POSSIBILITY OF DIALOG IN COMPUTER PROCESSING OF SPECTROSCOPIC DATA

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Spectroscopic data obtained under real conditions contain, aside from random errors, different instrumental distortions, owing primarily to the nonmonochromatic nature of the spectrum of the source of radiation and the finite resolution of the energy analyzer. Such distortions result in a significant complication of the spectra, whose unequivocal interpretation becomes difficult and often impossible.

The solution of the problem is to combine a spectrometer into a single measuring-computing system (MCS) with a computer, in which one of the main functions of the computer is to solve the problem of reconstructing the spectra.

In this paper we develop a dialog approach to the solution of inverse problems of reconstruction that permits including effectively the investigator in the process of analysis of the measurements on the MSC. The importance of dialog is determined by the following.

First, the investigator is the source of a priori information about the spectrum, the use of which (as will be shown below) significantly increases the quality of the solution of the problem of reconstruction of the spectrum. Since the investigator's knowledge consists of very specific data that is poorly formalized and not absolutely reliable, in this paper attention is devoted to methods for formalizing and taking into account a priori knowledge and means for monitoring subjective errors and estimation of the efficiency of these means.

Second, in most cases the investigator is the user of the results of analysis, since it is the investigator who makes the final decision about the structure of the spectrum. In this connection, controllable methods for processing measurements are implemented on the basis of the dialog approach; these methods make it possible to satisfy the subjective requirements and quality criteria, and performing iteration procedures of reconstruction, in which the investigator has real-time control over the course of the analysis. In this paper we also study the important question of visualizing the errors in the result of analysis with the help of methods of statistical simulation. Practical calculations have shown that visualization substantially increases the reliability of subjective conclusions, based on the reconstructed spectra. The possibilities of a dialog in the solution of the problem of reconstruction of indirect measurements on the basis of a statistical approach, where the knowledge of the investigator is formalized as an a priori statistical model of the spectrum being analyzed, are studied in [1, 2]. The present work is based on a fundamentally different determinate approach to the analysis of measurements; this approach is effective in spectroscopic applications and in it the knowledge of the investigator is formalized in the form of projection operators.

The described method was implemented on the basis of the SPEKTR–DIALOG dialog program system, intended for organizing a constructive dialog between the investigator and the computer in analysis of photo- and x-ray electronic spectra [3].

Reconstruction of Spectra Taking into Account A Priori Knowledge. For most spectroscopic measurements a linear finite-dimensional model is characteristic:

$$\xi_i = \int_a^b a_i(x) f(x)\, dx + \nu_i, \quad i = 1, \ldots, n, \tag{1}$$

where $\xi = (\xi_1 \ldots \xi_n)^* \in R_n$ is the vector of measurements; $a_i(x)$ is the instrumental function of the measuring apparatus, corresponding to the i-th measurement; $\nu = (\nu_1 \ldots \nu_n)^* \in R_n$ is the noise vector, an unbiased random vector with the correlation operator Σ. Most often $\Sigma = \mathrm{diag}(\sigma_1^2 \ldots \sigma_n^2)$, which is caused by the fact that separate points of the spectrum are independent; $f(x) \in L_2[a, b]$ is the ideal undistorted spectrum. In practical calculations one trans-

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fers from the model (1) to the discrete model

$$\xi = A\mathbf{f} + \mathbf{v}, \tag{2}$$

where $\mathbf{f} = (f_1 \ldots f_n)^* \in R_n$ is the vector of readings of the ideal spectrum and A is an $n \times n$ matrix.

The problem of reconstructing the spectrum $\mathbf{f}$ is formalized as a problem of constructing the operator R, giving in some sense an optimal $\hat{\mathbf{f}} = R\xi$ estimate of the unknown vector $\mathbf{f}$. Different formulations of the problem of reconstruction of indirect measurements are described in detail in [4]. In the most general case $R = A^-$, where $A^- = \lim_{\omega \to 0}(A^*A + \omega I)^{-1}A^*$ is a pseudoinverse operator. If A^{-1} (inverse operator) exists, then $A^- = A^{-1}$. However, the estimate $\hat{\mathbf{f}} = A^-\xi$, as a rule, is not good enough, i.e., it is associated with large errors, which is a consequence of the sparseness of information in the model (2).

On the basis of the dialog approach, instead of (2) we shall study the model

$$\xi = AP\mathbf{f} + \mathbf{v}, \tag{3}$$

in which it is assumed that signals belonging to $R(P) \subset R_n$, rather than an arbitrary signal from R_n, enter the device A. In this situation P is a projection operator (in the general case a nonlinear operator) that formalizes definite a priori knowledge of the investigator about the spectrum $\mathbf{f}$ under study. This formalization approach is convenient in practice and, as will be shown below, permits including in the analysis data of the most diverse type at the same time wihtout changing the processing algorithm. We shall give the most common forms of the projection operators.

a) Restriction to nonnegative spectra

$$P_1\mathbf{f} = \begin{cases} \mathbf{f}, & \mathbf{f} \geqslant 0 \\ 0, & \mathbf{f} < 0 \end{cases}, \quad \mathbf{f} \in R_n.$$

b) More detailed data about the spectrum – restriction of the "corridor" type on the intensity

$$P_2\mathbf{f} = \begin{cases} \mathbf{f}, & \underset{\sim}{\mathbf{f}} \leqslant \mathbf{f} \leqslant \tilde{\mathbf{f}} \\ \underset{\sim}{\mathbf{f}}, & \underset{\sim}{\mathbf{f}} > \mathbf{f} \\ \tilde{\mathbf{f}}, & \tilde{\mathbf{f}} < \mathbf{f} \end{cases}, \quad \underset{\sim}{\mathbf{f}}, \ \tilde{\mathbf{f}}, \ \mathbf{f} \in R_n,$$

where $\underset{\sim}{\mathbf{f}}$ and $\tilde{\mathbf{f}}$ are the lower and upper limits of the corridor, respectively.

c) Restriction on the extent of the spectrum

$$P_3\mathbf{f} = \begin{cases} \mathbf{f}, & \mathbf{f} \in R(P_3) \\ 0, & \mathbf{f} \bar{\in} R(P_3) \end{cases},$$

where $R(P_3) \subset R_n$ determines the region of the spectrum and P_3 is the orthogonal projector on $R(P_3)$.

d) Restriction on the frequency band, i.e., data on the regularity of the structure of the spectrum. The last operator corresponds to the filter

$$P_4 f(x) = \int \frac{\sin \omega_c (x - x')}{\pi (x - x')} f(x')\, dx',$$

where ω_c is the limiting frequency.

The use of numerical methods of spline approximation makes it possible to formalize the data on the smoothness of the spectrum $\mathbf{f}$. Then the operator P_5 projects on $R(P_5)$ – the set of splines of a type given by the investigator – and is determined from the condition

$$\|\mathbf{f} - P_5\mathbf{f}\| = \inf \{\|\mathbf{f} - \mathbf{v}\|; \quad \mathbf{v} \in R(P_5)\}.$$

The operator P in Eq. (3) can be both separately chosen P_i and the result of the combined action of all P_i, $P = P_4P_3P_2P_1$. Data on the maximum number of peaks in a given section, the type of structural features, etc., are also formalized analogously.

Nontraditional forms of projection operators are possible.

e) Let us assume that the investigator is drawing some reference spectrum $\mathbf{f}^*$ and asserts that the form of the ideal spectrum $\mathbf{f}$ in Eq. (1) must be similar to the form of $\mathbf{f}^*$. In many

cases it is obvious that the form of f^* is determined by the sections where f^* is monotonic, and the set $V(f^*)$ of spectra whose form is similar to that of the reference spectrum is determined by the following:

$$V(f^*) = \{f'(x) = \sum_{i=1}^{l} g_i(x)\chi_{a_i}(x);\ i = 1, \ldots, l\}.$$

Here $a_1, \ldots, a_l$ is the partition of the segment [a, b] into nonoverlapping sets, sections where $f^*(x)$ is monotonic; $g_i(x)$ are functions that are monotonic in a_i, analogously to $f^*(x)$;

$$\chi_{a_i}(x) = \begin{cases} 1, & x \in a_i \\ 0, & x \bar{\in} a_i \end{cases} \quad \text{— indicator functions.}$$

The projection operator P_6 is determined in this case from the condition

$$\| f - P_6 f \| = \inf \{\| f - v \|;\ v \in V(f^*)\}.$$

Thus it is possible to formalize the data on the maximum number of bands and their position without specifying the contour.

Knowledge formalized in the manner described above is based on the analysis of the starting measurement, data of a theoretical character, independent additional measurements, and even the intuition of the investigator. It should be noted that in practice graphical dialogue, which enables the investigator to draw directly on a display the corridor $\underset{\sim}{f}$ and $\tilde{f}$, indicate the limits of the spectrum, etc., is used to formalize the a priori knowledge

Thus, to reconstruct the spectrum f in the model (3) it is necessary to realize the operator $(AP)^-$. In so doing it is natural to expect that the quality of the solution $(AP)^-\xi$ will be higher than that of $A^-\xi$. The main difficulty arising in this case is connected with the possible nonlinearity of the operator AP. In this connection we realized the iteration algorithm

$$f^k = \lambda \cdot g + (I - \lambda \cdot A) P f^{k-1}, \tag{4}$$

where λ is an accelerating parameter, ensuring convergence of $\lim_{k\to\infty} Pf^k = (AP)^-\xi = \hat{f}$. In Eq. (4) it is assumed for simplicity that $A = A^*$. The solution $\hat{f}$ is stable with respect to random errors in the measurements, which makes the algorithm (4) more advantageous than the iteration algorithms traditionally employed in the reconstruction of spectra. For this, preliminary smoothing is performed $g = AA^-\xi = Af + AA^-v$, in which some of the noise v, equal to $(I - AA^-)v$, is filtered out without degrading the resolution of the signal Af.† The number of iterations sufficient for revealing the interesting features of the spectrum, the accelerating parameter, the smoothing parameter, and the accuracy of the a priori data all offer possibilities of controlling the algorithm (4). In the dialogue regime the investigator calculates the estimate $\hat{f}$ for different controlling parameters, choosing subjectively the best result. This is one additional method for taking into account the investigator's poorly formalized knowledge at the stage of analysis of the structure of the spectrum.

Figure 1 demonstrates the strong effect of using a priori data about the spectrum.

Monitoring of the Consistency of A Priori Knowledge and Measurements. Such a strong and often unpredictable effect of the a priori data on the solution of the problem of reconstructing the structure of the spectrum poses the question of monitoring the reliability of the investigator's knowledge and, as a consequence, the reliability of the result of the solution of the problem. It is understandable that data such as the nonnegativity of the spectrum, as a rule, do not give rise to any doubts. However, when the investigator contributes more detailed restrictions the question of their reliability must be resolved.

On the basis of the dialogue approach it is necessary to have a criterion that monitors the reliability of the representation (3). We shall study the discrepancy

$$t(\xi) = \| \xi - AP\hat{f} \| = \| Q_{AP}\xi \|, \tag{5}$$

where $\hat{f} = (AP)^-\xi$ and $Q_{AP} = I - AP(AP)^-$ is the orthogonal projector $R^{\perp}(AP)$ (it is assumed that the operator AP is linear).

It can be shown that the inequality

$$0 \leqslant t(\xi) \leqslant \delta + \Delta, \tag{6}$$

†Based on the properties of the psuedoinverse operator $AA^-A = A$.

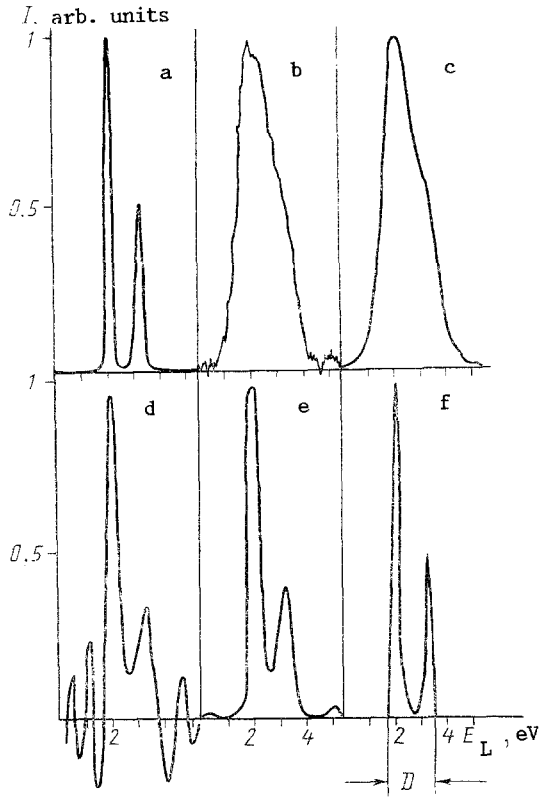

Fig. 1

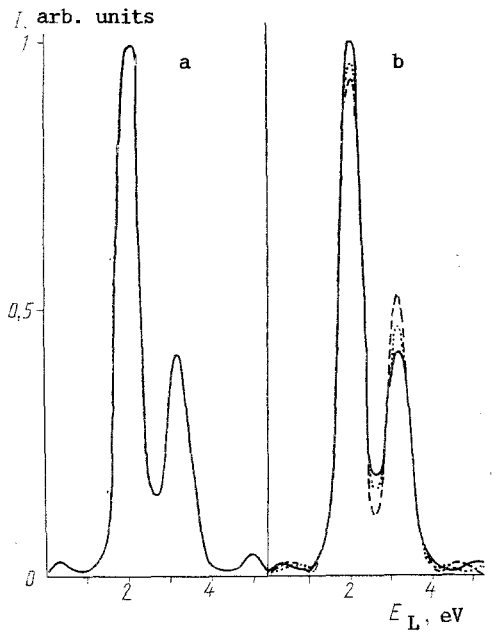

Fig. 2

Fig. 1. The use of a priori data in the problem of the reconstruction of spectra. The undistorted spectrum $\hat{f}$ (a); the spectrum $\xi = A\hat{f} + \nu$ modeled on a computer (b); the smoothed spectrum $g = AA^{-}\xi$ (c); the result of reconstruction $f^k = \lambda \cdot g + (I - \lambda \cdot A)f^{k-1}$, $k = 50$, neglecting a priori knowledge (d); the spectrum reconstructed taking into account restrictions for nonnegativeness and smoothness (e); effect of local data limiting the region D outside which the spectrum $\hat{f}$ is assumed to be equal to zero. Inside D no assumptions, aside from nonnegativity, are made about the structure of $\hat{f}$ (f).

Fig. 2. Simulation of the variability of the result of reconstruction. The result presented in Fig. 1e (a); simulation of the variability (b).

where $\Delta = \|Q_A pA\,(\tilde{f} - P\hat{f})\|$, and $\|\nu\| \leq \delta$, is satisfied. Based on Eqs. (5) and (6) it is possible to formulate a criterion A that monitors the reliability of the restriction $\tilde{f} = P\hat{f}$ based on the measurements ξ: if $t(\xi) > \delta$, then the a priori knowledge contradicts the measurement ξ and it must be regarded as disinformation; if $t(\xi) \leq \delta$, then the measurement ξ does not give any grounds for rejecting the a priori knowledge.

The reliability of the last solution is determined by the sensitivity of the criterion A. The point is that if $t(\xi) \leq \delta$, then this still does not mean that $\Delta = 0$; in particular, it is possible that $0 < \Delta \leq \Delta_0$, $\Delta_0 = t(\xi) + \delta$. The sensitivity determines the requirements that the a priori knowledge must satisfy. For example, if the sensitivity of the criterion is high, then the riskiest ideas about the spectrum $\hat{f}$ can be confidently included and vice versa.

In the case when $t(\xi) > \delta$, i.e., the a priori knowledge contradicts the measurement ξ (such a solution is absolutely reliable), the investigator must transfer to new data which do not contradict ξ. As a rule, this can be done by softening the a priori restrictions, for example, expanding the corridor $\tilde{f}$, $\tilde{\tilde{f}}$ to $\tilde{f} - \Delta f$, $\tilde{\tilde{f}} + \Delta f$, $\Delta f > 0$. The quality of the final solution of the problem of reconstructing $\hat{f}$ will, naturally, be reduced in the process.

Remark. The criterion A is also applicable in the case of nonlinear P. In this case, difficulties arise only in estimating the sensitivity of the criterion.

Simulation of the Variability of the Results of Reconstruction. Another important aspect of the reconstruction of spectroscopic measurements is estimation of the statistical

variability of the result of analysis, caused by random errors in the measurements.

In the case when the operator AP is linear and the linear reconstruction operator R can be calculated in an explicit form the correlation operator $\hat{\Sigma}$ of the error of reconstruction Rν can be calculated analytically, i.e., if $\hat{f} = RAPf + R\nu$, $\nu \sim N(0, \Sigma)$, then $R\nu \sim N(0, \hat{\Sigma})$, $\hat{\Sigma} = R\Sigma R^*$. The diagonal elements of the matrix Σ permit constructing the confidence corridor for the vector RAPf.

For nonlinear R this problem cannot be solved so easily analytically. Moreover, the error Rν even for uncorrelated initial noise ν is strongly correlated and in most cases it is manifested as spurious peaks, which makes it much more difficult to analyze the results of processing. In this sense the corridor is far from complete information about the random error Rν. Another difficulty is that the investigator is interested in the variability of the solution (4), not in the asymptotic case $k \to \infty$, but rather for a completely concrete number of iterations $k = k_0$.

These and other difficulties can be resolved with the help of the method of statistical simulation to estimate and visualize the variability of the results of processing. The main idea of the simulation approach is as follows: a probabilistic automatic device, intended for simulating the variability of the measurements ξ, i.e., for obtaining the realization $\tilde{\xi}$, is constructed based on the statistical sample S and the variability of the estimate $\hat{f} = f^k$ is simulated by repeated calculations $\tilde{f}^k = \lambda \cdot \tilde{g} + (I - \lambda \cdot A)P\tilde{f}^{k-1}$, $\tilde{g} = AA^-\tilde{\xi}$.

We shall study two particular cases of practical importance.

1. $S = \{\xi\}$, $\xi = (\xi_1 \ldots \xi_n)^*$ is the vector of measurements, and $\xi = Af + \nu$, $\nu = (\nu_1 \ldots \nu_n)^*$; ν_i, $i = 1, \ldots, n$ are independent identically distributed random quantities with unknown distribution $P_\nu(x)$. The coordinates of the vector $\xi - AA^-\xi$ are used as a sample of n independent random quantities, according to which the estimate $\tilde{P}_\nu(x)$ of the distribution $P_\nu(x)$ is calculated. The form of the estimate $\tilde{P}_\nu(x)$ depends on the a priori information about the smoothness or parametric nature of the distribution $P_\nu(x)$. A probabilistic automatic device, playing out, according to $\tilde{P}_\nu(x)$, the realizations $\tilde{\nu}$ and further $\tilde{\xi} = AA^-\xi + \tilde{\nu}$, is implemented on a computer. This approach works reliably when the useful signal Af is significantly more regular than the noise ν.

2. A commonly used device is an experiment performed in a serial fashion, in which the final result is $\xi = \frac{1}{m}\sum_{i=1}^{m} \xi^i$, where ξ^i are identically distributed random vectors. In this case $S = \{\xi^1 \ldots \xi^m\}$, and one of the simplest methods for modeling the realizations is the bootstrap method [5], which does not require any a priori information about the distribution of the vectors.

The possibility of using the simulation approach follows from the fact that the processing operator R is continuous.

The results of the simulation of the variability of the estimate $\hat{f} = f^k$ are displayed in the form of multiplication, which enables the investigator to trace the stability of his subjective conclusions regarding the structure of the spectrum under analysis. Figure 2 illustrates the variability of the solution, previously presented in Fig. 1e. One can see, for example, that the small peaks in the solution cannot be trusted, since noise can produce analogous peaks. At the same time the conclusion that two peaks are present in the central region is stable, but the intensities of the peaks can differ from the values obtained in Fig. 1e.

The complexity of the simulation approach lies in the necessity of performing repeated calculations of the estimate $\hat{f} = f^k$. The algorithm (4) which we used, especially for bonded matrices A, permits calculating $\hat{f}$ quite rapidly. It should be noted that parallel computing systems will give new motivation for using the simulation approach.

LITERATURE CITED

1. B. I. Volkov, Yu. P. Pyt'ev, and D. V. Yudin, Vestn. Mosk. Gos. Univ., Ser. Fiz., Astron., 28, No. 1, 3-8 (1987).
2. D. V. Yudin and V. V. Gorchakov, Zh. Prikl. Spektrosk., 49, No. 4, 642-647 (1988).
3. D. V. Yudin and V. V. Gorchakov, in: Abstracts of Reports at the 9th All-Union Conference on Physical and Mathematical Methods in Coordination Chemistry, Novosibirsk (1987), Vol. 2, p. 271.

4. Yu. P. Pyt'ev, Mat. Sb., 120, No. 2, 240-272 (1983).
5. D. Freedman and S. Peters, Technical Report, Univ. of California (1982), No. 10, pp. 167-175.

CALCULATION AND USE OF THE COEFFICIENTS IN DUNHAM'S FUNCTION TO DETERMINE THE SPECTROSCOPIC CHARACTERISTICS OF DIATOMIC MOLECULES

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In solving the Schröedinger equation for a diatomic molecule Dunham employed the potential function [1]

$$V = a_0 \xi^2 (1 + a_1 \xi + a_2 \xi^2 + a_3 \xi^3 + \ldots), \tag{1}$$

where $a_0 = \omega_e^2/4B_e$; ω_e is the frequency of small oscillations, in cm^{-1}; $B_e = h/8\pi^2\mu r_e^2 c$; μ is the reduced mass of the molecule; $\xi = (r - r_e)/r_e$, where r_e is the equilibrium and r is the variable internuclear distance. For brevity we shall call the constants a_i Dunham's constants. The energy levels of the molecule $E(v, K)$ obtained from the solution of Schröedinger's equation are equal to [1]

$$E(v,K) = \sum_i \sum_j Y_{ij} \left(v + \frac{1}{2}\right)^i [K(K+1)]^j, \tag{2}$$

where Y_{ij} are polynomials, which depend on ω_e, B_e, and a_i from Eq. (1).

On the other hand, it is known that [2, 3]

$$E(v,K) = \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 + \omega_e y_e \left(v + \frac{1}{2}\right)^3 + \ldots + \\ - B_e K(K+1) - \alpha_e \left(v + \frac{1}{2}\right) K(K+1) + \ldots \tag{3}$$

Comparing the coefficients in Eqs. (2) and (3) for equal powers of v and K we obtain equations relating Y_{ij} with the anharmonicity constants and the rotational constants α_e and B_e.

Thus, the spectroscopic characteristics of a diatomic molecule can be expressed in terms of B_e, ω_e, and a_i. From here one can see the importance of Dunham's coefficients for calculating the characteristics of the vibrational and rotational spectra of molecules.

In [4, 5] the coefficients a_1 and a_2 were obtained from experimental data for ω_e, B_e, α_e, and $\omega_e x_e$ – the first anharmonicity constant – from the formulas of [1]:

$$-a_1 = \frac{\alpha_e \omega_e}{6B_e^2} + 1, \tag{4}$$

$$a_2 = \frac{5}{4} a_1^2 - \frac{2\omega_e \chi_e}{3B_e}. \tag{5}$$

In [4] it is concluded that a_1 and a_2 are constant for all groups of molecules, with the exception of hydrogen and lithium compounds.

In this work we obtained expressions for a_i for any i in terms of a_1, starting from the model potential function proposed in [6] for a diatomic molecule:

$$V_r = V_{r_e} + \frac{1}{2} \alpha_e (r - d_{ij}'')^2 + \frac{Z_i Z_j e^2}{(r - d_{ij}')^2}, \tag{6}$$

where $Z_i e$ and $Z_j e$ are the effective charges of the constituent atoms i and j of the molecule; d_{ij}'' is the equilibrium distance between the atoms i and j in the absence of Coulomb repulsive forces; d_{ij}' is the sum of the displacements of the centers of the effective charges compared with the equilibrium position of the nuclei i and j.

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