Unrestricted Harmonic Balance

A General Method to Evaluate Periodic Structures in Time and/or Space of Arbitrary Stability for Non-linear Chemical Reaction and Reaction-Diffusion Systems.

I. Theory and Computer Program for Time-dependent Systems

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Periodic structures in chemical kinetic systems can be evaluated by an extension of the well-known method of harmonic balance, which yields very simple expressions in the case of linear systems containing only zero and first order reactions. The far more interesting non-linear systems containing e.g. second order reactions which in case of open systems far from thermodynamic equilibrium give rise to non-classical phenomena like oscillations, chemical waves, excitability, hysteresis, multistability, dissipative structures etc. can be treated in a similar way by introducing new pseudo-linear quantities utilizing certain group properties of harmonic expansions. The resulting complicated implicit non-linear algebraic equations are solved by a method developed by Powell and show good convergence. Since this method — in contrast to the conventional method of simulation — is independent from the stability of the periodic structure to be evaluated it can even be applied to unstable cases where the simulation method necessarily fails. An evaluation of the stability is included in the developed computer program.

1. Introduction

Models of realistic chemical reaction systems have to take account of some facts of elementary reactions as e.g. that there are only first and second order reaction steps, higher orders being extremely unprobable from a statistical point of view and being only the result of comprising several elementary steps into one. If some precursors of a substance are well buffered they form pools of constant concentrations each giving rise to zero order terms. Thus there are virtually only three types of terms in rate equations: a) Constant influxes (zero order), b) monomolecular or pseudolinear reactions (first order) and c) bimolecular reactions (second order) which are the only direct non-linear terms entering the rate equations.

As is well known since some decades (e.g. Prigogine and Glansdorff [1]) and is attracting increasing interest from different fields, non-classical features like oscillations, multistability, excitability, dissipative structures, monoflop- and flip-flop-behaviour,

chemical waves, hysteresis etc. are possible if the system is open, sufficiently far from thermodynamic equilibrium and non-linear. Recently, since the appearance of the Lorenz model [2], the so-called chaos or chemical turbulence has increased the list of these phenomena.

Systems of the described behaviour can be formulated as state vectors $\boldsymbol{x}(\boldsymbol{r}, t) \in \mathbb{R}_+{}^n$, where $\boldsymbol{r}$ is the 3-dimensional space and t is time, n is the number of independent reactants, each component of $\boldsymbol{x}$ is a concentration. Actually $\boldsymbol{x}$ depends on a vector of parameters $\boldsymbol{p} \in \mathbb{R}_+{}^m$ like rate constants, concentrations of catalysts, diffusion constants, constant influxes etc.

Purely time-dependent phenomena in autonomous systems are described by ordinary differential equations (including initial conditions)

$$\mathrm{d}x_i/\mathrm{d}t = f_i(\boldsymbol{x}), \quad i = 1, \ldots, n, \qquad (1)$$

the f_i's being non-linear functions established on the basis of the law of mass action.

Space- and time-dependent phenomena are most often found in reaction diffusion systems

$$\partial x_i/\partial t = D_i \nabla^2 x_i + f_i(\boldsymbol{x}), \quad i = 1, \ldots, n, \qquad (2)$$

where D_i is the diffusion constant, ∇ is the dif-

ferential operator $(\partial/\partial x, \partial/\partial y, \partial/\partial z)$ and the description of the system is supplemented by appropriate boundary conditions. In some cases the right-hand side of (2) has to be expanded by a convection term $-\nabla x_i \cdot \boldsymbol{v}_i$, where $\boldsymbol{v}_i$ is the velocity vector of compound i.

Considering spatially homogeneous systems (1) which do not depend on the space coordinates, $\boldsymbol{x}(t)$ is a trajectory for a given initial condition. There are singular or critical points, $\boldsymbol{x}_{\mathrm{cr}}$, for which $d\boldsymbol{x}/dt = 0$, which can be found by solving the non-linear algebraic system

$$f(\boldsymbol{x}_{\mathrm{cr}}) = 0, \tag{3}$$

and whose stability properties are defined by the eigenvalues of the Jacobian matrix $(\partial f/\partial \boldsymbol{x})_{\boldsymbol{x} = \boldsymbol{x}_{\mathrm{cr}}}$. But there are in many cases other limit sets known as limit cycles which can be found by numerical simulation techniques *if they are orbitally stable*. If this condition is not met it is normally impossible to get these unstable limit cycles by simulation. Since all the rest of the trajectories describes only transient behaviours of the system, it appears to be worthwhile to search for similar algebraic techniques like those for the evaluation of critical points. Authors like Willems [3] state that "... there is no general method for finding periodic solutions of non-linear autonomous systems." Actually there does exist a method introduced by Krylov and Bogoljubov for at least systems with weak non-linearities and this idea can be extended to general systems whose non-linearity comes only from terms like $k_{ij} x_i{}^k x_j{}^l$ $(k, l = 1, 2, \ldots)$: this method is known as the method of "harmonic balance" [4], is most often restricted to only the first harmonic, is applied to technical control systems, but was apparently never used in the treatment of chemical and related (biological, ecological) systems.

2. Group Properties of the State Variables in the Case of Periodic solutions for Mass-action Systems

The state vector $\boldsymbol{x}(t)$ is periodic, if there exists a constant time T called period for which $\boldsymbol{x}(t+T) = \boldsymbol{x}(t)$. The inverse of T, $\nu = 1/T$, can be called the fundamental frequency, $\omega = 2\pi\nu$ the fundamental radian frequency. It is possible then to expand $\boldsymbol{x}(t)$ in harmonics of ω:

$$x_i(t) = \bar{x}_i + \sum_{j=1}^{\infty} x_{cij} \cos(j\omega t)$$
$$+ \sum_{j=1}^{\infty} x_{sij} \sin(j\omega t) \tag{4}$$

or alternatively

$$x_i(t) = \bar{x}_i + \sum_{j=1}^{\infty} A_{ij} \sin(j\omega t + \delta_{ij}), \tag{5}$$

where

$$x_{cij} = A_{ij} \sin \delta_{ij}, \quad A_{ij} = \sqrt{x_{cij}^2 + x_{sij}^2},$$
$$x_{sij} = A_{ij} \cos \delta_{ij}, \quad \delta_{ij} = \arccos(x_{sij}/A_{ij})$$
$$\cdot \operatorname{sign}(x_{cij}) \tag{6}$$

ω, $\{\bar{x}_i\}$, $\{x_{cij}\}$ and $\{x_{sij}\}$ are the quantities to be determined.

In the following we shall prefer the more symmetric expansion (4) which does not need transcendental functions furtheron, but at computing explicitly $x_i(t)$ for given constants, (5) will need only half the number of computations of sine or cosine functions and will be the formulation of choice in that case. If a second component x_k is given in a similar way, the product $x_i x_k$ can be expressed in quite the same way showing group properties of the components of $\boldsymbol{x}$ with respect to multiplication. In the numerical treatment every expansion has to be truncated, say at the highest harmonic N.

So if to avoid an unnecessary accumulation of indices we rewrite

$$x_i(t) \equiv y(t) = \bar{y} + \sum_{j=1}^{N} y_{cj} \cos(j\omega t)$$
$$+ \sum_{j=1}^{N} y_{sj} \sin(j\omega t) \tag{7}$$

and

$$x_k(t) \equiv z(t) = \bar{z} + \sum_{j=1}^{N} z_{cj} \cos j\omega t$$
$$+ \sum_{j=1}^{N} z_{sj} \sin(j\omega t) \tag{8}$$

the product is of the same form, namely

$$y(t) z(t) \equiv p(t) = \bar{p} + \sum_{j=1}^{N} p_{cj} \cos(j\omega t)$$
$$+ \sum_{j=1}^{N} p_{sj} \sin(j\omega t) \tag{9}$$

with

$$\bar{p} = \bar{y} \cdot \bar{z} + \frac{1}{2} \sum_{j=1}^{N} (y_{cj} z_{cj} + y_{sj} z_{sj}), \tag{10}$$

$$p_{cj} = \bar{y} \cdot z_{cj} + \bar{z} \cdot y_{cj} + \underbrace{\tfrac{1}{2}(y_{c,j/2} \cdot z_{c,j/2} - y_{s,j/2} \cdot z_{s,j/2})}_{\text{for } j \text{ even}}$$

$$+ \underbrace{\tfrac{1}{2} \sum_{k=1}^{N-j} (y_{c,j+k} \cdot z_{ck} + y_{ck} \cdot z_{c,j+k} + y_{s,j+k} \cdot z_{sk} + y_{sk} \cdot z_{s,j+k})}_{\text{for } j \le N-1}$$

$$+ \underbrace{\tfrac{1}{2} \sum_{k=1}^{k_{\max}} (y_{c,j-k} \cdot z_{ck} + y_{ck} \cdot z_{c,j-k} - y_{s,j-k} \cdot z_{sk} - y_{sk} \cdot z_{s,j-k})}_{\text{for } j \ge 3}, \tag{11}$$

$$p_{sj} = \bar{y} \cdot z_{sj} + \bar{z} \cdot y_{sj} + \underbrace{\tfrac{1}{2}(y_{s,j/2} \cdot z_{c,j/2} + y_{c,j/2} \cdot z_{s,j/2})}_{\text{for } j \text{ even}}$$

$$+ \underbrace{\tfrac{1}{2} \sum_{k=1}^{N-j} (y_{s,j+k} \cdot z_{ck} - y_{sk} \cdot z_{c,j+k} - y_{c,j+k} \cdot z_{sk} + y_{ck} \cdot z_{s,j+k})}_{\text{for } j \le N-1}$$

$$+ \underbrace{\tfrac{1}{2} \sum_{k=1}^{k_{\max}} (y_{s,j-k} \cdot z_{ck} + y_{sk} \cdot z_{c,j-k} + y_{c,j-k} \cdot z_{sk} + y_{ck} \cdot z_{s,j-k})}_{\text{for } j \ge 3}, \tag{12}$$

$$k_{\max} = \text{INT}\left(\frac{j+1}{2}\right) - 1. \tag{13}$$

These results are gained from the well-known formulas

$$2 \sin(nx) \sin(mx) = \cos((n-m)x)$$
$$- \cos((n+m)x),$$
$$2 \cos(nx) \cos(mx) = \cos((n-m)x)$$
$$+ \cos((n+m)x),$$
$$2 \sin(nx) \cos(mx) = \sin((n-m)x)$$
$$+ \sin((n+m)x).$$

Higher products of the components of x can be formulated in the same way by repeated application of the transformations (7) through (13). Thus pseudo-linear expressions are gained for the new quantities p which in reality are non-linear in the coefficients of the components x_i of x. By gathering all terms containing neither cosine- nor sine-functions, and separately all terms containing the same $\cos(j\omega t)$ or $\sin(j\omega t)$ and setting all of them equal to zero we end up with $2N+1$ non-linear equations for each differential equation. Since each component of x contains one constant $\bar{x}_i$ and N coefficients for the sine- and cosine-functions each, there is a balance of equations and variables. The radian frequency ω

which has to be determined, too, does not need an additional equation for the following reason: (4) applied to all x_i would yield a redundancy caused by the arbitrariness of the time zero; setting one coefficient, say x_{c11}, equal to zero (equivalent to setting the phase shift of the first harmonic j, δ_{1j}, equal to 0) fixes the time zero, and effectively removes one variable for the system of non-linear algebraic equations; this place can be taken by ω.

Normally the number of implicit equations = number of variables is much less than $n(2N+1)$, because a) in most cases there exist linear combinations of the original differential equations that are purely linear and allow the expression of the coefficients of one component x_i by those of the others and b) very often other combinations are non-linear as a total, but one x_i enters only linearly so that explicit rather than implicit non-linear equations can be formulated for the latter. In special cases existing symmetries of the variables roughly half the number of equations, because only even or odd, respectively, coefficients enter. Representative examples for the different cases will be given in the

subsequent sections. The solution of the remaining implicit non-linear equations is quite straightforward and can be tackled by a number of different methods of numerical mathematics. Since the degree of nesting of true and intermediate (e.g. p of (9)) variables can be high, it is favourable to have methods at hand which only need the implicit functions, but no analytical expressions for derivatives. A method that fulfills these requirements and shows convenient convergence and stability properties is the method developed by Powell [5], which was used in all examples. The transformations (7) through (13) were written in a subroutine. No investigation of the influence of the truncation error was done so far; in some cases this question was treated empirically by using different N's.

3. Computer Program for Ordinary Differential Equations in Time, Including Evaluation of the Stability

According to the considerations outlined in the preceding section a computer program written in FORTRAN was developed. Since the stability and convergence of the Powell method of the solution of implicit nonlinear algebraic equations has nothing to do with the dynamical stability of the system itself, it can be expected and is just one advantage of this method that dynamically unstable periodic solutions are gained, too. In this case it is of great importance to know, if the found solution corresponds to a limit cycle amenable to simulation, i.e. to a *asymptotically orbitally stable solution*, so that a stability analysis had to be included.

The task of investigating the stability of a periodic solution which is a closed *curve* in $\mathbb{R}_+^n$ is more complicated than to test the stability of a critical *point*, but has certain similarities with it. Several existing theorems on the stability of periodic solutions were tried to develop an algorithm for computer application, but only one technique seemed to work. The following definitions, terms and theorems were adopted from Willems [3].

We assume that we have gained a periodic solution $p(t)$ of the nonlinear autonomous system $\dot{x} = f(x)$ by the method of harmonic balance and want to investigate its stability. The starting point of our consideration is the equation of the *first variation* about the motion $p(t)$ defined by

$$\dot{x} = A(t) x \tag{14}$$

with $A(t)$ being the time-dependent Jacobi matrix

$$A(t) = (\partial f / \partial x)_{x = p(t)}. \tag{15}$$

Since $p(t)$ is a solution of $\dot{x} = f(x)$, $\dot{p} = f(p)$ and by differentiation

$$\ddot{p} = (\partial f / \partial x)_{x = p} (dx/dt)_{x = p} = A(t) \dot{p}, \tag{16}$$

i.e. $\dot{p}$ is a solution of (14). But since $\dot{p}$ is periodic, too, it cannot vanish with $t \to \infty$, so the null solution of (14) is not asymptotically stable. The matrix $A(t)$ has at least one characteristic multiplier with modulus 1 or in other words, if there is a small perturbation in the direction of the periodic solution (the limit cycle) p itself, this point lies on the limit cycle, too, the deviation from the original point increases and decreases, but after one cycle (period T) it is exactly the same as at the beginning, the limit cycle is indifferent (neither stable nor unstable) against small perturbations in the direction of the tangent on p at any point. Whether the limit cycle is stable or unstable is determined by the stability characteristics of perturbations orthogonal to p. So the orbital asymptotical stability of p is given, if $n-1$ characteristic multipliers of $A(t)$ of (15) have a modulus smaller than 1, or equivalently, if $n-1$ characteristic exponents of $A(t)$ have negative real parts.

These quantities can be gained from the *transition matrix* $\boldsymbol{\Phi}(t, t_0)$, which is the particular fundamental matrix $\mathbf{F}(t, t_0)$ as a solution of the matrix differential equation

$$\dot{\mathbf{F}}(t, t_0) = A(t) \mathbf{F}(t, t_0), \tag{17}$$

whose initial value $\mathbf{F}(t_0, t_0) = \mathbf{I}$, i.e.

$$\boldsymbol{\Phi}(t, t_0) = \mathbf{F}(t, t_0) \mathbf{F}(t_0, t_0)^{-1}. \tag{18}$$

The trajectory $x(t)$ can be interpreted as a transformation of the starting point x_0 by means of the transition matrix

$$x(t; x_0, t_0) = \boldsymbol{\Phi}(t, t_0) x_0. \tag{19}$$

In a linear system with time-invariant A, $\dot{x} = A x$, the solution is

$$x(t) = \exp\{A(t - t_0)\} x_0$$
$$= \mathbf{W} \exp\{\boldsymbol{\Lambda}(t - t_0)\} \mathbf{W}^{-1} x_0,$$

$\boldsymbol{\Lambda}$ being the diagonal matrix of the eigenvalues and $\mathbf{W}$ being the matrix of the eigenvectors of A, so that in that case

$$\boldsymbol{\Phi}(t, t_0) = \exp\{A(t - t_0)\}$$
$$= \mathbf{W} \exp\{\boldsymbol{\Lambda}(t - t_0)\} \mathbf{W}^{-1}.$$

In a general nonlinear system with a periodic solution $p(t)$ and an equation of the first variation about $p(t)$ like (14) the transition matrix can be proved to be of the form

$$\boldsymbol{\Phi}(t, t_0) = \mathbf{P}(t) \exp\{\mathbf{R}(t - t_0)\} \mathbf{P}(t_0)^{-1}, \quad (20)$$

where $\mathbf{P}(t)$ is a non-singular periodic matrix with the same period T as the original system $\dot{\boldsymbol{x}} = \boldsymbol{f}(\boldsymbol{x})$ and $\mathbf{R}$ is a constant matrix. The eigenvalues of $\mathbf{R}$ are called *characteristic exponents* of $\mathbf{A}(t)$, the eigenvalues of

$$\mathbf{C} = e^{\mathbf{R}T} = \boldsymbol{\Phi}(T, 0) \quad (21)$$

are called *characteristic multipliers*; these are the entities which determine the asymptotic orbital stability of the periodic solution as mentioned above. If the periodic solution is known, they can be evaluated by numerical integration over a period T. Practically that means: at the starting point

$$\boldsymbol{x}_0 = \boldsymbol{x}(t_0), \quad \mathbf{A} = (\partial \boldsymbol{f}/\partial \boldsymbol{x})_{\boldsymbol{x} = \boldsymbol{p}}$$

is determined, its eigenvalues and eigenvectors are evaluated, which form the matrices $\boldsymbol{\Lambda}$ and $\mathbf{W}$, respectively,

$$\boldsymbol{\Phi}(t, t_0) = \mathbf{W}(t) \exp\{\boldsymbol{\Lambda}(t - t_0)\} \mathbf{W}(t_0)^{-1}$$

is computed which is for $t = t_0$ simply the unit matrix $\mathbf{I}$. This procedure is repeated for $t = t_0 + \Delta t$, $\boldsymbol{\Phi}(t_0 + \Delta t, t_0)$ is multiplied with $\boldsymbol{\Phi}(t_0, t_0) = \mathbf{I}$, then the same for $t = t_0 + 2\Delta t$ etc. until $t = t_0 + T$. Thus $\mathbf{C} = \boldsymbol{\Phi}(t_0 + T, t_0)$ is gained by repeated multiplication of the differential $\boldsymbol{\Phi}(t + \Delta t, t)$'s over one period.

The program is organized as given in Table 1, the superscripts on the name of the subroutines indicating the level of nesting. To avoid nearby singularities it uses double precision (24 digits) of the 48 bit computer TR 440 and consists of roughly (problem specific!) 1350 lines of FORTRAN. The original output of the Powell routine was altered to give only the sum of squares of residues during the iterations to indicate the progress of convergence.

Table 1. Structure of the FORTRAN-program.

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[1]Main program: input of parameters and starting vector, call of PWLL and ANALYS.

   [2]PWLL: Powell routine for the solution of implicit nonlinear algebraic equations.

      [3]CALFUN: problem specific part defining the implicit functions.

         [4]PROD: product formation according to (7) through (13).

      [3]MINV: inversion of a real matrix.

   [2]ANALYS: evaluation of the state variables as a function of time according to (5) and (6), computation of the local and the global transition matrix, $\boldsymbol{\Phi}(\tau + \Delta t, \tau)$ and $\boldsymbol{\Phi}(t, t_0) = \prod\limits_{\tau = t_0}^{\tau = t - \Delta t} \boldsymbol{\Phi}(\tau + \Delta t, \tau)$, determination of characteristic multipliers and exponents for the stability analysis.

      [3]EWEVRM: determination of the eigenvalues and eigenvectors of a real matrix by the EisPack [6] programs [4]BALANC, [4]ELMHES, [4]ELTRAN, [4]HQR2 and [4]BALBAK.

         [4]CINV: inversion of a complex matrix.

      [3]PLOTLO: plot of the state variables as functions of time or as 2-dimensional cross-sections through the state space.

   [2]SAVE2: storage of all relevant results on a disk file after each 10th iteration of the Powell routine and at the end.

         [4]QUOT: quotient formation as an inverse procedure of algorithm PROD.

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4. Representative Examples of Time-periodic Structures

a) Orbitally Stable Limit Cycle of a Simple System in $\mathbb{R}^2$

A well-known example in chemical system theory is the so-called brusselator of Prigogine and Nicolis [7]. Expressed in dimensionless variables x, y, t and parameters a and b it is reduced to

$$\dot{x} = a - bx - x + x^2 y,$$
$$\dot{y} = x - x^2 y. \quad (22)$$

It has only one critical point at $x_{cr} = a/b$, $y_{cr} = b/a$ which is unstable for $b \leqq 1$ and $a \leqq b\sqrt{1 - b}$ and is no saddle point. Since the system is stable in the large there exists one orbitally stable limit cycle in this case.

We use (4) for x and y each and transform $p \equiv x^2$ and $q \equiv py$ and get one linear and one pseudo-linear equation

$$\dot{x} + \dot{y} - a + bx = 0, \quad (23)$$
$$\dot{y} - x + x^2 y = \dot{y} - x + q = 0. \quad (24)$$

(23) yields directly

$$\bar{x} = \frac{a}{b} = x_{cr}, \quad (25)$$

$$\left.\begin{array}{l} y_{cj} = -x_{cj} + \dfrac{b}{j\omega} x_{sj}, \\[2mm] y_{sj} = -x_{sj} - \dfrac{b}{j\omega} x_{cj}, \end{array}\right\} \quad j = 1, \ldots, N,$$

thus eliminating these unknowns and (24) renders

$$
\left.\begin{array}{l}
j\omega y_{sj} - x_{cj} + q_{cj} = 0, \\
- j\omega y_{cj} - x_{sj} + q_{sj} = 0,
\end{array}\right\} \quad j = 1, \dots, N,
$$
$$
- \bar{x} + \bar{q} = 0, \tag{26}
$$

giving $2N+1$ implicit and via $\bar{q}$, $\{q_{cj}\}$ and $\{q_{sj}\}$ highly non-linear equations of $2N+1$ unknowns $\bar{y}$, ω, $x_{c2}, \dots, x_{cN}$, $x_{s1}, x_{s2}, \dots, x_{sN}$. The time zero is fixed by arbitrarily setting $x_{c1} = 0$. The result (amplitudes of x and y, $\bar{y}$ and ω) for $N = 24$ is given in Table 2. If each residual is called f_i, $F \equiv \sum_{i=1}^{2N+1} f_i^2$ is a measure of the accuracy, the ratio of the amplitudes A_N/A_1 defined by (5), expresses the convergence of harmonics.

b) Closed Trajectories Around a Centre Depending on the Initial Condition

The standard example of ecology is the Lotka-Volterra system [8] which reads in dimensionless quantities

$$
\dot{x} = x - xy, \quad \dot{y} = a(xy - y). \tag{27}
$$

It has a saddle point at $x_{cr1} = 0$, $y_{cr1} = 0$ and a centre at $x_{cr2} = 1$, $y_{cr2} = 1$ with an eigenvalue $\lambda = \pm i\sqrt{a}$, i.e. for small amplitudes oscillations occur with a radian frequency $\omega = \sqrt{a}$. For every initial condition $x(0) = x_0$, $y(0) = y_0$ we get a closed trajectory obeying

$$
a(x - x_0 - \ln(x/x_0)) + y - y_0 - \ln(y/y_0) = 0
$$

or

$$
a(x - \ln x) + y - \ln y = a(x_0 - \ln x_0)
$$
$$
+ y_0 - \ln y_0 = \text{const}. \tag{28}
$$

This relation can be used to test the accuracy of the method. Especially simple is the case $a = 1$, because then on reversing time $t \to -t$ we get $x \to y$ and $y \to x$ which means that the closed trajectories are symmetrical with respect to the line $x = y$.

If the initial conditions are chosen in such a way that the starting point lies on the symmetry axis, we get

$$
x(t) = \bar{x} + \sum_{j=1}^{N} x_{cj} \cos(j\omega t)
$$
$$
+ \sum_{j=1}^{N} x_{sj} \sin(j\omega t),
$$
$$
y(t) = \bar{x} + \sum_{j=1}^{N} x_{cj} \cos(j\omega t)
$$
$$
- \sum_{j=1}^{N} x_{sj} \sin(j\omega t). \tag{29}
$$

But since

$$
\dot{x} + \dot{y} - x + y = 0 \tag{30}
$$

we get

$$
x_{sj} = -j\omega x_{cj} \quad \text{for all} \quad j = 1, \dots, N, \tag{31}
$$

so that ω, $\bar{x}$ and $\{x_{cj}\}$ are the actual unknowns.

Application of (7) through (13) then yields for $p \equiv xy$

$$
\bar{p} = \bar{x}^2 + \tfrac{1}{2} \sum_{j=1}^{N} x_{cj}^2 (1 - j^2 \omega^2), \tag{32}
$$

Table 2. Results of the brusselator with $a = 0.33$, $b = 0.66$.

j	A_{xj}	A_{yj}	
1	0.237218	0.469575	$F = 4.8 * 10^{-22}$
2	0.089709	0.117980	$\bar{y} = 1.906080$
3	0.031907	0.036717	$\omega = 0.386338$
4	0.011062	0.012029	
5	0.003901	0.004123	$\left(\text{cf.: } y_{cr} = b/a = 2,\right.$
6	0.001437	0.001494	
7	0.000551	0.000568	$\omega_{cr} = \sqrt{\dfrac{a^2}{b} - \dfrac{1}{4}\left(1 - b - \dfrac{a^2}{b^2}\right)^2} = 0.403702\Big)$
8	0.000217	0.000222	
9	0.000086	0.000088	
10	0.000034	0.000035	moduli of characteristic multipliers =
.	.	.	0.999998 and 0.189932
.	.	.	real parts of characteristic exponents =
.	.	.	$-1.19787 * 10^{-7}$ and
24	$1.33 * 10^{-10}$	$1.34 * 10^{-10}$	-0.1021364

$$p_{cj} = 2\bar{x}x_{cj} + \underbrace{\tfrac{1}{2}x_{cj/2}^2(1+(j/2)^2\omega^2)}_{\text{for } j \text{ even}}$$

$$+ \underbrace{\sum_{k=1}^{N-j} x_{c,j+k}x_{ck}(1-(j+k)k\omega^2)}_{\text{for } j \leq N-1}$$

$$+ \underbrace{\sum_{k=1}^{\text{INT}\left(\frac{j+1}{2}\right)-1} x_{c,j-k}x_{ck}(1+(j-k)k\omega^2)}_{\text{for } j \geq 3}, \qquad (33)$$

$$p_{sj} = 0 \quad \text{for all} \quad j = 1, \ldots, N. \qquad (34)$$

From

$$\dot{x} - x + xy = \dot{x} - x + p = 0 \qquad (35)$$

we get from the terms containing neither $\cos(j\omega t)$ nor $\sin(j\omega t)$

$$\bar{x}^2 - \bar{x} + \tfrac{1}{2}\sum_{j=1}^{N} x_{cj}^2(1-j^2\omega^2) = 0 \qquad (36)$$

from those terms containing $\cos(j\omega t)$

$$x_{cj}(-j^2\omega^2 - 1 + 2\bar{x}) + \underbrace{\tfrac{1}{2}x_{cj/2}^2(1+(j/2)^2\omega^2)}_{\text{for } j \text{ even}}$$

$$+ \underbrace{\sum_{k=1}^{N-j} x_{cj+k}x_{ck}(1-(j+k)k\omega^2)}_{\text{for } j \leq N-1}$$

$$+ \underbrace{\sum_{k=1}^{\text{INT}\left(\frac{j+1}{2}\right)-1} x_{c,j-k}x_{ck}(1+(j-k)k\omega^2)}_{\text{for } j \geq 3} = 0,$$

$$j = 1, \ldots, N, \qquad (37)$$

whereas all the terms containing $\sin(j\omega t)$ vanish identically. But in reality (36) is redundant and has to be removed from the system of implicit equations; for summing (37) over all $j = 1, \ldots, N$ we get

$$\sum_{j=1}^{N} x_{cj}(2\bar{x} - 1 - j^2\omega^2) + \tfrac{1}{2}\sum_{j=2,\text{even}}^{N} x_{cj/2}^2(1+j/2)^2\omega^2)$$

$$+ \sum_{j=1}^{N-1}\sum_{k=1}^{N-j} x_{c,j+k}x_{ck}(1-(j+k)k\omega^2) \qquad (38)$$

$$+ \sum_{j=3}^{N}\sum_{k=1}^{\text{INT}\left(\frac{j+1}{2}\right)-1} x_{c,j-k}x_{ck}(1+(j-k)k\omega^2) = 0,$$

which is

$$\sum_{j=1}^{N} x_{cj}(2\bar{x} - 1 - j^2\omega^2) + \left(\sum_{j=1}^{N} x_{cj}\right)^2$$

$$- \tfrac{1}{2}\sum_{j=1}^{N} x_{cj}^2(1 - j^2\omega^2) = 0. \qquad (39)$$

As (35) has to be valid for $t = 0$, too, and as

$$x(0) = y(0) = \bar{x} + \sum_{j=1}^{N} x_{cji},$$

$$\dot{x}(0) = -\sum_{j=1}^{N} j^2\omega^2 x_{cj}$$

(39) is equivalent to

$$\left(\bar{x} + \sum_{j=1}^{N} x_{cj}\right)^2 - \bar{x}^2 - \sum_{j=1}^{N} x_{cj}(1 + j^2\omega^2)$$

$$- \tfrac{1}{2}\sum_{j=1}^{N} x_{cj}^2(1 - j^2\omega^2)$$

$$= \dot{x}(0) - x(0) + x(0)y(0) - \bar{x}^2 + \bar{x}$$

$$- \tfrac{1}{2}\sum_{j=1}^{N} x_{cj}^2(1 - j^2\omega^2)$$

$$= -\bar{x}^2 + \bar{x} - \tfrac{1}{2}\sum_{j=1}^{N} x_{cj}^2(1 - j^2\omega^2) = 0, \qquad (40)$$

and hence yields (36). On the other hand each initial condition $x(0) = y(0) = x_0$ on the line $x = y$ beyond $\bar{x}$ describes a special closed trajectory so that

$$x_0 = \bar{x} + \sum_{j=1}^{N} x_{cj} \qquad (41)$$

is an additional equation to be obeyed.

Table 3. Results of the symmetrical Lotka-Volterra-oscillator with $x_0 = y_0 = 2$.

j	$A_{xj} = A_{yj}$	
1	0.997673	$F = 2.02 * 10^{-22}$
2	0.383705	$\omega = 0.90521386$ (cf.: $\omega_{cr} = 1$)
3	0.148628	
4	0.058880	moduli of characteristic multipliers =
5	0.023668	$9.6719934. * 10^{-4}$ and 1.00000000,
6	0.009598	real parts of characteristic
7	0.003914	exponents =
8	0.001602	-1.00000000 and
9	0.000657	$-5.1627031 * 10^{-27}$
10	0.000270	(1000 integration points), maximal
.	.	relative error
.	.	$= \left\lvert \dfrac{x + y - \ln(xy) - c}{c} \right\rvert$
.	.	
.	.	$= 5.52 * 10^{-10}$
24	$1.13 * 10^{-9}$	with $c = x_0 + y_0 - \ln(x_0 y_0)$
		$= 4 - 2\ln 2$

The equilibrium between the number of equations ($N+1$) and the number of unknowns ($\bar{x}$, ω and N coefficients x_{cj}) can only be established under the assumption that $\bar{x}$ is equal to $x_{cr2} = 1$. This assumption is verified by the results given in Table 3 that show that the A_j converge rapidly. The dimension of the problem is, due to the symmetry and the possibility of formulating one linear equation, roughly one fourth of the maximum to be expected. Note the extremely small error of $< 10^{-9}$!

5. Conclusions

The method of unrestricted harmonic balance is universally applicable to the computation of closed trajectories — stable or unstable — of nonlinear chemical reaction systems as they are derived directly from the law of mass action. This was demonstrated for the limit cycle of the brusselator and the case of the Lotka-Volterra-system, which leads to a closed curve for any initial condition and is less representative, but whose trajectories obey an exact implicit equation and which can thus be used to test the accuracy. Although a thorough examination of the error in the general case was not made, it is felt that the relative amplitude A_N/A_1 is a measure of the accuracy in general.

Applications of the method to stiff differential equations, to chaotic systems including unstable limit cycles and to spatial structures (dissipative structures and chemical waves) in reaction-diffusion systems are underway and are planned to be the topics of further papers of this series.

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