chi}^{(1)}_{10}$ or $\tilde{\chi}^{(1)}_{01}$ must be in the composition of the subsystem. To construct the subsystem one can start from the equation of one of those matrix elements. Further, all the matrix elements being in resonance and being contained in this initial equation, are to be determined. Forming the equations of all these matrix elements, a part of the subsystem is constructed. If in this part new matrix elements occur, the equations of these elements are to be set up, etc.

In order to make this procedure more rational, it is important to know the coupling rules of the matrix elements. It is seen from (1.40) that all the matrix elements of the harmonics $\tilde{\chi}^{(1)}_{00}$, $\tilde{\chi}^{(1)}_{10}$, $\tilde{\chi}^{(1)}_{01}$ are coupled. Another type of coupling (direct coupling) is based on the terms of the type (1.43) in the equations (1.44).

Direct Coupling Rules

It is seen from (1.44) that the equation of the matrix element $<p|\tilde{\chi}^{(k)}_{nm}|r>$ contains the matrix element $<s|\tilde{\chi}^{(l)}_{ij}|t>$ only in the case if the following conditions are fulfilled:

A. $p = s$ or $r = t$ (a common energy level);

B. $l = k-1$ or $l = k+1$;

C. if $l = k-1$, then $i = n'$ and $j = m'$;
if $l = k+1$, then $i = n''$ and $j = m''$.

In order to represent these rules in graphical form, let us express any matrix element $<p|\tilde{\chi}^{(k)}_{nm}|r>$ in form of an arrow on the energy level diagram directed from p to r. An analogous arrow can be used to represent the matrix element $<s|\mathbf{D}_{+\lambda}|t>$.

This method of graphical representation of coupling rules is illustrated in Fig. 1. The diagram I in this Figure denotes that the equation of the matrix element $<a|\tilde{\chi}^{(k)}_{nm}|c>$ contains the matrix element $<b|\tilde{\chi}^{(l)}_{ij}|c>$ in the form of the term $i<a|\mathbf{D}_{+\lambda}|b><b|\tilde{\chi}^{(l)}_{ij}|c>$. The diagram II deno-

tes the fact that the equation of the matrix element $\langle b | \tilde{\chi}^{(l)}_{ij} | c \rangle$ contains the matrix element $\langle a | \tilde{\chi}^{(k)}_{nm} | c \rangle$ in the form of the term $i\langle b | \mathbf{D}_{-\lambda} | a \rangle \langle a | \tilde{\chi}^{(k)}_{nm} | c \rangle$. Both equations are, therefore, directly coupled.

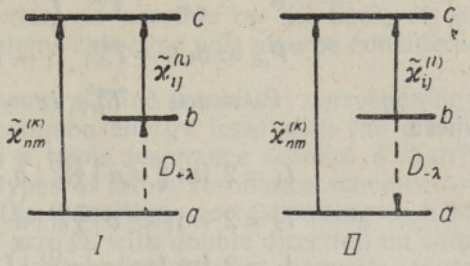

Fig. 1. Graphical representation of the direct coupling rules of matrix elements.

Note that the arrows of the elements $\langle a | \mathbf{D}_{+\lambda} | b \rangle$ and $\langle b | \tilde{\chi}^{(l)}_{ij} | c \rangle$ represent the arrow of the element $\langle a | \tilde{\chi}^{(k)}_{nm} | c \rangle$ as a vector sum. Associating to the matrix elements of the operators $\mathbf{D}_{\pm\lambda}$ harmonic numbers and orders as follows

	k	n	m
$\mathbf{D}_{\pm 1}$	± 1	0	0
$\mathbf{D}_{\pm 2}$	± 1	± 1	0
$\mathbf{D}_{\pm 3}$	± 1	0	± 1

(2.8)

it is seen from B and C that in addition to the vector sum rule an algebraic sum rule holds for any index. So, for example, on the diagram I $k = l + 1$, $n = i + 1$, $m = j$ if $\lambda = 2$. Taking into account the above-mentioned sum rules by constructing the diagrams of the types I and II, all the conditions A, B, C are satisfied.

Since a diagram of the type II corresponds to any diagram of the type I, the coupling between $\langle a | \tilde{\chi}^{(k)}_{nm} | c \rangle$ and $\langle b | \tilde{\chi}^{(l)}_{ij} | c \rangle$ is mutual.

The following simple but important consequence is directly seen from (1.45) and (2.8).

D. The matrix elements $\langle a | \tilde{\chi}^{(k)}_{nm} | c \rangle$ and $\langle b | \tilde{\chi}^{(l)}_{ij} | c \rangle$ are simultaneously in resonance only in the case if the difference between the non-common energy levels is equal to the corresponding frequency ω_λ.

Triple Resonance Schemes

Let us now consider the simplest case of triple resonance with all the frequencies ω_λ in resonance

$$\omega_1 \approx b - a, \qquad \omega_2 \approx d - c, \qquad \omega_3 \approx f - e$$

but with a, b, c, d, e, f all different. Because of this the condition A is not satisfied and the matrix elements $\langle a | \tilde{\chi}^{(1)}_{00} | b \rangle$, $\langle c | \tilde{\chi}^{(1)}_{10} | d \rangle$, $\langle e | \tilde{\chi}^{(1)}_{01} | f \rangle$ are not directly coupled with any other off-diagonal element. Together with the conjugated elements they are the only nonzero off-diagonal elements in the weak rf and weak relaxation approximation. The system of equations (1.44), (1.40) reduces then to

$$\begin{aligned} \Delta_{ab} \langle a | \tilde{\chi}^{(1)}_{00} | b \rangle &= i \langle a | \mathbf{D}_{+1} | b \rangle P_{ab}, \\ \Delta_{cd} \langle c | \tilde{\chi}^{(1)}_{10} | d \rangle &= i \langle c | \mathbf{D}_{+2} | d \rangle P_{cd}, \\ \Delta_{ef} \langle e | \tilde{\chi}^{(1)}_{01} | f \rangle &= i \langle e | \mathbf{D}_{+3} | f \rangle P_{ef}, \end{aligned} \tag{2.9}$$

$$P_{ab} = q\omega_0 - T^{ab}_{ba1}\, I_1 - T^{cd}_{ba1}\, I_2 - T^{ef}_{ba1}\, I_3,$$
$$P_{cd} = q\omega_0 - T^{ab}_{dc1}\, I_1 - T^{cd}_{dc1}\, I_2 - T^{ef}_{dc1}\, I_3, \qquad (2.10)$$
$$P_{ef} = q\omega_0 - T^{ab}_{fe1}\, I_1 - T^{cd}_{fe1}\, I_2 - T^{ef}_{fe1}\, I_3,$$

where

$$I_1 = 2\ \mathrm{Im}\{ \langle a | \tilde{\chi}^{(1)}_{00} | b \rangle \langle b | \mathbf{D}_{-1} | a \rangle \},$$
$$I_2 = 2\ \mathrm{Im}\{ \langle c | \tilde{\chi}^{(1)}_{10} | d \rangle \langle d | \mathbf{D}_{-2} | c \rangle \}, \qquad (2.11)$$
$$I_3 = 2\ \mathrm{Im}\{ \langle e | \tilde{\chi}^{(1)}_{01} | f \rangle \langle f | \mathbf{D}_{-3} | e \rangle \}.$$

The solution of this system of equations is considered in the next part. At this place we shall deal with the case of monoresonance only.

If only ω_1 is in resonance, only $\langle a | \tilde{\chi}^{(1)}_{00} | b \rangle \neq 0$ and $I_2 = I_3 = 0$. Then from the first equation of (2.9)—(2.11) one obtains the well-known [5] result

$$\langle a | \tilde{\chi}^{(1)}_{00} | b \rangle = \frac{\langle a | \mathbf{D}_{+1} | b \rangle T_{ab2}\, q\omega_0 (i + \Delta\omega_1 T_{ab2})}{1 + (\Delta\omega_1 T_{ab2})^2 + 2 | \langle a | \mathbf{D}_{+1} | b \rangle |^2 T^{ab}_{ba1}\, T_{ab2}}, \qquad (2.12)$$

where

$$\Delta\omega_1 = \omega_1 - (b - a). \qquad (2.13)$$

In the above-mentioned simplest triple resonance case only the first-order matrix elements of the harmonics $\tilde{\chi}_{00}$, $\tilde{\chi}_{10}$, $\tilde{\chi}_{01}$ have nonzero values. In order to possess nonzero matrix elements of other orders and of other harmonics, at least two of the above-mentioned first-order matrix elements must have a common energy level. This is the direct consequence of the coupling rule D. Therefore, two first-order matrix elements corresponding to the frequencies ω_1, ω_2 and possessing an energy level in common will give rise to one additional matrix element of the order two or zero. In accordance with this, one receives two possible types of double resonance schemes given in Fig. 2. The double resonance scheme on the left side of Fig. 2 is referred to by Freeman and Anderson [19] as type $\Lambda = 2$ scheme, the scheme on the right side of Fig. 2 corresponds to the type $\Lambda = 0$.

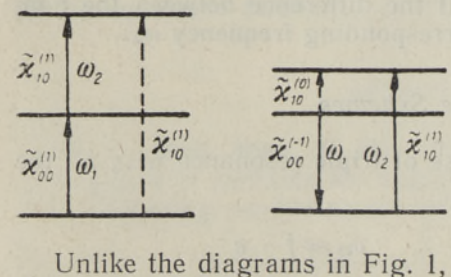

Fig. 2. Two possible types of double resonance schemes. The $\Lambda = 2$ type on the left, the $\Lambda = 0$ type on the right.

Unlike the diagrams in Fig. 1, the arrows corresponding to the matrix elements of the operators $\mathbf{D}_{\pm\lambda}$ are omitted in the diagrams of Fig. 2. In fact, the arrows of the second and zeroeth order elements in Fig. 2 are vector sums of the first-order elements and the algebraic sum rule of the indices holds as well. This is the consequence of the fact that the first-order terms and the corresponding elements of the operators $\mathbf{D}_{\pm\lambda}$ have the same indices (see Eq. (2.8)). Thus, both diagrams in Fig. 2 present a system of three directly coupled equations of the type (1.44). Because of the importance of this double resonance problem in the theory of triple resonance spectra, it will be discussed in the next part.

If two matrix elements in resonance corresponding to the frequencies ω_1 and ω_2, respectively, are coupled according to a double resonance scheme, but a third first-order matrix element in resonance corresponding to fre-

quency ω_3 has no energy level in common with the first two, a type of triple resonance appears, the analysis of which is possible on the basis of the solution of the double resonance problem. This type will also be considered in the next part.

If now to a double resonance scheme a third transition corresponding to frequency ω_3 and possessing a common energy level with the double resonance scheme is added, one gets a triple resonance scheme of matrix elements. The five possible general types of triple resonance schemes are given in Fig. 3. In this Figure only the transitions corresponding to first-order matrix elements are given. The arrows with double direction on some diagrams denote the fact that both conjugated matrix elements corresponding to one transition are to be included in the coupled system of equation (1.44). The arrows with broken lines correspond to the first-order matrix elements giving rise to signals at combined frequencies.

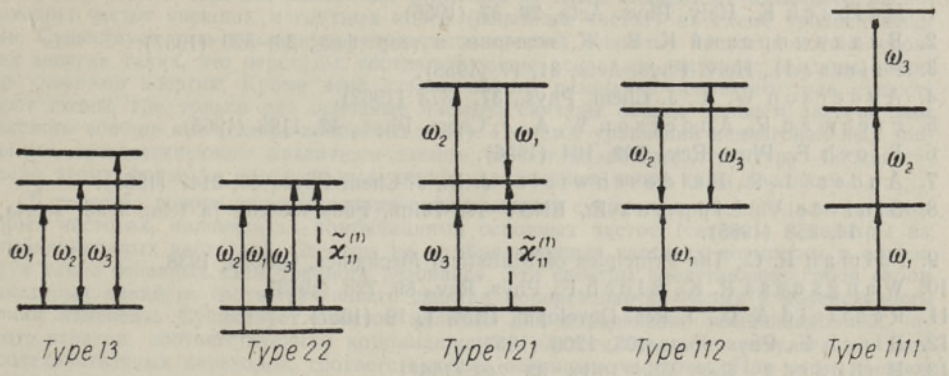

Fig. 3. General types of triple resonance schemes.

Each diagram in Fig. 3 consists of four energy levels. The diagrams differ in the distribution of these levels between different values of the quantum number M (the eigenvalue of the operator F_z). Each diagram is denoted by a type number giving the energy level distribution by increasing (or decreasing) the value of M. Note that by this convention the double resonance types in Fig. 2 are to be noted as type 111 and 12, resp.

In the case of a double resonance scheme a zeroeth or second-order matrix element appears (in addition to the initial first-order matrix elements). Those zeroeth and second-order matrix elements also occur in the triple resonance schemes. In the case of types 13 and 112 they will cause only the coupling of the initial first-order matrix elements. As there are more matrix elements than in the case of double resonance, more complicated shapes of lines in a frequency-swept spectrum are to be expected.

In the case of types 1111, 121 and 22, new types of matrix elements appear. Starting from a second-order matrix element a third-order matrix element can appear (type 1111). Starting from a second or zeroeth-order matrix element a new first-order matrix element can appear (types 121 and 22). It may be shown that the arrow of the new first-order matrix element is a vector sum of the initial first-order matrix elements and the algebraic sum rule of indices holds. The harmonic numbers of the new first-order matrix elements, therefore, differ from the harmonic numbers of the initial first-order matrix elements. Since first-order matrix elements occur in the signal formula (1.23), these new first-order matrix elements will cause signals at frequencies different from the initial frequencies ω_λ. These signals (and

spectra) will be further referred to as signals and spectra at combined frequencies.

The frequency at which the new signals are to be detected can be calculated on the basis of harmonic numbers or simply with the use of the algebraic sum rule of the initial frequencies ω_λ. So, for example, this frequency in Fig. 3 equals to $\omega_1 + \Omega_2 + \Omega_3 = \omega_2 + \omega_3 - \omega_1$. To calculate line shapes and line intensities in these spectra, the system of equation (1.44) is to be set up and solved.

The author is greatly indebted to L. Vahtra for her kind help in correcting the manuscript.

REFERENCES

1. Halbach K., Helv. Phys. Acta, **29**, 37 (1956).
2. Владимирский К. В., Ж. эксперим. и теор. физ., **33**, 529 (1957).
3. Primas H., Helv. Phys. Acta, **31**, 17 (1958).
4. Anderson W. A., J. Chem. Phys., **37**, 1373 (1962).
5. Freeman R., Anderson W. A., J. Chem. Phys., **42**, 1199 (1965).
6. Bloch F., Phys. Rev., **102**, 104 (1956).
7. Anders L. R., Baldeschwieler J. D., J. Chem Phys., **43**, 2147 (1965).
8. Sinivee V., Lippmaa E., ENSV TA Toim., Füüs.-matem. ja tehn. tead. seeria, **14**, 258 (1965).
9. Tolman R. C., The Principles of Statistical Mechanics, Oxford, 1938.
10. Wangsness R. K., Bloch F., Phys. Rev., **89**, 728 (1953).
11. Redfield A. G., J. Res. Developm. IBM, **1**, 19 (1957).
12. Bloch F., Phys. Rev., **105**, 1206 (1957).
13. Hubbard P., Rev. Mod. Phys., **33**, 249 (1961).
14. Файн В. М., Ж. эксперим. и теор. физ., **42**, 1075 (1962).
15. Argyres P. N., Kelley P. L., Phys. Rev., **134A**, 98 (1964).
16. Lösche A., Kerninduktion, Berlin, 1957.
17. Sinivee V., ENSV TA Toim., Füüs.-matem. ja tehn. tead. seeria, **15**, 182 (1966).

Academy of Sciences of the Estonian SSR
Institute of Cybernetics

Received
March 13, 1967

V. SINIVEE

TUUMSE MAGNETILISE KOLMIKRESONANTSI SPEKTRITE TEOORIA NÕRKADE RAADIOSAGEDUSLIKE VÄLJADE PUHUL. I

Esitatakse üldine probleemi käsitlemise formalism.

В. СИНИВЕЭ

ТЕОРИЯ СПЕКТРОВ ЯДЕРНОГО МАГНИТНОГО ТРОЙНОГО РЕЗОНАНСА В СЛУЧАЕ СЛАБЫХ РАДИОЧАСТОТНЫХ ПОЛЕЙ. I

На основе квантовокинетических уравнений Блоха—Редфильда рассматривается теория спектров ядерного магнитного тройного резонанса высокого разрешения. При этом предполагаются выполненными следующие условия: система ядерных спинов исследуемого типа молекулы гомонуклеарна, не имеет вырожденных уровней энергии и равных разниц энергии, радиочастотные магнитные поля и релаксация слабые (в бло-

ховском смысле). В настоящем, первом сообщении представлен общий формализм для трактовки проблемы.

Кинетическое уравнение (1.8) преобразуется с помощью преобразования (1.16) и рассматривается в энергетическом представлении (1.7). Стационарное решение преобразованного кинетического уравнения (1.17) ищется в виде двойного тригонометрического ряда (1.19). Это приводит к системе алгебраических уравнений (1.21), связывающей матричные элементы вообще различных гармоник. Путем введения подходящих параметров релаксации (1.35), (1,39), определяемых системой уравнений (1.36), проблему нахождения диагональных матричных элементов (1.26) можно отделить от проблемы недиагональных элементов. Последние подчиняются системе уравнений (1.44), (1.40). В случае слабых р. ч. полей и слабой релаксации (1.12) только ограниченное число недиагональных элементов, «находящихся одновременно в резонансе», в первом приближении отличны от нуля. Поэтому система (1.44), (1.40) содержит в рассматриваемом приближении ограниченное число уравнений. Решение этой системы уравнений и подстановка результата в (1.22), (1.23) позволяет вычислить форму и интенсивность наблюдаемых спектральных линий.

Число недиагональных элементов, отличных от нуля, зависит от взаимного расположения частот внешних магнитных полей (основных частот) на схеме уровней энергии. Существует пять различных типов расположения основных частот на схеме уровней энергии таких, что переходы, соответствующие основным частотам, связаны общими уровнями энергии. Кроме этих схем тройного резонанса основного типа существуют схемы, где только две основные частоты связаны общим уровнем энергии или такового вообще нет (схемы побочного типа). Системы уравнений недиагональных элементов, соответствующие различным схемам, имеют различную структуру. Соответственно этому формулы спектральных линий у различных типов схем различны.

В качестве нового явления теория предсказывает существование сигналов на некоторых частотах, являющихся комбинациями основных частот (сигналы и спектры на комбинационных частотах). Спектры на комбинационных частотах возможны в случае двух типов основных схем тройного резонанса. Эти спектры представляют собой отбор некоторых линий из соответствующего спектра монорезонанса. Форма и интенсивность линий изменены. Существует простое правило для определения комбинационных частот: переход, соответствующий комбинационной частоте, является результатом трех последовательных переходов, соответствующих основным частотам. При этом предполагается, что каждый из четырех переходов удовлетворяет правилу отбора $\Delta M = \pm 1$.