in 55% yield.

Acknowledgement. The authors are grateful to the Organic Chemistry Research Center (OCRC) for the financial support. The use of a Varian Gemini 300 NMR spectrometer is financially supported by the OCRC.

References

1. Gutsche, C. D. *Calixarenes*; Stoddart, J. F. Ed.; Royal Society of Chemistry; London, 1989.
2. *Calixarenes: A Versatile Class of Macrocyclic Compounds*, Vicens, J.; Bohmer, V. Eds.; Kluwer Academic Publishers; Dordrecht, **1991**.
3. Gutsche,C. D.; Bauer, L. *J. Tetrahedron Lett.* **1981**, *22*, 4763.
4. Gutsche,C. D.; Dhawan, B.; No, K. H.; Muthukrishnan, R. *J. Am. Chem. Soc.* **1981**, *103*, 3782.
5. Bocchi,V.; Foina,D.; Pochino, A.; Ungaro, R.; Andreetti,C. D. *Tetrahedron*, **1982**, *38*, 373.
6. Iqbal, M.; Mangiafico, T.; Gutsche, C. D. *Tetrahedron* **1987**, *43*, 4917.
7. Gutsche, C. D.; Reddy, P. A. *J. Org. Chem.* **1991**, *56*, 4783.
8. Jaime, C.; Mendoza, J.; Prados, P.; Nieto, P. M.; Sanchez, C. *J. Org. Chem.* **1991**, *56*, 3372.
9. Still, W. C.; Kahn, M.; Mitra, M. *J. Org. Chem.* **1978**, *43*, 2923.
10. Gutsche, C. D.; Dahwan, B.; Levine, J. A.; No, K. H.; Bauer, L. *J. Tetrahedron* **1983**, *39*, 409.
11. Rizzoli, C.; Andreetti, C. D.; Ungaro, R.; Pochini, A. *J. Molec. Struct.* **1982**, *82*, 133.
12. Gutsche, C. D. Bauer, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 6052.
13. No, K. H.; Noh, Y. J.; Kim, Y. H. *Bull. Korean Chem. Soc.* **1986**, *7*, 442.
14. Gutsche, C. D.; Rogers, J. S.; Stewart, D.; See, K. *Pure Appl. Chem.* **1990**, *62*, 485.
15. Gibbs, C. G.; Gutsche, C. D. *J. Am. Chem. Soc.* **1993**, *115*, 5338.
16. Iwamoto, K.; Araki, K.; Shinkai, S. *J. Org. Chem.* **1991**, *56*, 4955.
17. Araki, K.; Iwamoto, K.; Shinkai, S.; Matsude, T. *Chem. Lett.* **1989**, 1474.
18. Groenen, L. C.; van Loon, J-D.; Verboom, W.; Harkema, S.; Casnati, A.; Ungaro, R.; Pochini, A.; Ugozzoli, F.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1991**, *113*, 2385.
19. Bott, S. G.; Coleman, A. W.; Atwood, J. L. *J. Inclusion Phenom.* **1987**, *5*, 747.
20. No, K. H.; Noh, Y. J. *Bull. Korean Chem. Soc.* **1986**, *7*, 314.
21. Gutsche, C. D.; Levine, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2652.

A Nonlinear Theory for the Oregonator Model with an External Input

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Received February 23, 1994

An approximate nonlinear theory of the Oregonator model is obtained with the aid of an ordinary perturbation method when the system is perturbed by some kinds of external input. The effects of internal and external parameters on the oscillations are discussed in detail by taking specific values of the parameters. A simple approximate solution for the Oregonator model under the influence of a constant input is obtained and the result is compared with the numerical result. For other types of external inputs the approximate solutions up to the fourth order expansion are compared with the numerical results. For a periodic input, we found that the entrainment depends crucially on the difference between the internal and external frequencies near the bifurcation point.

Introduction

With the aid of the star expansion method, originally proposed by Houard and his coworkers[1-3], two[4] of us have obtained approximate nonlinear solutions for the Schlögl models[5] under the influence of some kinds of external input and compared the numerical predictions with the exact solution available for some cases and also with the linearized solutions and the approximate ones obtained by the Feynman method. Although the approximate solution based on the star expansion method and that obtained by the Feynman method numerically agree well with each other, the former is more systematic and simpler. We also have extended the star expansion method to the Lotka-Volterra model, which is the two-component chemical reaction model exhibiting the sustained oscillation and then discussed the effects of nonlinearity, amplitude and frequency of the external input on the chemical oscillations in the model by taking specific values of the model parameters[6].

The purpose of the present paper is to discuss the effects of external inputs on nonlinear oscillations in the Oregonator model[7] proposed by Field and Noyes for the Belousov-Zhabotinskii reaction. There are three intermediates in the Oregonator which make the application of the star expansion method too complicated contrary to other models mentioned above. Therefore, we adopt Feynman's theory of ordinary perturbation method instead of the star expansion method in this work. In section II we present the general method to be used for the Oregonator. In section III we obtain a simple approximate solution for the Orgonator under the influence of the constant input and compare them with the numerical results obtained by using the differential equation solver, subroutine DGEAR of IMSL[8]. For the cases of different kinds of external input the approximate solutions up to the fourth order expansion are numerically compared with the numerical results.

Theory

Probably the best characterized homogeneous self-oscillatory chemical reaction is the Belousov-Zhabotinskii (BZ) reaction involving the cerium ion catalyzed oxidation of malonic acid by acidic bromate. Field, Körös and Noyes proposed a complex system of 10 chemical reactions with 7 intermediates as a model for the BZ reaction in batch system[9]. From this system Field and Noyes abstracted a simple model called the Oregonator.

$$A+Y\xrightarrow{k_1}X, \qquad X+Y\xrightarrow{k_2}P,$$
$$B+X\xrightarrow{k_3}2X+Z, \qquad 2X\xrightarrow{k_4}Q,$$
$$Z\xrightarrow{k_5}fY, \tag{1}$$

where A and P are the reactant, BrO_3^- and product, HOBr, respectively; X, Y, and Z are the intermediates, $HBrO_2$, Br^-, and Ce^{4+}, respectively; and k's are the rate constants. From now on, the concentration will be represented by its chemical species for the notational simplicity, for example, $A=[A]$. The numerical values of k_1 through k_4, as well as A and B are[7]

$$A=B\cong 0.06\ \mathrm{M},\ k_1\cong 1.34\ \mathrm{M^{-1}s^{-1}},\ k_2\cong 1.6\times 10^9\ \mathrm{M^{-1}s^{-1}}$$
$$k_3\cong 8\times 10^3\ \mathrm{M^{-1}s^{-1}},\ k_4\cong 4\times 10^7\ \mathrm{M^{-1}s^{-1}} \tag{2}$$

The stoichiometric factor f and the rate constant k_5 are the controllable parameters. It is convenient to introduce the following scaled variables:

$$x=\frac{k_2}{k_1A}X\cong 2.0\times 10^{10}X,\ y\cong\frac{k_2}{k_3B}Y\cong 3.3\times 10^6 Y,$$
$$z=\frac{k_2k_5}{k_1k_3AB}Z\cong 2.0\times 10^7 Z,\ s=\left\{\frac{k_3B}{k_1A}\right\}^{1/2}\cong 77.27,$$
$$t=(k_1k_3AB)^{1/2}\tau\cong 6.25\ \tau,$$
$$q=\frac{2k_1k_4A}{k_2k_3B}\cong 8.375\times 10^{-6},\ w\cong\frac{k_5}{(k_1k_3AB)^{1/2}}\cong 0.161$$
$$\xi(t)=\frac{k_2}{(k_1{}^3k_3A^3B)^{1/2}}\zeta(t)\cong 2.47\times 10^9\zeta(t) \tag{3}$$

where τ and $\xi(t)$ are the real time and the external input, respectively. The dimensionless rate equations with the scaled external input may be written as

$$\frac{dx}{dt}=s(y-xy+x-qx^2)+\xi,$$
$$\frac{dy}{dt}=s^{-1}(-y-xy+fz)$$
$$\frac{dz}{dt}=w(x-z) \tag{4}$$

Defining the fluctuating variables due to the external input near the steady state (x_0, y_0, z_0) as

$$x_1=x-x_0,\ x_2=y-y_0,\ x_3=z-z_0, \tag{5}$$

where

$$x_0=z_0=\frac{1-f-q+[(1-f-q)^2+4q(1+f)]^{1/2}}{2q},\ y_0=\frac{f\,x_0}{1+x_0}, \tag{6}$$

we may obtain the following equation

$$\frac{d}{d\tau}(x_1,\ x_2,\ x_3)^T=\mathbf{M}(x_1,\ x_2,\ x_3)^T+\mathbf{A}(x_1,\ x_2,\ x_3)^T+(\zeta,\ 0,\ 0)^T, \tag{7}$$

where

$$\mathbf{M}=\begin{bmatrix} s(1-2qx_0-y_0) & s(1-x_0) & 0\\ -y_0/s & -(1+x_0)/s & f/s\\ w & 0 & -w\end{bmatrix},\ \mathbf{A}=\begin{bmatrix} -sx_2 & 0 & 0\\ 0 & -x_1/s & 0\\ 0 & 0 & 0\end{bmatrix},$$

It should be noted that in Eq. (7) we have neglected the qx_1^2 term in the nonlinear part on the ground of the fact that the quantity q is so small that its effect is negligible compared to the other nonlinear parts. The eigenvalue of $\mathbf{M}$ satisfies

$$\lambda^3+A_0\lambda^2+B_0\lambda+C_0=0; \tag{8}$$

where

$$A_0=[s(1-y_0-2qx_0)-s^{-1}(1+x_0)-w],$$
$$B_0=[s^{-1}w(1+x_0)-sw(1-y_0-2qx_0)-(1+x_0)(1-y_0-2qx_0)],$$
$$C_0=[w(1+x_0)(1-y_0-2qx_0)-wf(1-x_0)-y_0(1-x_0)],$$

Let ψ^i and ϕ_i be the left and right eigenvectors of $\mathbf{M}$ with eigenvalue $-\lambda_i$, that is,

$$\Psi^i\cdot\mathbf{M}=-\lambda_i\Psi^i;\ \Psi^i=(\Psi_1^i,\ \Psi_2^i,\ \Psi_3^i)^T\ (i=1,\ 2,\text{ or }3). \tag{9}$$

There exist six eigenvectors corresponding to $-\lambda_i$. Three independent eigenvectors are

$$\Psi^i(1)=\left\{1-\frac{s(1-x_0)}{\lambda_i-s^{-1}(1+x_0)},\ \frac{sw(1-x_0)}{[\lambda_i-s^{-1}(1+x_0)](\lambda_i-w)}\right\}^T,$$
$$\Psi^i(2)=\left\{-\frac{\lambda_i-s^{-1}(1+x_0)}{s(1-x_0)},\ 1,\ -\frac{s^{-1}f}{\lambda_i-w}\right\}^T,$$
$$\Psi^i(3)=\left\{-\frac{[\lambda_i-s^{-1}(1+x_0)](\lambda_i-w)}{(1-x_0)f},\ \frac{\lambda_i-w}{f},\ 1\right\}^T, \tag{10}$$

With the aid of Eq. (9), Eq. (7) reduces to

$$\frac{d\mu}{dt}=-\lambda\mu+B\mu+\eta, \tag{11}$$

where

$$\mu=\psi x,\ \lambda\begin{bmatrix}\lambda_1 & 0 & 0\\ 0 & \lambda_2 & 0\\ 0 & 0 & \lambda_3\end{bmatrix},\ B=\psi A\phi,\ \eta=\psi(\xi,\ 0,\ 0)^T,$$

$$\psi=(\psi^1,\ \psi^2,\ \psi^3),\ \phi=(\phi_1,\ \phi_2,\ \phi_3). \tag{12}$$

Using the complicated procedures, the components of the matrix B are

$$b_{11}=\alpha_{11}\mu_1+\alpha_{12}\mu_2+\alpha_{13}\mu_3,\ b_{12}=\beta_{11}\mu_1+\beta_{12}\mu_2+\beta_{13}\mu_3,$$
$$b_{13}=\gamma_{11}\mu_1+\gamma_{12}\mu_2+\gamma_{13}\mu_3,\ b_{21}=\alpha_{21}\mu_1+\alpha_{22}\mu_2+\alpha_{23}\mu_3,$$
$$b_{22}=\beta_{21}\mu_1+\beta_{22}\mu_2+\beta_{23}\mu_3,\ b_{22}=\gamma_{21}\mu_1+\gamma_{22}\mu_2+\gamma_{23}\mu_3,$$
$$b_{31}=\alpha_{31}\mu_1+\alpha_{32}\mu_2+\alpha_{33}\mu_3,\ b_{32}=\beta_{31}\mu_1+\beta_{32}\mu_2+\beta_{33}\mu_3,$$
$$b_{33}=\gamma_{31}\mu_1+\gamma_{32}\mu_2+\gamma_{33}\mu_3, \tag{13}$$

where

$$\alpha_{1j}=-s\psi_1^1\phi_{11}\phi_{2j}-s^{-1}\psi_2^1\phi_{21}\phi_{1j},\ \alpha_{2j}=-s\psi_1^1\phi_{12}\phi_{2j}-s^{-1}\psi_2^1\phi_{22}\phi_{1j}$$
$$\alpha_{3j}=-s\psi_1^1\phi_{13}\phi_{2j}-s^{-1}\psi_2^1\phi_{23}\phi_{1j},\ \beta_{1j}=-s\psi_1^2\phi_{11}\phi_{2j}-s^{-1}\psi_2^2\phi_{21}\phi_{1j}$$
$$\beta_{2j}=-s\psi_1^2\phi_{12}\phi_{2j}-s^{-1}\psi_2^2\phi_{22}\phi_{1j},\ \beta_{3j}=-s\psi_1^2\phi_{13}\phi_{2j}-s^{-1}\psi_2^2\phi_{23}\phi_{1j}$$
$$\gamma_{1j}=-s\psi_1^3\phi_{11}\phi_{2j}-s^{-1}\psi_2^3\phi_{21}\phi_{1j}\quad \gamma_{2j}=-s\psi_1^3\phi_{12}\phi_{2j}-s^{-1}\psi_2^3\phi_{22}\phi_{1j}$$
$$\gamma_{3j}=-s\psi_1^3\phi_{13}\phi_{2j}-s^{-1}\psi_2^3\phi_{23}\phi_{1j}\quad (j=1,\ 2,\ \text{or}\ 3). \tag{14}$$

Introducing the variable $p(t)$ as

$$p(t)=\exp(\lambda t)\mu(t), \tag{15}$$

Eq. (11) becomes

$$\frac{d}{dt}p(t)=\mathbf{C}\cdot z(t)+\eta'(t), \tag{16}$$

where

$$\eta'(t)=\exp(\lambda t)\cdot\eta. \tag{17}$$

and the components of matrix $\mathbf{C}$ are given as

$$C_{ij}=b_{ij}\ \exp[(\lambda_i-\lambda_j)t] \tag{18}$$

The general solution of Eq. (16) as

$$p_i(t)=\sum_{j=1}^{3}\int_0^t d\tau\ G_{ij}(t,\tau)\eta'_j(\tau), \tag{19}$$

where the retarded Green function $\mathbf{G}(t,\tau)$ satisfies

$$\frac{d}{dt}\mathbf{G}(t,\tau)=-\mathbf{C}(\tau)\cdot\mathbf{G}(t,\tau). \tag{20}$$

The solution of the Green function is

$$G_{ij}(t,\tau)=\delta_{ij}+\sum_{k=1}^{3}\int_\tau^t d\tau'\ C_{ik}(\tau')G_{kj}(t,\tau'), \tag{21}$$

Expanding G_{ij} and C_{ij} in tes of the external input, we have

$$G_{ij}(t,\tau)=\sum_{n=0}G_{ij}^{(n)}(t,\tau),\ C_{ij}(t)=\sum_{m=1}C_{ik}^{(m)}(t), \tag{22}$$

The n-th order of the Green function corresponding to the $(n-1)$-th order of the input is

$$G_{ij}^{(n)}(t,\tau)=\sum_{l=1}\sum_{m=0}\sum_{k=1}^{3}\int_\tau^t d\tau' C_{ik}^{(l)}(\tau')G_{kj}^{(m)}(t,\tau'),$$
$$G_{ij}^{0}(t,\tau)=\delta_{ij}\qquad\qquad (l+m=n\geq 1) \tag{23}$$

Then, $\mu_i(t)$ has the following solution

$$\mu_i(t)=\sum_{n=1}\mu_i^{(n)}(t)=\exp(-\lambda_i t)\sum_{n=1}\sum_{k=1}\int_0^t d\tau\ G_{ik}^{(n-1)}(t,\tau)\eta'_k(\tau). \tag{24}$$

Discussion

It is well known that the oscillatory behavior of the Oregonator depends on the values of k_5 and f. Field and Noyes[10] carried out normal mode analysis to investigate the stability of the Oregonator and constructed a bifurcation diagram numerically indicating both stable and unstable regions in the k_5-f plane. Across the bifurcation line dividing the stable and unstable regions the Oregonator shows the Hopf bifurcation phenomenon. Let us discuss the nonlinear responses in two cases. In the first case, the system is in the stable region far from the Hopf bifurcation[7] and in the second case it is extremely close to the bifurcation point. An example of the first case is obtained when $f=0.5002000$ and $k_5=1\ s^{-1}$. The choice of the value of $k_5=1\ s^{-1}$ corresponds to experimental observation. The choice of the value of f is somewhat arbitrary but we choose this value for which noticeable nonlinear response can be observed. Following the analysis of Field and Noyes, we found in this case numerically that the system has the following eigenvalues.

$$\lambda_{1(2)}=0.06398+(-)\ i\ 2.433,\ \lambda_3=811 \tag{25}$$

A Hopf bifurcation point can be obtained by increasing the value of f while keeping the value of k_5 at the constant value of $1\ s^{-1}$. Thus, an example of the second case is obtained at $f=0.5010695$. At this point the eigenvalues are

$$\lambda_{1(2)}=1.67\times10^{-6}+(-)\ i\ 2.431,\ \lambda_3=809.7 \tag{26}$$

In both cases the eigenvalue λ_3 is so large that the modes containing this eigenvalue can be neglected.

The responses of the Oregonator are discussed for three kinds of external input by taking specific values of the parameters. The kinds of external input are

$\eta(t)=\eta$: constant input,
$\eta(t)=\eta\ \exp(-\kappa t)$: exponentially decaying input,
$\eta(t)=\eta\ \sin(\omega t)$: periodic input.

In each figure, the results of the approximate solution and the numerical results obtained from Eq. (4) are displayed in parts (a) and (b), respectively, and the odd (even) numbered figures indicate that the system is far from (extremely close to) the bifurcation point.

Constant Input. The linear solution is

$$\mu_i^{(1)}(t)=\frac{\eta_i}{\lambda_i}\{1-\exp(-\lambda_i t)\}\qquad (i=1,\ 2\ \text{or}\ 3) \tag{27}$$

The detailed procedure to obtain the nonlinear solution for $\mu_1(t)$ is given in the previous section. From Eq. (24), the 2nd order expansion term is

$$\mu_1^{(2)}(t)=\exp(-\lambda_1 t)$$
$$\times\int\Big[G_{11}^{(1)}(t,\tau)\eta_1(\tau)+G_{12}^{(1)}(t,\tau)\eta_2(\tau)+G_{13}^{(1)}(t,\tau)\eta_3(\tau)\Big]d\tau \tag{28}$$

The first term in the integral denoted by $\mu_{11}^{(2)}(t)$ is easily obtained as

$$\mu_{11}^{(2)}(t) \simeq \frac{\eta_1}{\lambda_1}\frac{A_{10}}{\lambda_1} - \frac{\eta_1}{\lambda_1}(A_{10}-A_{11})\, t \exp(-\lambda_1 t)$$
$$-\left[\frac{\eta_1}{\lambda_1}\frac{1}{\lambda_1}(A_{10}+A_{11}) + \frac{\eta_1}{\lambda_1-\lambda_2}\frac{A_{12}}{\lambda_2}\right]\exp(-\lambda_1 t)$$
$$+\frac{\eta_1}{\lambda_1}\frac{A_{12}}{\lambda_1-\lambda_2}\exp(-\lambda_2 t) + \frac{A_{11}\eta_1}{\lambda_1^2}\exp(-2\lambda_1 t)$$
$$+\frac{\eta_1}{\lambda_1}\frac{A_{12}}{\lambda_2}\exp[-(\lambda_2+\lambda_2)t], \tag{29}$$

where

$$A_{ik} = -\frac{\alpha_{ik}\eta_k}{\lambda_k} \qquad A_{i0} = -\sum_{k=1}^{3} A_{ik} \tag{30}$$

The above solution is relatively simple. However, as the order of expansion becomes higher, the procedure and solution become much more complicated. Thus, let us compare the effects of the modes on the solution to obtain a simpler solution. When the system is far from the bifurcation point, the other modes except the constant mode decay exponentially. Thus, the constant mode plays the most important role after long time. As the system approaches extremely close to the bifurcation point, the main contribution mode is $t\exp(-\lambda_1 t)$ after long time. Thus, we may obtain the approximate solution for $\lambda_{11}^{(2)}(t)$ after long time, when the system exists between the two extreme cases.

$$\mu_{11}^{(2)}(t) \simeq \frac{\eta_1}{\lambda_1}\left[\frac{A_{10}}{\lambda_1} - (A_{10}-A_{11})\; t\exp(-\lambda_1 t)\right] \tag{31}$$

Including the most dominant parts from the other parts in the integral, $\mu_1^{(2)}(t)$ becomes after long time

$$\mu_1^{(2)}(t) \simeq \frac{\eta_1}{\lambda_1}\frac{A_{10}}{\lambda_1} + \frac{\eta_2}{\lambda_2}\frac{A_{10}'}{\lambda_1} + \frac{\eta_3}{\lambda_3}\frac{A_{10}''}{\lambda_1}$$
$$+\left[\frac{\eta_1}{\lambda_1}(-A_{10}+A_{11}) + \frac{\eta_2}{\lambda_2}A_{11}' + \frac{\eta_3}{\lambda_3}A_{11}''\right] t\exp(-\lambda_1 t), \tag{32}$$

where

$$A_{ik}' = -\frac{\beta_{ik}\eta_k}{\lambda_k}, \qquad A_{i0}' = -\sum_{k=1}^{3} A_{ik}'$$
$$A_{ik}'' = -\frac{\gamma_{ik}\eta_k}{\lambda_k}, \qquad A_{i0}'' = -\sum_{k=1}^{3} A_{ik}'' \tag{33}$$

The magnitudes of the parameters given in Eqs. (30) and (33) depend on the eigenvectors defined in Eq. (10). Let $\mu_{1-j}^{(2)}(t)$ be the solution $\mu_1^{(2)}(t)$ based on the eigenvector $\psi^1(j)$. In this case the magnitudes of $\eta_3 A_{10}''/\lambda_3\lambda_1$ and $\eta_3 A_{11}''/\lambda_3$ are less than other parameters. Thus, the approximate solution is

$$\mu_{1-1}^{(2)}(t) \simeq \frac{\eta_1}{\lambda_1}\frac{A_{10}}{\lambda_1} + \frac{\eta_2}{\lambda_2}\frac{A_{10}'}{\lambda_1}$$
$$+\left[\frac{\eta_1}{\lambda_1}(A_{11}-A_{10}) + \frac{\eta_2}{\lambda_2}A_{11}'\right] t\exp(-\lambda_1 t), \tag{34}$$

Including the higher order terms, we may express an approximate solution for $\mu_{1-1}(t)$ as

$$\mu_{1-1}(t) \simeq \frac{\eta_1}{\lambda_1}\left(1+\frac{A_{10}}{\lambda_1-A_{10}}\right) + \frac{\eta_2}{\lambda_2}\frac{A_{10}'}{\lambda_1}\frac{\lambda_1+A_{10}}{\lambda_1-A_{10}}$$
$$+\left[-\frac{\eta_1}{\lambda_1}\exp(2A_{10}t) + \frac{\eta_2}{\lambda_2}\frac{A_{11}''t}{1-A_{10}t}\right]\exp(-\lambda_1 t) \tag{35}$$

where the series converges only when the following conditions are satisfied:

$$\frac{A_{10}}{\lambda_1} < 1, \qquad 2A_{10}t < 1. \tag{36}$$

Defining the solution for μ_{1-j} as

$$\mu_{1-j}(t) \simeq u_{1-j} + u_{2-j}\ \exp(-\lambda_1 t),$$
$$\mu_{2-j}(t) \simeq u_{1-j}' + u_{2-j}'\ \exp(-\lambda_2 t),$$
$$\mu_{3-j}(t) \simeq u_{1-j}'' \tag{37}$$

the solutions according to the basis eigenvectors are given in the Table 1. With the aid of Eq. (10) we may obtain x_{i-j}. Thus, the general solution for $x_i(t)$ is the linear combination of x_{i-1}, x_{i-2}, and x_{i-3}, that is,

$$x_i(t) = C_{i-1}\ x_{i-1}(t) + C_{i-2}\ x_{i-2}(t) + C_{i-3}\ x_{i-3}\ (t). \tag{38}$$

The coefficients can be obtained by comparing the linear results in Eq. (28) and the numerical linear result from the differential equation solver, subroutine DGEAR of IMSL[8]. As shown in the table, the functions based on the eigenvector $\psi^i(1)$ have the same form as the functions based on $\psi^i(2)$. However, the magnitudes are quite different. Comparing the linear results, we obtain x_i's approximately as

$$x_1(t) \cong 2.0x_{1-1} + 0.0010x_{1-3},$$
$$x_2(t) \cong -1.5\times10^{-5}x_{1-2},$$
$$x_3(t) \cong 0.013x_{3-1} - 1.3x_{3-3}, \tag{39}$$

Table 1. The Functions Based on the Eigenvectors

eigenvector \ Function	u_{1-j}	u_{2-j}	u_{1-j}'	u_{2-j}'	u_{2-j}''
$\psi^i(1)$	$\frac{\eta_1}{\lambda_1}\left(1+\frac{A_{10}}{\lambda_1-2A_{10}}\right)$	$-\frac{\eta_1}{\lambda_1}\exp(2A_{10}t)$	$\frac{\eta_2}{\lambda_2}\left[1+\frac{2A_{20}'}{\lambda_2}\right.$	$-\frac{\eta_2}{\lambda_2}$	$\frac{\eta_3}{\lambda_1}+\frac{\eta_1}{\lambda_1}\frac{A_{30}}{\lambda_3}\frac{\lambda_1}{\lambda_1-A_{10}}$
$\psi^i(2)$	$+\frac{\eta_2}{\lambda_2}\frac{A_{10}'}{\lambda_1}\frac{\lambda_1+A_{10}}{\lambda_1-A_{10}}$	$+\frac{A_{11}'}{1-A_{11}'t}t+A_{11}'t$ $-\ln(1+A_{11}'t)$	$\left.\times\left(1+\frac{A_{10}}{\lambda_2}\frac{\lambda_2}{\lambda_2+2A_{20}}\right)\right]$	$\times\exp(2A_{20}'t)$	$+\frac{\eta_2}{\lambda_2}\frac{A_{30}'}{\lambda_3}\frac{\lambda_1}{\lambda_1-A_{10}}$
$\psi^i(3)$	$\frac{\eta_3}{\lambda_1}+\frac{\eta_1}{\lambda_3}$ $\times\left[1+\frac{\lambda_1 A_{10}}{(\lambda_1-A_{10})^2}\right]$	The same as the above.	$\frac{\eta_2}{\lambda_2}\left[1+\frac{A_{20}'}{\lambda_2}\frac{\lambda_1}{(\lambda_1-A_{10})}\right]$ $+\frac{\eta_3}{\lambda_3}\frac{A_{20}'}{\lambda_2-A_{30}'}$	The same as the above.	$\frac{\eta_3}{\lambda_3}+\frac{\eta_1}{\lambda_1}\frac{A_{30}}{\lambda_3-A_{30}''}$

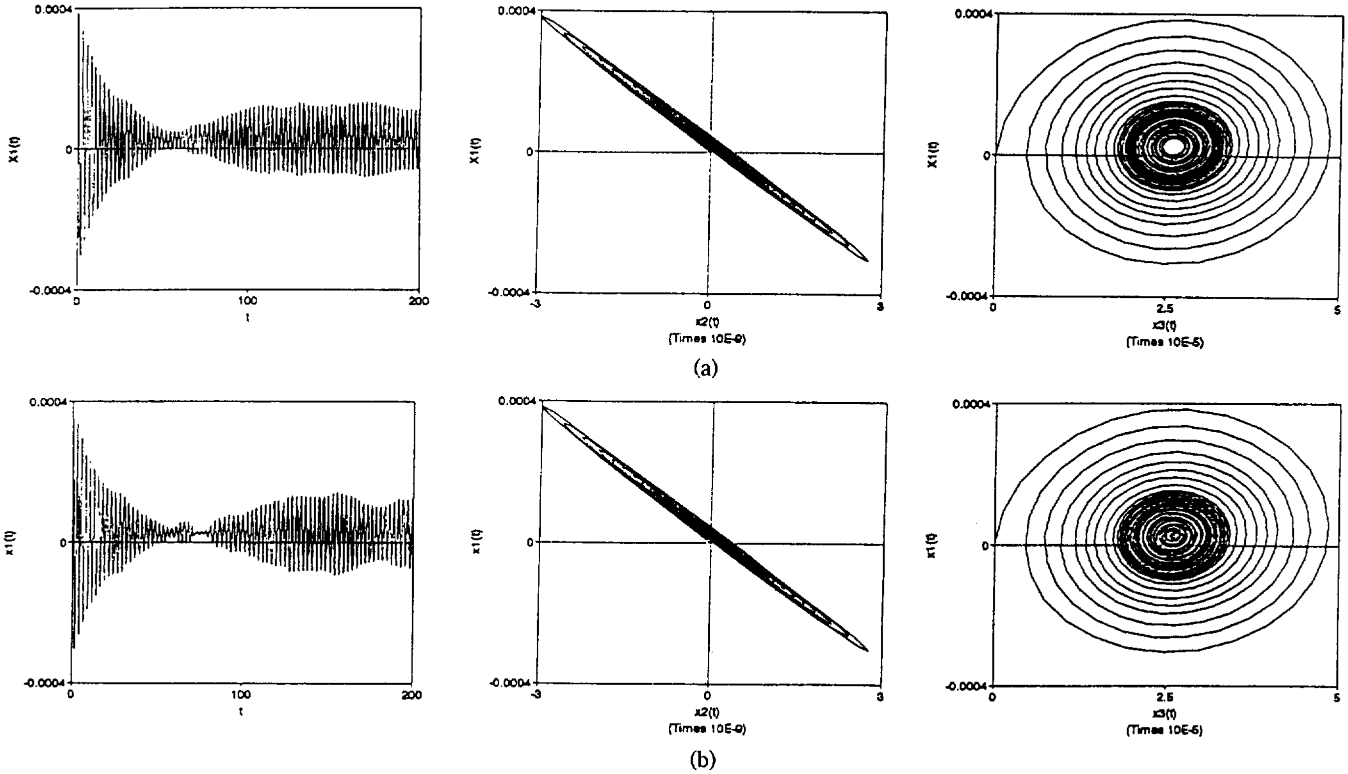

Figure 1. The oscillation of the system far from the bifurcation point under constant input with $\xi=0.001$. (a) approximate and (b) numerical results.

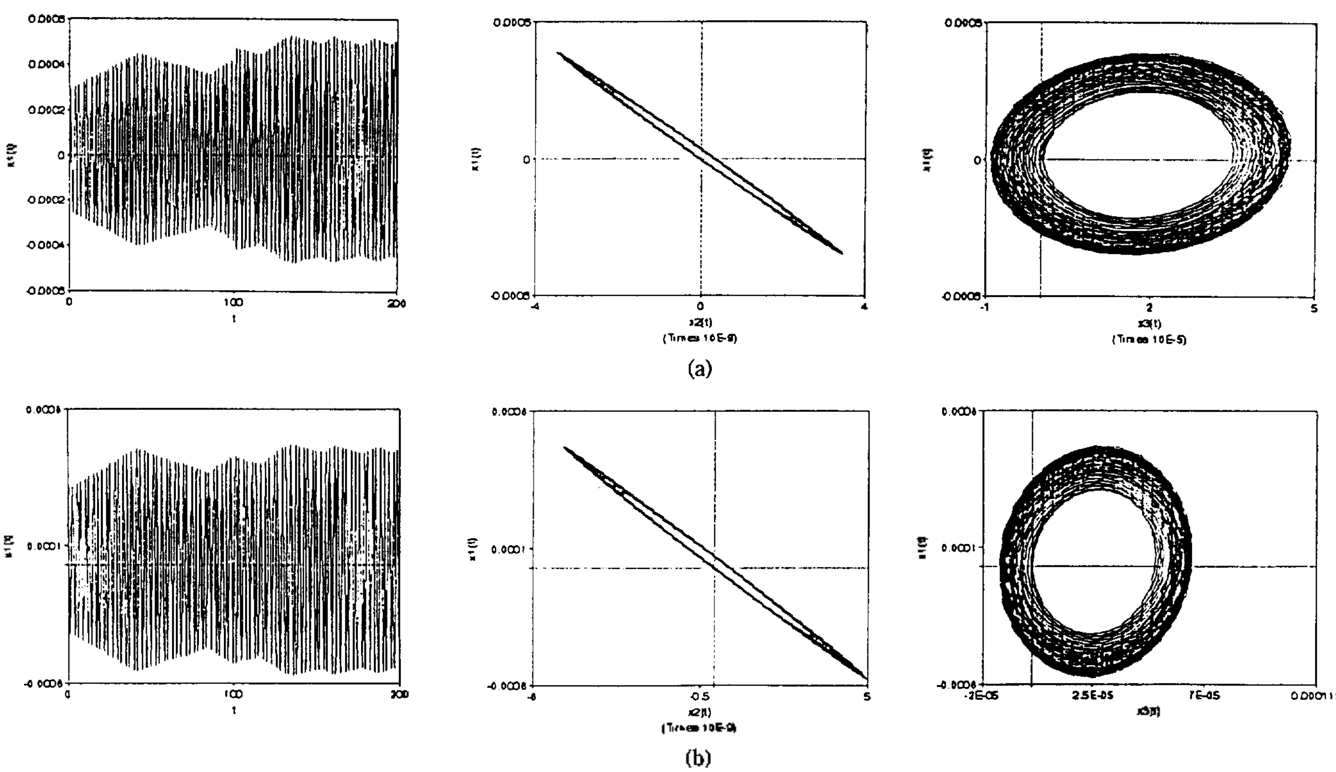

Figure 2. The oscillation of the system extremely close to the bifurcation point under constant input with $\xi=0.001$. (a) approximate and (b) numerical results.

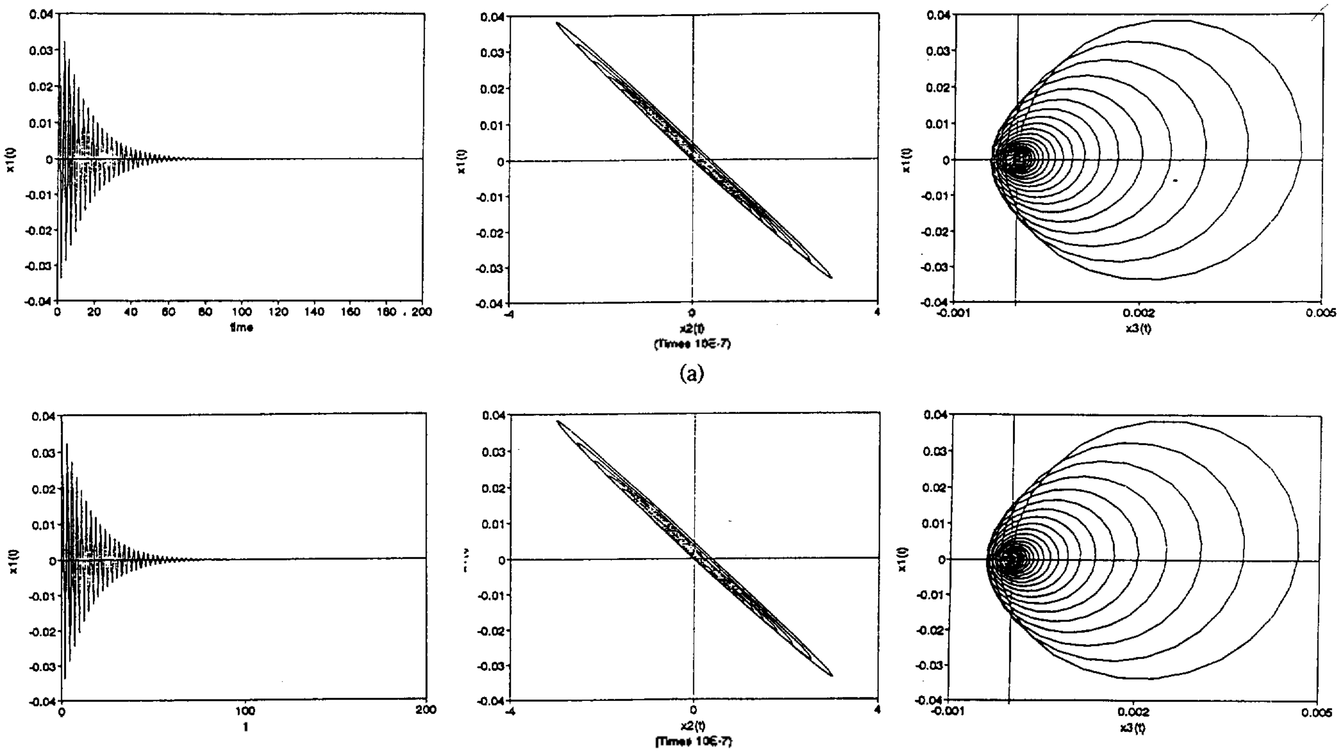

Figure 3. The oscillation of the system far from the bifurcation point under exponentially decaying input with $\xi=0.1$ and $\kappa=0.1$. (a) approximate and (b) numerical results.

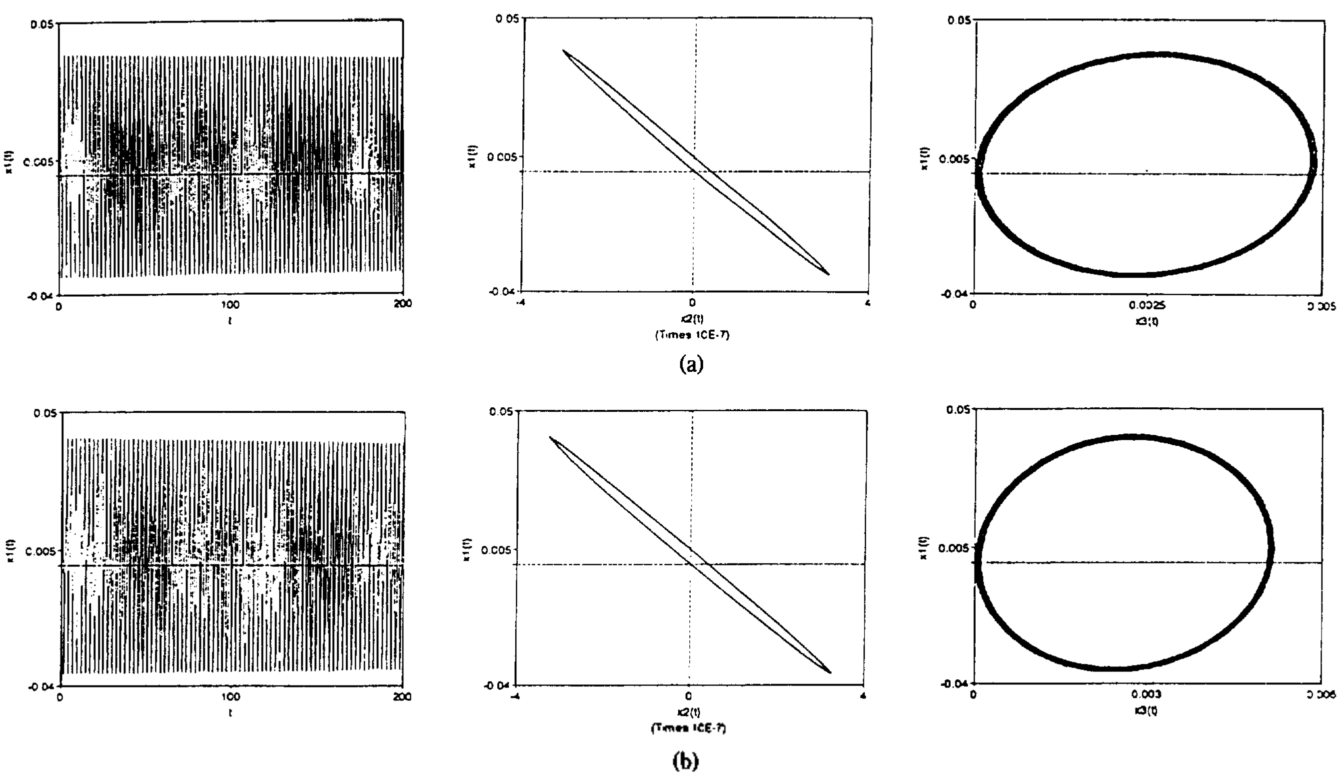

Figure 4. The oscillation of the system extremely close to the bifurcation point under exponentially decaying input with $\xi=0.1$ and $\kappa=0.1$. (a) approximate and (b) numerical results.

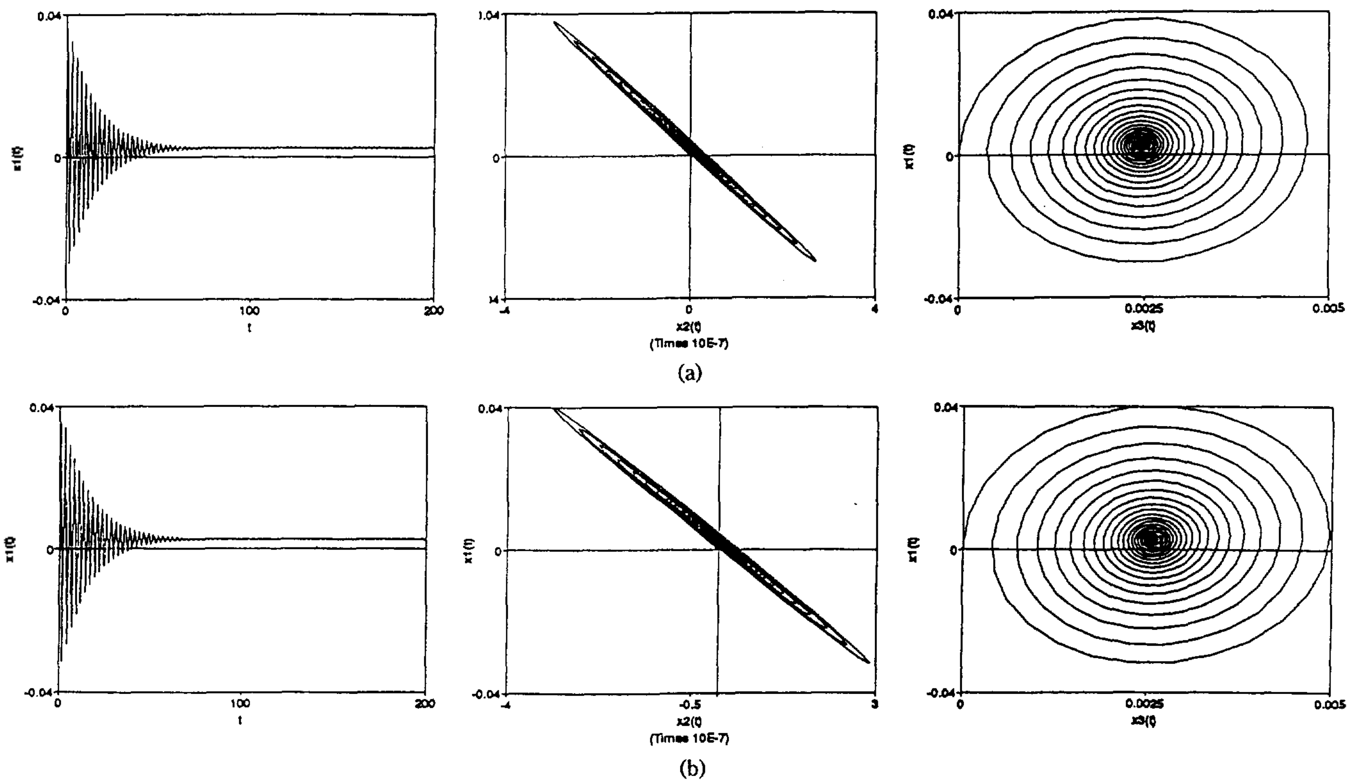

Figure 5. The oscillation of the system far from the bifurcation point under periodic input with $\xi=0.1$ and $\omega=2$. (a) approximate and (b) numerical results.

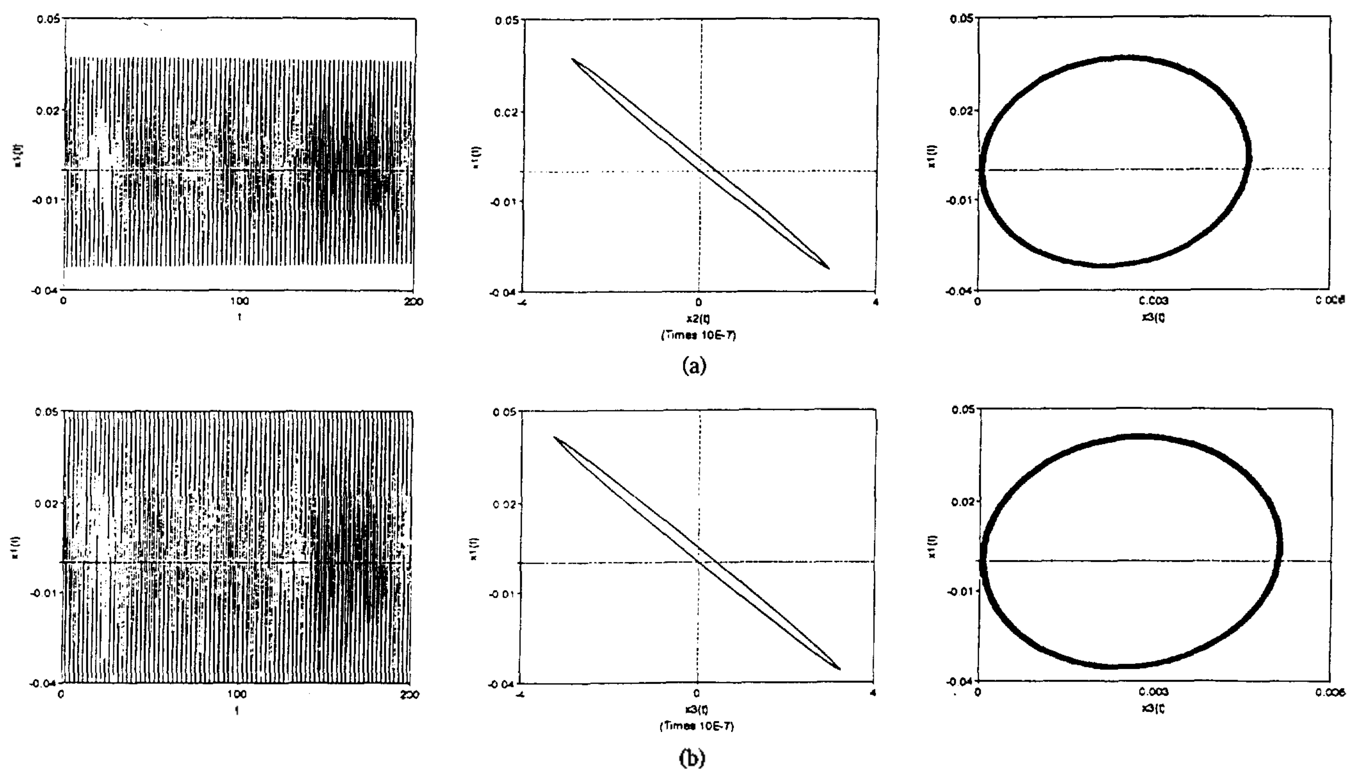

Figure 6. The oscillation of the system extremely close to the bifurcation point under periodic input with $\xi=0.1$ and $\omega=2$. (a) approximate and (b) numerical results.

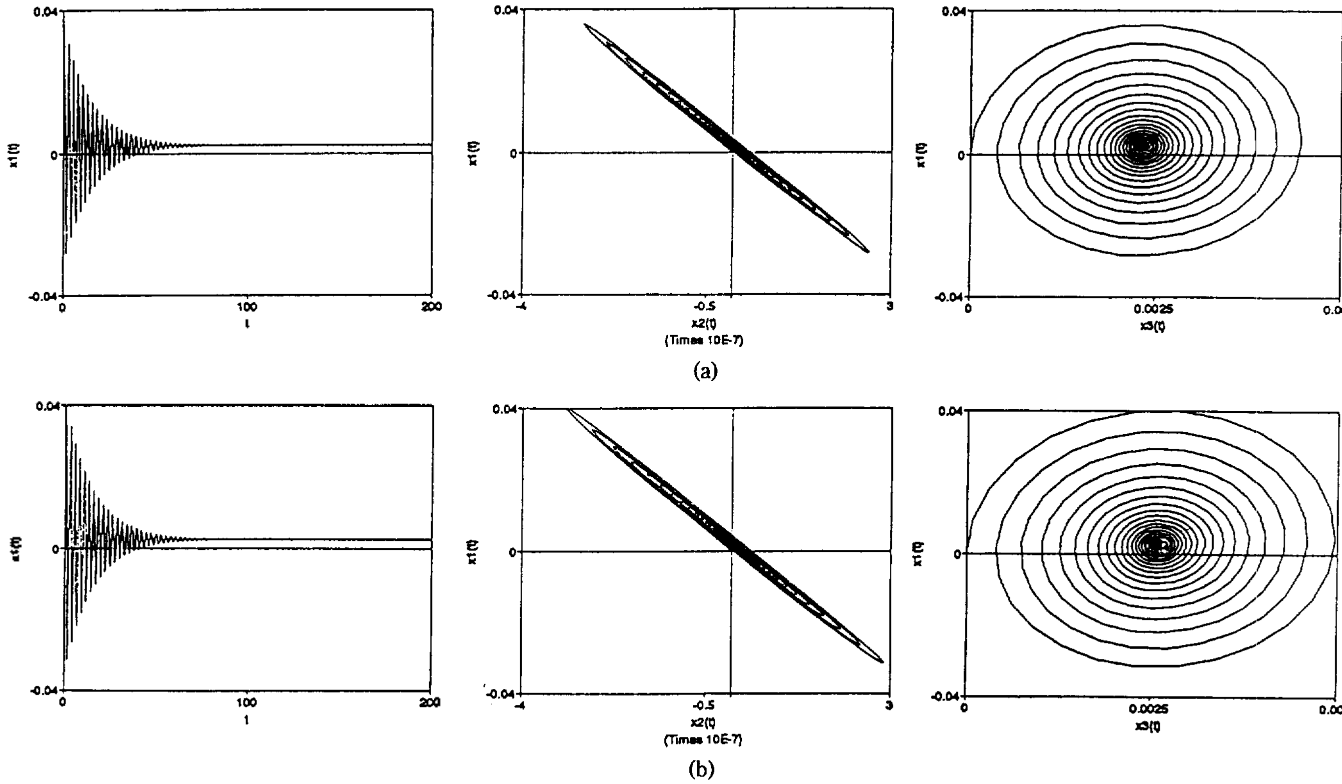

Figure 7. The oscillation of the system far from the bifurcation point under periodic input with $\xi=0.1$ and $\omega=2.5$. (a) approximate and (b) numerical results.

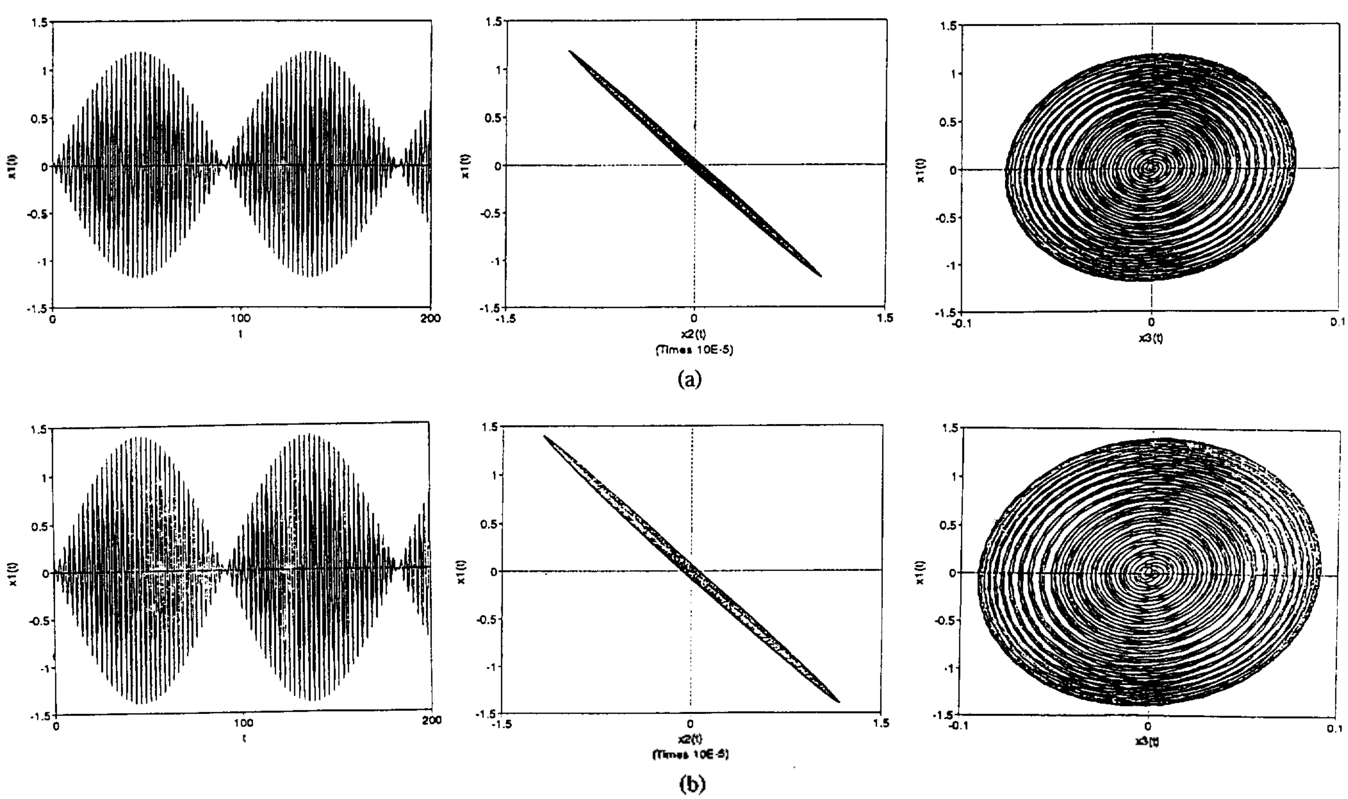

Figure 8. The oscillation of the system extremely close to the bifurcation point under periodic input with $\xi=0.1$ and $\omega=2.5$. (a) approximate and (b) numerical results.

With the aid of the above result the approximate result for the system far from the bifurcation point is given in Figure 1 and compared with the numerical result. From now on the first figures in (a) and (b) show $x_1(t)$ as the function of time and the second and third figures represent the phase trajectories between x_1 and x_2, and x_1 and x_3, respectively. The figures show that the approximate results deviate a lot from the exact numerical solutions. The main reasons for the difference are that the approximate results are oversimplified and hold in the long time region. In spite of the difference both results show similar trend, that is the approach to the new stable focus[6]. In the case of the system extremely close to the bifurcation point it takes very long time to arrive at the stable focal point. This behavior can be seen most clearly in the x_1 *vs.* x_3 phase trajectory (see Figure 2).

Exponentially decaying input. When the system is perturbed by a decaying input, the oscillations of the system are quasi-periodic. In this case, the linear solution is

$$\mu_i(t)=\frac{\eta_i}{\lambda_i-\kappa}[\exp(-\kappa t)-\exp(-\lambda_i t)] \tag{40}$$

When the system is far from the bifurcation point, the oscillation decays very rapidly and approaches to 0, as shown in Figure 3, since all the modes have decaying exponential form. If the system is very close to the critical point, the oscillation is decaying periodic for some time and then becomes periodic due to the internal modes (see Figure 4).

Periodic input. If the response of the nonlinear oscillating system to the periodic input is also periodic with the external input, the response is called the entrainment[7]. The entrainments are shown in Figures 5-8.

When the system is far from the bifurcation point, the oscillations are decaying periodic for some time and then becomes periodic due to the external modes (see Figures 5 and 7). The phenomena are independent of the difference between the external and internal frequencies. Of course, the period depends on the external frequency.

For the system extremely close to (and at) the bifurcation point the oscillating phenomena severely depend on the difference between the internal and external frequencies. When the difference is large, the oscillation is simply periodic as given in Figure 6. If the difference is very small compared with the internal frequency, the phenomenon of beats oscillation occurs as shown in Figure 8[6].

We have discussed the responses of the Oregonator to some kinds of external input. Let us summarize the important results.

(1) For the case of a constant input, the oscillation is simple and thus may be expressed by a simple approximate nonlinear solution, even though there is some quantitative difference. It is very difficult to improve the result by including minor effects. The system at any state approaches to the new focal point[6].

(2) When the system far from (and extremely close to (and at) the bifurcation point is perturbed by decaying input, the oscillation transits from a quasi-periodic to simply decaying to (periodic around) the original steady state.

(3) For periodic input, the entrainment severely depends on the difference between the internal and external frequencies for the Oregonator extremely close to (and at) the bifurcation point[6]. Far from the bifurcation point the entrainment is simply periodic, its period being dependent on the external frequency.

Acknowledgement. This work was supported by a grant (No. BSRI-91-311) from the Basic Science Research Program, Ministry of Education of Korea, 1991.

References

1. Houard, J. C. *Lett. Nuovo Cimento*, **1982**, *33*, 519.
2. Houard, J. C.; Irac-Astaud, M. *J. Math. Phys.* **1983**, *24*, 1997.
3. Houard, J. C.; Irac-Astaud, M. *J. Math. Phys.* **1984**, *25*, 3451.
4. Ryu, M. H.; Lee, D. J.; Kim, I. D. *Bull. Korean Chem. Soc.* **1991**, *12*, 383.
5. Schlögl, F. *Z. Physik*, **1972**, *263*, 147.
6. Yang, M.; Lee, S.; Kim, S. K.; Shin, K. J.; Ryu, M. H.; Lee, S. H.; Lee, D. J. *Bull. Korean Chem. Soc.* **1992**, *13*, 560.
7. Field, R. J.; Burger, M. *Oscillations and Travelling Waves in Chemical Systems*; John Wiley & Sons: New York, 1985. and a lot of references therein.
8. International Mathematical and Statistical Libraries, Inc., *IMSL Library Reference Manual*; 9th ed; Houston, Texas; **1982**.
9. Field, R. J.; Körös, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649.
10. Field, R. J.; Noyes, R. M. *J. Chem. Phys.* **1974**, *60*, 1877.