Approximate Methods in Analysis of NMR Spectra
I. Application of Perturbation Theory to Decomposition of Many-Spin Systems

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Abstract

By means of perturbation theory, expressions for transition frequencies and intensities have been derived for many-spin systems which can be decomposed into several weakly interacting subsystems. The way in which these expressions have to be modified in cases where the basic system is symmetrical has also been shown.

Keywords: HR-NMR, NMR spectroscopy, Analysis of spectra, Perturbation theory

APPROXIMATE METHODS IN ANALYSIS OF NMR SPECTRA. I.

APPLICATION OF PERTURBATION THEORY TO DECOMPOSITION OF MANY-SPIN SYSTEMS

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By means of perturbation theory, expressions for transition frequencies and intensities have been derived for many-spin systems which can be decomposed into several weakly interacting subsystems. The way in which these expressions have to be modified in cases where the basic system is symmetrical has also been shown.

NMR spectra of complicated spin systems are usually analysed by direct calculation of the spectrum from trial parameters (chemical shifts and coupling constants) with subsequent refinement by an iteration procedure. The size of the computational work necessary for the direct spectrum calculation itself increases very rapidly with the number of the nuclei considered, and the possibilities of present computational techniques do not practically reach beyond the general nine spin system. Systematic studies of possible approximate procedures are therefore of considerable importance for the analysis of many-spin systems.

All the present approximate methods are either based on, or can be derived from the perturbation theory. This is, first of all, the well known "first-order analysis", in which all spin–spin interactions are considered as a perturbation, with subsequent application of the first order perturbation theory[1]. This method is satisfactory only in those cases where all the coupling constants are small compared with the corresponding chemical shifts. This limitation is partly removed by the "effective frequency" method introduced by Pople and Schaefer[2] and later generalized by Diehl and coworkers[3] (so called "subspectral analysis"); this can in principle be applied to any system in which the coupling of several nuclei (or groups of equivalent nuclei) with the remaining (inner) part of the system is weak. If this coupling is considered as a perturbation, it can be shown that the spectrum of the inner part of the system behaves approximately as the sum of subspectra each of which corresponds to a certain spin state of the weakly coupled nuclei. All the subspectra can be calculated from the Hamiltonian of the inner part of the system in which the parameters (chemical shifts) have been modified following very simple rules. The number of cases to which subspectral analysis can be applied is strongly limited by the requirement that the inner part of the system should weakly interact only with individual, mutually noninteracting nuclei or groups of equivalent nuclei.

In this paper, a different approach to the application of perturbation theory in the analysis of many-spin systems is used. In many cases the whole system can be divided into two or more mutually weakly coupled subsystems G_α (Fig. 1). We expect intuitively that in these cases the spectrum will consist of a superposition of the spectra of the individual subsystems. The spectrum of each subsystem in turn is expected to consist of a series of subspectra corresponding to different spin states of the remaining subsystems. Individual subspectra can be determined so that the dependence of the frequency and intensity of each resonance transition on the spin state of the remaining subsystems is determined.
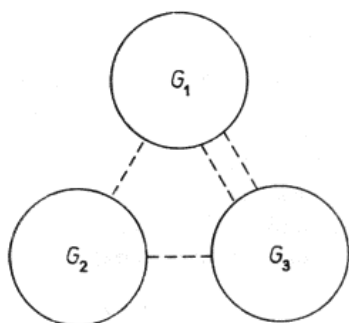

FIG. 1

Schematic Decomposition of a System into Subsystems
Couplings between subsystems are indicated by dashed lines.

Perturbation Treatment

The Hamiltonian of the above system can be written in the form

$$H = H_0 + H', \quad H_0 = \sum_{\alpha=1}^{N} H_\alpha \tag{1}$$

$$H' = -\sum_{s,t} J_{st}\, \bar{I}_s \cdot \bar{I}_t, \quad s \in G_\sigma, \ t \in G_\tau, \ G_\sigma \neq G_\tau,$$

where N is the number of subsystems, H_α is the Hamiltonian of the isolated subsystem G_α and H' is the perturbation part involving only interactions between different subsystems.

Let the number of nuclei in subsystem G_α be n_α. If the eigenvalues $\varepsilon_\alpha(k)$ of the Hamiltonian H_α are arranged in a diagonal matrix $\bar{\varepsilon}_\alpha$ (of order 2^{n_α}) and the corresponding eigenfunctions $\varphi_\alpha(k)$ in a vector $\bar{\varphi}_\alpha$, we can write

$$H_\alpha \bar{\varphi}_\alpha = \bar{\varepsilon}_\alpha \bar{\varphi}_\alpha . \tag{2}$$

The energies $\varepsilon_\alpha(k)$ and functions $\varphi_\alpha(k)$ can be obtained for each subsystem by conventional methods and in the following they will be cosidered as known.

The eigenfunctions of the unperturbed Hamiltonian H_0 are represented by the 2^n

(n is the total number of nuclei) functions of type

$$\Phi_{0j} = \prod_{\alpha=1}^{N} \varphi_\alpha(k_\alpha), \quad k_\alpha = 1, 2, \ldots, 2^{n_\alpha}. \tag{3}$$

The corresponding eigenvalues of H_0 are given by the additive relation

$$E_{0j} = \sum_{\alpha=1}^{N} \varepsilon_\alpha(k_\alpha). \tag{4}$$

The functions Φ_{0j} can be again arranged in a vector $\bar{\phi}_0$ and schematically be written as

$$\bar{\phi}_0 = \prod_{\alpha=1}^{N} \bar{\varphi}_\alpha, \quad H_0\bar{\phi}_0 = \bar{E}_0\bar{\phi}_0, \tag{5}$$

with the symbol $\overline{\overline{\prod}}$ designating the cartesian product and $\bar{E}_0$ the diagonal matrix of the energies E_{0j}.

The matrices $\bar{H}'$ and $\bar{C}$ can now be formed according to the relations

$$\bar{H}' = \langle \bar{\phi}_0 | H' \bar{\phi}_0^t \rangle \tag{6}$$

$$\bar{C}_{km} = \left\langle \begin{array}{ll} H'_{km}/(E_{0k} - E_{0m}) & \text{for } k \neq m \\ 0 & \text{for } k = m. \end{array} \right. \tag{7}$$

According to the Rayleigh-Schrödinger perturbation theory, the diagonal matrix $\bar{E}$ of the eigenvalues of the Hamiltonian H and the corresponding vector of eigenfunctions $\bar{\psi}$ can be expanded

$$\bar{E} = \bar{E}_0 + \bar{E}_1 + \bar{E}_2 + \ldots \tag{8}$$

$$\bar{\psi} = \bar{\phi}_0 + \bar{\phi}_1 + \ldots \tag{9}$$

with the first order corrections with respect to H' being

$$(\bar{E}_1)_{ij} = H'_{ii}\delta_{ij} \text{ (diagonal part of matrix } \bar{H}'), \tag{10}$$

$$\bar{\phi}_1 = C\bar{\phi}_0 \tag{11}$$

and the second order corrections

$$(\bar{E}_2)_{ij} = (\bar{H}'\bar{C})_{ii}\delta_{ij} \text{ (diagonal part of matrix } \bar{H}'\bar{C}). \tag{12}$$

From relations $(6)-(11)$ it can be seen that the first order corrections are linear and the second order corrections quadratic with respect to the coupling constants J_{st} between nuclei of different subsystems.

In the application of the preceding relations we have to consider the symmetry of the basic system G_0 arising from the complete system by removal of the couplings between the individual subsystems G_α.

A. Unsymmetrical Basic System

In this case no new degenerations are formed by the connection of the Hamiltonians H_α. If the interactions between subsystems are sufficiently weak, then

$$\overline{C}_{km} \ll 1 \tag{13}$$

and only first order corrections may be considered.

For the elements of the matrix $\overline{H}'$, the relation

$$\overline{H}'_{km} = -\sum_{s,t} J_{st} \cdot e_{\sigma,\tau}(k, m), \quad s \in G_\sigma, \ t \in G_\tau, \ G_\sigma \neq G_\tau, \tag{14}$$

is obtained from equation (6) by a simple rearrangement, with the coefficients $e_{\sigma,\tau}(k, m)$ given only by the eigenfunctions of the Hamiltonians H_σ, H_τ:

$$e_{\sigma,\tau}(k, m) = \gamma_{\sigma,\tau}(k, m) \cdot \langle \varphi_\sigma(k)\varphi_\tau(k) \mid \overline{I}_s \cdot \overline{I}_t \varphi_\sigma(m)\varphi_\tau(m) \rangle \tag{15}$$

$$\gamma_{\sigma,\tau}(k, m) = \begin{cases} 1 & \text{if } \varphi_\alpha(k) \equiv \varphi_\alpha(m) \text{ for all } \alpha \neq \sigma, \tau \\ 0 & \text{in all other cases.} \end{cases}$$

Let us now consider how the transitions of a given subsystem G_σ are affected by the perturbation. A transition from state ψ_k to state ψ_l (abbreviated as $k \to l$) can be classified as a transition inside subsystem G_σ, if

$$\varphi_\sigma(k) \neq \varphi_\sigma(l),$$
$$\varphi_\alpha(k) \equiv \varphi_\alpha(l) = \varphi_\alpha(k, l) \text{ for all } \alpha \neq \sigma. \tag{16}$$

According to (10), (14) and (15), for such a transition the frequency change given by mutual interactions of subsystems, is equal to

$$\Delta v_\sigma(k, l) = \overline{H}'_{ll} - \overline{H}'_{kk} =$$
$$\sum_{s,t} J_{st} \cdot \langle \varphi_\tau(kl) \mid I_{tz}\varphi_\tau(kl) \rangle \{ \langle \varphi_\sigma(k) \mid I_{sz}\varphi_\sigma(k) \rangle - \langle \varphi_\sigma(l) \mid I_{sz}\varphi_\sigma(l) \rangle \}$$
$$s \in G_\sigma, \ t \in G_\tau, \ \tau \neq \sigma. \tag{17}$$

This relation can be expressed as rule I:

Each interaction between the nuclei $s \in G_\sigma$ and $t \in G_\tau$ affects the frequency of the transition $k \rightarrow l$ in the subsystem G_σ by a value which in the first approximation is equal to the product of the coupling constant J_{st}, the density of the operator I_z on nucleus t and the change of the density of operator I_z on nucleus s resulting from the transition $k \rightarrow l$.

If the structure and eigenfunctions of all subsystems are known, the frequency of any transition in subsystem G_σ can be calculated by means of relation (17) for any spin state of the other subsystems. But even in those cases where the structure of some subsystems is not known, or is too complicated for an explicit solution, useful informations about the sensitivity limits of various transitions in G_σ to the state of the other subsystems can be obtained. From relation (17)

$$|\Delta v_\sigma(kl)| < \tfrac{1}{2} \cdot \sum_{s,t} |J_{st}| \cdot |\langle \varphi_\sigma(k)| \, I_{sz}\varphi_\sigma(k)\rangle - \langle \varphi_\sigma(l) \, I_{sz}\varphi_\sigma(l)\rangle| \, . \tag{18}$$

The so determined upper limit for $\Delta v_\sigma(kl)$ is given only by the properties of the isolated subsystem G_σ. This can be used *e.g.* for the estimation of the maximum error caused by substituting a smaller fragment for a large system in the analysis of the transitions on a certain nucleus or group of nuclei.

Relation (17) can be supplemented by an analogous relation for the change of transition intensities. The intensity P_{kl} of the transition $k \rightarrow l$ is given by

$$P_{kl} = |\langle \psi_k | \, I_x\psi_l\rangle|^2 \, . \tag{19}$$

Using equations (9) and (11), and taking into account only first order members with respect to H', we obtain

$$\Delta P_{kl} = P_{kl} - P_{0kl} = 2p_{kl} \cdot \sum_m (C_{km}p_{ml} - p_{km}C_{ml}) \, , \tag{20}$$

where $p_{mn} = \langle \Phi_{0m} | \, I_x\Phi_{0n}\rangle$ a $P_{0kl} = |p_{kl}|^2$ is the intensity of transition $k \rightarrow l$ in unperturbed state. The quantities p_{mn} can be represented as elements of a matrix $\bar{\mathbf{p}}$ and equation (20) transformed into the interesting form

$$\Delta P_{kl} = 2p_{kl}[\bar{\mathbf{C}}, \bar{\mathbf{p}}]_{kl} \, . \tag{21}$$

If $P_{0kl} = 0$, then also $p_{kl} = 0$ and according to (19) also $P_{kl} = 0$. From this, rule II can be derived:

Selection rules operating in the isolated subsystem G_σ remain valid (to first order with respect to J_{st}) also after the consideration of the interactions with other subsystems.

B. *Symmetrical Basic System*

Let us assume that the decomposition of the system into subsystems is symmetrical, *i.e.* that the symmetry group of the whole system is an invariant subgroup of the symmetry group $\mathscr{T}$ of the basic system G_0. In the opposite case there arise approximate degenerations of the Hamiltonian H_0 and the conditions (13) can be severely violated for some C_{km}.

Two possibilities can now arise:

a) Any of the subsystems G_α is invariant with respect to all the elements of group $\mathscr{T}$. In this case new degenerations do not arise from the connection of the Hamiltonians H_α, so that the results of the previous paragraph for unsymmetrical systems can be directly applied.

b) Some of the subsystems G_α are transformed by some elements R of group $\mathscr{T}$ into different subsystems. Then by the operation of element R on the eigenfunction Φ_{0k} of Hamiltonian H_0 a different eigenfunction Φ_{0l}

$$\Phi_{0l} = R(\Phi_{0k}) \tag{22}$$

is in general obtained. The functions Φ_{0l} and Φ_{0k} correspond to equal energy, so that the Hamiltonian H_0 is degenerate and the corresponding coefficient C_{kl} is not defined. In this case it is therefore necessary to symmetrize the system of basic functions Φ_{0l} according to the irreducible representations of group $\mathscr{T}$ and to apply the relations $(6)-(11)$ after the symmetrization.

As the simplest example let us consider a system composed of two subsystems, mutually symmetric with respect to the plane σ with a single interaction $J_{ss'}$ between the nuclei s and s'. For a given arrangement of the eigenfunctions $\varphi_{\alpha k}$ $(k = 1, 2, \ldots, 2^{n_\alpha})$ of the isolated subsystem G_α, the arrangement of the eigenfunctions of subsystem G_β is determined by symmetry:

$$\varphi_{\beta k} = \sigma(\varphi_{\alpha k}) . \tag{23}$$

In this case we can designate the functions Φ_0 by means of a pair of indices k, l so that

$$\Phi_{0k,l} = \varphi_{\alpha k}\varphi_{\beta l}, \quad \Phi_{0l,k} = \sigma(\Phi_{0k,l}) . \tag{24}$$

The symmetrized basis consists of a symmetrical and antisymmetrical set:

$$\text{Symmetrical set} - \begin{cases} \Phi_0^+(kk) = \Phi_{0k,k} \\ \Phi_0^+(kl) = (\Phi_{0k,l} + \Phi_{0l,k})/(2)^{1/2} \end{cases}$$

$$\text{Antisymmetrical set} \quad \Phi_0^-(kl) = (\Phi_{0k,l} - \Phi_{0l,k})/(2)^{1/2} \tag{25}$$

A conventional evaluation of the matrix elements H' in the basis (25) leads to the relation

$$\langle \Phi_0^{\pm}(mn) \mid H'\Phi_0^{\pm}(mn)\rangle = -J_{ss'} \cdot \{(\mathbf{I}_{sz})_{mm} \cdot (\mathbf{I}_{sz})_{nn} \pm \tfrac{1}{2}|(\mathbf{I}_{sx})_{mn}|^2\}, \qquad (26)$$

where $A_{ij} = \langle \varphi_i \mid \mathbf{A}\varphi_j\rangle$ for any operator $\mathbf{A}$.

Let us designate the matrix element $p_{mn} = (\mathbf{I}_x)_{mn}$ as the amplitude of the transition $m \to n$ (see also equation (20)). Therefore the quantity $(\mathbf{I}_{sx})_{mn}$ in equation (26) is to be understood as the contribution of nucleus s to the amplitude of the transition $m \to n$.

The transition $k \to m$ in the isolated subsystem G_α corresponds to the transitions $\Phi_0^{\pm}(kl) \to \Phi_0^{\pm}(ml)$ $(l = 1, 2, \ldots, 2^{n_\alpha})$. The frequency change of such a transition caused by interaction between the systems is according to (26) equal to

$$\Delta v_1(km) =$$
$$= -J_{ss'} \cdot \{((\mathbf{I}_{sz})_{mm} - (\mathbf{I}_{sz})_{kk}) \cdot (I_{sz})_{11} \pm \tfrac{1}{2}(|(\mathbf{I}_{sx})_{ml}|^2 - |(\mathbf{I}_{sx})_{kl}|^2)\}. \qquad (27)$$

The upper sign in this equation corresponds to symmetrical and the lower to antisymmetrical transitions. In cases where both systems are coupled through more pairs of nuclei s, s', a summation over all these pairs has to be introduced into relation (27).

Without loss of generality we can further assume that $(\mathbf{I}_z)_{mm} - (\mathbf{I}_z)_{kk} = 1$. We can then obtain rule III from relation (27).

A coupling $J_{ss'}$ between two equal subsystems G_α, G_β leads to a splitting of the transition $k \to m$ of subsystem G_α into a symmetrical and antisymmetrical component. The center of transition shifts as a function of the spin state l of the subsystem G_β similarly as in unsymmetrical case (rule I). The magnitude of the splitting between the symmetrical and antisymmetrical line is equal to:

$a)$ 0 for $(\mathbf{I}_z)_{11} - (\mathbf{I}_z)_{mm} > 1$ or $(\mathbf{I}_z)_{kk} - (\mathbf{I}_z)_{11} > 1$,

$b)$ $J_{ss'} \cdot |(\mathbf{I}_{sx})_{kl}|^2$ for $(\mathbf{I}_z)_{kk} - (\mathbf{I}_z)_{11} = 1$ or $(\mathbf{I}_z)_{11} = (\mathbf{I}_z)_{mm}$,

$c)$ $-J_{ss'} \cdot |(\mathbf{I}_{sx})_{ml}|^2$ for $(\mathbf{I}_z)_{11} - (\mathbf{I}_z)_{mm} = 1$ or $(\mathbf{I}_z)_{11} = (\mathbf{I}_z)_{kk}$.

CONCLUSION

The method described makes it possible to express explicitly the effect of weak coupling between several spin subsystems upon transitions inside these subsystems (rules I and II). The modifications necessary in cases where the basic system is symmetrical have also been indicated. As an example, transition frequencies have been derived for a system composed of two mutually coupled equal subsystems (rule III).

If neither of the subsystems contains more than two spin $^1/_2$ nuclei, the above theory leads to explicit expressions for transition frequencies and intensities. More important, however, is the fact that a) this method makes possible analysis in cases where the whole system is too extensive for direct treatment, and b) it yields an upper limit of error in analysis by means of fragments.

In the preceding text only spin 1/2 nuclei have been considered. However, the relations derived remain valid (but for a trivial modification of the inequality (18)) also for systems with higher spin values (only the numbers of basic functions have to be changed).

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