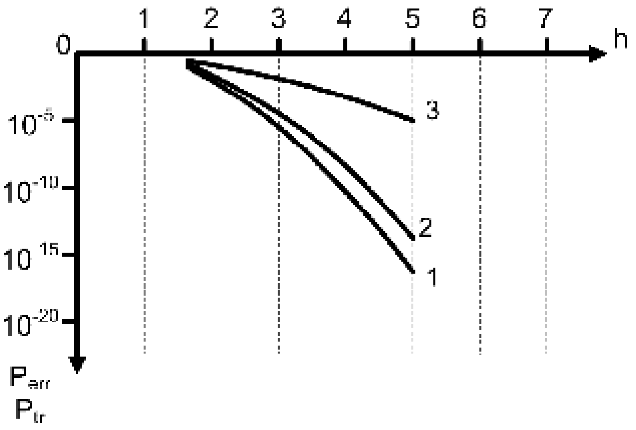

Fig. 3. The noise immunity of IRAM at $k = 0,7$ and $INV_l = 1$; $INV_i = 2; 3; 4; 5; 6; 7$.
Curve 1is the probability of the pairwise transition into IRAM under non-correlativity of the noise readings (theoretical limit; Curve 2 is the probability of the pairwise transition of IRAM at $R = 0,7$; Curve 3 is the error probability of the classical AM

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A. E. Novikov
Siberian Federal University, Russia, Krasnoyarsk

E. A. Novikov
Institute of Computational Modelling, Russian Academy of Sciences, Siberian Branch, Russia, Krasnoyarsk

THE NUMERICAL MODELING OF A CESIUM CYCLE IN THE UPPER ATMOSPHERE BY AN L-STABLE METHOD OF SECOND-ORDER ACCURACY*

An algorithm of right-hand side and Jacobian formation of differential equations of chemical kinetics is described. Numerical simulation of the cesium cycle in the upper atmosphere is conducted by means of the L-stable method of the second order of accuracy with the control accuracy. The results of the computation are presented.

Keywords: chemical kinetics, cesium cycle, stiff problem, L-stable method, accuracy control.

The modeling of chemical reactions kinetics’ is applied in the studies of various chemical processes. The subject of this study is the time dependence on concentration of reagents being a solution for the Cauchy problem and for systems of ordinary differential equations. Difficulties in solving such problems are related to stiffness and a large scale. In modern methods for the solving stiff problems, an inversion of the Jacobi matrix of the equations’ system is used. In the case of the original problem’s large scale, the decomposition of the given matrix essentially defines a total of computational work. To improve calculation efficiency, in a number of algorithms the freezing of the Jacobi matrix, i. e. the application of the same matrix at several iteration steps, is used [1–2]. This approach is used in advantage to algorithms based on the multistep methods, in particular the formula for backward differentiation [3]. The situation is worse in algorithms for integrations based on known iteration-free methods among which are the Rozenbrok type methods and their modifications [1]. Here is an algorithm for the construction of the right-hand side and the Jacobi matrix of the differential chemical kinetics’ equations. Results of numerical modeling of an ionization-deionization cesium cycle in the upper atmosphere with an L-stable method of second-order accuracy, in which the numerical freezing as well as analytical Jacobi matrix is allowed, are given here.

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* The work was supported by the Russian Foundation of Fundamental Researches (grant №08-01-00621) and by the Presidential grant NSh-3431.2008.9.

A kinetic scheme of a chemical reaction consisting of elementary stages which are written in formula [4]

$$\sum_{i=1}^{N_r} \alpha_{ij} x_i \xrightarrow{k_j} \sum_{i=1}^{N_r} \beta_{ij} x_i, \qquad (1)$$

where x_i, $1 \le I \le N_r$ are reagents; k_j, $1 \le j \le N_s$ are constants of stages' rates; N_r and N_s are a number of reagents and a number of stages respectively; α_{ij} and β_{ij}, $1 \le I \le N_r$, $1 \le j \le N_s$ are stoichiometric coefficients. In the framework of an isothermal reactor of a constant volume lumped model, to the process (1) corresponds a system of ordinary differential equations

$$C' = A^T V \qquad (2)$$

with a given initial condition $C(0) = C_0$. Here A^T is a stoichiometric matrix, C and V are vectors of reagent concentrations and rates of stages respectively. When a reaction occurs in non-isothermal conditions, the heat balance equation is

$$T' = [Q^T V - \alpha(T - T_{01})] / C_V^T C, \qquad (3)$$

where T is the temperature of a reactor mixture, T_{01} is temperature of reactor walls, Q^T is a vector of specific heat of stages, C^T_V is a vector of the reagents' heat capacity, $\alpha = \alpha s/r$, α is a heat transfer coefficient, s and r are an area of a surface and the volume of a reactor respectively, is added to the system (2). The superscript T of the vectors Q^T and C^T_V means transposition. Heat capacity of reagents and a heat transfer coefficient may be the functions of reagent concentration α may depend on temperature as well.

When the reaction occurs in an isothermal reactor of a constant volume with an agent change (an open system, a reactor of the ideal mixing), a system of differential equations is written in the formula

$$C' = AV^T + \frac{1}{\Theta}(C_p - C), \qquad (4)$$

where C_p is a vector of reagent concentration in the inlet, Θ is time of the mixture being in the reactor, $\Theta = r/u$, u is volume velocity of the mixture flow through a reactor. When a reaction occurs in non-isothermal conditions, the heat balance equation is

$$T' = [Q^T V - \alpha(T - T_{01})] / C_V^T C - \frac{1}{\Theta}(T - T_{02}), \qquad (5)$$

where T_{02} is the temperature of a mixture at the inlet of a reactor, is added to the system (4). The temperature of a reacting mixture can be given as a function of time and concentration, i. e. $T = T(t,C)$.

If a stage is reversible, then the difference of rates W_s^+ and W_s^- (of direct and inverse processes) respectively, is conventionally taken as a rate W_s of a stage, i. e.

$$W_s = W_s^+ + W_s^-, \quad 1 \le s \le N_s.$$

If the third particle is involved in the reaction, then a rate is recalculated by the formula

$$V_s = P_s W_s, \quad P_s = \sum_{i=1}^{N_r + N_{in}} \varepsilon_{si} c_i,$$

where ε_{si}, $1 \le i \le N_r$ are efficiencies of the third particles, N_{in}, ε_{si} and c_i, $N_r + 1 \le i \le N_r + N_{in}$ are quantity, efficiencies and concentrations of inert agents, respectively. The values of the components of the vector W_s are determined from scheme (1) of a chemical reaction by the relations

$$W_s^+ = k_s \prod_{i=1}^{N_r + N_{in}} c_i^{\alpha_{si}}, \; W_s^- = k_{-s} \prod_{i=1}^{N_r + N_{in}} c_i^{\beta_{si}},$$

where k_s and k_{-s}, $1 \le s \le N_s$ are constants of rates of direct and reverse stages, respectively. Constants of rates are calculated by the formula

$$k_j = A_j T^{n_j} \exp(-E_j / RT),$$

where T is temperature of the mixture in the reactor; A_j, n_j and E_j/R are the given constants. The immediate use of this formula may lead to a wrong result or arithmetic overflow because of the large constant data spread [5–6]. Therefore for calculating constants of stages' rates the following relation is used:

$$k_j = \exp(\ln A_j + n_j \ln T - E_j / RT).$$

The stoichiometric matrix A^T with entries α_{ij} is formed from the kinetic scheme (1) by the following rule: a stage number coincides with a column number and a reagent number coincides with a number of the row of the matrix A^T. If x_i is an initial reagent then $a_{ij} = -\alpha_{ij}$, if x_i is a product then $a_{ij} = \beta_{ij}$. If x_i is an initial reagent and a product simultaneously then $a_{ij} = \beta_{ij} - \alpha_{ij}$. Usually a small number of reagents take part in an elementary stage, i. e. a stoichiometric matrix is sparse. For the system (2) the j-th column b_j of the Jacobi matrix defined by the formula

$$b_j = A^T \frac{\partial V}{\partial c_j}, \quad 1 \le j \le N_r. \qquad (6)$$

In the case that the system (2), (3) is solved simultaneously, the row $b_{Nr+1,i}$, the column $b_{i,Nr+1}$ and the corner element $b_{Nr+1,Nr+1}$, which are determined the following way:

$$b_{N_r+1,i} = \{Q^T \frac{\partial V}{\partial c_i} - \frac{\partial \alpha}{\partial c_i}(T - T_{01}) +$$

$$+ [\alpha(T - T_{01}) - Q^T V] c_{vi} / C_V^T C\} / C_V^T C,$$

$$b_{i,N_r+1} = (A \frac{\partial V}{\partial T})_i, \quad 1 \le i \le N_r,$$

$$b_{N_r+1,N_r+1} = [Q^T \frac{\partial V}{\partial T} - \frac{\partial \alpha}{\partial T}(T - T_{01}) - \alpha] / C_V^T C -$$

$$-[Q^T V - \alpha(T - T_{01})](\frac{\partial C_V^T}{\partial T} C) / (C_V^T C)^2,$$

are added to the matrix. For a flow reactor, the diagonal elements of the obtained matrix are adjusted considering the component $1/\Theta$. Observe that the components of the vector $\partial V/\partial c_i$ have the form

$$\partial v_s / \partial c_i = \alpha_{si} p_s k_s c_i^{\alpha_{si} - 1} \prod_{k=1, k \ne i}^{N_r + N_{in}} c_i^{\alpha_{sk}} -$$

$$-\beta_{si} p_s k_{-s} c_i^{\beta_{si} - 1} \prod_{k=1, k \ne i}^{N_r + N_{in}} c_i^{\beta_{sk}} - \varepsilon_{si}(W_s^+ - W_s^-), \qquad (7)$$

and for the components of the vector $\partial V/\partial T$ we have the following reactions:

$$\partial v_s / \partial T = p_s \frac{\partial k_s}{\partial T} \prod_{i=1}^{N_r + N_{in}} c_i^{\alpha_{si}} -$$

$$-p_s \frac{\partial k_{-s}}{\partial T} \prod_{i=1}^{N_R + N_{in}} c_i^{\beta_{si}}, \quad 1 \le s \le N_s.$$

If at the s-th stage there is no third particle, then in the expressions for $\partial v_s/\partial c_i$ and $\partial v_s/\partial T$ one should put $p_s = 1$ and $\varepsilon_{si} = 0$.

To determine the entries b_{ij}, $1 \le i, j \le N_r$ of the Jacobi matrix with the help of (6), we can apply the formula

$$b_{ij} = \sum_{s=1}^{N_s} a_{js} \frac{\partial v_s}{\partial c_i}, \quad 1 \le i, j \le N_r .$$

Consider the individual term (7), i. e.

$$\alpha_{js} p_s k_s \alpha_{si} c_i^{\alpha_{si}-1} \prod_{k=1, k \ne i}^{N_r + N_{in}} c_i^{\alpha_{sk}} -$$

$$-\alpha_{js} p_s k_{-s} \beta_{si} c_i^{\beta_{si}-1} \prod_{k=1, k \ne i}^{N_r + N_{in}} c_i^{\beta_{sk}} + a_{js} \varepsilon_{si} (W_s^+ - W_s^-).$$

To determine this expression, it is necessary to perform three steps. Repeating them in a loop allows the forming of the relations (8). At the first step $a_{js} p_s k_s \alpha_{si}$ and $a_{js} p_s k_{-s} \beta_{si}$, are formed with $p_s k_s$ or $p_s k_{-s}$ assumed to be calculated. At the second step we define

$$c_i^{\alpha_{si}-1} \prod_{k=1, k \ne i}^{N_r + N_{in}} c_i^{\alpha_{sk}}, \qquad c_i^{\beta_{si}-1} \prod_{k=1, k \ne i}^{N_r + N_{in}} c_i^{\beta_{sk}}.$$

In the case that the third particles are involved in the scheme of a reaction, for the third step $a_{js} \varepsilon_{si} (W_s^+ - W_s^-)$ is given.

We describe a numerical method which is applied for numerical integration of an ionization-deionization cesium cycle in the upper atmosphere. For the numerical solution of the Cauchy problem in a system of ordinary differential equations

$$y' = f(t, y), \quad y(t_0) = y_0, \quad t_0 \le t \le t_k, \tag{8}$$

where y and f are real N-dimensional vector functions, t is an independent variable, we consider the (m, k)-method of the form [7]

$$y_{n+1} = y_n + a k_1 + (1-a) k_2, \quad a = 1 - \frac{\sqrt{2}}{2},$$

$$D_n k_1 = h_n f(t_n + \beta h, y_n), \quad D_n k_2 = k_1. \tag{9}$$

Here k_1 and k_2 are stages of the method; $D_n = E - a h_n A_n$; E is the identity matrix; h_n is an integration step; A_n is a matrix which can be represented in the form $A_n = f'_n + hB_n + O(h^2)$; $f'_n = \partial f(y_n)/\partial y$ is the Jacobi matrix of the system (8); B_n is a matrix which does not depend on an integration step. We can apply the method (9) of freezing the numerical as well as the analytical Jacobi matrix. Using the Taylor expansion of the stages, a local error δ_n of the method (9) can be written in formula

$$\delta_n = (a - 1/3) h^3 f_y'^2 f + h^3 [\frac{1}{24} f''_{tt} + \frac{1}{6} f''_{yy} f^2 +$$

$$+ \frac{1}{3} f''_{yt} f - \frac{1}{2} f'_y f'_t - \frac{1}{2} B_n f] + O(h^4).$$

Then, according to [8], for the accuracy control in (9) we can use the error estimation of the form

$$\varepsilon_n = (a - \frac{1}{3}) h^2 f'_y f + O(h^3).$$

Taking into account

$$k_2 - k_1 = a h^2 f'_{y,n} f_n + O(h^3)$$

we can estimate ε_n within the order terms of $O(h^3)$ using this formula

$$\varepsilon_n = a^{-1} (a - \frac{1}{3}) [k_2 - k_1].$$

As a result, in the accuracy control for the method (9) we can apply the inequality

$$\varepsilon(j_n) = \| D_n^{1-j_n} (k_2 - k_1) \| \le \frac{a\varepsilon}{1/3 - a},$$

where ε is a required accuracy of integration, ||·|| is some norm in R^N, and the value of the parameter j_n, $1 \le j_n \le 2$, is taken the least one for which this inequality holds. In precise calculations the norm in the inequality had been calculated with the formula

$$\| D_n^{1-j_n} (k_2 - k_1) \| = \max_{1 \le i \le N} \frac{| [D_n^{1-j_n} (k_2 - k_1)]_i |}{| y_n^i | + tr},$$

where i is the number of the component of the approximate solution, tr is a positive parameter. If for the i-th component of a solution the inequality $|y_n^i| < tr$ holds then the absolute error $tr \cdot \varepsilon$ is controlled, in the opposite case the relative error e is controlled. In the calculations the parameter tr is chosen so that for all components of the solution the actual accuracy is not worse than the given one.

In the numerical calculation of the Jacobi matrix a step r_j, $1 \le j \le N$ of numerical differentiation is taken by the formula $r_j = \max(10^{-14}, 10^{-7}|y_j|)$. Usually in the solution of stiff problems double precision is used since the Jacobi matrix of the system (9) is ill-conditioned. Now the j-th column a_n^j of the matrix A_n in (9) is calculated by the formula

$$a_n^j = \frac{f(y_1, ..., y_j + r_j, ..., y_N) - f(y_1, ..., y_j, ..., y_N)}{r_j},$$

i. e., calculation of the matrix A_n requires N calculations of the right-hand side of the problem (8). An attempt to use the previous matrix D_n is performed after each successful integration step. To ensure that the stability property of a numerical scheme holds, the integration step remains constant when freezing the matrix D_n. Unfreezing of the matrix takes place in the following cases:

– the accuracy of calculations is violated;

– the number of steps with a frozen matrix achieves a given maximal value I_h;

– the predicted step is Q_h times greater than the last successful one;

– $\varepsilon(1) > \varepsilon(2)$.

The choice of I_h and Q_h can have influence on redistribution of computational work. For $I_h = 0$ and $Q_h = 0$ freezing a matrix does not take place, with increasing I_h and Q_h the number of calculations of the right-hand side of the problem (8) increases and the number of inversions of the Jacobi matrix decreases. Efficiency of the integration algorithm depends on I_h and Q_h by the choice of which the algorithm can be adjusted for a concrete type of problems. They are chosen depending on the ratio of the computational cost of the function f to that of the decomposition of the Jacobi matrix.

Now we consider a model of the ionization-deionization cesium cycle in the upper atmosphere. The presented model is obtained from a large kinetic scheme and is widely used abroad as a typical example of a stiff problem of kinetics [9]. The scheme of the reaction has the form

1) $O_2^- + C_s^+ \to C_s + O_2$,
2) $C_s^+ + e \to C_s$,
3) $C_s \to C_s^+ + e$,
4) $O_2 + C_s + M \to C_s O_2 + M$,
5) $O_2 + e + M \to O_2^- + M$,
6) $O_2^- \to O_2 + e$,

where the constants of rates are the following: $k_1 = 3{,}0 \cdot 10^{10}$,

$k_2 = 6{,}0 \cdot 10^5$, $k_3 = 3{,}24 \cdot 10^{-3}$, $k_4 = 3{,}63 \cdot 10^4$, $k_5 = 3{,}63 \cdot 10^4$, $k_6 = 4{,}0 \cdot 10^{-1}$. The reaction occurs with participation of the inert substance N_2, its concentration is $[N_2] = 3{,}32 \cdot 10^{-3}$. Efficiencies of the third substances are equal to 1 for all reagents with the exception of the efficiency of O_2 at the fifth stage which is equal to 12,4. We denote the concentrations of the reagents in the following way:

$$c_1 = [e],\ c_2 = [O_2^-],\ c_3 = [C_s],$$
$$c_4 = [C_s O_2],\ c_5 = [C_s^+],\ c_6 = [O_2].$$

The corresponding system involves 6 differential equations of the form

$$\begin{aligned} c_1' &= -k_2 c_1 c_5 + k_3 c_3 - k_5 p_2 c_1 c_6 + k_6 c_2, \\ c_2' &= -k_1 c_2 c_5 + k_5 p_2 c_1 c_6 - k_6 c_2, \\ c_3' &= k_1 c_2 c_5 + k_2 c_1 c_5 - k_3 c_3 - k_4 p_1 c_3 c_6, \\ c_4' &= k_4 p_1 c_3 c_6, \\ c_5' &= -k_1 c_2 c_5 - k_2 c_1 c_5 + k_3 c_3, \\ c_6' &= k_1 c_2 c_5 - k_4 p_1 c_3 c_6 - k_5 p_2 c_1 c_6 + k_6 c_2, \end{aligned} \qquad (10)$$

where

$$p_1 = c_1 + c_2 + c_3 + c_4 + c_5 + c_6 + [N_2],$$
$$p_2 = c_1 + c_2 + c_3 + c_4 + c_5 + 12.4 c_6 + [N_2].$$

Integration is performed over the segment [0.1000] with initial step 10^{-5} for the following initial concentrations of the reagents:

$$c_1 = [e] = 1.66 \cdot 10^{-16},$$
$$c_2 = [O_2^-] = 8.63 \cdot 10^{-16},$$
$$c_3 = [C_s] = 1.66 \cdot 10^{-6},$$
$$c_4 = [C_s O_2] = 0.0,$$
$$c_5 = [C_s^+] = 1.03 \cdot 10^{-15},$$
$$c_6 = [O_2] = 5.98 \cdot 10^{-4}.$$

The presented algorithm was compared in efficiency with the known *dlsode* method of Gear in the implementation of A. Hindmarsh [10] for accuracy $\varepsilon = 10^{-2}$ of calculations. Poor accuracy of calculations is related to the fact that the method (9) is of second-order accuracy and there is no sense in using it in high-accuracy calculations. The number *if* of calculations of the right-hand side and the number *ij* of decompositions of the Jacobi matrix of the problem (10) on the integration interval are taken as an efficiency criterion. To solve the problem (10), the constructed algorithm requires 101 calculations of the right-hand side and 14 decompositions of the Jacobi matrix. In the *dlsode* method the required accuracy of 10^{-2} is achieved for $\varepsilon = 10^{-3}$ with computational costs *if* = 192 and *ij* = 22.

The numerical results show that the proposed algorithm has the advantage for the number of calculations of the right-hand side almost by a factor of two, whereas the advantage for the number of decompositions of the Jacobi matrix is about by a factor of 1.5. This integration algorithm is assumed to have the most efficient application for stiff problems for accuracy $\varepsilon = 10^{-2}$ of calculations (of order of one percent) and lower.

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