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Nuclear Magnetic Resonance with Stochastic High-Frequency Fields

(A simple example to the theory of systems with a stochastic hamiltonian)

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Zusammenfassung: Ausgehend von einer Funktionalentwicklung der Dichteoperator-Gleichung wurde ein Theorem für den Ensemble-Mittelwert der linearen Response eines quantenmechanischen Systems mit stochastischem Hamilton-Operator hergeleitet, um davon ausgehend für Ein-Spin- und Zwei-Spin-System das Verhalten bei magnetischen Doppelresonanz-Experimenten mit einem starken stochastischen Hochfrequenzfeld zu untersuchen.

Im Gegensatz zu den üblichen Doppelresonanz-Experimenten mit einem deterministischen Hochfrequenzfeld ist hier eine Störung möglich, welche die Rotationssymmetrie bezüglich der z-Achse des Problems nicht stört. Dadurch wird das Spektrum wesentlich beeinflusst, insbesondere wird die maximale Linienzahl stark eingeschränkt. Es ist damit gezeigt, dass die Verletzung der Rotationsinvarianz für das Auftreten von Doppelresonanz-Effekten nicht entscheidend ist.

1. Introduction

The purpose of this paper is twofold. Firstly it deals with an extension of the double resonance methods in nuclear magnetic resonance (*nmr*). It is not claimed to give a practical new method of spin decoupling but the main interest is to clear up some questions of the physical mechanism of double resonance phenomena. The second purpose of these calculations is a methodical one. The spin systems of *nmr* spectroscopy are mathematically so simple, that they form the ideal field for testing new mathematical methods. In a former paper[1]) we developed a general formal method for treating quantum mechanical systems with a strong, time-dependent stochastic perturbation. Because of the great importance of such systems in physics, chemistry and biology it seems to be worthwhile to work out this formal theory on a simple but nontrivial example. Because our point of view here is more or less methodical, we will discuss only the principal methods of approach and give the main results without any detailed proof. For the detailed calculations, the reader is referred to the thesis of R. R. ERNST[2]).

The organisation of the paper it as follows: In Chapter 2 we discuss the origin of the problem and its reduction to an abstract problem. Chapter 3 gives then the main theorem which allows the calculation of the ensemble average of the linear response of a system with a strong time dependent stochastic perturbation. In the following Chapter 4 this theory is applied first to an one-spin and then to a two-spin system with a scalar coupling. The question of convergence is discussed and a relation between level shift and line broadening is stated. The *nmr* spectra are described in relation to the shape of the power spectrum of the stochastic perturbation.

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2. Reduction of a double resonance experiment to an abstract problem

In *nmr*-spectroscopy the double resonance methods have become a powerful mean for determining molecular structure. The most important applications of double resonance techniques in high-resolution *nmr* spectroscopy are due to the simplification of the *nmr*-spectra caused by a partial decoupling of the nuclear spins in a molecule. For the practical spectroscopist it would be ideal if he could remove *all* spin-spin couplings at the same time. With the usual methods this is often an almost impossible task because one would be forced to irradiate with strong *rf*-fields simultaneously at a great number of different, discrete frequencies dependent on the structure of the spectrum. Because the exact structure is in general unknown before having done the experiment, the necessary frequencies of the *rf*-fields are not known at the beginning. This difficulty suggests itself to replace this multitude of discrete frequencies by a continuous stochastic spectrum. By choosing an appropriate shape of the power spectrum of the strong «double»-resonance field it should be possible to get a *nmr* spectrum with all spin-spin couplings simultaneously removed. Of course, we are aware of the practical difficulties of such an experiment, but for the purpose of this paper we may be allowed to ignore all possible difficulties of the hereto necessary electronic instrumentation. The set up of our «Gedankenexperiment» is shown in Figure 1.

In the hypothetical experiment, time averaging of the output voltage of the phase-sensitive detector would be used to eliminate the stochastic part of the signal. Without having a proof exactely for this case, we assume the validity of an ergodic theorem stating the equivalence of time and ensemble average. Therefore one is allowed to replace the time average by an ensemble average which is theoretically much easier to work with than the time average. In contrast to the time average, the ensemble average commutes with the action of the phase-sensitive detector. Thus it is possible to neglect in the theoretical treatment the phase-sensitive detector.

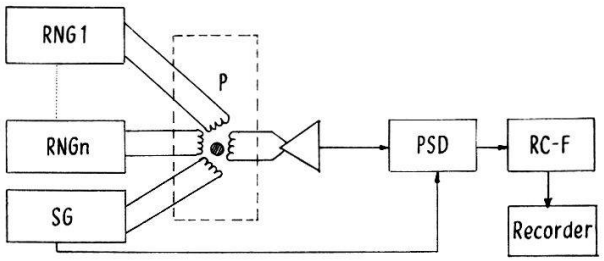

Fig. 1
Block diagram of the proposed *nmr* spectrometer

RNGn: Random noise generators with appropriate power spectra driving n transmitter coils in the *nmr* measuring probe assembly *P*

SG: Signal generator generating the weak *rf*-field $B_1 \cos\omega_1 t$ for measurement

P: Probe assembly consisting of the sample probe, the transmitting coils and the receiving coil. The sample probe is placed in a homogenous static magnetic field B_0 in the z-direction. The signal voltage induced in the receiving coil by the time-dependent magnetisation of the sample is amplified and fed to the phase-sensitive detector *PSD*

RC-F: *RC*-Filter with a large time constant causing the output to be essentially the time average of the input voltage

The *rf*-field $B_1 \cos\omega_1 t$ for measurement is assumed to be sufficiently weak. As usual in *nmr* spectroscopy, we are only interested in the linear response to this weak perturbation.

Therefore we can formulate the general problem as follows: Find the ensemble average of the linear response of a quantum mechanical system with a strongly time-dependent stochastic Hamiltonian. This is shown schematically in Figure 2.

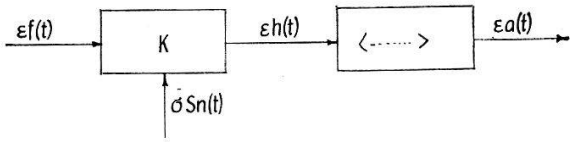

Fig. 2
Diagram of the general problem

$\boldsymbol{K}$*) is the Hamiltonian of the unperturbed system under the influence of one or several strong time dependent stochastic perturbations $\sigma\, s_n(t)$ acting by means of the Operators $\boldsymbol{V}_n$. $\varepsilon \cdot f(t)$ is the weak deterministic perturbation for measurement, acting by the operator $\boldsymbol{H}_1$. $h(t)$ represents the linear response of the system to $f(t)$ and $a(t)$ finally is the ensemble average of $f(t)$. The observable will be denoted by $\boldsymbol{A}$. σ and ε are parameters.

The Hamiltonian characterizing the system, all perturbations included, has therefore the structure

$$\boldsymbol{H}(t) = \boldsymbol{K} + \varepsilon \cdot f(t)\, \boldsymbol{H}_1 + \sigma \sum_n s_n(t)\, \boldsymbol{V}_n \,. \tag{2-1}$$

$\boldsymbol{H}_1$ and $\boldsymbol{V}_n$ are hermitian, time-independent operators. The functions $s_n(t)$ are assumed to be stationary, uncorrelated, Gaussian, stochastic functions:

$$\langle s_n(t)\, s_m(\tau)\rangle = \delta_{n\,m}\, \mathcal{K}_m(t-\tau) \,. \tag{2-2}$$

with the correlation function $\mathcal{K}_n(t)$.

3. Ensemble average of the linear response of a time-dependent quantum mechanical system

This chapter deals with the deduction of a general equation for the ensemble average of the linear response of a stochastically time-dependent system. The linear response $\varepsilon \cdot h(t)$ to the non-stochastic input function $\varepsilon \cdot f(t)$ of a time-dependent system can be calculated by means of its Green's function $g'(t, \tau)$ through a convolution integral:

$$h(t) = \int_{-\infty}^{t} g'(t, \tau)\, f(\tau)\, d\tau \,, \tag{3-1}$$

*) Bold face capital letters represent operators over the Hilbert space; $Tr(\boldsymbol{A})$ means the trace of the operator $\boldsymbol{A}$; $\langle \boldsymbol{A} \rangle$ is the ensemble average of $\boldsymbol{A}$. A tilde is used to denote the Fourier-transform

$$\tilde{a}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} a(t)\, e^{-i\omega t}\, dt \,.$$

where the condition of causality is assumed to be fulfilled.

The ensemble average $a(t)$ of the linear response $h(t)$ is given by

$$a(t) = \langle h(t) \rangle = \int_{-\infty}^{t} \langle g'(t, \tau) \rangle \, f(\tau) \, d\tau \, . \tag{3-2}$$

If it is assumed that the system is stationary (that is, the time-dependence of the system is entirely given by a set of stationary stochastic parameters), then the ensemble average of the Green's function depends only on the difference $t - \tau$:

$$\langle g'(t, \tau) \rangle = g(t - \tau) \, . \tag{3-3}$$

The ensemble average of the linear response is now given by

$$a(t) = \int_{0}^{\infty} g(x) \, f(t - x) \, dx \, . \tag{3-4}$$

On the other hand, the linear response $h(t)$ is given by the quantum statistical expection value of the appropriate observable $\boldsymbol{A}$

$$h(t) = Tr\{\boldsymbol{A} \, \boldsymbol{P}_1(t)\} \, , \tag{3-5}$$

where $\boldsymbol{P}_1$ is the linear part in ε of the density operator $\boldsymbol{P}(t)$ of the system,

$$\boldsymbol{P}(t) = \boldsymbol{P}_0(t) + \varepsilon \, \boldsymbol{P}_1(t) + \varepsilon^2 \, \boldsymbol{P}_2(t) + \cdots . \tag{3-6}$$

Therefore we get for the ensemble average $a(t)$ of $h(t)$

$$a(t) = Sp\{\boldsymbol{A} \, \boldsymbol{\Pi}_1(t)\} \tag{3-7}$$

with

$$\boldsymbol{\Pi}_1(t) = \langle \boldsymbol{P}_1(t) \rangle \, .$$

Instead of starting with the correct density operator of the whole system including spin system and the interacting environment, we assume that the density operator of the spin system alone satisfies the differential equation of KARPLUS, SCHWINGER[3])*):

$$\dot{\boldsymbol{P}}(t) = -i \, [\boldsymbol{H}(t), \, \boldsymbol{P}(t)] - \Gamma\{\boldsymbol{P}(t) - \boldsymbol{P}_c(t)\} \, . \tag{3-8}$$

This is justified by the fact that the exact form of the relaxation mechanism is not of importance in considering double resonance phenomena. It is sufficient to assume a general relaxation mechanism with a single relaxation time $1/\Gamma$. We suppose further that the relaxation is weak, Γ shall be very small, but different from zero. $\boldsymbol{P}_c(t)$ is the density operator of the canonical ensemble.

By means of a functional expansion with respect to σ[1]), it is possible to obtain starting from (3-8) an integro-differential equation for the ensemble average $\boldsymbol{\Pi}(t)$ of the density operator and by a further expansion with respect to ε an equation for $\boldsymbol{\Pi}_1(t)$. These rather extensive calculations shall not be reproduced here[2]).

*) Energies are expressed here throughout in units of rad/sec. In these units is $\hbar = 1$.

By analogy with the Green's function $g(t)$ we define a Green's operator $\boldsymbol{G}(t)$ and it is possible to write:

$$\boldsymbol{\Pi}_1(t) = \int_0^\infty \boldsymbol{G}(x)\, f(t-x)\, dx \tag{3-9}$$

and

$$g(t) = Tr\{\boldsymbol{A}\, \boldsymbol{G}(t)\}\,. \tag{3-10}$$

The integro-differential equation for the Green's operator $\boldsymbol{G}(t)$ can be solved by a Fourier-transformation. Therewith one gets the following theorem:

Theorem for the calculation of the ensemble average of the linear response of a quantum mechanical system with a stochastic time-dependent Hamiltonian.

Assumptions:

1. The system shall be characterized by a Hamiltonian of the following structure:

$$\boldsymbol{H}(t) = \boldsymbol{K} + \varepsilon\, f(t)\, \boldsymbol{H}_1 + \sigma \sum_n s_n(t)\, \boldsymbol{V}_n\,. \tag{3-11}$$

$\boldsymbol{K}$, $\boldsymbol{H}_1$ and $\boldsymbol{V}_n$ are time-independent, hermitian operators operating on a d-dimensional, finite Hilbert space. σ and ε are parameters, $f(t)$ a non-stochastic time function and $s_n(t)$ are independent, Gaussian, stationary stochastic functions with the correlation functions $\mathcal{K}_n(t-\tau)$:

$$\langle s_n(t)\, s_m(\tau)\rangle = \delta_{n\,m}\, \mathcal{K}_n(t-\tau)\,; \quad \langle s_n(t)\rangle = 0 \tag{3-12}$$

and with the power spectrum $P_n(\omega)$

$$P_n(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathcal{K}_n(t)\, e^{-i\omega t}\, dt\,. \tag{3-13}$$

It is further assumed that

$$Tr\{\boldsymbol{V}_n\} = 0\,. \tag{3-14}$$

2. The density operator $\boldsymbol{P}(t)$ of the system shall be described by the differential equation

$$\dot{\boldsymbol{P}}(t) = -\,i\,[\boldsymbol{H}(t),\, \boldsymbol{P}(t)] - \Gamma\{\boldsymbol{P}(t) - \boldsymbol{P}_c(t)\} \tag{3-15}$$

with

$$\boldsymbol{P}_c(t) = \chi \exp\{-\beta\, \boldsymbol{H}(t)\} \tag{3-16}$$

and

$$\chi^{-1} = Tr\big(\exp\{-\beta\, \boldsymbol{H}(t)\}\big)\,, \quad \beta = 1/k\,T\,.$$

k is the Boltzmann constant and T the absolute temperature.

3. The system is subjected to some restrictions:

a) Γ shall be sufficiently small, but $\Gamma > 0$.

b) It is supposed that $\beta^{-1} \gg \Omega_{max}$. Ω_{max} is the maximum value of the greatest eigenvalue of $\boldsymbol{H}(t)$.

c) $$\pi\, d\, \sigma^2 \sum_n \left| P_n(\omega) + i\, Q_n(\omega) \right|_{max} \cdot \frac{\| \boldsymbol{V}_n \|^2}{\| \boldsymbol{K} \|} \ll 1 \,, \tag{3-17}$$

d) $$d^2\, \sigma^2 \sum_n \left| \frac{\partial}{\partial \omega} \left(P_n(\omega) + i\, Q_n(\omega) \right) \right|_{max} \cdot \frac{\| \boldsymbol{V}_n \|^2}{\| \boldsymbol{H}_1 \|} \ll 1 \,. \tag{3-18}$$

$Q_n(\omega)$ is the Hilbert transform of the power spectrum $P_n(\omega)$:

$$Q_n(\omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} P_n(x)\, (x - \omega)^{-1}\, dx \,. \tag{3-19}$$

Theorem:

The ensemble average $a(t)$ of the linear response to the input function $f(t)$ and with the observable $\boldsymbol{A}$ is given by

$$a(t) = \int_0^{\infty} Tr\{ \boldsymbol{A}\, \boldsymbol{G}(x) \}\, f(t - x)\, dx \,, \tag{3-20}$$

$$\boldsymbol{G}(t) = \mathscr{F}^{-1} \{ \tilde{\boldsymbol{G}}(\omega) \} \,. \tag{3-21}$$

$\tilde{\boldsymbol{G}}(\omega)$ is determined by the subsequent linear equation*):

$$\left.\begin{aligned} i\, \omega\, \tilde{\boldsymbol{G}}(\omega) + i\, [\boldsymbol{K}, \tilde{\boldsymbol{G}}(\omega)] + \Gamma\, \tilde{\boldsymbol{G}}(\omega) + \sigma^2\, \tilde{\boldsymbol{a}}_2 \{ \tilde{\boldsymbol{G}}(\omega) \} + \sigma^4\, \tilde{\boldsymbol{a}}_4 \{ \tilde{\boldsymbol{G}}(\omega) \} \\ = - i\, [\boldsymbol{H}_1, \boldsymbol{\Pi}_0] \end{aligned}\right\} \tag{3-22}$$

with

$$\tilde{\boldsymbol{a}}_2 \{ \tilde{\boldsymbol{G}}(\omega) \} = \sum_n \int_0^{\infty} e^{-\Gamma x}\, e^{-i\omega x}\, \mathscr{K}_n(x) \left[\boldsymbol{V}_n, e^{-i\boldsymbol{K}x} [\boldsymbol{V}_n, \tilde{\boldsymbol{G}}(\omega)]\, e^{i\boldsymbol{K}x} \right] dx \,. \tag{3-23}$$

$$\left.\begin{aligned} \tilde{\boldsymbol{a}}_4 \{ \tilde{\boldsymbol{G}}(\omega) \} = \sum_m \sum_n \int_{-\infty}^{\infty} d\omega_1\, P_m(\omega_1) \int_{-\infty}^{\infty} d\omega_2\, P_n(\omega_2) \Big\{ \Big[\boldsymbol{V}_m, \frac{1}{\Gamma + i(\boldsymbol{k} + \omega - \omega_1)} \\ \times \Big[\boldsymbol{V}_n, \frac{1}{\Gamma + i\,(\boldsymbol{k} + \omega - \omega_1 - \omega_2)} \\ \times \Big[\boldsymbol{V}_m, \frac{1}{\Gamma + i\,(\boldsymbol{k} + \omega - \omega_2)} [\boldsymbol{V}_n, \tilde{\boldsymbol{G}}(\omega)] \Big] \Big] \Big] \\ + \Big[\boldsymbol{V}_m, \frac{1}{\Gamma + i\,(\boldsymbol{k} + \omega - \omega_1)} \Big[\boldsymbol{V}_n, \frac{1}{\Gamma + i\,(\boldsymbol{k} + \omega - \omega_1 - \omega_2)} \\ \times \Big[\boldsymbol{V}_n, \frac{1}{\Gamma + i\,(\boldsymbol{k} + \omega - \omega_1)} [\boldsymbol{V}_m, \tilde{\boldsymbol{G}}(\omega)] \Big] \Big] \Big] \Big\} \,. \end{aligned}\right\} \tag{3-24}$$

The superoperator $\boldsymbol{k}$ (compare [4])) is defined by

$$\boldsymbol{k}\{\boldsymbol{A}\} = [\boldsymbol{K}, \boldsymbol{A}] \,. \tag{3-25}$$

$\boldsymbol{\Pi}_0$ can be calculated from

$$i\, [\boldsymbol{K}, \boldsymbol{\Pi}_0] + \Gamma\, \boldsymbol{\Pi}_0 - \Gamma\, \boldsymbol{\chi}(\boldsymbol{1} - \beta\, \boldsymbol{K}) + \sigma^2\, \boldsymbol{a}_2 \{ \boldsymbol{\Pi}_0 \} + \sigma^4\, \boldsymbol{a}_4 \{ \boldsymbol{\Pi}_0 \} = 0 \tag{3-26}$$

*) Small bold face letters represent superoperators, i.e. operators over the algebra generated by the observables (compare [4])).

with

$$\boldsymbol{a}_2\{\boldsymbol{\Pi}_0\} = \sum_n \int_0^\infty e^{-\Gamma x}\, \mathscr{K}_n(x)\, [\boldsymbol{V}_n, e^{-iKx}[\boldsymbol{V}_n, \boldsymbol{\Pi}_0]\, e^{iKx}]\, dx\,, \tag{3-27}$$

$$\begin{aligned} a_4\{\boldsymbol{\Pi}_0\} = -\sum_m \sum_n \int_0^\infty dx_1 \int_0^\infty dx_2 \int_0^\infty dx_3\, e^{-\Gamma(x_1+x_2+x_3)} \{\mathscr{K}_m(x_1+x_2) \\ \times \mathscr{K}_n(x_2+x_3)\, [\boldsymbol{V}_m, e^{-iKx_1}[\boldsymbol{V}_n, e^{-iKx_2}[\boldsymbol{V}_m, e^{-iKx_3} \\ \times [\boldsymbol{V}_n, \boldsymbol{\Pi}_0]\, e^{iKx_3}]\, e^{iKx_2}]\, e^{iKx_1}] \\ + \mathscr{K}_m(x_1+x_2+x_3)\mathscr{K}_n(x_2)\, [\boldsymbol{V}_m, e^{-iKx_1}[\boldsymbol{V}_n, e^{-iKx_2}[\boldsymbol{V}_n, e^{-iKx_3} \\ \times [\boldsymbol{V}_m, \boldsymbol{\Pi}_0]\, e^{iKx_3}]\, e^{iKx_2}]\, e^{iKx_1}]\}\,. \end{aligned} \tag{3-28}$$

These relations have been calculated by a functional expansion with respect to σ. All terms with σ^6 and higher powers were neglected. The convergence of this expansion has to be prooved in any special application of this theorem. *A general criterion for the convergence can not be stated.* If the terms $\boldsymbol{a}_4(\boldsymbol{\Pi}_0)$ and $\tilde{\boldsymbol{a}}_4(\tilde{\boldsymbol{G}}(\omega))$ are not small enough to be neglected, it is to be assumed that the convergence is insufficient.

4. Application of the general theory to spin systems

41. *General remarks*

We restrict ourselves here to systems with spin 1/2 coupled together by scalar spin-spin interactions and being in an external magnetic field B_0 in the z-direction. The Hamiltonian K of the unperturbed system has therefore the structure[5][6]:

$$\boldsymbol{K} = \sum_j \Omega_j\, \boldsymbol{I}_j^0 + \sum_{j \neq k} \sum J_{jk}\, \boldsymbol{I}_j\, \boldsymbol{I}_k \tag{41-1}$$

with the «Zeeman»-frequencies

$$\Omega_j = \gamma_j\, B_0(1 - \sigma_j)\,. \tag{41-2}$$

γ_j is the gyromagnetic ratio of the spin j and σ_j the appropriate chemical shift. J_{jk} represents the scalar coupling constant between the spins j and k. $\boldsymbol{I}_j$ is the j-th spin vector with the spherical components

$$\boldsymbol{I}_j^- = \boldsymbol{I}_{jx} - i\, \boldsymbol{I}_{jy}\,, \quad \boldsymbol{I}_j^0 = \boldsymbol{I}_{jz}\,, \quad \boldsymbol{I}_j^+ = \boldsymbol{I}_{jx} + i\, \boldsymbol{I}_{jy} \tag{41-3}$$

and with the commutation relations

$$[\boldsymbol{I}_{jx}, \boldsymbol{I}_{ky}] = i\, \delta_{j,k}\, \boldsymbol{I}_{jz} \quad \text{and cycl.} \tag{41-4}$$

The Hamiltonian K is invariant against rotation about the z-axis,

$$[\boldsymbol{K}, \boldsymbol{F}_z] = 0\,, \quad \text{with} \quad \boldsymbol{F}_z = \sum_j \boldsymbol{I}_{jz}\,. \tag{41-5}$$

It is advantageous to choose a perturbation which does not destroy the symmetry of the problem. Therewith it should be possible to simplify the solution of the density operator equation considerably.

Experimentally, the perturbations are restricted to magnetic dipole interactions. To get transitions with the time-dependent perturbation, it is necessary that the perturbation does not commute with the unperturbed hamiltonian $\boldsymbol{K}$. Using exclusively *non-stochastic*, time-dependent perturbations, the operator

$$\boldsymbol{M}^0 = \sum_j \gamma_j(1 - \sigma_j)\, \boldsymbol{I}_j^0$$

is the only possible rotation-invariant perturbation operator which does not commute with the hamiltonian $\boldsymbol{K}$.

For spins with only small differencies Δ_{ik} of their Zeeman-frequencies Ω_i and with weak couplings J_{ik}, the resulting transition probabilities become very small in this case. The ratio of these transition probabilities p_0 to the transition probabilities $p_{x,y}$ obtained in the usual magnetic resonance experiments by the perturbation operators $\boldsymbol{M}_{x,y} = \sum_j \gamma_j(1 - \sigma_j)\, \boldsymbol{I}_{jx,y}$ equals approximately to

$$\frac{p_0}{p_{x,y}} \sim \frac{J_{ik}\,\Delta_{ik}}{\sqrt{J_{ik}^2 + \Delta_{ik}^2}} \cdot \frac{2}{(\Omega_i + \Omega_k)}\,. \tag{41-6}$$

If one investigates the nuclear magnetic resonance of systems consisting of spins with equal gyromagnetic ratios (a.g.hydrogen), this ratio $p_0/p_{x,y}$ has the order of magnitude of 10^{-6}. Such effects, of course, are too small to be observed.

With an appropriate *stochastic* perturbation nevertheless it is possible even by the use of the perturbation operators $\boldsymbol{M}_{x,y}$ to get a rotation-invariant equation for the ensemble average of the linear response to a second, non-stochastic perturbation. The resulting transition probabilities will be of the same order of magnitude as in the usual magnetic resonance experiments.

We assume now a system of spins with equal gyromagnetic ratios and with only small differencies in the chemical shifts. It is easy to show that it is allowed in this case to replace the operators $\boldsymbol{M}_{x,y}$ by $\{\text{const} \cdot \boldsymbol{F}_{x,y}\}$ with

$$\boldsymbol{F}_{x,y} = \sum_j \boldsymbol{I}_{jx,y}\,.$$

If one inserts in equation (3-11) a stochastic perturbation of the form

$$\sum_n s_n(t)\, \boldsymbol{V}_n = s_1(t)\, \boldsymbol{F}_x + s_2(t)\, \boldsymbol{F}_y\,. \tag{41-7}$$

($s_1(t)$ and $s_2(t)$ have to satisfy the equations (3-12) with the same correlation function $\mathscr{K}(t)$), it can be shown[2]) that the equation (3-26) and the left side of equation (3-22) become invariant against rotation about the z-axis. Only be choosing two uncorrelated stochastic perturbations with the same power spectrum and applying them in the x- and in the y-direction respectively, a rotation-invariant ensemble average is resulting. No similar result is possible without taking the ensemble average.

It is well-known that any stationary stochastic function and its Hilbert transformed stochastic function are completely uncorrelated[16]) and have the same correlation functions. It is further known that the output function of a broadband 90° phase shift network is the Hilbert transform of its input function[17]). Therefore

one can get the stochastic function $s_2(t)$ from $s_1(t)$ simply by means of a 90° phase shift network, i.e. the electronic equipment would be quite similar as in a usual *nmr*-experiment with a rotating *rf*-field.

It is to be noticed that the structure of the equation for the ensemble average $\boldsymbol{\Pi}(t)$ of the density operator is much more complicated than the structure of the equation for the density operator $\boldsymbol{P}(t)$. It is impossible to reduce the equation for $\boldsymbol{\Pi}(t)$ to the simple density operator equation (3-8) by introduction of a certain model Hamiltonian.

The choise of a rotation invariant structure of the equations has an essential influence on the selection rules of the transitions induced by the stochastic perturbation and therefore on the resulting spectrum too. The mathematical problem of solution is thereby greatly simplified. The result shows that the phenomena of double resonance is not due to a violation of the invariance with respect to rotations about the z-axis. In the subsequent chapters a perturbation of this form is always assumed.

42. *Nuclear magnetic resonance of a one-spin system under the influence of a strong stochastic perturbation*

It is here assumed that the system consists of one particle with spin 1/2. Of course no real double resonance effects are here to be expected. There result only line shifts by generalized Bloch-Siegert effects[7][8]) and line broadenings. The one-spin system is suitable to study the direct effects of the stochastic perturbation on the observed resonance line. In the more complicated systems these effects exist additionally to the real double resonance features.

Because it is hard to state a valuable criterion for convergence of the functional expansion, the convergence shall first be discussed by means of a simple example in Chapter 421. The features of the spectrum of the one-spin system will then be discussed in Chapter 412.

421. *Example for the convergence of the functional expansion with respect to* σ

The shape of the normalized power spectrum $P(\omega)$ of the two stochastic processes is supposed to be a Lorentzian function:

$$P(\omega) = \frac{1}{2\pi} \cdot \frac{\delta}{\delta^2 + (\omega_1 - \omega)^2} \,. \tag{421-1}$$

δ is the line width and ω_1 the central frequency of the Lorentzian function.

It has been found that $\tilde{\boldsymbol{a}}_4(\tilde{\boldsymbol{G}}(\omega))$ [equation (3-24)] can be neglected compared with $\tilde{\boldsymbol{a}}_2(\tilde{\boldsymbol{G}}(\omega))$ if the subsequent condition is fulfiled:

$$\frac{9}{4}\sigma^2 \frac{1}{(\Gamma + \delta)(\Gamma + 2\delta)} \ll 1 \,. \tag{421-2}$$

This condition is sufficient to neglect too $\boldsymbol{a}_4(\boldsymbol{\Pi}_0)$ compared with $\boldsymbol{a}_2(\boldsymbol{\Pi}_0)$. The condition (421-2) is contained in the following simplified form

$$\sigma/\delta \ll 1 \,. \tag{421-3}$$

These two conditions are practically equivalent because the width δ of the power spectrum is usually large compared with the line width Γ.

The convergence of the functional expansion is therefore guaranteed if the variance σ of the stochastic process is small compared with the width δ of its power spectrum. It has been shown[1]) that for white noise ($\delta \to \infty$) the first term of the functional expansion alone gives the exact solution. On the other hand, it is seen from equation (421-3) that for a discrete spectrum of the perturbation, the functional development does not converge at all. It is therefore possible to state in a qualitative manner that the convergence will be better as broader the noise power spectrum is.

Although it is difficult to generalize the condition for the convergence, the equation (421-3) gives an intuitive measure for the convergence even if the power spectrum has not shape of a Lorentzian function.

There is some evidence that the functional expansion here used to get an equation for the ensemble average of the density operator has an asymptotic character and delivers therefore useful results even if the convergence is not sufficient. For example formula (422-5) gives the correct line shift for a perturbation with a discret frequency spectrum although the development does not converge, as mentioned above.

422 *Intensity, line width and resonance frequency of the one-spin system*

If a condition of the form of equation (421-2) is fulfiled, the spectrum of a one-spin system under the influence of a stochastic perturbation with an arbitrary power spectrum is given by

$$\tilde{a}(\omega) = a_0 \frac{\Gamma}{\Gamma + 2\pi\sigma^2 P'(\Omega)} \cdot \frac{\Gamma + \pi\sigma^2 P'(\omega)}{(\Gamma + \pi\sigma^2 P'(\omega)^2) + (\omega - \Omega + \pi\sigma^2 Q'(\omega))^2} . \qquad (422\text{-}1)$$

$P'(\omega)$ is the corrected power spectrum which takes into consideration the influence of the finite line width Γ and which is calculated by a convolution integral:

$$P'(\omega) = \int_{-\infty}^{\infty} P(\omega + \omega') \frac{\Gamma}{\omega'^2 + \Gamma^2} d\omega' . \qquad (422\text{-}2)$$

$Q'(\omega)$ again is the Hilbert transform of $P'(\omega)$. Ω represents the resonance frequency of the unperturbed system and a_0 is a constant dependent on the polarisation of the unperturbed system.

It is seen that in general a complicated spectrum is resulting. If $P'(\omega)$ and $Q'(\omega)$ are slowly variable functions of the frequency in the vicinity of the resonance line, the spectrum comes to be again a Lorentzian function.

The resulting spectrum has the subsequent properties:

1. It results a reduction of the intensity by a factor f:

$$f = \frac{\Gamma}{\Gamma + 2\pi\sigma^2 P'(\Omega)} . \qquad (422\text{-}3)$$

2. The stochastic high-frequency field causes a line broadening γ:

$$\gamma = \pi \sigma^2 P'(\Omega) . \tag{422-4}$$

3. The resonance frequency is shifted by

$$\Delta\omega = \pi \sigma^2 Q'(\Omega) . \tag{422-5}$$

Line broadening and line shift are consequently Hilbert transforms of each other.

The line shift is the result of a generalized Bloch-Siegert effect[7][8]). It is worthy to note that the equation (422-5) delivers the correct line shift even for a non-stochastic time-dependent perturbation although the functional expansion does not converge in this case, as it has been stated in Chapter 421. A difference between the effects of stochastic and non-stochastic perturbations lies in the fact that a stochastic perturbation causes a line broadening whereas a non-stochastic *rf*-field does not influence the line width.

43. *Nuclear magnetic resonance of a two-spin system under the influence of a strong stochastic perturbation*

Two cases are to be distinguished here:

1. weak spin-spin coupling: $J \ll \Delta$,
2. strong spin-spin coupling: $J \sim \Delta$.

$\Delta = \Omega_1 - \Omega_2$ is the difference of the two resonance frequencies of the uncoupled system and J represents the spin-spin coupling constant. It is easy to solve the problem approximately for $J/\Delta \ll 1$, but in the case of strong coupling, there exist considerable difficulties which can be overcome in general only by the use of an electronic computer. We suppose for the power spectrum of the stochastic perturbation the subsequent idealised form*):

$$P(\omega') = \pi \sigma^2 \{\vartheta(|\omega'| - \omega - \omega_a) + \vartheta(\omega - \omega_a - |\omega'|)\} \tag{43-1}$$

with

$$\vartheta(x) = \begin{cases} 0 \text{ for } x < 0 \\ 1 \text{ for } x \geq 0 . \end{cases}$$

ω is here the frequency of the weak non-stochastic *rf*-field by which the spectrum is investigated. The relative positions of the four resonance frequencies k_1^1, k_2^1, k_3^1, k_4^1 of the unperturbed system with respect to the noise power spectrum are seen from Figure 3.

By the equation (43-1), a fixed relation is established between the frequency ω of the measuring field and the power spectrum of the stochastic field. The power

*) One has to pay attention to the two different definitions of the parameter σ implied by the equations (421-1) and (43-1). Even the dimensions are different. In the case of a normalizable power spectrum (as in chapter 421), it is convenient to use the normalized power spectrum $P(\omega)$. The parameter σ^2 has here the meaning of the mean square of the stochastic function and has the dimension of frequency^2. If the power spectrum is not normalizable (as in the following chapters), σ^2 can be defined as the power density of the stochastic function and has therefore the dimension of frequency.

spectrum is symmetrical with respect to the frequency ω and therefore the Hilbert transform $Q(\omega)$ equals to zero. This spectrum could be realized experimentally by amplitude modulation of the carrier frequency ω. The stochastic modulation signal of the appropriate shape can be produced by a high-pass filter with a cut-off frequency ω_d starting from a white noise power spectrum. It is to be pointed out that severe experimental difficulties would arise from the necessary high power in the two side bands.

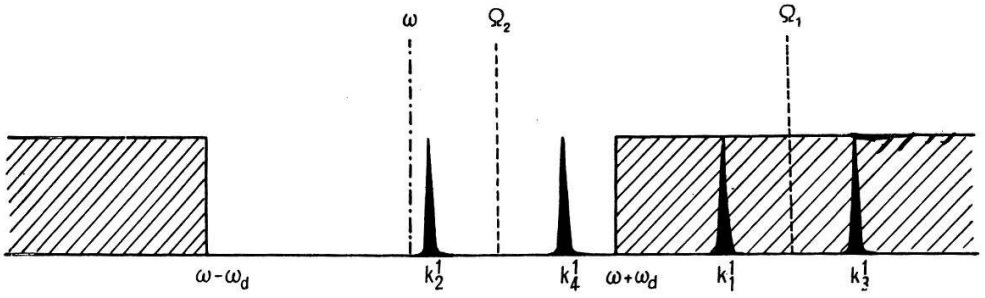

Fig. 3
Power spectrum of the stochastic process

We suppose here again a perturbation of the form (41-7) which guaranties a rotation-invariant form of the resulting systems of equations, and leads to an essential simplification. The system of equations resulting from (3-26) for the computation of zero-order ensemble average $\boldsymbol{\Pi}_0$ of the density operator consists of five coupled, linear equations. The corresponding system of equations for the Green's operator $\tilde{\boldsymbol{G}}(\omega)$ has the dimension four. This fact implies the existence of at most four different resonance frequencies. In the general case of an arbitrary perturbation, 15 different resonance frequencies can be found. In the usual double resonance with a rotating *rf*-field 12 different lines are possible[9]).

431. *Two-spin system with weak spin-spin coupling:* $J \ll \Delta$

We limit now the sweep range by the equation

$$\Omega_2 - J \leq \omega \leq \Omega_2 + J \tag{431-1}$$

and put for the width of the 'hole' in the power spectrum of the stochastic perturbation

$$\omega_d = \sqrt{J\,\Delta}\,. \tag{431-2}$$

With these assumptions all Hilbert transforms $Q'(\omega')$ in the equations for the zero-order ensemble average $\boldsymbol{\Pi}_0$ of the density operator can be neglected for the case of weak coupling. $\boldsymbol{\Pi}_0$ was calculated by expansion of the equation (3-27) in a Neumann series. We used hereby the assumption

$$\pi\,\sigma^2 \gg \gamma\,. \tag{431-3}$$

This implies that the two resonance lines with the resonance frequencies k_1^1 and k_3^1 are strongly saturated. The Green's operator $\tilde{\boldsymbol{G}}(\omega)$ can be estimated by the appli-

cation of perturbation theory. The expansion parameter is J/Δ. The result shows that it is sufficient to consider the approximation of zero-order to understand the main features of the resulting spectrum. The first and higher orders deliver only slight line broadenings and frequency shifts.

a) *Zero-order perturbation:*

In the vicinity of the frequency Ω_2, there exist in general two resonance lines. To characterize these lines, it is necessary to distinguish three different cases:

$$J < 2\pi\sigma^2 ,$$
$$J = 2\pi\sigma^2 ,$$
$$J > 2\pi\sigma^2 .$$

The respective data can be found in Table 1.

Table 1

Intensity, line width and resonance frequency of the two lines in the vicinity of Ω_2

case	line	relative intensity	half line width	resonance frequency
$J > 2\pi\sigma^2$	1	$\dfrac{1+\dfrac{1}{\sqrt{J^2/4\pi^2\sigma^4-1}}}{1+\pi\sigma^2/\Gamma}$	$\Gamma+\pi\sigma^2$	$\tilde{\Omega}_2+\frac{1}{2}\sqrt{J^2-4\pi^2\sigma^4}$
	2	$\dfrac{1-\dfrac{1}{\sqrt{J^2/4\pi^2\sigma^4-1}}}{1+\pi\sigma^2/\Gamma}$	$\Gamma+\pi\sigma^2$	$\tilde{\Omega}_2-\frac{1}{2}\sqrt{J^2-4\pi^2\sigma^4}$
$J = 2\pi\sigma^2$	1	$\dfrac{2}{1+J/2\Gamma}$	$\Gamma+J/2$	$\tilde{\Omega}_2$
	2	$\dfrac{\Gamma}{J}\dfrac{1}{\left(\Gamma/J+\frac{1}{2}\right)^2}$	$\Gamma(+J/2)\sqrt{\sqrt{5}-2}$	$\tilde{\Omega}_2$
$J < 2\pi\sigma^2$	1	$\dfrac{1+\dfrac{1}{\sqrt{1-J^2/4\pi^2\sigma^4}}}{1+\dfrac{1}{\Gamma}\left(\pi\sigma^2-\frac{1}{2}\sqrt{4\pi^2\sigma^4-J^2}\right)}$	$\Gamma+\pi\sigma^2-\frac{1}{2}\sqrt{4\pi^2\sigma^4-J^2}$	$\tilde{\Omega}_2$
	2	$\dfrac{1-\dfrac{1}{\sqrt{1-J^2/4\pi^2\sigma^4}}}{1+\dfrac{1}{\Gamma}\left(\pi\sigma^2+\frac{1}{2}\sqrt{4\pi^2\sigma^4-J^2}\right)}$	$\Gamma+\pi\sigma^2+\frac{1}{2}\sqrt{4\pi^2\sigma^4-J^2}$	$\tilde{\Omega}_2$

The relative intensity is defined by the ratio of the maxima of the absorption line shapes with and without the perturbation. $\tilde{\Omega}_2$ is defined by

$$\tilde{\Omega}_2 = \Omega_2 + \frac{1}{2} \Delta \left(1 - \sqrt{J^2/\Delta^2 + 1}\right) \tag{431-4}$$

and has the meaning of a 'corrected' Zeeman frequency of spin 2 under the influence of spin 1 (central frequency between the two doublet lines of spin 2).

The line shape is generally a Lorentzian function with the exeption of the special case $J = 2\pi\sigma^2$. In this case the line shape of line 2 has a more complicated form*). It has to be noticed that the intensity of the line 2 can get a negative sign; this means that the line is reversed and becomes negativ. But it can be shown that nevertheless the overall absorption signal, e. g. the sum of the two lines 1 and 2 never becomes negativ. The distance of the two lines is diminished by the influence of the stochastic perturbation. Simultaneously it occurs a line broadening proportional to the strength of the stochastic field. For $J = 2\pi\sigma^2$, the two lines are collapsing. In the case $J < 2\pi\sigma^2$ there results again a sharpening of one of the two collapsing lines meanwhile the intensity of the other line tends to zero. For $2\pi\sigma^2 \to \infty$, the spectrum consists of a single line with the initial line width Γ, and with twice the intensity of an initial single line. In the intermediate region, the overall absorption signal becomes asymmetric.

The behaviour of the spectrum for a typical value of $J/\Gamma = 8$ is shown in Figure 4.

The integral I of the whole spectrum of spin 2 is independent of the field strength of the stochastic perturbation. This statement holds only for the zero-order approximation

$$I = \int_{-\infty}^{\infty} \tilde{a}_0(\omega)\, d\omega\,. \tag{431-5}$$

It is important to note that in the limiting case, $2\pi\sigma^2 \to \infty$, the resonance frequency does not approach the resonance frequency Ω_2 of the uncoupled system but becomes equal to the corrected frequency $\tilde{\Omega}_2$. Although these two frequencies are identical for $J/\Delta \to 0$, they differ essentially for $J/\Delta \sim 1$. This means that the asymptotic resonance frequency for $2\pi\sigma^2 \to \infty$ is strongly dependent on the coupling constant J.

This is of course of great practical interest because it is therewith shown that it is not possible to measure with this new double resonance experiment immediately the chemical shifts independent of the various couplings. *This is a common property of all known double resonance experiments.*

The rotational invariance of this stochastic double resonance experiment causes a quite different spectrum compared with the usual double resonance methods with

*) For $J = 2\pi\sigma^2$, the line 2 in the absorption mode equals to

$$\text{const.}\ \frac{(\omega - \tilde{\Omega}_2)^2 - (\gamma + J/2)^2}{(\omega - \tilde{\Omega}_2)^2 + (\gamma + J/2)^2}\,.$$

This resonance line has a central positive peak, two zeros and two negative tails. The line width indicated in Table 1 is the half width of the central peak.

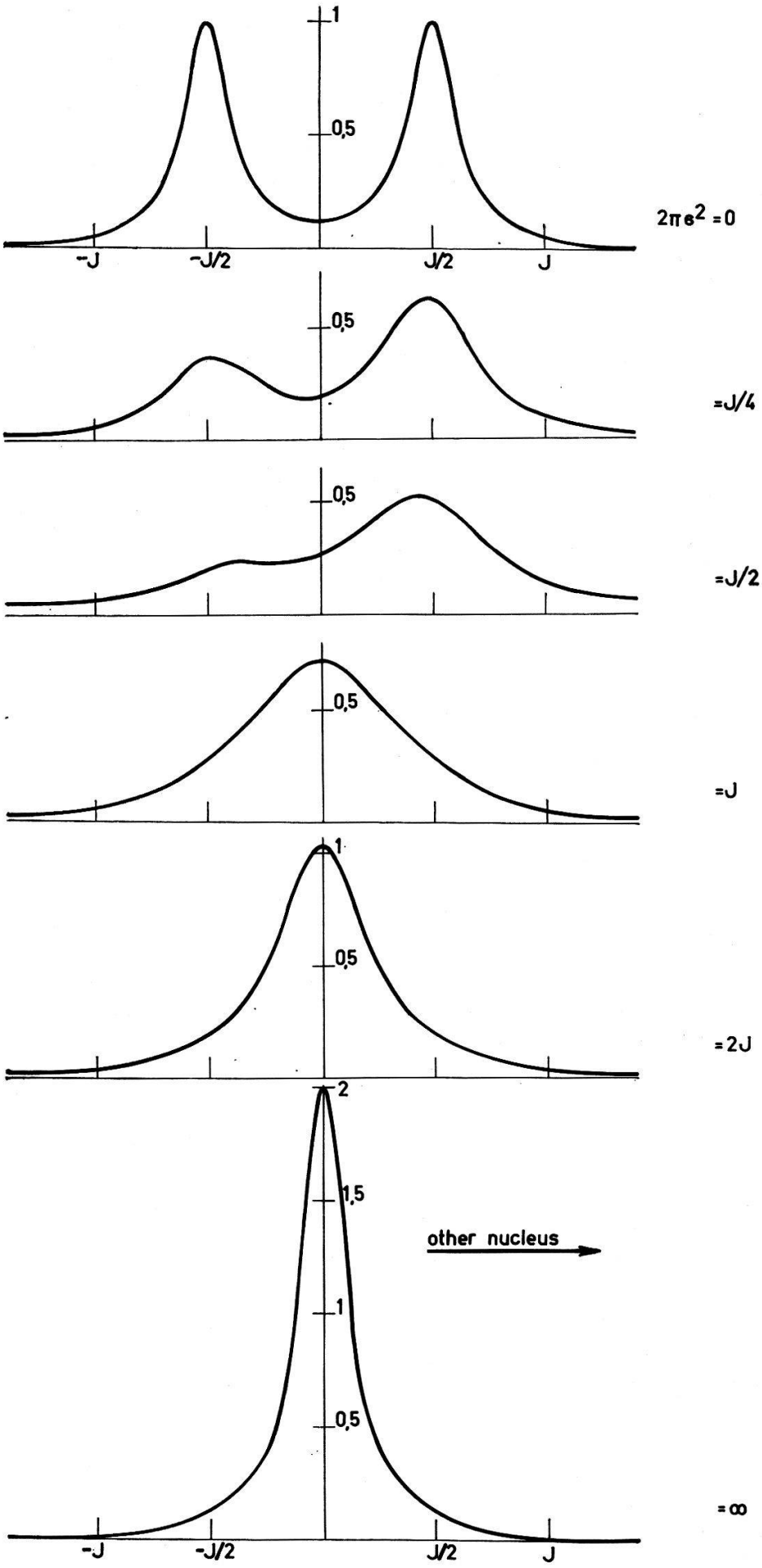

Fig. 4

Double resonance spectrum of a weakly coupled two-spin system with $J/\Gamma = 8$ for various strengths of the stochastic perturbation

a strong *rf*-field of definite frequency[9-13]). The here described experiment is essentially a field sweep method[12]); the difference between the frequencies the two *rf*-fields remains constant during the experiment; but nevertheless it has to be compared with the frequency sweep experiments of double resonance because the power spectrum of the stochastic *rf*-field does not change in the neighbourhood of the characteristic frequencies k_1^1, k_3^1, $\omega \pm \Delta$, $\Omega_1 + \Omega_2 - \omega$, of the spin system.

The double resonance spectrum of a weak coupled two-spin system with a rotating non-stochastic perturbation shows in general four lines in the vicinity of Ω_2[11])[12]). If the strength of the double resonance *rf*-field is increased, the distance of the two inner lines and the intensity of the two outer lines are diminished and the distance of the two outer lines and the intensity of the two inner lines are enhanced. In the limiting case a single line is resulting. If the double resonance frequency equals exactly Ω_2, the two inner lines are replaced by a single line with a frequency independent of the field strength of the perturbing field.

b) *First-order perturbation*

The contribution of the first-order perturbation produces a line broadening of both lines by

$$(J/\Delta)^2 \frac{\pi \sigma^2}{2} .$$

Therefore, the line width for $\pi \sigma^2 \to \infty$ is no more Γ, but gets a part proportional to the strength of the perturbing field. In the case of $J/\Delta \ll 1$, this line broadening can usually be neglected.

The Hilbert transform of the power spectrum causes simultaneously a weak line shift. This is not a proper Bloch-Siegert effect because the power spectrum is symmetrical with respect to the measuring frequency ω. This effect can accordingly be designated as an indirect Bloch-Siegert effect because it is a Bloch-Siegert effect with respect to the other spin which influences the spin under examination through the spin-spin coupling. In the case of $J/\Delta \ll 1$, this effect can be neglected too.

432. *Two-spin system with strong spin-spin coupling*

As a preliminary example, the case of a perturbation with a white power spectrum will be discussed.

a) *Perturbation with a white power spectrum*

The perturbation with a white power spectrum (power density independent on frequency) is mathematically the simplest case because any Bloch-Siegert effects are eliminated. The spectrum is symmetrical with respect to any frequency. The resulting line shifts are therefore pure double resonance effects. As mentioned above [1]), the approximation of second order in the parameter σ is exact for a white power spectrum. All terms of higher order vanish.

These effects would be very difficult to measure experimentally because the intensity of the resonance lines tends to zero with increasing field strength of the perturbation. Simultaneously, the line width grows considerably. Here we are interested only in the line shifts. The correlation function $\mathcal{K}(t)$ of the stochastic processes $s_n(t)$ is assumed to be

$$\mathcal{K}(t) = 2 \pi \delta(t) . \qquad (432\text{-}1)$$

Further it is supposed that the inequality holds:

$$\pi \sigma^2 \gg \Delta \,. \tag{432-2}$$

Only under this condition, a simple spectrum is to be expected, as the results for weak coupling suggest.

The properties of the resulting spectrum are the following: There are three resonance lines, all with the relative intensity

$$\frac{\Gamma}{\Gamma + 4\,\pi\,\sigma^2}$$

and the line width $\Gamma + 2\,\pi\,\sigma^2$. The three resonance frequencies are

$$\frac{\Omega_1 + \Omega_2}{2} = \frac{\tilde{\Omega}_1 + \tilde{\Omega}_2}{2}\,.$$

$$\left.\begin{aligned} \Omega_1 - \Delta\left(1 - \sqrt{J^2/\Delta^2 + 1}\right) &= \tilde{\Omega}_1\,, \\ \Omega_2 + \Delta\left(1 - \sqrt{J^2/\Delta^2 + 1}\right) &= \tilde{\Omega}_2\,. \end{aligned}\right\} \tag{432-3}$$

The line shape of all three lines are Lorentzian functions. It is again seen that the double resonance spectrum of a strongly coupled systems does not include lines at the resonance frequencies of the uncoupled system, even if the Bloch-Siegert shifts can be neglected. It is significant that in the middle of the two frequencies Ω_1 and Ω_2 a new line is produced. This reminds to the effects of multiple-quantum transitions[14])[15]). But of course, in the linear response which we have calculated here, no real multiple-quantum transitions can be obtained.

b) *Perturbation with a power spectrum according to Figure 3:*

The power spectrum here assumed shall have again the form (43-1) of Figure 3. For an exact discussion, it would be unavoidable to calculate the spectrum with an electronic computer. But for the purposes here pursued, it is sufficient to show that no enough simple spectrum can result, useful for the determination of the chemical shifts. If the spectrum is calculated for a stochastic *rf*-field of high field strength:

$$\pi \sigma^2 \gg \Delta\,, \tag{432-4}$$

neglecting the Hilbert transform of the power spectrum, four resonance lines are obtained. Three of these lines have a line width proportional to $\pi \sigma^2$, whilst the last line with the resonance frequency $(\Omega_1 + \Omega_2)/2$ has a line width which tends asymptotically for $\pi \sigma^2 \to \infty$ towards the initial line width γ. The intensities of all the four lines go to zero for a strong perturbation. It is easy to show that in the intermediate region $\pi \sigma^2 \sim \Delta$ likewise no simple spectrum is resulting. The effect of the hereby neglected Hilbert transform of the power spectrum is essentially a small shift of the three broad lines. It is seen that the chemical shift differencies will be eliminated too by applying a perturbation strong enough to eliminate the effects of the spin-spin coupling. Additionally, the strong coupling causes all intensities to become very small. This means that it is scarcely possible to get any valuable information in a simple form about the strongly coupled system under investigation by applying this double resonance method.

5. Conclusions

In a double resonance experiment with an appropriate stochastic perturbation, it is possible to save the rotational invariance of the equations. The resulting spectrum will be simplified thereby considerably with respect to the usual double resonance method with a rotating field of definite frequency which destroys the rotational symmetry. It is important to take the ensemble average of the linear response of the system to restore the invariance.

In the two-spin system with two spins 1/2, the spectrum resulting by the application of such a stochastic perturbation consists at most of only four different resonance frequencies. On the other hand in the case of a rotating deterministic field, 12 different lines can be observable.

For weak spin-spin coupling, this simplification is only essential in intermediate region of a fairly strong perturbation: $2\pi\sigma^2 \sim J$. In the limiting case $2\pi\sigma^2 \gg J$, both methods result in a single sharp line and are therefore equivalent. Both methods could be used to determine the chemical shifts. The intermediate region is of some practical interest in certain special applications of double resonance experiments, e.g. the determination of the relative signs of the spin-spin coupling constants.

In the case of strong spin-spin coupling, no simple useful spectrum results. In particular, no resonance frequencies are produced at the positions of the Zeeman frequencies of the uncoupled spins. By the application of a very strong perturbing, stochastic field a single sharp resonance line with very small intensity is caused in the proximity of $(\Omega_1 + \Omega_2)/2$.

This example shows that the here used and elsewhere described[1]) functional expansion of the density operator is useful to calculate the effects of strong stochastic perturbations on a quantum mechanical system. In most cases it is sufficient to consider the first term of the expansion only.

Acknowledgment

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