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Analysis of NMR Spectra of Magnetically Inequivalent Nuclei Using Perturbation Theory

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A method of analysis of NMR spectra based upon degenerate-state perturbation theory is developed. The technique can be applied to the analysis of NMR spectra of sets of nuclei which are magnetically inequivalent, *i. e.*, sets of nuclei which have different couplings between chemically equivalent groups. The method is illustrated by analysis of the spectrum of 1-indanone, which is of the type AA′BB′. Satisfactory results can be obtained by a second order analysis, even for quite strongly coupled spectra. Closed form expressions have been derived for the AA′BB′ spectrum which are correct to second order.

Für die Analyse von Kernresonanzspektren wird eine Methode angegeben, die auf der Störungsrechnung für entartete Systeme beruht und die auch im Fall mehrerer Kopplungskonstanten zwischen zwei unter sich chemisch äquivalenten Gruppen von Protonen gilt. Als Beispiel dafür wird das Spektrum des 1-Indanons (Typ AA′BB′) behandelt, wobei bereits die zweite Näherung befriedigende Ergebnisse liefert und in geschlossener Form angegeben wird.

Sur base de la théorie des perturbations des états dégenerés, nous avons développé une méthode pour analyser des spectres NMR. Cette méthode s'applique à des molécules, qui ont de couplages différents entre plusieurs groupes d'atomes équivalents. Le procédé est illustré par l'analyse du spectre de 1-indanone du type AA′BB′. Le second ordre du calcul rend de résultats satifaisants, même au case de couplages assez forts. Des expressions closes, correctes jusqu'au second ordre, sont dérivées pour le spectre AA′BB′.

1. Introduction

The essential features involved in the analysis of NMR spectra have been clearly understood for quite some time, and have been discussed at length in such standard reference works as POPLE, SCHNEIDER, and BERNSTEIN [*11*]. An excellent review devoted entirely to NMR spectrum analysis has also been given by CORIO [*4*]. The assignment of transitions can often be simplified by the use of such techniques as moment analysis [*2*], double irradiation [*1*], excitation of multiple quantum transitions [*14*], isotopic substitution [*12*]; and group theoretical methods are frequently useful for the simplification of the calculations [*9*]. However, the basic problem remains one of a solution of secular equations for the transition frequencies and intensities based on a set of estimated parameters. The successive adjustment of these parameters to fit the calculated with the experimental spectrum can be accomplished automatically by computer analysis in many cases [*13, 14*].

There are limitations on the number of nuclei which can be treated by such calculations, and it appears that about 6 — 8 nuclei constitutes a practical upper limit on the number of magnetic nuclei which can be conveniently handled in a complete treatment with modern computational facilities. Although a complete solution is to be preferred if feasible, one may have to rely on approximation methods in many cases. A treatment based upon perturbation theory has been given by ANDERSON [*1*] and applied with success to the analysis of the spectrum of ethyl alcohol by ARNOLD [*3*]. ANDERSON'S approach can be used to analyze the NMR spectrum of any number of sets of equivalent nuclei, subject to the restriction that there is only one coupling constant between nuclei in any given pair of sets. It is well known that in such a case, the spectrum is independent of the coupling between nuclei within a set.

It is equally well known that much more information can be obtained from spectra which show magnetic inequivalence between chemically equivalent sets. In such cases the coupling between chemically equivalent nuclei can be determined by a complete analysis of the spectrum. The best known example of this occurs in the A_2B_2 spectra of molecules which are rigid so that averaging of the coupling between the A and B nuclei cannot occur. The above-mentioned perturbation cannot be applied in such cases. It is the purpose of this paper to present a method of analysis based upon degenerate-state perturbation theory which is sufficiently general to include the case of magnetic inequivalence.

2. Outline of the Method

The appropriate Hamiltonian operator for NMR spectrum analysis is [*11*],

$$H = \sum_i \nu_i I_z(i) + \sum_{i<j} J_{ij} \boldsymbol{I}(i) \cdot \boldsymbol{I}(j) \tag{1}$$

where $\nu_i = \frac{1}{2\pi} \gamma_i (1 - \sigma_i) H_0$. γ_i is the magnetogyric ratio of the nucleus in question, and σ_i is the electronic screening constant. The first term in Eq. (1) thus represents the energy of interaction of the nucleus with the externally applied magnetic field, H_0, and the second term gives the energy of nuclear spin-spin coupling as represented by the magnitude of the constant J_{ij}. The state functions are taken to be the products of spin functions of the individual nuclei and are classified with respect to the expectation value of the total z-component of spin $\sum_i I_z(i)$.

Following the usual perturbation theory procedure, H is assumed to be of the form,

$$H = H^{(0)} + \lambda H^{(1)} \tag{3}$$

Using the definition, $I_\pm = I_x \pm i I_y$, the spin coupling term can be written

$$\sum_{i<j} J_{ij} [I_z(i) I_z(j) + \tfrac{1}{2} I_+(i) I_-(j) + \tfrac{1}{2} I_-(i) I_+(j)] .$$

It is obvious that no mixing of energy states occurs as a result of the first term, so that it is convenient to group it with the external field interaction term to obtain, for the zeroth-order Hamiltonian,

$$H^{(0)} = \sum_i \nu_i I_z(i) + \sum_{i<j} J_{ij} I_z(i) I_z(j) . \tag{4}$$

The perturbation Hamiltonian is then taken to be

$$H^{(1)} = \tfrac{1}{2} \sum_{i<j} J_{ij} [I_+(i) I_-(j) + I_-(i) I_+(j)] . \tag{5}$$

The appropriate matrix elements can readily be constructed using simple rules [*4*, *11*]. Due to the nature of the perturbation problem involving degenerate zeroth-order states, it is doubtful that convenient closed form expressions for the energies are possible. A considerable factorization is accomplished by the above choice of a zeroth-order Hamiltonian, however, so that much smaller secular equations are involved.

Results which are correct to the second-order have been given by KEMBLE [*8*], and were used in the present investigation. The third-order results have been derived similarly, with the energy being given as a root of the equation

$$\widehat{U}^{(0)}\,(kl;\,ki)\,E_{ki}^{(3)} + \widehat{U}^{(1)}\,(kl;\,ki)\,E_{ki}^{(2)} + \sum_{l'''} G\,(kl;\,kl''')\,\widehat{U}^{(0)}\,(kl''';\,ki) = 0 \qquad (6)$$

where the matrix G is defined by

$$G\,(kl;\,kl''') = \sum_{k' \neq k}\sum_{l'} \frac{(E_{ki}^{(1)} - E_{k'l'}^{(1)})}{(E_{k}^{(0)} - E_{k'}^{(0)})^2}\,\widehat{H}^{(1)}\,(kl;\,k'l')\,\widehat{H}^{(1)}\,(k'l';\,kl''') +$$
$$+ \sum_{k' \neq k}\sum_{l'}\sum_{k'' \neq k}\sum_{l''} \frac{\widehat{H}^{(1)}\,(k\,l;\,k'\,l')\,\widehat{H}^{(1)}\,(k'\,l';\,k''\,l'')\,\widehat{H}^{(1)}\,(k''\,l'';\,k\,l''')}{(E_{k'}^{(0)} - E_{k}^{(0)})(E_{k}^{(0)} - E_{k''}^{(0)})}\,.$$

The notation corresponds to that used by KEMBLE, and it is necessary to sum Eq. (6) only over the states which remain degenerate in the first order.

It might be noted that the zeroth-order wave functions, as contained in $U^{(0)}$, are completely determined in the first order only if the degeneracy is entirely removed; otherwise, the calculation must be extended to the second order for their determination. Similarly, the first order corrections, $U^{(1)}$, in general, necessitate a calculation of the third order energies. Thus, it will not prove very useful to rely on the intensities for an assignment of transitions in any but the most simple cases.

3. The AA′ BB′ System

Although mathematically one could treat magnetic inequivalence in an AA′B system, the simplest case in which it occurs in practice is in the AA′BB′ spectrum. (The obvious convention used here is the designation of nuclei which differ only through magnetic inequivalence by primes.) The characteristics of this type spectrum have been investigated by several authors [*5*, *6*, *9*, *10*] with explicit expressions for the A_2X_2 limit having been given by MCCONNELL, MCLEAN, and REILLY [*9*]. Of the 54 transitions possible for a general four-spin system, only 24 are observed, and these occur as two sets of "mirror images" which are symmetric about $(\nu_A + \nu_B)/2$.

The calculation of the spectrum based upon the method outlined in the last section is quite simple in this case. The straight-forward evaluation of the matrix elements of $H^{(0)}$ shows that the largest set of secular equations which must be solved is of order 2 × 2. Thus, explicit expressions can be obtained for the transition frequencies using the perturbation theory approach. These energies, correct to second order, are shown in Tab. 1 together with the appropriate zeroth-order wave functions. The notation introduced by MCCONNELL, MCLEAN, and REILLY [*9*] is used throughout:

$$K = J_{AA'} + J_{BB'} \qquad L = J_{AB} - J_{A'B}$$
$$M = J_{AA'} - J_{BB'} \qquad N = J_{AB} + J_{A'B}\,.$$

Table 1. *Energies of the* AA′ BB′ *system, correct to second order*

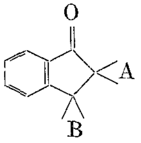
State	ΣI_z	ψ_0	E_0	E_1	E_2
1	2	$\alpha\alpha\alpha\alpha$	$\nu_A + \nu_B + \frac{1}{4}K + \frac{1}{2}N$	0	0
2	1	$\frac{1}{\sqrt{2}}(\alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha)$	$\nu_A + \frac{1}{4}M$	$\frac{1}{4}(K - M)$	$\frac{\frac{1}{4}N^2}{\nu_A - \nu_B + \frac{1}{2}M}$
3	1	$\frac{1}{\sqrt{2}}(\alpha\alpha\alpha\beta - \alpha\alpha\beta\alpha)$	$\nu_A + \frac{1}{4}M$	$-\frac{1}{4}(K - M)$	$\frac{\frac{1}{4}L^2}{\nu_A - \nu_B + \frac{1}{2}M}$
4	1	$\frac{1}{\sqrt{2}}(\alpha\beta\alpha\alpha + \beta\alpha\alpha\alpha)$	$\nu_B - \frac{1}{4}M$	$\frac{1}{4}(K + M)$	$\frac{-\frac{1}{4}N^2}{\nu_A - \nu_B + \frac{1}{2}M}$
5	1	$\frac{1}{\sqrt{2}}(\alpha\beta\alpha\alpha - \beta\alpha\alpha\alpha)$	$\nu_B - \frac{1}{4}M$	$-\frac{1}{4}(K + M)$	$\frac{-\frac{1}{4}L^2}{\nu_A - \nu_B + \frac{1}{2}M}$
6	0	$\alpha\alpha\beta\beta$	$\nu_A - \nu_B + \frac{1}{4}K - \frac{1}{2}N$	0	$\frac{\frac{1}{8}(N-L)^2}{\nu_A - \nu_B + \frac{1}{2}K - \frac{1}{2}(N+L)} + \frac{\frac{1}{8}(N+L)^2}{\nu_A - \nu_B + \frac{1}{2}K - \frac{1}{2}(N-L)}$
7	0	$\frac{1}{\sqrt{2}}(\alpha\beta\alpha\beta + \beta\alpha\beta\alpha)$	$-\frac{1}{4}K + \frac{1}{2}L$	0	$\frac{K^2}{4L} + \frac{1}{8}(N-L)^2 \left\{\frac{(N+L-K)}{\frac{1}{4}(N+L-K)^2 - (\nu_A - \nu_B)^2}\right\}$
8	0	$\frac{1}{\sqrt{2}}(\alpha\beta\beta\alpha + \beta\alpha\alpha\beta)$	$-\frac{1}{4}K - \frac{1}{2}L$	0	$\frac{-K^2}{4L} + \frac{1}{8}(N+L)^2 \left\{\frac{(N-K-L)}{\frac{1}{4}(N-K-L)^2 - (\nu_A - \nu_B)^2}\right\}$
9	0	$\frac{1}{\sqrt{2}}(\alpha\beta\beta\alpha - \beta\alpha\alpha\beta)$	$-\frac{1}{4}K - \frac{1}{2}L$	0	$\frac{-\frac{1}{4}M^2}{\frac{1}{2}K + L}$
10	0	$\frac{1}{\sqrt{2}}(\alpha\beta\alpha\beta - \beta\alpha\beta\alpha)$	$-\frac{1}{4}K + \frac{1}{2}L$	0	$\frac{\frac{1}{4}M^2}{\frac{1}{2}K + L}$
11	0	$\beta\beta\alpha\alpha$	$-\nu_A + \nu_B + \frac{1}{4}K - \frac{1}{2}N$	0	$\frac{\frac{1}{8}(N-L)^2}{-\nu_A + \nu_B + \frac{1}{2}K - \frac{1}{2}(N+L)} + \frac{\frac{1}{8}(N+L)^2}{-\nu_A + \nu_B + \frac{1}{2}K - \frac{1}{2}(N-L)}$
12	−1	$\frac{1}{\sqrt{2}}(\alpha\beta\beta\beta + \beta\alpha\beta\beta)$	$-\nu_B - \frac{1}{4}M$	$\frac{1}{4}(K + M)$	$\frac{\frac{1}{4}N^2}{\nu_A - \nu_B - \frac{1}{2}M}$

Table 1 (Continued)

State	ΣI_z	ψ_0	E_0	E_1	E_2
13	−1	$\frac{1}{\sqrt{2}}(\alpha\beta\beta\beta - \beta\alpha\beta\beta)$	$-\nu_B - \frac{1}{4}M$	$-\frac{1}{4}(K+M)$	$\frac{\frac{1}{4}L^2}{\nu_A - \nu_B - \frac{1}{2}M}$
14	−1	$\frac{1}{\sqrt{2}}(\beta\beta\alpha\beta + \beta\beta\beta\alpha)$	$-\nu_A + \frac{1}{4}M$	$\frac{1}{4}(K-M)$	$\frac{\frac{1}{4}N^2}{-\nu_A + \nu_B + \frac{1}{2}M}$
15	−1	$\frac{1}{\sqrt{2}}(\beta\beta\alpha\beta - \beta\beta\beta\alpha)$	$-\nu_A + \frac{1}{4}M$	$-\frac{1}{4}(K-M)$	$\frac{\frac{1}{4}L^2}{-\nu_A + \nu_B + \frac{1}{2}M}$
16	−2	$\beta\beta\beta\beta$	$-\nu_A - \nu_B + \frac{1}{4}K + \frac{1}{2}N$	0	0

Based upon these zeroth-order wave functions, the spectrum given in Tab. 2 can be derived. It will be noted that there are slight asymmetries in the spectrum to this degree of approximation, which depend on the magnitude of M compared to $2\,|\nu_A - \nu_B|$.

As a specific illustration of the method, the aliphatic part of the spectrum of 1-indanone,



has been calculated, and is shown in Fig. 1 and 2, together with the experimental spectrum. This spectrum (60 Mc) has been previously analyzed [7], with the reported results

$$\begin{aligned} J_{AA'} &= 1.9 \text{ cps} \\ J_{BB'} &= 3.8 \text{ cps} \\ J_{A'B'} = J_{AB} &= 8.9 \text{ cps} \\ J_{A'B} = J_{AB'} &= 3.5 \text{ cps} \end{aligned}$$

$$\nu_A = \nu_{A'} = -\nu_B = -\nu_{B'} = 15.5 \text{ cps [relative to } (\nu_A + \nu_B)/2] \, .$$

The assignment of A and B protons was made on the basis of the broadened downfield portion of the spectrum, which was attributed to unresolved coupling of the B protons with those of the aromatic ring.

Fig. 1 shows the result of calculations based on the zeroth-order wave functions. It appears that an assignment might be made on the basis of the energies alone. The calculations were extended to third order so that the first order intensities could be evaluated as shown in Fig. 2. It is interesting to note that even in a fairly strongly coupled case such as this, the third order corrections shifted the frequencies by 0.2 cps at most, with most peaks less effected. For this reason the third-order spectrum is not shown. It is in essence the same as the second order

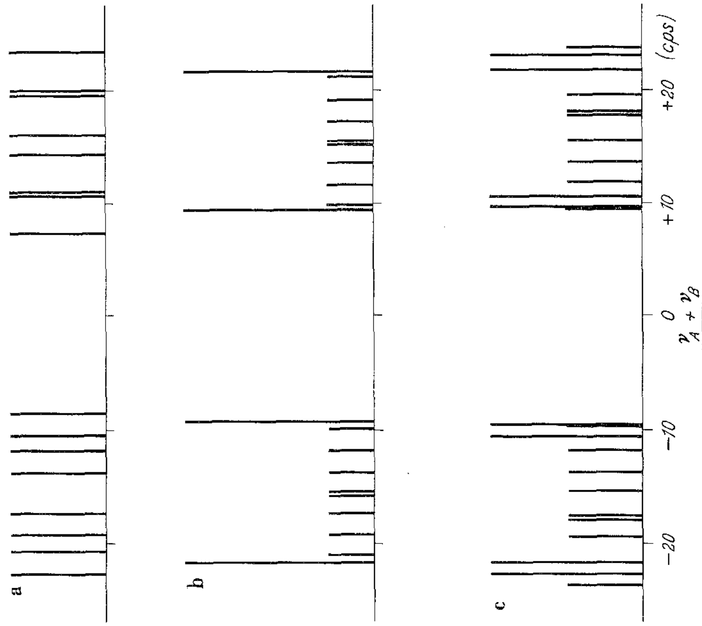


Fig. 1. Calculated aliphatic A_2B_2 portion of 1-indanone NMR spectrum using zeroth-order intensities. a) Zeroth-order, b) First-order, c) Second-order

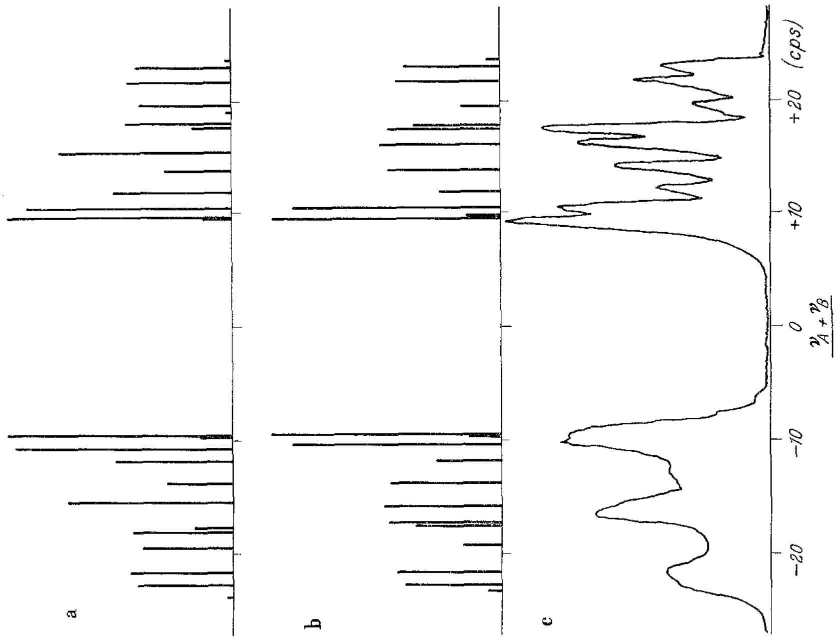


Fig. 2. Aliphatic A_2B_2 portion of the NMR spectrum of 1-indanone. a) Second-order calculated spectrum with first-order intensity corrections, b) Exact calculated spectrum obtained by complete solution of secular equations, c) Experimental spectrum

spectrum, with the slight asymmetries mentioned above between the A and B sets further reduced.

In general, it will still be necessary to use numerical methods to diagonalize the smaller secular determinants, although in the case of the AA′BB′ spectrum considered here, the energies can be expressed to any desired degree of approximation

Table 2. *Frequencies of* A_2B_2 *transitions, correct to second order*

Zeroth Order Intensity	A Transitions		B Transitions	
1	$14 \to 8$	$\nu_A - \frac{1}{2}K - \frac{1}{2}L - \frac{K^2}{4L} + \frac{\frac{1}{4}N^2}{\nu_A - \nu_B - \frac{1}{2}M} +$ $+ \frac{1}{8}(N+L)^2\left[\frac{(N-K-L)}{\frac{1}{4}(N-K-L)^2 - (\nu_A - \nu_B)^2}\right]$	$8 \to 4$	$\nu_B + \frac{1}{2}K + \frac{1}{2}L + \frac{K^2}{4L} - \frac{\frac{1}{4}N^2}{\nu_A - \nu_B + \frac{1}{2}M} -$ $- \frac{1}{8}(N+L)^2\left[\frac{(N-K-L)}{\frac{1}{4}(N-K-L)^2 - (\nu_A - \nu_B)^2}\right]$
2	$12 \to 6$	$\nu_A - \frac{1}{2}N - \frac{\frac{1}{4}N^2}{\nu_A - \nu_B - \frac{1}{2}M} +$ $+ \frac{\frac{1}{8}(N-L)^2}{\nu_A - \nu_B + \frac{1}{2}K - \frac{1}{2}(N+L)} + \frac{\frac{1}{8}(N+L)^2}{\nu_A - \nu_B + \frac{1}{2}K - \frac{1}{2}(N-L)}$	$6 \to 2$	$\nu_B + \frac{1}{2}N + \frac{\frac{1}{4}N^2}{\nu_A - \nu_B + \frac{1}{2}M} -$ $- \frac{\frac{1}{8}(N-L)^2}{\nu_A - \nu_B + \frac{1}{2}K - \frac{1}{2}(N+L)} - \frac{\frac{1}{8}(N+L)^2}{\nu_A - \nu_B + \frac{1}{2}K - \frac{1}{2}(N-L)}$
2	$16 \to 12$	$\nu_A - \frac{1}{2}N + \frac{\frac{1}{4}N^2}{\nu_A - \nu_B - \frac{1}{2}M}$	$2 \to 1$	$\nu_B + \frac{1}{2}N - \frac{\frac{1}{4}N^2}{\nu_A - \nu_B + \frac{1}{2}M}$
1	$10 \to 3$	$\nu_A + \frac{1}{2}M - \frac{1}{2}L - \frac{\frac{1}{4}M^2}{\frac{1}{2}K + L} + \frac{\frac{1}{4}L^2}{\nu_A - \nu_B + \frac{1}{2}M}$	$9 \to 5$	$\nu_B - \frac{1}{2}M + \frac{1}{2}L + \frac{\frac{1}{4}M^2}{\frac{1}{2}K + L} - \frac{\frac{1}{4}L^2}{\nu_A - \nu_B + \frac{1}{2}M}$
1	$15 \to 9$	$\nu_A - \frac{1}{2}M - \frac{1}{2}L - \frac{\frac{1}{4}M^2}{\frac{1}{2}K + L} + \frac{\frac{1}{4}L^2}{\nu_A - \nu_B - \frac{1}{2}M}$	$13 \to 10$	$\nu_B + \frac{1}{2}M + \frac{1}{2}L + \frac{\frac{1}{4}M^2}{\frac{1}{2}K + L} - \frac{\frac{1}{4}L^2}{\nu_A - \nu_B - \frac{1}{2}M}$
1	$7 \to 2$	$\nu_A + \frac{1}{2}K - \frac{1}{2}L - \frac{K^2}{4L} + \frac{\frac{1}{4}N^2}{\nu_A - \nu_B + \frac{1}{2}M} -$ $- \frac{1}{8}(N-L)^2\left[\frac{(N+L-K)}{\frac{1}{4}(N+L-K)^2 - (\nu_A - \nu_B)^2}\right]$	$12 \to 7$	$\nu_B - \frac{1}{2}K + \frac{1}{2}L + \frac{K^2}{4L} - \frac{\frac{1}{4}N^2}{\nu_A - \nu_B - \frac{1}{2}M} +$ $+ \frac{1}{8}(N-L)^2\left[\frac{(N+L-K)}{\frac{1}{4}(N+L-K)^2 - (\nu_A - \nu_B)^2}\right]$
1	$9 \to 3$	$\nu_A + \frac{1}{2}M + \frac{1}{2}L + \frac{\frac{1}{4}M^2}{\frac{1}{2}K + L} + \frac{\frac{1}{4}L^2}{\nu_A - \nu_B + \frac{1}{2}M}$	$10 \to 5$	$\nu_B - \frac{1}{2}M - \frac{1}{2}L - \frac{\frac{1}{4}M^2}{\frac{1}{2}K + L} - \frac{\frac{1}{4}L^2}{\nu_A - \nu_B + \frac{1}{2}M}$

Table 2 (Continued)

1	14 → 7	$\nu_A - \frac{1}{2}K + \frac{1}{2}L + \frac{K^2}{4L} + \frac{\frac{1}{4}N^2}{\nu_A - \nu_B - \frac{1}{2}M} + \frac{1}{8}(N-L)^2\left[\frac{(N+L-K)}{\frac{1}{4}(N+L-K)^2 - (\nu_A-\nu_B)^2}\right]$	7 → 4	$\nu_B + \frac{1}{2}K - \frac{1}{2}L - \frac{K^2}{4L} - \frac{\frac{1}{4}N^2}{\nu_A - \nu_B + \frac{1}{2}M} - \frac{1}{8}(N-L)^2\left[\frac{(N+L-K)}{\frac{1}{4}(N+L-K)^2 - (\nu_A-\nu_B)^2}\right]$
1	15 → 10	$\nu_A - \frac{1}{2}M + \frac{1}{2}L + \frac{\frac{1}{4}M^2}{\frac{1}{2}K + L} + \frac{\frac{1}{4}L^2}{\nu_A - \nu_B - \frac{1}{2}M}$	13 → 9	$\nu_B + \frac{1}{2}M - \frac{1}{2}L - \frac{\frac{1}{4}M^2}{\frac{1}{2}K + L} - \frac{\frac{1}{4}L^2}{\nu_A - \nu_B - \frac{1}{2}M}$
2	11 → 4	$\nu_A + \frac{1}{2}N - \frac{\frac{1}{4}N^2}{\nu_A - \nu_B + \frac{1}{2}M} + \frac{\frac{1}{8}(N-L)^2}{\nu_A - \nu_B - \frac{1}{2}K + \frac{1}{2}(N+L)} + \frac{\frac{1}{8}(N+L)^2}{\nu_A - \nu_B - \frac{1}{2}K + \frac{1}{2}(N-L)}$	14 → 11	$\nu_B - \frac{1}{2}N + \frac{\frac{1}{4}N^2}{\nu_A - \nu_B - \frac{1}{2}M} - \frac{\frac{1}{8}(N-L)^2}{\nu_A - \nu_B - \frac{1}{2}K + \frac{1}{2}(N+L)} - \frac{\frac{1}{8}(N+L)^2}{\nu_A - \nu_B - \frac{1}{2}K + \frac{1}{2}(N-L)}$
2	4 → 1	$\nu_A + \frac{1}{2}N + \frac{\frac{1}{4}N^2}{\nu_A - \nu_B + \frac{1}{2}M}$	16 → 14	$\nu_B - \frac{1}{2}N - \frac{\frac{1}{4}N^2}{\nu_A - \nu_B - \frac{1}{2}M}$
1	8 → 2	$\nu_A + \frac{1}{2}K + \frac{1}{2}L + \frac{K^2}{4L} + \frac{\frac{1}{4}N^2}{\nu_A - \nu_B + \frac{1}{2}M} - \frac{1}{8}(N+L)^2\left[\frac{(N-K-L)}{\frac{1}{4}(N-K-L)^2 - (\nu_A-\nu_B)^2}\right]$	12 → 8	$\nu_B - \frac{1}{2}K - \frac{1}{2}L - \frac{K^2}{4L} - \frac{\frac{1}{4}N^2}{\nu_A - \nu_B - \frac{1}{2}M} + \frac{1}{8}(N+L)^2\left[\frac{(N-K-L)}{\frac{1}{4}(N-K-L)^2 - (\nu_A-\nu_B)^2}\right]$

in closed form. The determination of the eigenvectors requires higher order approximations, so that the method is most readily applied to spectra which are sufficiently close to first order that an assignment of the transitions can be made on the basis of the frequencies alone.

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