ON THE PROCESSING OF ROTATIONAL SPECTRA OF MOLECULES IN RADIO SPECTROSCOPY

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An algorithm is given that realizes the inverse problem of processing rotational spectra. The statistical properties of model parameters obtained by processing are characterized by the correlation matrix. The algorithm does not result in balking for an incorrectly stated inverse problem and can be used as the basis for development of a method for automatic identification of a spectrum.

As new possibilities appear in submillimeter radio spectroscopy and are accompanied by the recording of rotational spectra containing hundreds and thousands of lines, a serious effort is required to develop an apparatus for the processing of these spectra. In developing and making practical use of programs implementing the solution of direct and inverse problems in spectroscopy within the framework of the asymmetric nonrigid top model we met with certain difficulties that forced us to a certain degree of revision of current practice in calculation and representation of output data:

a) a situation often arises in which it is difficult to make an a priori choice of a model that will on the one hand give a good description of the experimental spectrum and on the other hand contain no parameters inessential to its description. As a rule, we must work with models having redundant parameters. Thus it is important that in the course of solving the inverse problem definite combinations of parameters be found "automatically," i.e., the algorithm must determine the independent constraints imposed on the model parameters by the experimental data. The version in which the number of constraints equals the number of parameters and the latter can be determined uniquely must be taken only as a special case;

b) the model parameters obtained by solution of the inverse problem are functions of the random experimental data — i.e., they are themselves random variables. The model parameters are usually statistically dependent, but in the literature their probability properties (for a normal distribution) are characterized solely by the variances — i.e., just by the diagonal elements of the correlation matrix. Such an approach may lead to substantial error in estimating the accuracy with which spectral-line frequencies are calculated from the computed model parameters. Thus the algorithm realizing the inverse problem must fully determine the probability properties of the constraints imposed on the model parameters by the experimental data and, consequently, the probability properties of the model parameters themselves if they are uniquely determined.

We shall briefly consider an algorithm meeting the above requirements; we have made practical use of it to process the rotational spectra of molecules.

1. Determining Model Parameters or Independent Combinations of Them (Inverse Problem)

Let $x_1, x_2, \ldots, x_N$ be a set of experimental data for identified transitions; the random quantities x_i are independent and normally distributed, while $\xi_1, \xi_2, \ldots, \xi_N$ are the theoretical analogs of the experimental data and depend on the model parameters $A_1, A_2, \ldots, A_s$. The maximum likelihood criterion then places a requirement on the model parameters that is equivalent to prescribing the least-squares method [2]:

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TABLE 1. Rotational and Centrifugal Constants of H_2CO

$A = 281938{,}6 \pm 5{,}9$ MHz	$D_{11} = -37{,}8 \pm 2{,}2$ MHz $2 \cdot D_{12} = -2{,}553 \pm 0{,}038$ MHz
$B = 38835{,}083 \pm 0{,}038$ MHz	$D_{22} = -0{,}09775 \pm 0{,}00015$ MHz $2 \cdot D_{13} = -0{,}359 \pm 0{,}038$ MHz
$C = 34003{,}186 \pm 0{,}038$ MHz	$2 \cdot D_{23} = -0{,}12857 \pm 0{,}00036$ MHz $D_{33} = -0{,}05611 \pm 0{,}00014$MHz

TABLE 2. Model-parameter Correlation Coefficient Matrix for H_2CO

	A	B	C	D_{11}	$2 \cdot D_{12}$	D_{22}	$2 \cdot D_{13}$	$2 \cdot D_{23}$	D_{33}
A	1	−0,98	+0,98	+0,98	+0,98	−0,20	−0,98	−0,49	−0,11
B	−0,98	1	−0,98	−1,00	−1,00	+0,20	+1,00	+0,42	+0,11
C	+0,98	−0,98	1	+1,00	+1,00	−0,29	−1,00	−0,48	−0,20
D_{11}	+0,98	−1,00	+1,00	1	+1,00	−0,26	−1,00	−0,45	−0,16
$2 \cdot D_{12}$	+0,98	−1,00	+1,00	+1,00	1	−0,25	−1,00	−0,46	−0,16
D_{22}	−0,20	+0,20	−0,29	−0,25	−0,25	1	+0,25	+0,47	+0,99
$2 \cdot D_{13}$	−0,98	+1,00	−1,00	−1,00	−1,00	+0,25	1	+0,45	+0,16
$2 \cdot D_{23}$	−0,49	+0,42	−0,48	−0,45	−0,46	+0,47	+0,45	1	+0,45
D_{33}	−0,11	+0,11	−0,20	−0,16	−0,16	+0,99	+0,16	+0,45	1

TABLE 3. Experimental and Theoretical Frequencies of Series of H_2CO lines

$Jk_{-1}k_{+1} \rightarrow J'k'_{-1}k'_{+1}$	f^e, MHz, Δf^e, MHz	f^e, MHz, Δ, MHz	Δ^*, MHz	$f^e - f^t$ MHz
4 3 2 — 4 3 1	4,5730 ± 0,0002	4,57269 ± 0,00004	0,002	+ 0,0003
15 5 11 — 15 5 10	6,212 ± 0,001	6,2124 ± 0,0002	0,014	— 0,0004
4 2 3 — 4 2 2	1065,85 ± 0,2	1065,878 ± 0,004	0,13	— 0,028
1 1 1 — 1 1 0	4829,6600 ± 0,0001	4829,6600 ± 0,0001	0,075	+ 0,0000
3 2 2 — 3 2 1	28974,85 ± 0,1	28974,808 ± 0,001	0,45	+ 0,042
11 2 10 — 11 4 9	48612,7 ± 5,0	48617,74 ± 0,10	5,4	— 5,0
0 0 0 — 1 0 1	72837,974 ± 0,024	72837,987 ± 0,007	0,053	— 0,013
5 2 4 — 6 2 5	436584,1 ± 0,6	436585,59 ± 0,087	1,3	— 1,5
6 0 6 — 7 0 7	505830.0 ± 0,6	505830,83 ± 0,20	0 42	— 0,83
7 3 5 — 8 3 6	583142,2 ± 0,6	583141,78 ± 0,19	3,9	+ 0,42

Note. Δ, Δ^* are the mean square deviations of the calculated frequency from the average value with and without allowance for the nondiagonal elements of the correlation matrix.

$$\varphi(A) = \sigma^2 \sum_i \left[\frac{x_i - \xi_i(A)}{\sigma_i} \right]^2 = \min, \tag{1}$$

where σ_i^2 is the variance of the random variable x_i; $\sigma^2 = 1/[\sum_i (1/\sigma_i^2)]$ is a normalizing constant.

Let us assume that we know (from structural considerations, for example) a crude solution of the inverse problem, A^0, such that when searching for an exact solution we can linearize the theoretical relationships:

$$\xi_i(A) = \xi_i(A^0) + \left. \frac{\partial \xi_i}{\partial A_p} \right|_0 a_p = \xi_i^0 + \gamma_p^i a_p. \tag{2}$$

It is then simple to write the functional (1) in the form

$$\varphi(a) = \langle a | V | a \rangle - 2\langle t | a \rangle + d^2. \tag{3}$$

Here

$$V = \sigma^2 \sum_i \frac{|\alpha^{(i)}\rangle \langle \alpha^{(i)}|}{\sigma_i^2},$$

$$|t\rangle = \sigma^2 \sum_i \frac{x_i - \xi_i^0}{\sigma_i^2} |\alpha^{(i)}\rangle, \quad d^2 = \sigma^2 \sum_i \left(\frac{x_i - \xi_i^0}{\sigma_i} \right)^2.$$

The operator V is a symmetric operator which operates in a finite-dimensional space. For operators of this class we have very good iteration algorithms with which to seek the eigenvalues and eigenvectors (viz., in particular [3]).

Let $|y_n\rangle$, λ_n be an orthonormalized system of eigenvectors and corresponding eigenvalues of the operator V. Then letting

$$|a\rangle = c_n |y_n\rangle, \tag{4}$$

we obtain

$$\varphi = c_n^2 \lambda_n - 2c_n \langle t | y_n \rangle + d^2. \tag{5}$$

The coefficients c_n of the expansion are chosen from the minimization condition for (5). As a result we have

$$c_n = \frac{\langle t | y_n \rangle}{\lambda_n} \qquad (\lambda_n \neq 0), \tag{6}$$

where

$$\varphi_{\min} = d^2 - \sum_n \frac{|\langle t | y_n \rangle|^2}{\lambda_n}. \tag{7}$$

Summation in (7) is carried out only over those n for which the eigenvalues are nonzero.* The quantity c_n (corresponding to $\lambda_n \neq 0$) fixes a certain linear combination of the model parameters. In fact, from (4) it follows that

$$c_n = \langle y_n | a \rangle = y_p^{(n)} a_p. \tag{8}$$

We shall refer to such linear combinations of parameters as "determinable." If the functional has characteristic directions with $\lambda_n = 0$ it is not possible to make a unique determination of the model parameters from the experimental data used, and we are forced to content ourselves with relationships of the type (8) (of course, in this case it always remains possible to introduce certain additional information in order to obtain a unique answer). It is important, however, that with the solution method described the incorrectness of the inverse problem does not lead to balking against the algorithm, since it will find all the possible information in the given case in the form (8). †

* It follows from (1) that $\varphi \geq 0$; i.e., the functional is bounded from above. Thus all $\lambda_n \geq 0$; here if $\lambda_n \to 0$ then $\langle t | y_n \rangle \to 0$ as well.

† When practical use is made of the algorithm, the $\lambda_n = 0$ criterion is indefinite, since machine calculations are of finite accuracy, and we must use instead the confidence criterion for the calculated values of c_n. The solution to this problem depends on the particular computer employed and on the specific algorithm used to search for the eigenvalues and eigenvectors.

2. Determining the Probability Characteristics of Model Parameters or Their Independent Combinations (Inverse Problem)

The quantities c_n ($\lambda_n \neq 0$) are linear functions of statistically independent normally distributed variables x_i. Thus the c_n are also normally distributed [2]. We shall show that they are independent random quantities. This will be so if and only if the correlation matrix $B^{(c)}_{kl} = \overline{(c_k - \bar{c}_k)(c_l - \bar{c}_l)}$ is diagonal:

$$B^{(c)}_{kl} = \frac{\sigma^4}{\lambda_k \lambda_l} \langle y_k | \sum_{ij} \overline{\frac{x_i - \bar{x}_i}{\sigma_i^2} \frac{x_j - \bar{x}_j}{\sigma_j^2}} | \alpha^{(i)} \rangle \langle \alpha^{(j)} | y_l \rangle =$$

$$= \frac{\sigma^2}{\lambda_k \lambda_l} \langle y_k | V | y_l \rangle = \frac{\sigma^2}{\lambda_k} \delta_{kl}.$$

Thus $c_n - \bar{c}_n$ are normally distributed independent quantities with mean square deviations

$$\sqrt{\overline{(\Delta c_n)^2}} = \sigma / \lambda^{1/2}.$$

For measurements of equal accuracy, $\sigma^2 = \sigma_1^2/N$, and (9) goes over to the form $\sqrt{\overline{(\Delta c_n)^2}} = (\sigma_1/\sqrt{N})(1/\sqrt{\lambda})$.

We shall assume that each characteristic direction of the operator V corresponds to a determinable combination of model parameters. Then all of the output data can be uniquely written in the form of the model parameters in accordance with (4). The quantities a_k are also normally distributed, but are statistically dependent; their correlation matrix is

$$B^{(a)}_{kl} = \overline{(a_k - \bar{a}_k)(a_l - \bar{a}_l)} = \sum_n y^{(a)}_k y^{(a)}_l \frac{\sigma^2}{\lambda_n}. \tag{10}$$

It is more convenient to characterize the statistical relationship between the model parameters by means of the correlation coefficient matrix

$$r^{(a)}_{kl} = \frac{B^{(a)}_{kl}}{\left[B^{(a)}_{kk} B^{(a)}_{ll} \right]^{1/2}}. \tag{11}$$

3. Determining the Probability Properties of Spectral Characteristics found from the Computed Model Parameters (Direct Problem)

An important role is played in the solution of the direct problem by estimating the variance of the spectral characteristics to be determined; this variance is associated with errors in determination of the model parameters (particularly the variance estimate for the frequencies of the spectral absorption lines). This quantity characterizes the degree of confidence in the calculations. It is not difficult to find that

$$\overline{(\xi_i - \bar{\xi}_i)^2} = B^{(a)}_{kl} \alpha^{(i)}_k \alpha^{(i)}_l. \tag{12}$$

In the general case $\overline{(\Delta \xi_i)^2}$ depends essentially on the nondiagonal elements of the correlation matrix.

4. Practical Utilization of Algorithm

The algorithm under discussion was used in a program designed to process molecular rotational spectra within the framework of the nonrigid asymmetric top model. As an example, let us look at the processing of the rotational spectrum of H_2CO. The initial data for the model-parameter search were the experimentally measured frequencies of 84 indentified lines given in [4, 5]. The relative accuracy of measurement varied from $2 \cdot 10^{-8}$ to $6 \cdot 10^{-4}$. We note that the only data taken from [4] are those for transitions having a quantum number of the total angular momentum $J \leq 18$, since the molecules are so light that for a given measurement accuracy at higher values of J centrifugal effects of higher order than those taken into account by our expression for the rotational energy of a molecule become substantial (see the Appendix).

The calculations gave the values of rotational and centrifugal constants of H_2CO shown together with their mean square deviations in Table 1, as well as the matrix of correlation coefficients (Table 2) which indicates the strong statistical dependence of the model parameters. The data obtained were used

in the direct problem. Table 3 shows the theoretical and experimental frequency values for some of the H_2CO lines; the computational accuracy (mean square deviation) was evaluated both with and without allowance for the nondiagonal elements of the correlation matrix. The sharp difference in the estimates is associated with the "weak" correctness of the problem statement. The H_2CO molecule is in fact plane, so that description of it without allowance for the "planarity" conditions must inevitably lead to inaccurate determination of certain combinations of model parameters (the accuracy with which combinations, i.e., c_n, are determined varies from $0.79 \cdot 10^{-5}$ MHz to $0.62 \cdot 10$ MHz). Allowance for the correlation characteristics in this case becomes fundamental, since it is precisely these characteristics that permit us to pick out those transitions for which poor accuracy of certain combinations is unimportant in the determination of their frequencies. This is an extremely useful fact in identification of a spectrum. As a role, we are initially able to identify only a small part of the transitions, and this results in inaccurate determination of certain combinations of model parameters. Despite this, in calculations for the direct problem the correlation properties enable us to pick out those transitions for which the effect is weak and which can, as a consequence, be additionally identified. Repeating this process, we can interpret the spectrum completely.

Appendix

The rotational energy of a molecule can be represented in the form

$$W(J, \tau) = Q_\alpha \langle P_\alpha^2 \rangle + D_{\alpha\beta} \langle P_\alpha^2 \rangle \langle P_\beta^2 \rangle \qquad (D_{\alpha\beta} = D_{\beta\alpha}), \tag{A.1}$$

where P_α is the operator for the component of the total angular momentum along the α axis in the coordinate system associated with the molecule. Averaging is carried out with the aid of wave functions of the Hamiltonian $H_0 = Q_\alpha P_\alpha^2$. It can be shown that (A.1) is strictly equivalent to the expression ordinarily employed for the energy levels of a nonrigid top that can be described by the Hamiltonian

$$H = q_\alpha P_\alpha^2 + H_1 = q_\alpha P_\alpha^2 + \frac{1}{4} \tau_{\alpha\alpha\beta\beta} P_\alpha^2 P_\beta^2, \tag{A.2}$$

obtained in first-order perturbation theory for the operator H_1.

From the computational viewpoint it is very convenient to use the set of parameters Q_α, $D_{\alpha\beta}$ in solving both the direct and inverse spectroscopy problems [6]. The relationships between the set of parameters Q_α, $D_{\alpha\beta}$ and q_α, $\tau_{\alpha\alpha\beta\beta}$ may be written as

$$\begin{aligned} Q_\alpha &= q_\alpha + \Delta_\alpha, \\ D_{\alpha\alpha} &= \frac{1}{4} \tau_{\alpha\alpha\alpha\alpha}, \\ D_{\alpha\beta} &= \frac{1}{4} \tau_{\alpha\alpha\beta\beta} + \frac{1}{2} \Delta\gamma \qquad (\alpha \neq \beta \neq \gamma). \end{aligned} \tag{A.3}$$

Here

$$\begin{aligned} \Delta_x = \frac{1}{12} (&- L_x L_z^{-1} \tau_{xxxx} + L_y \tau_{yyyy} + L_y^{-1} \tau_{zzzz} + \\ &+ 2L_z^{-1} \tau_{xxyy} + 2L_x \tau_{xxzz} - 2\tau_{yyzz}) \end{aligned} \tag{A.4}$$

and

$$L_x = \frac{q_y - q_z}{q_x - q_z}, \tag{A.5}$$

while Δy, Δz and L_y, L_z can be obtained from (A.4) and (A.5), respectively, by cyclic permutation of the indices x, y, z.

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