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

IV. Extension to Transcendental Functions

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The method of Unrestricted Harmonic Balance (UHB) as exposed and applied to purely time-dependent systems, stiff systems, and chemical waves in the preceding 3 papers is extended to the case of transcendental functions. So, e. g., exponential functions even in mass action kinetics systems occur, if a wider range of temperature is considered as is the case in continuous stirred tank reactors (CSTR). Here the reaction heat is removed by heat exchangers, but since the volume is in most cases considerable, the system cannot be kept strictly isothermal and instabilities are known to arise. Here the oscillatory case is treated with the method of UHB.

1. Introduction

In paper I of this series [1] the method of UHB was introduced and demonstrated for typical examples of time-dependent periodic kinetic systems (chemical oscillations). The principle of this method is that periodic state variables can be expressed as Fourier series, e.g.

$$x(t) = \bar{x} + \sum_{j=1}^{\infty} x_{c_j} \cos(j\,\omega\,t) + \sum_{j=1}^{\infty} x_{s_j} \sin(j\,\omega\,t). \quad (1)$$

As is known, the products of sine- and cosine-functions are again sine- and cosine-functions so that state variables of the form (1) preserve their group property under multiplication (under addition trivially anyhow). In practical applications the Fourier series have to be truncated at some highest harmonic, say N, so that each state variable is represented by a $(2N+1)$-dimensional vector and the product, the complicated formulas of which were derived in [1], can be interpreted as a particular vector product.

In paper II [2] it was shown that this method even works for stiff differential equations and in paper III [3] the method was applied to running and standing chemical waves, i.e. to partial differential equations in time and space.

As was explicitly stated in paper I the only realistic non-linearities in chemical reaction systems with mass-action kinetics are products of concentrations, to which the product algorithm can be applied, if necessary repeatedly. This is true for *isothermal* systems; this assumption in turn is fairly well fulfilled in *small* systems in biochemistry or laboratory chemistry, because here the turnover is so small that the removal of the reaction heat is no problem. Or stated in another way: since heat production is proportional to volume and therefore $\propto l^3$, if l is a typical length parameter of the extension of the reaction vessel, and since the heat flow occurs through the surface $\propto l^2$, the temperature difference between inside the vessel and some temperature bath outside can be easily kept arbitrarily small for small systems. But for bigger plants as they occur in technical CSTRs, special heat exchangers have to be provided and nevertheless a considerable temperature change can basically be expected.

Thus temperature enters as an additional state variable and the rate constants can no longer be considered as being strictly constant, but are strongly temperature dependent, in the simplest case as expressed by the Arrhenius equation

$$k(T) = k_0 \cdot \exp(-E_a/RT). \quad (2)$$

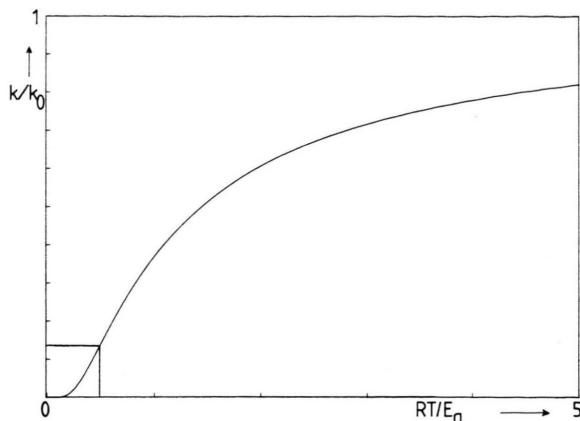Here E_a is the positive activation energy (per mole), T is the temperature, R is the universal gas constant,

Fig. 1. Plot of $k/k_0 = \exp(-E_a/RT)$ in the interval [0,1] vs. dimensionless temperature RT/E_a in the interval [0,5]. The point of inflection with its coordinates is particularly displayed.

and k_0 is the preexponential factor, which is seen to be equal to $\lim_{T \to \infty} k$. In most cases the characteristic temperature $\theta = E_a/R$ is so high that at the considered temperature range the curve $k(T)$ as shown in Fig. 1 is far from the saturation region, but is in the range of a dramatic increase with T. This gives rise to a kind of autocatalysis by the heat and is responsible for the known intrinsic instabilities of such systems [4].

Since the exponential function e^x can be expressed as an infinite series and *is* actually used in this form at its evaluation in computers, the exponential of some $2N+1$-dimensional state *vector x* of the form (1) (with N instead of ∞) is of exactly the same series form, if each multiplication by x (to yield some higher power of x) is performed by application of the product procedure as given in part I. The truncation of the series should be controlled by the expected or needed accuracy by a reasonable criterion. Of course each exponential needs several product formations and is therefore more time consuming than one simple product, but this is true for the exponential of some scalar in comparison with the product of two scalars in the same way.

2. ODE-System for a CSTR with Heat Removal by a Heat Exchanger

A CSTR for a simple first order reaction with removal of the reaction heat by a heat exchanger was treated by Wicke [5], and Gilles [6] showed by application of the *restricted* harmonic balance method (truncation at $N=1$, which is tolerable only for very small amplitudes) that for certain values of the parameters undamped oscillations (limit cycle oscillations) can occur. As these equations are needed for the UHB treatment later on, the most important formulas are reproduced here, but in some of them other designations are introduced, which seem to be more convenient.

Let be V the volume of the CSTR, v its volume flow velocity, c the concentration of the reactant inside the CSTR, c_0 the concentration at its inlet, k the rate constant of the first order reaction, then

$$\frac{dc}{dt} = \frac{v}{V}(c_0 - c) - k\,c. \tag{3}$$

If in addition T is the temperature inside the CSTR, T_0 the temperature at its inlet, T_c the temperature of the coolant, ΔH the reaction enthalpy, which is negative for an exothermal reaction, $\varrho\, c_p$ the heat capacity per volume unit, its actual change during the reaction being neglected, and $\varkappa A$ is the heat flow through the surface (area) A of the heat exchanger per degree temperature difference, then

$$\frac{dT}{dt} = \frac{(-\Delta H)}{\varrho\, c_p} k\,c - \frac{v}{V}(T - T_0) - \frac{\varkappa A}{\varrho\, c_p V}(T - T_c). \tag{4}$$

The last two terms of the right-hand side of (4) represent terms of heat removal and can be formulated analogous to the term $(v/V)(c_0 - c)$ in (3) by defining a temperature T_{0c} characteristic for the device as

$$T_{0c} = \frac{v\,\varrho\, c_p T_0 + \varkappa A T_c}{v\,\varrho\, c_p + \varkappa A} \tag{5}$$

and ΔT_{ad},

$$\Delta T_{ad} = \frac{(-\Delta H)\, c_0}{\varrho c_p} \tag{6}$$

which is the increase in temperature for an adiabatic reaction at which T would be stationary.

By introducing a dimensionless constant

$$\mu = \frac{\varkappa A}{v\,\varrho\, c_p}. \tag{7}$$

(4) can be reformulated as

$$\frac{dT}{dt} = \frac{\Delta T_{ad}}{c_0} k\,c - \frac{v}{V}(1 + \mu)(T - T_{0c}). \tag{8}$$

The steady state is characterized by the fact that (3) and (8) are equal to zero, defining steady state concentration c_{ss} and steady state temperature T_{ss} and by means of (2) the steady state rate constant k_{ss} by

$$c_{ss} = c_0 \frac{v}{v + k_{ss} V}, \tag{9}$$

$$T_{ss} = T_{0c} + \frac{\Delta T_{ad} k_{ss} V}{(v + k_{ss} V)(1 + \mu)}, \tag{10}$$

and

$$k_{ss} = k_0 \exp(-E_a/R T_{ss}), \tag{11}$$

so that in a way analogous to (3) and (8) for the deviations $\Delta c = c - c_{ss}$ and $\Delta T = T - T_{ss}$ from the steady state variables

$$\frac{d\Delta c}{dt} = -\frac{v}{V} \Delta c + k_{ss} c_{ss} \left(1 - \frac{k c}{k_{ss} c_{ss}}\right), \tag{12}$$

$$\frac{d\Delta T}{dt} = -\frac{v}{V}(1 + \mu) \Delta T - \frac{\Delta T_{ad}}{c_0} k_{ss} c_{ss} \left(1 - \frac{k c}{k_{ss} c_{ss}}\right), \tag{13}$$

where

$$k/k_{ss} = \exp[(E_a/R T_{ss})(\Delta T/(T_{ss} + \Delta T))]. \tag{14}$$

With the following abbreviations using dimensionless variables and parameters throughout

$$\xi = \Delta T/T_{ss}, \tag{15}$$

$$\eta = \Delta c/c_{ss}, \tag{16}$$

$$\tau = k_{ss} t, \tag{17}$$

$$\alpha = E_a/R T_{ss}, \tag{18}$$

$$\beta = v/k_{ss} V, \tag{19}$$

and

$$\gamma = \frac{\Delta T_{ad}}{T} \frac{c_{ss}}{c_0} \tag{20}$$

we get finally

$$d\xi/d\tau = -\beta(1 + \mu) \xi \tag{21}$$
$$- \gamma[1 - \exp(\alpha \xi/(1 + \xi)) \cdot (1 + \eta)],$$

$$d\eta/d\tau = -\beta \eta + 1 - \exp(\alpha \xi/(1 + \xi)) \cdot (1 + \eta) \tag{22}$$

which have to be solved for given parameters α, β, γ, μ.

3. UHB-Treatment

Equations (21) and (22) are basically identical with those of Gilles [6], save a) slightly different designations, b) that Gilles introduced the superfluent approximation $\exp(\alpha \xi/(1 + \xi)) \approx \exp(\alpha \xi) \cdot (1 - \alpha \xi^2)$.

The term containing the exponential function is the only non-linearity and appears fortunately in both differential equations in the same way so that one purely linear equation can be formulated

$$\frac{d\xi}{d\tau} + \gamma \frac{d\eta}{d\tau} + \beta(1 + \mu) \xi + \beta \gamma \eta = 0. \tag{23}$$

The non-linear equation is

$$\frac{d\xi}{d\tau} + \beta(1 + \mu) \xi \tag{24}$$
$$+ \gamma[1 - \exp(\alpha \xi/(1 + \xi)) \cdot (1 + \eta)] = 0.$$

We set $\xi_{c1} = 0$ and choose frequency ω, $\bar{\xi}$, $\{\xi_{c_j}\}\backslash\xi_{c1}$ and $\{\xi_{s_j}\}$ $(j = 1, \ldots, N)$ as the $2N + 1$ unknowns.

From (23) we get

$$\bar{\eta} = -((1 + \mu)/\gamma) \bar{\xi}, \tag{25}$$

$$j \omega \xi_{s_j} + j \omega \gamma \eta_{s_j} + \beta(1 + \mu) \xi_{c_j} + \beta \gamma \eta_{c_j} = 0, \tag{26}$$

$$-j \omega \xi_{c_j} - j \omega \gamma \eta_{c_j} + \beta(1 + \mu) \xi_{s_j} + \beta \gamma \eta_{s_j} = 0 \tag{27}$$

which yield with the abbreviations

$$a_{c_j} = (-\beta(1 + \mu) \xi_{c_j} - j \omega \xi_{s_j})/\gamma, \tag{28}$$

$$a_{s_j} = (j \omega \xi_{c_j} - \beta(1 + \mu) \xi_{s_j})/\gamma, \tag{29}$$

$$\eta_{c_j} = \frac{\beta a_{c_j} - j \omega a_{s_j}}{\beta^2 + j^2 \omega^2}, \tag{30}$$

$$\eta_{s_j} = \frac{j \omega a_{c_j} + \beta a_{s_j}}{\beta^2 + j^2 \omega^2}, \tag{31}$$

so that η is expressed by ξ.

In (24) the exponential needs a special treatment. Since $|\xi| \ll 1$, a MacLaurin expansion appears to be appropriate

$$f(x) = f(0) + x f'(0) + \frac{1}{2} x^2 f''(0) + \ldots$$
$$= \sum_{n=0}^{\infty} \frac{x^n}{n!} f^{(n)}(0). \tag{32}$$

Here

$$f(\xi) = \exp(\alpha \xi/(1 + \xi)) \tag{33}$$

and the factors $f^{(n)}(0)/n!$ are constants which have to be determined only once and stored for iterative use. We get

$$f(\xi) = \exp(\alpha \xi/(1 + \xi)),$$

$$f'(\xi) = \exp(\alpha \xi/(1 + \xi)) \cdot \frac{\alpha}{(1 + \xi)^2},$$

$$f''(\xi) = \exp(\alpha\,\xi/(1+\xi)) \cdot \left[\frac{-2\,\alpha}{(1+\xi)^3} + \frac{\alpha^2}{(1+\xi)^4}\right],$$

$$f'''(\xi) = \exp(\alpha\,\xi/(1+\xi))$$
$$\cdot \left[\frac{6\,\alpha}{(1+\xi)^4} - \frac{6\,\alpha^2}{(1+\xi)^5} + \frac{\alpha^3}{(1+\xi)^6}\right], \qquad (34)$$

$$f^{(4)}(\xi) = \exp(\alpha\,\xi/(1+\xi))$$
etc.
$$\cdot \left[\frac{-24\,\alpha}{(1+\xi)^5} + \frac{36\,\alpha^2}{(1+\xi)^6} - \frac{12\,\alpha^3}{(1+\xi)^7} + \frac{\alpha^4}{(1+\xi)^8}\right],$$

and

$$f(0) = 1, \qquad f''(0) = -2\alpha + \alpha^2,$$
$$f'(0) = \alpha, \qquad f'''(0) = 6\alpha - 6\alpha^2 + \alpha^3,$$
$$f^{(4)}(0) = -24\alpha + 36\alpha^2 - 12\alpha^3 + \alpha^4. \qquad (35)$$

So

$$\exp(\alpha\,\xi/(1+\xi)) = 1 + \sum_{n=1}^{\infty} \frac{f^{(n)}(0)}{n!}\,\xi^n \qquad (36)$$

with

$$\frac{f^{(n)}(0)}{n!} = \sum_{i=1}^{n} b_i^{(n)} \qquad (37)$$

and the recursion formulas

$$b_1^{(1)} = \alpha, \quad b_1^{(n)} = -b_1^{(n-1)}, \quad b_n^{(n)} = \frac{\alpha}{n}\,b_{n-1}^{(n-1)} \quad (38)$$

and

$$b_i^{(n)} = \frac{-(i+n-1)\,b_i^{(n-1)} + \alpha\,b_{i-1}^{(n-1)}}{n} \qquad (39)$$

for $i = 2, \ldots, n-1$.

Since here ξ and each power of ξ is not a scalar, but a $(2N+1)$-dimensional vector, each product $\xi^n = (\xi^{n-1}) \odot \xi$ has to be performed according to the algorithm of the harmonic vector product formation as given in [1]. The unavoidable truncation of the MacLaurin expansion has to be controlled by the wanted accuracy of the overall procedure in a suitable way.

So if

$$u = \exp(\alpha\,\xi/(1+\xi)) \qquad (40)$$

as computed by a special subprogram and

$$v = 1 + \eta, \qquad w = u \odot v \qquad (41), (42)$$

the $2N+1$ non-linear algebraic equations derived from (24) are

$$\beta(1+\mu)\,\bar{\bar{\xi}} + \gamma(1-\bar{w}) = 0, \qquad (43)$$

$$\left.\begin{array}{l} j\,\omega\,\xi_{s_j} + \beta(1+\mu)\,\xi_{c_j} - \gamma\,w_{c_j} = 0 \\ -j\,\omega\,\xi_{c_j} + \beta(1+\mu)\,\xi_{s_j} - \gamma\,w_{s_j} = 0 \end{array}\right\} \; j = 1, \ldots, N \quad \begin{array}{l} (44) \\ (45) \end{array}$$

which are again solved iteratively by the Powell method [7].

4. Conditions for Oscillations

Going back to (21) and (22) the steady state is characterized by $\xi_{ss} = \eta_{ss} = 0$ in accordance with the definitions of ξ and η, (15) and (16), respectively. The Jacobian df/dx is given by

$$J \equiv \frac{df}{dx} = \qquad (46)$$

$$\begin{pmatrix} -\beta(1+\mu) + \gamma\exp(\alpha\,\xi/(1+\xi)) \cdot \dfrac{\alpha}{(1+\xi)^2} \cdot (1+\eta) \\ \gamma\exp(\alpha\,\xi/(1+\xi)) - \beta - \exp(\alpha\,\xi/(1+\xi)) \\ -\exp(\alpha\,\xi/(1+\xi)) \cdot \dfrac{\alpha}{(1+\xi)^2} \cdot (1+\eta) \end{pmatrix}$$

the Jacobian at the steady state by

$$J_{ss} = \begin{pmatrix} -\beta(1+\mu) + \alpha\gamma & \gamma \\ -\alpha & -\beta-1 \end{pmatrix} \qquad (47)$$

which yields for the eigenvalues λ at the steady state the characteristic polynomial

$$(-\beta(1+\mu) + \alpha\gamma - \lambda)(-\beta-1-\lambda) = 0 \qquad (48)$$

or

$$\lambda^2 + \lambda(1 + \beta + \beta(1+\mu) - \alpha\gamma)$$
$$+ \beta(1+\beta)(1+\mu) - \alpha\beta\gamma = 0. \qquad (49)$$

Necessary condition for oscillations is that the critical point $\xi_{ss} = \eta_{ss} = 0$ is an unstable node or unstable focus, which means that simultaneously

$$\beta(1+\beta)(1+\mu) - \alpha\beta\gamma > 0 \qquad (50)$$

and

$$1 + \beta + \beta(1+\mu) - \alpha\gamma < 0 \qquad (51)$$

which can be united to

$$1 + \beta + \beta(1+\mu) < \alpha\gamma < (1+\beta)(1+\mu). \quad (52)$$

This shows that for the qualitative behaviour of the system actually only *three* parameters exist, namely $(\alpha\gamma)$, β and $(1+\mu)$. To have a gap for $\alpha\gamma$ at all, means that

$$1 + \beta + \beta(1+\mu) < (1+\beta)(1+\mu) \qquad (53)$$

equivalent to

$$\beta < \mu. \qquad (54)$$

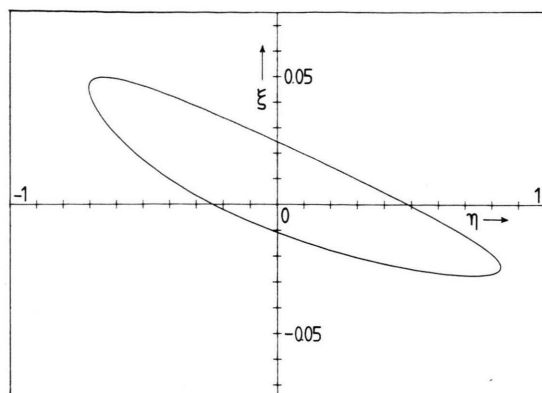Fig. 2a. Plot of $\xi(\tau)$ in the interval $[-0.075, 0.075]$ vs. $\eta(\tau)$ in the interval $[-1, 1]$.

Fig. 2b. Plot of $10\,\xi$ and η in the interval $[-1, 1]$ vs. $\omega\,\tau$ for one period.

Since this condition is a prerequisite for (52), β and μ stand highest in the hierarchy of parameters, $(\alpha\,\gamma)$ is lowest.

5. Result for the Example Treated by Gilles

In order to test the UHB method, the same model system with exactly the same parameters as that computed by Gilles [6] was treated. Inserting the particular values given there the parameter set is $\alpha = 30.40$, $\beta = 0.1604$, $\gamma = 0.0616$ and $\mu = 2.73$, the criterion (52) for instability is with $1.759 < 1.873 < 4.328$ fulfilled. The frequency of the linearized system with vanishing amplitudes would be 0.62497, the real part of the pair of conjugated complex eigenvalues of (49) 0.0570. Using the method of restricted harmonic balance (only first harmonic considered) Gilles found a frequency of 0.6672. The actual frequency after the UHB method is however 0.7339, oscillations are not around (0,0), but around $\bar\xi = -2.785 \cdot 10^{-3}$ and $\bar\eta = 0.16864$. The drop of amplitudes from $j = 1$ to $j = N = 12$ is from $3.1776 \cdot 10^{-2}$ to $7.1895 \cdot 10^{-5}$ for ξ and from 0.70968 to $1.171 \cdot 10^{-3}$ for η indicating that the neglect of higher harmonics leads to a considerable error. This
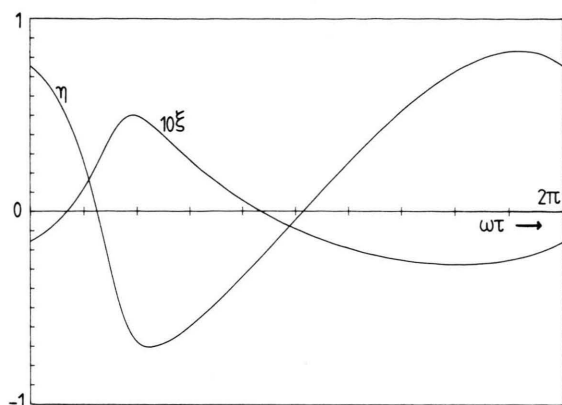
fact is conspicuously demonstrated by the plots of ξ vs. η and $10\,\xi$ and η vs. $\omega\,\tau$ as given in Figure 2.

6. Conclusions

In this paper it is demonstrated that the method of Unrestricted Harmonic Balance is applicable in a far broader range than was originally expected and intended. The extension to transcendental functions $f(x)$ is executed for the particular case of $f(x) = \exp\{a\,x/(1 + x)\}$, but there is no doubt that any other function could be treated as well. So the range of tractable non-linear problems is extended so much that hardly any limitation can be seen. The truncation of the series expansion of the transcendental functions can be easily controlled by adapting the convergence to the drop of amplitudes of the harmonics. In the preceding example the truncation occurred typically after x^8 in the final pass ($N = 12$).

7. Acknowledgement

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[7] M. J. D. Powell, in: Numerical Methods for Nonlinear Algebraic Equations, Ed. P. Rabinowitz, Gordon & Breach Science Publ., London 1970.