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Computation of periodic orbits in a three-dimensional kinetic model of catalytic hydrogen oxidation *

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Summary. An iterative method for solving periodical boundary-value problem (BVP) for autonomous ordinary differential equations (ODEs) is applied to calculations of periodic orbits and their stability in a three-dimensional kinetic model of catalytic hydrogen oxidation.

According to the method, the periodic orbit is decomposed into pieces by local cross-sections $\{\pi_i\}$ and between π_i and π_{i+1} the integration of the system is to be accomplished. Hence we obtain an α-pseudo-orbit and then construct the generalized Poincare map. Thus the BVP for ODEs is reduced to a system of nonlinear algebraic equations that takes into account both the boundary conditions of periodicity and condition of the solution continuity at boundary points of pieces. Being linearized, the algebraic system has a band structure and for solving such a system the orthogonal sweep method is extremely effective.

In the model considered we find numerically periodic orbits of rather complex structure, give an example of weakly stable dynamics,

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and show the role of successive period doubling bifurcations in the creation of weakly stable dynamics.

Key words: periodic orbit, numerical solution of ordinary differential equations, chemical kinetic model, period doubling bifurcation, weakly stable dynamics

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1. Introduction

It is common knowledge that a major disadvantage of the single shooting method is the roundoff error accumulation which occurs when an unstable periodic orbit or a periodic solution with a long period has to be integrated [1–5]. Therefore a decomposition of the periodic orbit into pieces and computation of α-pseudo-orbits is the most challenging task in the process of long-term numerical integration of ODEs or in so-called "a chase of canards" [13].

In this paper we present a decomposition strategy based on local cross-sections, α-pseudo-orbits and the generalized Poincare return map construction [8–9]. The α-pseudo-orbits are essentially realized in numerical iterations. If α is very small, then it implies that, while a computer may not calculate the orbit which you hope for, what it does find is nonetheless an approximation to some true hyperbolic orbit of the system. Some aspects of the problem formulation considered here have been discussed in earlier publications [3–7,15]. The method as it is proposed has an advantage over similar methods developed earlier [5] in that the number of unknown parameters to be found is decreased after the Houscholder transformation of the generalized Poincare map which we shall discuss in Sections 3 and 4.

In Section 6 we present an analysis of a three-dimensional mathematical model of the heterogeneous reaction of hydrogen oxidation on metallic catalysts as an illustration of computations using this method.

2. Poincare Return Map

We consider the differential equation

$$\frac{dx}{dt} = f(x) \tag{1}$$

for a vector $x = (\mathrm{x}_1, \ldots, \mathrm{x}_n)$ with n components and assume that a structurally stable periodic solution $x = x(t)$ exists. Let $a_1, \ldots, a_N$ be points in a certain neighborhood of the periodic solution $x(t)$. Let $b_1, \ldots, b_N$ be vectors such that $(b_i, f(a_i)) = (1 - \varepsilon_i)\|f(a_i)\|\,\|b_i\| > 0$, where $\varepsilon_i > 0$.

For each point a_i we take a local "cross section" of dimension $n-1$ passing through a_i

$$\pi_i = \{x \in \mathbf{R}^n : \quad (x - a_i, b_i) = 0\}.$$

The hyperplane π_i is transverse to the flow generated by the vector field f.

Let vector-functions $x_1(t, a_1)$, ..., $x_N(t, a_N)$ satisfy initial-value problems

$$\frac{dx_i}{dt} = f(x_i), \quad x_i(t_i, a_i) = a_i, \qquad t_i \le t \le t_{i+1}, \quad i = 1, \ldots, N,$$

and additional conditions

$$x_1(t_2, a_1) \in \pi_2, \quad \ldots, \quad x_{N-1}(t_N, a_{N-1}) \in \pi_N, \quad x_N(t_{N+1}, a_N) \in \pi_1.$$

It is convenient to introduce the new independent variables ξ_i for each $i \in [1, N]$ by setting

$$\xi_i = \frac{t - t_i}{t_{i+1} - t_i}, \tag{2}$$

and the functions y_i through

$$y_i(\xi_i, a_i) = x_i(t_i + \xi_i(t_{i+1} - t_i), a_i), \tag{3}$$

so that $y_i(\xi_i, a_i)$ will be defined on the interval $[0, 1]$ in ξ_i. Because of equations (2) and (3) the functions y_i satisfy the initial-value problems

$$\frac{dy_i}{d\xi_i} = F_i(y_i), \quad y_i(0, a_i) = a_i, \qquad 0 \le \xi_i \le 1,$$

where $F_1(y_1) = (t_2 - t_1)f(y_1)$, ..., $F_N(y_N) = (t_{N+1} - t_N)f(y_N)$.

It can be proved that for each $i \in [1, N]$ a function $\xi_i(a) \in \mathbf{C}^1$ exists such that

$$y_i(\xi_i(a), a) \in \pi_{i+1},$$

if $a \in \pi_i$ and a is in a certain neighborhood of the point a_i [10].

Let us introduce euclidian space U_i by means of a translation along the vector a_i:

$$U_i = \{u_i \in \mathbf{R}^n : \quad u_i = x - a_i, \quad x \in \mathbf{R}^n\}.$$

Now under this transformation the hyperplane π_i will go over into its image set forming the hyperplane

$$\Pi_i = \{u_i \in U_i : \quad (u_i, b_i) = 0\}\,. \tag{4}$$

Let U be $(N \times n)$-dimensional space

$$U = U_1 \oplus \cdots \oplus U_N,$$

that is a direct sum of n-dimensional vector spaces $U_i, \ \ i = 1, \ldots, N$. Let us define a subspace Π in U as

$$\Pi = \Big\{u = (u_1, \ldots, u_N)^T \in U : \quad u_i \in \Pi_i, \ \ i = 1, \ldots, N\Big\}.$$

We now proceed to construct the generalized Poincare return map of the subspace Π into itself $T : \Pi \to \Pi$ which can therefore be written in the form

$$\begin{bmatrix} \tilde{u}_1 \\ \tilde{u}_2 \\ \vdots \\ \tilde{u}_N \end{bmatrix} = \begin{bmatrix} y_N(\xi_N(a_N + u_N), a_N + u_N) - a_1 \\ y_1(\xi_1(a_1 + u_1), a_1 + u_1) - a_2 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ y_{N-1}(\xi_{N-1}(a_{N-1} + u_{N-1}), a_{N-1} + u_{N-1}) - a_N \end{bmatrix}.$$

The point u is a fixed point of the generalized Poincare map if $T(u) = u$, and there is a mutual one–to–one relationship between fixed points of this map and periodic solutions of the equation (1). Namely, points $a_i + u_i$ for $i = 1, \ldots, N$ lie on a periodic solution $x(t)$ if the point u is a fixed point of the generalized Poincare map, i.e.

$$\begin{bmatrix} u_1 \\ u_2 \\ \vdots \\ u_N \end{bmatrix} = \begin{bmatrix} y_N(\xi_N(a_N + u_N), a_N + u_N) - a_1 \\ y_1(\xi_1(a_1 + u_1), a_1 + u_1) - a_2 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ y_{N-1}(\xi_{N-1}(a_{N-1} + u_{N-1}), a_{N-1} + u_{N-1}) - a_N \end{bmatrix}. \tag{5}$$

Thus the problem of finding a periodic solution of the equation (1) is reduced to that of solving algebraic equation (5).

3. Transformation of the Poincare Map

Let us choose b_i so that $||b_i|| = 1$ for each $i \in [1, N]$. It is further convenient to introduce the Householder transformation $\mathcal{P}_i$ as follows

$$\mathcal{P}_i u_i = u_i - 2\frac{(u_i, b_i - e)}{||b_i - e||}(b_i - e),$$

where $e = (0, \dots, 0, 1)$. Now under this transformation the hyperplane Π_i will go over onto the hyperplane $S_i = \{u_i \in U_i : \ u_i^n = 0\}$.

For our purposes it is more suitable to introduce the transformation $\mathcal{P}$ so that

$$\mathcal{P}u = \begin{bmatrix} \mathcal{P}_1 & & 0 \\ & \ddots & \\ 0 & & \mathcal{P}_N \end{bmatrix} \begin{bmatrix} u_1 \\ \vdots \\ u_N \end{bmatrix}.$$

Consider a subspace S in U such that

$$S = \Big\{ u = (u_1, \dots, u_N)^T \in U : \quad u_i \in S_i, \quad i = 1, \dots, N \Big\}.$$

It is then immediately seen that under the transformation $\mathcal{P}$ the subspace Π goes over onto the subspace S. Moreover, since $\mathcal{P}_i^2 = I$ for each $i \in [1, N]$, then

$$\mathcal{P}^2 = \begin{bmatrix} \mathcal{P}_1^2 & & 0 \\ & \ddots & \\ 0 & & \mathcal{P}_N^2 \end{bmatrix} = \begin{bmatrix} I & & 0 \\ & \ddots & \\ 0 & & I \end{bmatrix}.$$

We denote by $\mathcal{R} = \mathcal{P} \circ T \circ \mathcal{P}$ the transformation under which S goes over onto itself:

$$S \xrightarrow{\mathcal{P}} \Pi \xrightarrow{T} \Pi \xrightarrow{\mathcal{P}} S.$$

It is not difficult to see that if the transformation T has a fixed point $u = T(u)$, $u \in \Pi$, then the transformation $\mathcal{R}$ also has a fixed point

$$v = \mathcal{R}(v), \tag{6}$$

where $v = \mathcal{P}(u)$.

4. Linearization

The technique of solving the nonlinear algebraic equations (5) or (6) is based on the Newton method. Let u_i be a small perturbation of a_i (initially guessed approximate value of $x(t_i)$) in the hyperplane π_i such that the point $a_i + u_i$ lies on the periodic solution. And let τ_i correspond to a small perturbation of the interval $[t_i, t_{i+1}]$ length so that $y_i(1 + \tau_i, a_i + u_i) \in \pi_{i+1}$.

It is further convenient to introduce instead of the functions $y_i(1+\tau_i, a_i + u_i)$ the functions $F_i(y_i(1, a_i))$, $D_i(1)$ obtained by expanding y_i in powers of τ_i and u_i around the point $(\tau_i, u_i) = (0, 0)$:

$$y_i(1 + \tau_i, a_i + u_i) = y_i(1, a_i) + \tau_i F_i(y_i(1, a_i)) + D_i(1)u_i. \tag{7}$$

Here $D_i(1)$ is, of course, a matrix and in the right part of (7) we keep only three terms in Taylor expansion. The matrix $D_i(s)$ should satisfy the equation

$$\frac{d}{ds}D_i(s) = (F_i)'_y(y_i(s,a_i)) \cdot D_i(s), \qquad D_i(0) = I.$$

We can rewrite (7) for $i = 1,\dots,N$ in the form

$$(8) \qquad y_i(1+\tau_i, a_i+u_i) - a_{i+1} = \\ = \tau_i F_i(y_i(1,a_i)) + D_i(1)u_i + y_i(1,a_i) - a_{i+1},$$

where $a_{N+1} = a_1$. Note that the left part of the relation (8) is equal to u_{i+1} by definition, where $u_{N+1} = u_1$. So, defining

$$h_i = y_i(1,a_i) - a_{i+1}$$

and recalling (4) we are left to solve a set of $(n+1)\times N$ linear algebraic equations

$$(9) \qquad u_{i+1} = \tau_i F_i(y_i(1,a_i)) + D_i(1)u_i + h_i, \\ (u_i, b_i) = 0, \qquad i = 1,\dots,N.$$

For this purpose we subject the system (9) to the transformation defined in the section 3. Introducing the vector v by

$$u = \mathcal{P}v.$$

we come from the system (9) to the next one

$$(10) \quad \mathcal{P}_{i+1}v_{i+1} = \tau_i F_i(y_i(1,a_i)) + D_i(1)\mathcal{P}_i v_i + h_i, \qquad i = 1,\dots,N,$$

where $\mathcal{P}_{N+1} = \mathcal{P}_1$. Since $\mathcal{P}^2_{i+1} = I$, then we can rewrite the equations (10) as follows

$$v_{i+1} = \tau_i \mathcal{P}_{i+1} F_i(y_i(1,a_i)) + \mathcal{P}_{i+1} D_i(1)\mathcal{P}_i v_i + \mathcal{P}_{i+1} h_i,$$

or in the vector form
(11)

$$\begin{bmatrix} v^1_{i+1} \\ \vdots \\ v^{n-1}_{i+1} \\ 0 \end{bmatrix} = \tau_i \begin{bmatrix} g^1_i \\ \vdots \\ g^{n-1}_i \\ g^n_i \end{bmatrix} + \begin{bmatrix} H^i_{11} & \dots\, H^i_{1n} \\ \multicolumn{2}{c}{\dots\dots\dots\dots\dots} \\ H^i_{n-1,1} & \dots\, H^i_{n-1,n} \\ H^i_{n,1} & \dots\, H^i_{n,n} \end{bmatrix} \begin{bmatrix} v^1_i \\ \vdots \\ v^{n-1}_i \\ 0 \end{bmatrix} + \begin{bmatrix} \varphi^1_i \\ \vdots \\ \varphi^{n-1}_i \\ \varphi^n_i \end{bmatrix},$$

where

$$g_i = \mathcal{P}_{i+1} F_i(y_i(1,a_i)), \qquad \varphi_i = \mathcal{P}_{i+1}(y_i(1,a_i) - a_{i+1}), \\ H_i = \mathcal{P}_{i+1} D_i(1) \mathcal{P}_i, \qquad i = 1,\dots,N.$$

Let us express the value τ_i for $i = 1, \dots, N$ from the last equation of the system (11)

$$\tau_i = -\frac{H^i_{n1}}{g^n_i} v^1_i - \dots - \frac{H^i_{n,n-1}}{g^n_i} v^{n-1}_i - \frac{\varphi^n_i}{g^n_i}.$$

Then the system (11) can be written as a matrix equation

$$\begin{bmatrix} -A_1 & I & 0 & \dots & 0 & 0 \\ 0 & -A_2 & I & \dots & 0 & 0 \\ 0 & 0 & -A_3 & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & \dots & -A_{N-1} & I \\ I & 0 & 0 & \dots & 0 & -A_N \end{bmatrix} \begin{bmatrix} \bar{v}_1 \\ \bar{v}_2 \\ \bar{v}_3 \\ \vdots \\ \bar{v}_{N-1} \\ \bar{v}_N \end{bmatrix} = \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \vdots \\ \psi_{N-1} \\ \psi_N \end{bmatrix}, \tag{12}$$

where

$$A_i = \begin{bmatrix} H^i_{11} - \frac{H^i_{n,1}}{g^n_i} g^1_i & \dots & H^i_{1,n-1} - \frac{H^i_{n,n-1}}{g^n_i} g^{n-1}_i \\ \dots & \dots & \dots \\ H^i_{n-1,1} - \frac{H^i_{n,1}}{g^n_i} g^1_i & \dots & H^i_{n-1,n-1} - \frac{H^i_{n,n-1}}{g^n_i} g^{n-1}_i \end{bmatrix},$$

$$\bar{v}_i = \begin{bmatrix} v^1_i \\ \vdots \\ v^{n-1}_i \end{bmatrix}, \qquad \psi_i = \begin{bmatrix} \varphi^1_i - \frac{\varphi^n_i}{g^n_i} g^1_i \\ \vdots \\ \varphi^{n-1}_i - \frac{\varphi^n_i}{g^n_i} g^{n-1}_i \end{bmatrix}.$$

Examining (12) we see that it is now apparent that the nonlinear problem (6) where

$$v_i = \begin{bmatrix} \bar{v}_i \\ 0 \end{bmatrix}, \qquad i = 1, \dots, N,$$

proceeds by solving a sequence of linear problems (12). Recalling that $u = \mathcal{P} v$ we can generate a sequence of iterates

$$\tilde{a}_i = a_i + u_i, \quad \tilde{t}_{i+1} = t_{i+1} + \tau_i (t_{i+1} - t_i), \quad i = 1, \dots, N.$$

5. Factorization Method

Consider a system of linear equations

$$u_{i+1} = \mathcal{A}_i u_i + \mathcal{F}_i, \qquad i = 1, \dots, N, \tag{13}$$
$$u_1 = \mathcal{A}_N u_N + \mathcal{F}_N,$$

according to N unknown n-dimensional vectors $u_1, \dots, u_N$. It is possible to write the system in a more convenient form

$$\mathcal{A}u = \mathcal{F}, \tag{14}$$

where

$$u = (u_1, \dots, u_N)^T, \qquad \mathcal{F} = (\mathcal{F}_1, \dots, \mathcal{F}_N)^T,$$

$$\mathcal{A} = \begin{bmatrix} -\mathcal{A}_1 & I & 0 & 0 \dots & 0 & 0 \\ 0 & -\mathcal{A}_2 & I & 0 \dots & 0 & 0 \\ 0 & 0 & -\mathcal{A}_3 & I \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & 0 \dots & -\mathcal{A}_{N-1} & I \\ I & 0 & 0 & 0 \dots & 0 & -\mathcal{A}_N \end{bmatrix}.$$

The elements of matrix $\mathcal{A}$ are equal to zero except the elements from the main diagonal and the blocks lying nearest to them from the right and the element from the lower left corner.

To solve the equation (14) we can use a rather effective factorization technique. Assume the matrixes $\mathcal{A}_1, \dots, \mathcal{A}_N$ are nonsingular. Consider a vector of $2n$-components

$$\begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = \begin{bmatrix} u_1 \\ \mathcal{A}_1 u_1 + \mathcal{F}_1 \end{bmatrix} = \begin{bmatrix} I & 0 \\ \mathcal{A}_1 & \mathcal{F}_1 \end{bmatrix} \begin{bmatrix} u_1 \\ 1 \end{bmatrix}. \tag{15}$$

Then we perform a decomposition of the matrix placed in the right hand side of (15) in the form

$$\begin{bmatrix} I & 0 \\ \mathcal{A}_1 & \mathcal{F}_1 \end{bmatrix} = \begin{bmatrix} \mathcal{P}_1 & \varphi_1 \\ \mathcal{Q}_1 & \psi_1 \end{bmatrix} \begin{bmatrix} \mathcal{R}_1 & \tau_1 \\ 0 & 1 \end{bmatrix}, \tag{16}$$

where

$$\mathcal{P}_1^\star \mathcal{P}_1 + \mathcal{Q}_1^\star \mathcal{Q}_1 = I, \qquad \mathcal{Q}_1 \tau_1 + \psi_1 = \mathcal{F}_1, \qquad \mathcal{P}_1 \tau_1 + \varphi_1 = 0, \tag{17}$$

and $\mathcal{R}_1$ is an upper triangular matrix. The first relation in (17) means that the columns of the composite matrix with the elements $\mathcal{P}_1$ and $\mathcal{Q}_1$ are orthonormal. Then from (15) and (16) we obtain the presentation of the composite vector

$$\begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = \begin{bmatrix} \mathcal{P}_1 & \varphi_1 \\ \mathcal{Q}_1 & \psi_1 \end{bmatrix} \begin{bmatrix} T_1 \\ 1 \end{bmatrix},$$

where

$$T_1 = \mathcal{R}_1 u_1 + \tau_1.$$

Let the presentation

$$\begin{bmatrix} u_1 \\ u_j \end{bmatrix} = \begin{bmatrix} \mathcal{P}_{j-1} & \varphi_{j-1} \\ \mathcal{Q}_{j-1} & \psi_{j-1} \end{bmatrix} \begin{bmatrix} T_{j-1} \\ 1 \end{bmatrix}. \tag{18}$$

of a composite vector $(u_1, u_j)^T$ to be valid for a certain j where $2 \le j \le N-1$. Let us consider the vector $(u_1, u_{j+1})^T$. Using the equalities (13) and (18) we can obtain the following formula

$$\begin{bmatrix} u_1 \\ u_{j+1} \end{bmatrix} = \begin{bmatrix} u_1 \\ \mathcal{A}_j u_j + \mathcal{F}_j \end{bmatrix} = \begin{bmatrix} \mathcal{P}_{j-1} T_{j-1} + \varphi_{j-1} \\ \mathcal{A}_j(\mathcal{Q}_{j-1} T_{j-1} + \psi_{j-1}) + \mathcal{F}_j \end{bmatrix} = \tag{19}$$

$$= \begin{bmatrix} \mathcal{P}_{j-1} & \varphi_{j-1} \\ \mathcal{A}_j \mathcal{Q}_{j-1} & \mathcal{A}_j \psi_{j-1} + \mathcal{F}_j \end{bmatrix} \begin{bmatrix} T_{j-1} \\ 1 \end{bmatrix}.$$

Now we perform a decomposition of the matrix from the right hand side of the equation (19) as follows

$$\begin{bmatrix} \mathcal{P}_{j-1} & \varphi_{j-1} \\ \mathcal{A}_j \mathcal{Q}_{j-1} & \mathcal{A}_j \psi_{j-1} + \mathcal{F}_j \end{bmatrix} = \begin{bmatrix} \mathcal{P}_j & \varphi_j \\ \mathcal{Q}_j & \psi_j \end{bmatrix} \begin{bmatrix} \mathcal{R}_j & \tau_j \\ 0 & 1 \end{bmatrix}, \tag{20}$$

where

$$\mathcal{P}_j^\star \mathcal{P}_j + \mathcal{Q}_j^\star \mathcal{Q}_j = I, \quad \mathcal{Q}_j \tau_j + \psi_j = \mathcal{A}_j \psi_{j-1} + \mathcal{F}_j, \quad \mathcal{P}_j \tau_j + \varphi_j = \varphi_{j-1},$$

and R_j is an upper triangular matrix. From relations (19) and (20) we have

$$\begin{bmatrix} u_1 \\ u_{j+1} \end{bmatrix} = \begin{bmatrix} \mathcal{P}_j & \varphi_j \\ \mathcal{Q}_j & \psi_j \end{bmatrix} \begin{bmatrix} T_j \\ 1 \end{bmatrix}$$

where

$$T_j = R_j T_{j-1} + \tau_j.$$

So by means of mathematical induction we have proved the validity such a formula for $j = 1, 2, \ldots, N$.

Since

$$\begin{bmatrix} u_1 \\ \mathcal{A}_N u_N + \mathcal{F}_N \end{bmatrix} = \begin{bmatrix} \mathcal{P}_N & \varphi_N \\ \mathcal{Q}_N & \psi_N \end{bmatrix} \begin{bmatrix} T_N \\ 1 \end{bmatrix},$$

where $T_N = R_N T_{N-1} + \tau_N$, then

$$\mathcal{P}_N T_N + \varphi_N = \mathcal{Q}_N T_N + \psi_N,$$

$$T_N = (\mathcal{P}_N - \mathcal{Q}_N)^{-1}(\psi_N - \varphi_N).$$

6. Dynamics of Catalytic Hydrogen Oxidation

In this section we present some new results concerning complex dynamics in a three-dimensional kinetic model of heterogeneous hydrogen oxidation on metallic catalysts [1,2,11–13]:

$$(21)\qquad \begin{cases} \dot{x} = k_1(1-x-y)^2 - k_{-1}x^2 - 2k_3(y)\cdot x^2 y, \\ \dot{y} = k_2(1-x-y)^2 - k_{-2}y^2 - k_4(y,z)\cdot y - k_3(y)\cdot x^2 y, \\ \dot{z} = \varepsilon\left[y(1-z) - \alpha z(1-x-y)\right], \end{cases}$$

where x, y are the catalyst surface coverages by hydrogen and oxygen adsorbed, respectively, so that $x \geq 0$, $y \geq 0$ and $x + y \leq 1$; z is the concentration of oxygen dissolved into the subsurface layer, $0 \leq z \leq 1$; $k_{\pm 1}$, $k_{\pm 2}$, k_3, k_4, and $k_{\pm 5}$ are the rate constants of the reaction mechanism steps, $\alpha = k_{-5}/k_5$, $\varepsilon = k_5$, and

$$k_3(y) = k_{30}\ exp(-\mu_3 y), \qquad k_4(y,z) = k_{40}\ exp(-\mu_4 y - \mu_5 z)$$

due to the assumption that the activation energies of the reaction rates depend upon the oxygen concentrations y and z. Note that ε is a small parameter because the dissolution into the subsurface layer is a relatively slow process as compared to the chemical reaction or adsorption onto the catalyst surface.

Periodic orbits. Let γ be a periodic orbit of the system (21). We first take local cross-sections π_i of dimension 2. Each hyperplane π_i must be chosen so that the flow is everywhere transverse to it. Denote the (unique) point where γ intersects π_i by $'i'$. We illustrate in Fig. 1 the behavior of the stable periodic solution γ by numerical simulation.

Fig. 2 illustrates the sensitive dependence of the condition number of the matrix $\mathcal{A}$ on variations in the number of partition points along the periodic orbit γ. This parametric sensitivity leads to an interesting conclusion, already hinted at in the sensitive dependence on initial conditions, which appears in the three-variable system (21) with fast, intermediate and slow variables due to existence of canard cycles which occur in the one-parameter family of two-variable subsystems for x and y. Such sort of orbits can exhibit an unusual degree of instability. For more information see the paper [13].

We let parameters k_1 and k_{40} vary while fix the other parameters $k_{-1} = 0.008$, $k_2 = 20$, $k_{-2} = 0$, $k_{30} = 100$, $\mu_3 = 30$, $\mu_4 = 12$, $\mu_5 = -10$, $\alpha = 7.88$, and $\varepsilon = 0.0024$. Physically it means that the hydrogen partial pressure in the gas mixture over the catalyst surface is varied. Note that k_1 and k_{40} depend linearly upon it.

Now we give an example to illustrate that an unstable limit cycle exists (see Fig. 3). We take three local cross sections π_1, π_2

and π_3 passing through the points $a_1 = (0.28899502, 0.64086281, 0.51238075)$, $a_2 = (0.33714826, 0.57187779, 0.49312216)$ and $a_3 = (0.38548260, 0.52092294, 0.44677296)$. It allows us to decompose the periodic orbit into three pieces with intervals of integration T_i from π_i to π_{i+1} where $T_1 = 395.66180572$, $T_2 = 283.61493869$ and $T_3 = 598.30280382$. Thus, the period equals 1277.57954823. We remark that in this example the multipliers of the unstable closed orbit are $(1.8133, 0, 1)$ and hence a two-dimensional stable invariant manifold exists. The local dynamical behavior "transverse" to this manifold is relatively simple, since it is controlled by the exponentially contracting flow in the local stable manifold (see Fig. 4). Solutions in the stable manifold are expanding.

Weakly stable dynamics. Numerical integration of the system (21) appears to yield trajectories that are not asymptotically periodic. In fact, in some cases we observe weakly stable dynamics followed by asymptotically periodic motions (see Fig. 5–8). Following [14,16] we refer to the local expansion and consequent "independent" behavior of orbits starting arbitrary close together as sensitive dependence on initial conditions or weakly stable dynamics.

Since such "simple" differential equations of dimension three play an important role in the kinetic modelling of heterogeneous catalytic reactions [12] and can posses solutions of stunning complexity, an understanding of typical structures of their solutions is essential.

Period Doubling Sequence. We consider the role of successive period doubling bifurcations in the creation of weakly stable dynamics in Fig. 5. Following [15], we make first one remark about relationship of the Poincare return map with eigenvalue -1 at a fixed point, to the continuous flow around the corresponding periodic orbit. The trajectories of the Poincare map alternate from one side of the fixed point to the other along the direction of the eigenvector to -1. It means that the two-dimensional center manifold for the periodic orbit of the three-variable system is twisted around the periodic orbit like a Mobius band around its center line.

We have found numerically a sequence of flip bifurcations in the system (21). In Fig. 9–11 we show periodic orbits for several values of k_1 and k_{40}. Using the techniques of previous paragraphs we show that for a value k_1' where $0.146 < k_1' < 0.147045$ the periodic orbit of period T has bifurcated to an orbit of period $2T$ and then for k_1'' where $0.145 < k_1'' < 0.146$ the periodic orbit of period $2T$ has bifurcated to an orbit of period $4T$. In such a way, an infinite number of families of periodic orbits can be created in flip bifurcations as k_1 decrease. Thus, a stable orbit with period longer then any preassigned period can be found if we let k_1 vary in the interval $0.144 \leq k_1 < 0.145$. Such orbits are indistinguishable in the numerical integration from bounded non-periodic motions.

We suggest that for $k_1 = 0.144$ such orbits may constitute the attractor observed in a long-term numerical integration (see Fig. 5).

7. Conclusion

In the paper an original iterative algorithm proved to be efficient and accurate for calculations of periodic orbits and their stability in a three-dimensional kinetic model of catalytic hydrogen oxidation.

Our analysis of this model demonstrates that for some parameters there exists an attractor with sensitive dependence on initial conditions. To get a clearer idea of the structure of the attracting set we find successive period doubling bifurcations in which the flow becomes progressively more complex until the attractor appears.

We believe that the results obtained are of importance for understanding the reasons of weakly stable dynamics in different heterogeneous catalytic systems.

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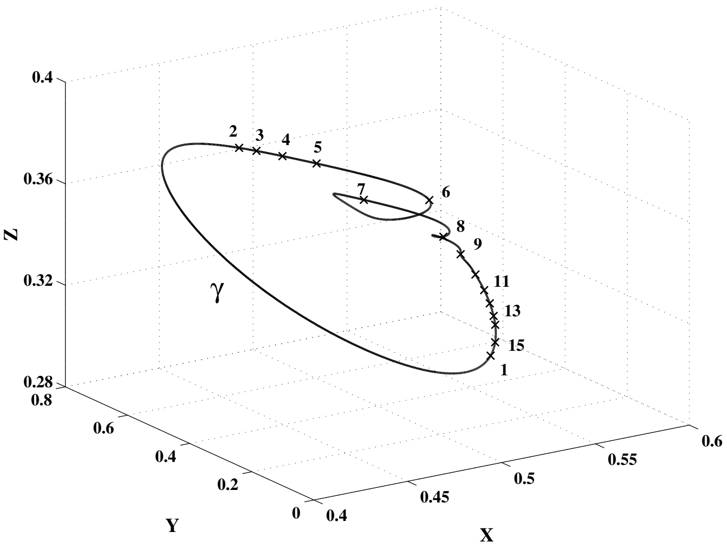

Fig. 1. Periodic orbit of the system (21) for parameters: $k_1 = 0.2$, $k_{-1} = 0.008$, $k_2 = 15$, $k_{-2} = 0$, $k_{30} = 100$, $k_{40} = 2$, $\mu_3 = 30$, $\mu_4 = 12$, $\mu_5 = -10$, $\alpha = 7.88$, $\varepsilon = 0.0029$. Points where γ intersects cross-sections π_i $(i = 1, \dots, 15)$ are shown as '$\times$'.

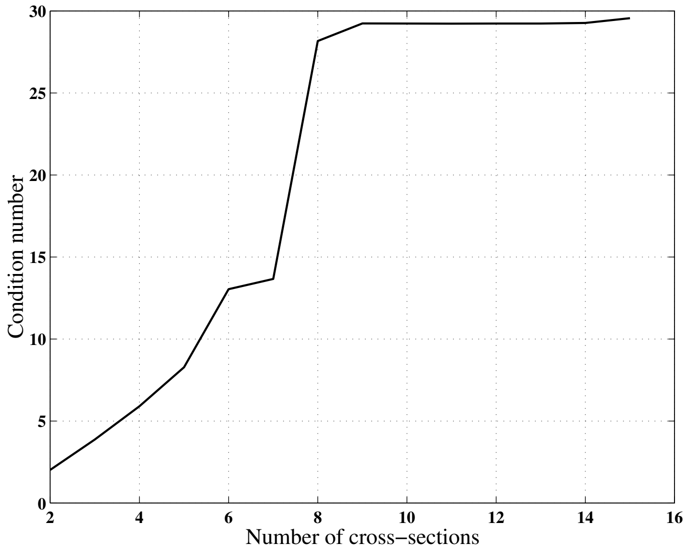

Fig. 2. Dependence of the condition number of the matrix $\mathcal{A}$ on the partition number.

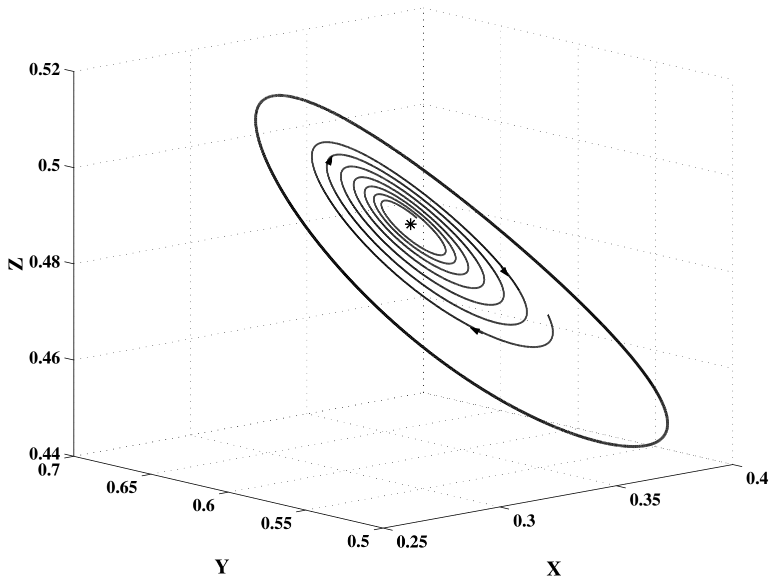

Fig. 3. Unstable limit cycle with a trajectory inside it of the system (21) for $k_1 = 0.135824260$, $k_{40} = 2$. The stable steady state is (0.3252466,0.5958083,0.4892114) with eigenvalues -1.9004268 and $-1.9769 \cdot 10^{-4} \pm i \cdot 5.05856 \cdot 10^{-3}$.

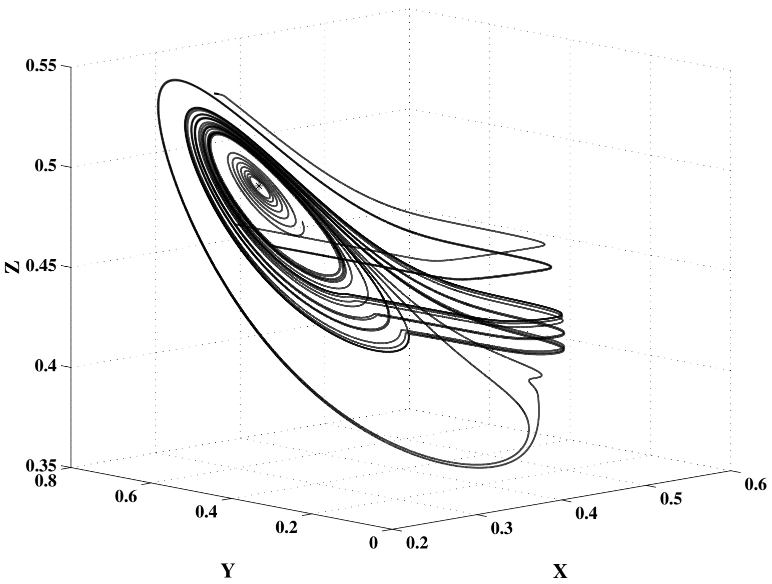

Fig. 4. Unstable limit cycle with two trajectories around it of the system (21). Parameters are the same as in Fig. 3.

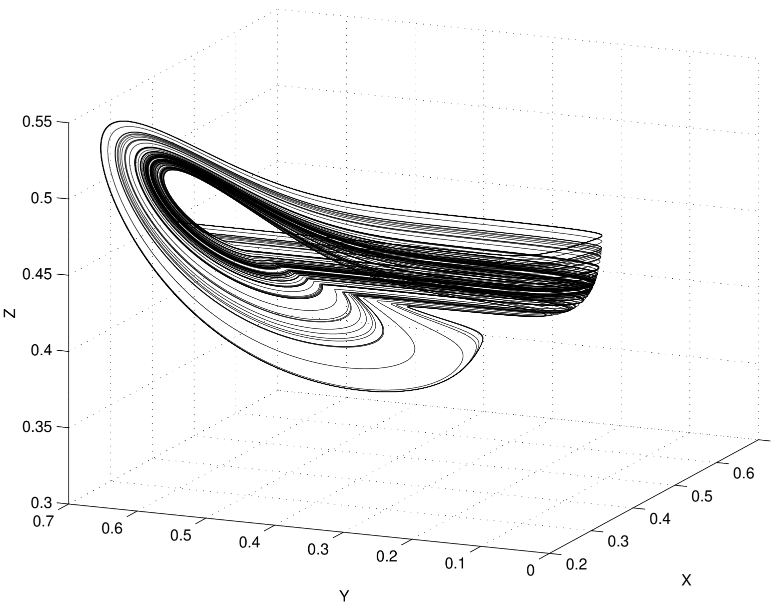

Fig. 5. Weakly stable dynamics. Numerical solution of the system (21) for $k_1 = 0.144$, $k_{40} = 1.92$. The initial condition is chosen arbitrary close to the attractor.

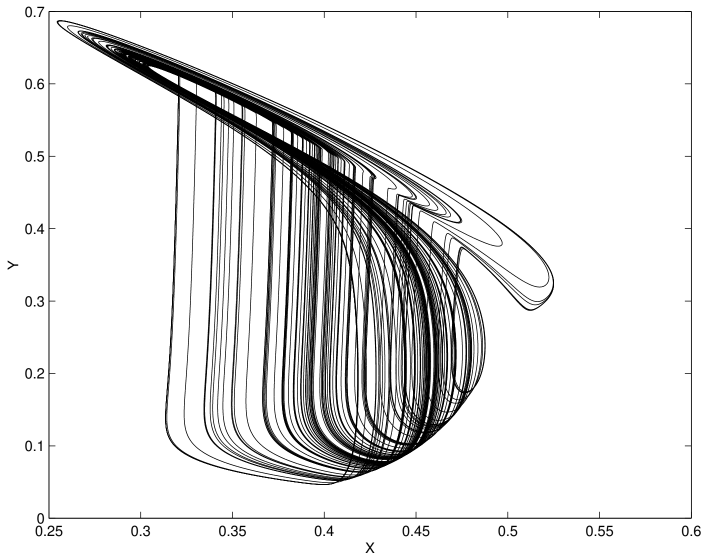

Fig. 6. Weakly stable dynamics: (x, y)-projection of the numerical solution of the system (21) for $k_1 = 0.144$, $k_{40} = 1.92$ which is shown in Fig. 5.

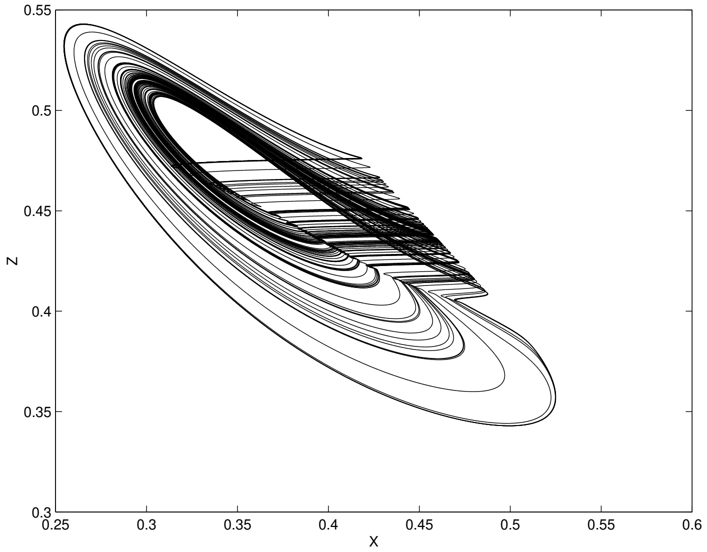

Fig. 7. Weakly stable dynamics: (x, z)-projection of the numerical solution of the system (21) for $k_1 = 0.144$, $k_{40} = 1.92$ which is shown in Fig. 5.

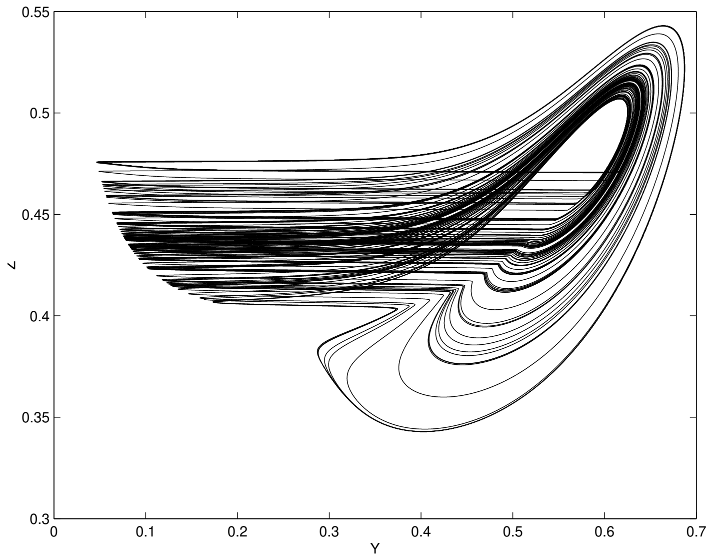

Fig. 8. Weakly stable dynamics: (y, z)-projection of the numerical solution of the system (21) for $k_1 = 0.144$, $k_{40} = 1.92$ which is shown in Fig. 5.

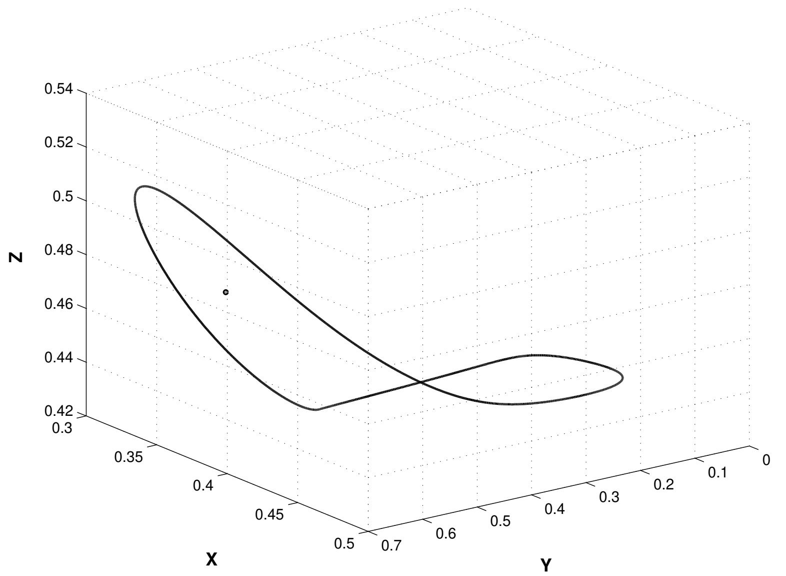

Fig. 9. T-periodic solution of the system (21) for $k_1 = 0.147045$, $k_{40} = 1.9606$. The unstable steady state is (0.3487194,0.5699204,0.4706045) with the eigenvalues -1.931873 and $7.17146 \cdot 10^{-4} \pm i \cdot 5.14812 \cdot 10^{-3}$. Period equals 970.4344.

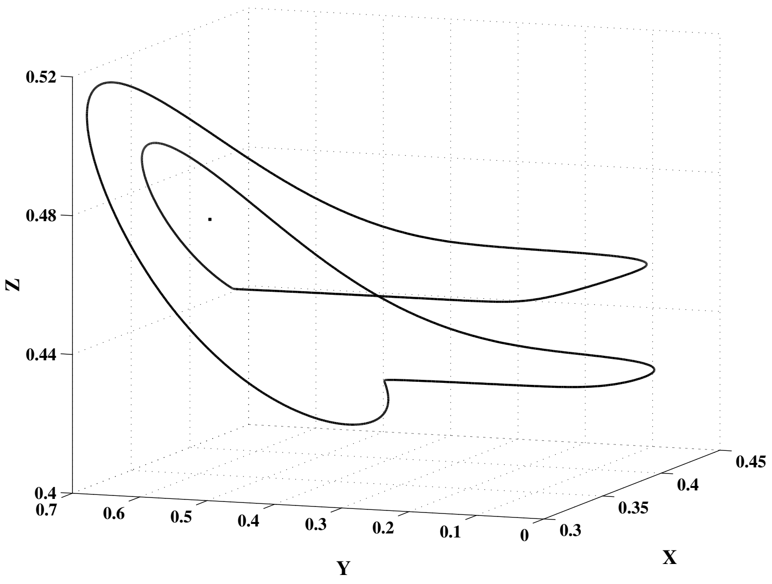

Fig. 10. $2T$-periodic solution of the system (21) for $k_1 = 0.1460$, $k_{40} = 1.94666$. Period equals 1931.1277.

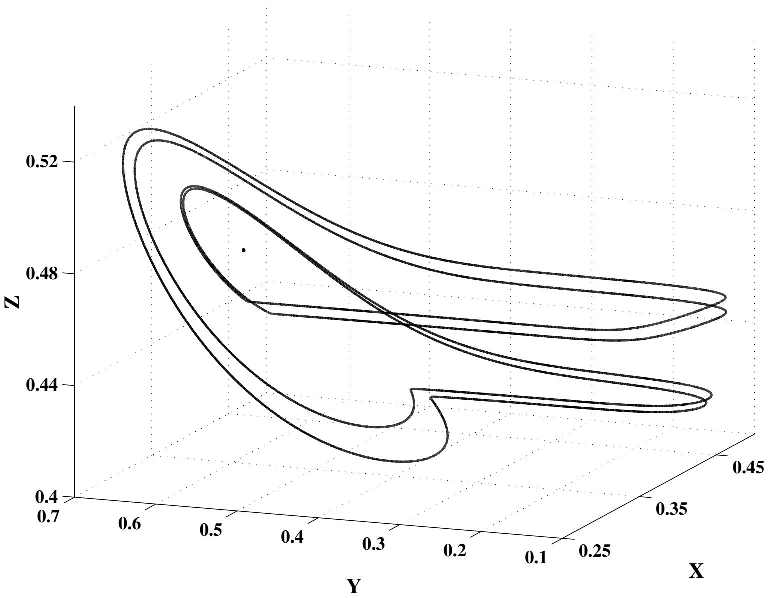

Fig. 11. $4T$-periodic solution of the system (21) for $k_1 = 0.1450$, $k_{40} = 1.9334$. Period equals 3949.9572.