A Nonlinear Theory for the Lotka-Volterra Model with an External Input

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A new perturbation theory called the star expansion method is used to obtain an approximate nonlinear solution of the Lotka-Volterra model under the influence of some kinds of external input. The effects of nonlinearity, amplitude and frequency of the external input on the chemical oscillations in the model are evaluated by taking specific values for the model parameters, and the results are discussed in detail.

Introduction

By using the star expansion method, originally proposed by Houard and his coworker[1-3], two of us[4] have recently obtained approximate nonlinear solutions for the Schlögl model[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.

The purpose of the present paper is to extend the method[4] to the Lotka-Volterra model[6], which exhibits the sustained oscillation near the steady state. In section II, we first transform the equations arising in the Lotka-Volterra model with an external input such a way that the linear coupling term becomes diagonalized. Extending the results in ref. 4, we then obtain an approximate nonlinear solution in a straightforward way. In section III, we calculate the numerical results by taking specific values for the model parameters, and discuss in detail the response of the concentrations of intermediates to the external input. Linear stability analysis of the Lotka-Volterra model under a constant input reveals that the stability of the steady state is changed from marginally stable state to stable state.

Theory

The Lotka-Volterra model is one type of chemical reaction mechanisms that exhibits the sustained oscillation[6] with internal frequency, $\Omega=(k_1k_3A)^{1/2}$, and is expressed as

$$A+X\xrightarrow{k_1}2X,\ X+Y\xrightarrow{k_2}2Y,\ \text{and}\ Y\xrightarrow{k_3}P. \tag{1}$$

Here k's are the rate constants, and A and P are the reactant and product, respectively. The concentrations of the reactant and product, which will be denoted also as A and P for the brevity of notation, are assumed to be controlled externally. The concentrations of intermediates are governed by the deterministic rate equations,

$$\frac{d}{dt'}X=k_1AX-k_2XY,\ \text{and}\ \frac{d}{dt'}Y=k_2XY-k_3Y, \tag{2}$$

with the nonvanishing steady values given by

$$X^\circ=k_3/k_2,\quad\text{and}\quad Y^\circ=k_1A/k_2 \tag{3}$$

We suppose that the system deviates from the steady state due to an external input, $\phi_i(t')$ ($i=x$ or y) at time $t'=0$. To study the nonlinear response of the system it is convenient to define a new set of dimensionless variables such as

$$\begin{gathered} t=(k_1k_3A)^{1/2}t',\qquad s=(k_1A/k_3)^{-1/2}\\ x_1(t)=X(t)/X^\circ-1,\qquad x_2(t)=Y(t)/Y^\circ-1\\ \xi_1(t)=(k_2/k_3^2)s\phi_x(t),\qquad \xi_2(t)=(k_2/k_1k_3A)s\phi_y(t)\\ \omega_o\equiv\Omega(k_1k_3A)^{-1/2}=1. \end{gathered}\tag{4}$$

Rewriting Eq. (2) in these reduced variables, we obtain

$$\frac{d}{dt}\begin{bmatrix}x_1\\x_2\end{bmatrix}=M\cdot\begin{bmatrix}x_1\\x_2\end{bmatrix}+A\cdot\begin{bmatrix}x_1\\x_2\end{bmatrix}+\begin{bmatrix}\xi_1\\\xi_2\end{bmatrix}\tag{5}$$

where

$$M=\begin{bmatrix}0&-s^{-1}\\s&0\end{bmatrix}\ \text{and}\ A=\begin{bmatrix}-s^{-1}x_2&0\\0&sx_1\end{bmatrix}.$$

The left and the right eigenvectors of M can be used to form transformation matrices that convert M into diagonal form. With the transformation, Eq. (5) becomes

$$\frac{d}{dt}\begin{bmatrix}y\\y^*\end{bmatrix}=\begin{bmatrix}i&0\\0&-i\end{bmatrix}\cdot\begin{bmatrix}y\\y^*\end{bmatrix}+B+\begin{bmatrix}\xi\\\xi^*\end{bmatrix}\tag{6}$$

where

$$B=\frac{1}{2}\begin{bmatrix}(i+s)[y^2-(y^*)^2]\\(i-s)[y^2-(y^*)^2]\end{bmatrix},$$

$$\begin{bmatrix}y\\y^*\end{bmatrix}=\frac{1}{2}\begin{bmatrix}1&i/s\\1&-i/s\end{bmatrix}\cdot\begin{bmatrix}x_1\\x_2\end{bmatrix},\ \begin{bmatrix}\xi\\\xi^*\end{bmatrix}=\frac{1}{2}\begin{bmatrix}1&i/s\\1&-i/s\end{bmatrix}\cdot\begin{bmatrix}\xi_1\\\xi_2\end{bmatrix}\tag{7}$$

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Here, asterisk denotes the complex conjugate. To eliminate the linear term, we replace $y(t)$ by

$$y(t)=\exp(-it)z(t). \tag{8}$$

Then the matrix equation, Eq. (6), can be decomposed into the component equations as

$$\frac{d}{dt}z(t)=\alpha(t)[z(t)]^2+\beta(t)[z^*(t)]^2+\eta(t) \tag{9}$$

$$\frac{d}{dt}z^*(t)=\alpha^*(t)[z^*(t)]^2+\beta^*(t)[z(t)]^2+\eta^*(t) \tag{10}$$

where

$\alpha(t)=[(s+i)/2]\exp(it),\ \beta(t)=-[(s+i)/2]\exp(-3it);$

$\eta(t)=\exp(-it)\zeta(t).$

We can solve Eq. (9) and (10) approximately by adapting the propagator, originally developed for a one-component system with quadratic nonlinear term in ref. 3. The formal solution of Eq. (9) is given as

$$z(t)=M_o(t,\ \tau)K(t,\ \tau) \tag{11}$$

where the operator $M_o(t,\tau)$ and the propagator $K(t,\tau)$ are defined, respectively, by

$$M_o(t,\ \tau)\equiv\int_0^t d\tau\,\eta(\tau)+\int_0^t d\tau\,\beta(\tau)[z^*(\tau)]^2 \tag{12}$$

and

$$K(t,\ \tau)\equiv\exp\left[\int_\tau^t d\tau'\alpha(\tau')z(\tau')\right] \tag{13}$$

The propagator $K(t,\tau)$ satisfies the following differential equation:

$$\frac{d}{d\tau}K(t,\ \tau)=-\alpha(\tau)z(\tau)K(t,\ \tau). \tag{14}$$

Inserting the expression of $z(t)$ given by Eq. (11) into Eq. (14), we obtain

$$\frac{d}{d\tau}K(t,\ \tau)=-\alpha(\tau)M_o(t,\ \tau_1)K(\tau,\ \tau_1)K(t,\ \tau). \tag{15}$$

With the help of the composition relations[3],

$$K(\tau,\ \tau_1)=K(t,\ \tau_1)K(\tau,\ t)$$

and

$$K(t,\ \tau)K(\tau,\ t)=K(\tau,\ t)K(t,\ \tau)=1,\ \forall t,\ \tau,\ \tau_1, \tag{16}$$

we get

$$\frac{d}{d\tau}K(t,\ \tau)=-\alpha(\tau)M_o(\tau,\ \tau_1)K(t,\ \tau_1). \tag{17}$$

Integrating this equation gives

$$\begin{aligned}K(t,\ \tau)&=1+\int_\tau^t d\tau'\alpha(\tau')M_o(\tau',\ \tau_1)K(t,\ \tau_1)\\&=1+\int_\tau^t d\tau'\alpha(\tau')\int_0^{\tau'}d\tau_1\{\eta(\tau_1)+\beta(\tau_1)[z^*(\tau_1)]^2\}K(t,\ \tau_1).\end{aligned} \tag{18}$$

Permuting the integrations, Eq. (18) becomes

$$K(t,\ \tau)=1+M(t,\ \tau,\ \tau_1)K(t,\ \tau_1) \tag{19}$$

where the operator, $M(t,\tau,\tau_1)$, is defined by

$$M(t,\ \tau,\ \tau_1)\equiv M_o(t,\ \tau_1)\int_{\sup(\tau,\ \tau_1)}^t\alpha(\tau')d\tau' \tag{20}$$

By an iterative procedure, we may obtain a series solution for $K(t,\tau)$ as

$$K(t,\ \tau)=\sum_{n=0}^\infty K_n(t,\ \tau) \tag{21}$$

where

$$K_n(t,\ \tau)=\left[\prod_{m=1}^{n}{}' M(t,\ \tau_{m-1},\ \tau_m)\right]K_o(t,\ \tau_n)\ \text{ for } n\geq 1 \tag{22}$$

and

$$K_o(t,\ \tau)\equiv 1.$$

Here, the prime on the product denotes index ordering and $\tau_{m=0}=\tau$.

Substituting Eq. (21) into Eq. (11), we obtain $z(t)$ as

$$z(t)=\sum_{n=0}^\infty Z_n(t) \tag{23}$$

where

$$Z_n(t)\equiv M_o(t,\ \tau)K_n(t,\ \tau). \tag{24}$$

If the amplitude of an external input is weak and consequently $|z^*(t)|$ is much less than one, we can approximate $z^*(\tau)$ in the expression of $M_o(t,\tau)$ [Eq. (12)] as the leading term of the formal solution of Eq. (11) which becomes

$$z^*(t)\cong\int_0^t d\tau\,\eta^*(\tau).$$

$Z_n(t)$ satisfies the following recursion relation:

$$\frac{d}{dt}Z_n(t)=n\,\alpha(t)Z_{n-1}(t)Z_0(t) \tag{25}$$

whose validity can be verified easily by differentiating the expression of $Z_n(t)$, Eq. (24). It will be more convenient to use Eq. (25) rather than Eq. (22).

Discussion

In this section we will discuss the responses of the system to several kinds of external input by taking specific values of the parameters. The kinds of external input to be considered are

$\xi_1(t)=\xi_2(t)=\xi$: constant input (A)

$\xi_1(t)=\xi_2(t)=\xi\exp(-\gamma t)$: exponentially decaying input (B)

$\xi_1(t)=\xi_2(t)=\xi\sin(\omega t)$: periodic input (C)

The time region where the series solution, Eq. (23), converges depends on the values of the control parameters, s, ξ, γ, and ω. When the amplitude of the external input is small, the series solution converges up to fairly large time. If the amplitude of the external inupt is very weak, our approximate solution taken to the second order term shows nearly complete coincidence with the numerical result. However, when the external input has a sizable magnitude, the series solution diverges eventually in th long time limit. Hence the validity of the star expansion method would be restricted to a short time region in such cases. Since the number of terms appearing in each order of the series soliution is very large and the manipulation of them requires a lengthy algebra, we include in the calculation only the zeroth order and the first order, and the dominating parts of the second order terms of the solution. The remaining parts of the second order terms and the higher order terms are neglected.

In each figure, the results of our approximate solution are displayed in part (a) and the numerical results obtained by using the differential equation solver, subroutine DGEAR of IMSL[7], in part (b).

Constant Input. When the external input is constant, a steady state is attained at long times. For this steady state, $dx_1/dt=0$ and $dx_2/dt=0$. Therefore, the equation we have to solve, *i.e.*, Eq. (5) becomes

$$M\cdot\begin{bmatrix} x_1^s \\ x_2^s \end{bmatrix}+A\cdot\begin{bmatrix} x_1^s \\ x_2^s \end{bmatrix}+\begin{bmatrix} \xi \\ \xi \end{bmatrix}=\begin{bmatrix} 0 \\ 0 \end{bmatrix}. \tag{26}$$

Here, x_1^s and x_2^s denote the steady-state values of x_1 and x_2 attained at long times under a constant input. x_1^s and x_2^s can be obtained easily by a simple algebra as following:

$$x_1^s=[-a\pm(a^2-4\xi/s)^{1/2}]/2,\quad x_2^s=[a-2\pm(a^2-4\xi/s)^{1/2}]/2 \tag{27}$$

where $a\equiv 1+(s+1/s)\xi$. Here, a, ξ, and s are all positive and so x_1^s is always negative, that is, at the newly attained steady state the concentration of the species X should be less than X°[see Eq. (3)]. There are two available steady states under a constant input. However, one of them will be shown to be unstable by the linear stability analysis.

We will briefly argue about the local stability of the newly attained steady state. To determine the local stability of a given steady state we need to know whether infinitesimally small perturbations of the system about that state will grow or decay. Suppose that a given steady state is perturbed by an external or an internal fluctuation. Then, the reduced concentrations X and Y become

$$x_1(t)=x_1^s+x_1',\quad x_2(t)=x_2^s+x_2' \tag{28}$$

where $x_1'\ll 1$ and $x_2'\ll 1$. Substituting Eq. (28) into Eq. (5) and neglecting the squares and higher-order powers of x_1' and x_2' because of the assumption that the perturbations is infinitesimally small, we obtain the following equation:

$$\frac{d}{dt}\begin{bmatrix} x_1' \\ x_2' \end{bmatrix}=J\cdot\begin{bmatrix} x_1' \\ x_2' \end{bmatrix} \tag{29}$$

where

$$J\equiv\begin{bmatrix} -s^{-1}x_2^s & -s^{-1}(1+x_1^s) \\ s(1+x_2^s) & sx_1^s \end{bmatrix} \tag{30}$$

The local stability of the system is determined by the eigenvalues of the matrix J. The eigenvalues λ_1 and λ_2 are given by the roots of the quadratic equation

$$\lambda^2-tr(J)\lambda+\det(J)=0, \tag{31}$$

that is,

$$\lambda_1=[\mathrm{tr}(J)+\{tr(J)^2-4\det(J)\}^{1/2}],$$
$$\lambda_2=[\mathrm{tr}(J)-\{tr(J)^2-4\det(J)\}^{1/2}] \tag{32}$$

where $tr(J)$ is the trace of J,

$$tr(J)=sx_1^s-s^{-1}x_2^s \tag{33}$$

and $\det(J)$ is the determinant of J,

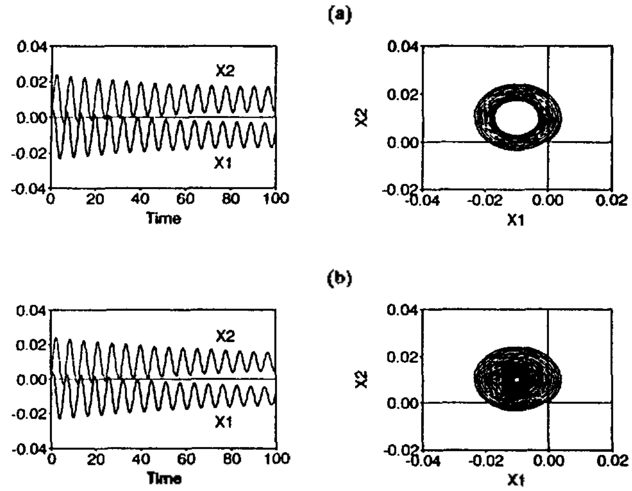

Figure 1. The oscillation under constant input with $s=1.0$, $\xi=0.01$.

$$\det(J)=1+x_1^s+x_2^s=\pm(a^2-4\xi/s)^{1/2}.\quad (a^2-4\xi/s>0) \tag{34}$$

Here, two signs of $\det(J)$ come from two steady states. One of two steady states with the plus sign in Eq. (27) has the negative sign of $\det(J)$ and therefore λ_1 must be positive. In this case the steady state is unstable and so it cannot be attained.

The stability of the steady state with the minus sign depends only on the sign of $tr(J)$ since $\det(J)>0$. In the Appendix, we show that the sign of $tr(J)$ is always negative regardless of the magnitude of external input and the system parameter, s, or the concentration of precursor, A. Therefore, we expect the steady state attained under a constant external input to show the behavior of stable focus (damped oscillatory approach) or stable node (monotonic approach). The discriminant,

$$\Delta=tr(J)^2-4\det(J) \tag{35}$$

is the criterion of the behavior, that is, a stable node prevails when $\Delta\geq 0$ and a stable focus does when $\Delta<0$. The curve satisfying $\Delta=0$ in $\xi-s$ parameter plane is the boundary between node and focus. The expression for the boundary curve is rather complicated and, therefore, it is not algebraically tractable but it can be easily computed numerically.

Figure 1 shows the system under a constant input has a stable focal point attained at long times which is displaced from that of the unperturbed system. The analytic value of the focal point is given as $x_1^s=-0.0099$ and $x_2^s=0.0101$ by Eq. (27) and $\Delta<0$ when the model parameters in Figure 1 are used. The temporal oscillation is decaying quasi-periodic approaching the focal point. The numerical result shows that the focal point at long times agrees with the analytic result. Our approximate result shows the tendency of approaching the focal point but it starts to diverge at about $t=100$ and the trajectory is truncated at $t=100$ in Figure 1(a). If we include higher order terms in our solution, it will show a better agreement with the numerical result. The zeroth order solution has the following expression:

$$Z_0(t)=\xi[1-\exp(-it)]$$
$$-(s+i)\xi^2[\{1-\exp(-3it)\}/3$$

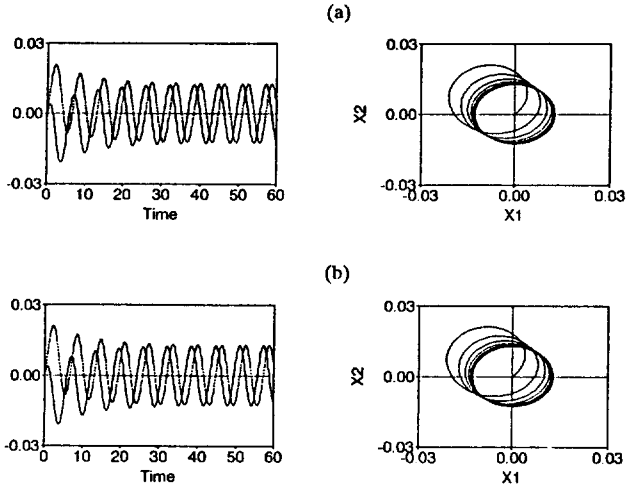

Figure 2. The oscillation under exponentially decaying input with the parameters, $s=1.0$, $\xi=0.01$, and $\gamma=0.1$. Solid line: $x_1(t)$, Dashed line: $x_2(t)$

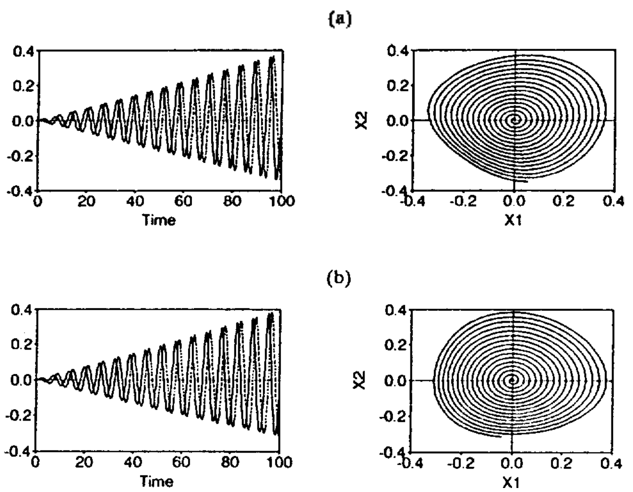

Figure 3. The entrainment with $s=1.0$, $\omega=1.0$, and $\xi=0.005$. Solid line: $x_1(t)$, Dashed line: $x_2(t)$

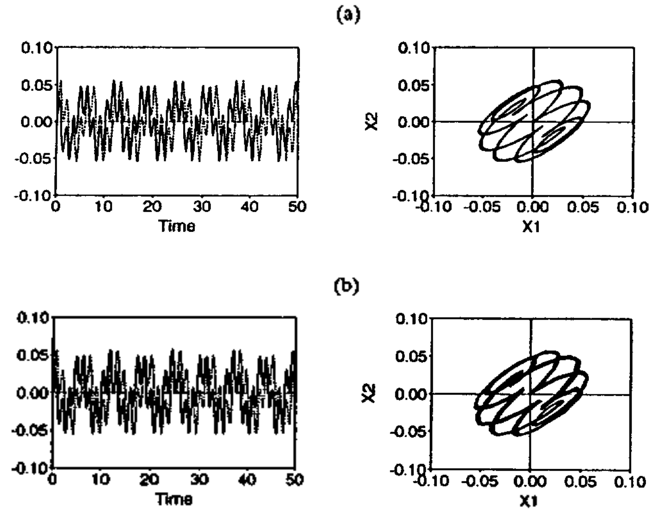

Figure 4. The entrainment with $s=1.0$, $\omega=4.5$, and $\xi=0.1$. Solid line: $x_1(t)$, Dashed line: $x_2(t)$

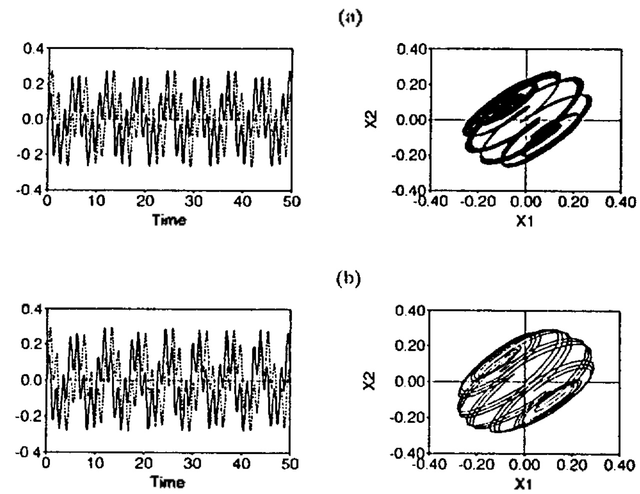

Figure 5. The distorted entrainment with $s=1.0$, $\omega=4.5$, and $\xi=0.5$. Solid line: $x_1(t)$, Dashed line: $x_2(t)$

$$-\{\exp(-it)-\exp(-2it)\}]/2 \tag{36}$$

The first and the higher order terms are complicated and, therefore, they are omitted here.

Exponentially Decaying Input. When the system is perturbed by a decaying input, the oscillation of concentration is temporally quasi-periodic. However, after a decay time, γ^{-1}, the concentrations of intermediates oscillate periodically with internal frequency, ω_o. The response of the system to a decaying input is displayed in Figure 2. In the case of an exponentially decaying input, the zeroth order solution becomes

$$\begin{aligned} Z_0(t)=&\eta[1-\exp(-(\gamma+i)t)]-(s+i)(\eta^*)^2 \\ &\times[\{1-\exp(-3it)\}/3i \\ &-2\{1-\exp(-(\gamma+2i)t)\}/(\gamma+2i) \\ &+\{1-\exp(-(2\gamma+i)t)\}]/(2\gamma+i)]/2 \end{aligned} \tag{37}$$

where $\eta\equiv\xi(\gamma-i)(s+i)/2s/(\gamma^2-1)$.

Periodic Input. If the response of the nonlinear oscillating system to the periodic perturbation is also periodic with the external frequency, the response is called as the entrainment [8]. The entrainments are shown in Figures 3-6.

When the external input is periodic, the perturbative solutions take the different expressions regarding the external frequency, ω. By Eq. (24), the zeroth order solution is given as

$$Z_0=\eta_o(t)+\beta_o(t) \tag{38}$$

where

$$\eta_o(t)\equiv\int_0^t d\tau\ \eta(\tau);\ \beta_o\equiv\int_0^t d\tau\ \beta(\tau);\ \left[\int_0^\tau d\tau'\eta^*(\tau)\right]^2. \tag{39}$$

with

$$\begin{aligned} \eta(t)=&(\xi/4)(s^{-1}-i)\{\exp[-i(1-\omega)t] \\ &-\exp[-i(1+\omega)t]\} \end{aligned} \tag{40}$$

which gives a different functional dependence on t under the integration in the case of $\omega=\pm1$ from the other cases

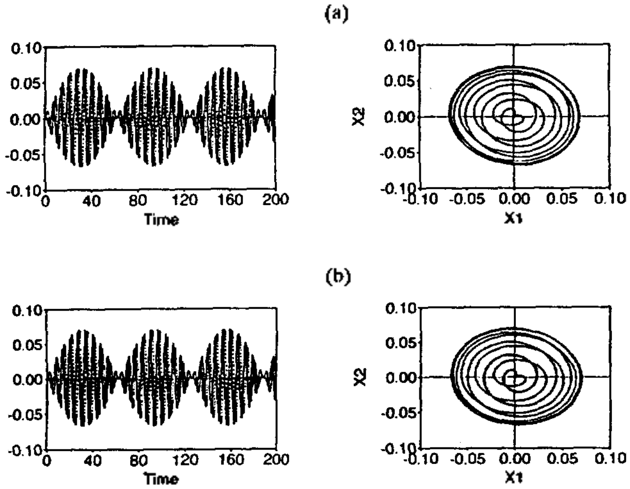

Figure 6. The beats oscillation with $s=1.0$, $\omega=0.9$, and $\xi=0.005$. Solid line: $x_1(t)$, Dashed line: $x_2(t)$

of $\omega\neq\pm 1$. In addition to the case of $\omega=\pm 1$, a similar behavior can be observed in other specific cases of $\omega=\pm 2$, $\omega=\pm 1/2$, $\cdots$ in each order term. So we must carefully calculate the perturbative solution case by case. Taking a typical example, we in Figure 3, display the response of the system when $\omega=1$, *i.e.*, when the external frequency is the same as the internal frequency. The zeroth order term of our approximate solution when $\omega=1$ (resonant case) is

$$\eta_o(t)=\xi(s^{-1}-i)[t-\{1-\exp(-2it)\}/2i]/4, \tag{41}$$

$$\beta_o(t)=-(s+i)(\xi/4)^2(s^{-1}-i)^2[(it^2/3+5t/9-29i/108)\exp(-3it)-(t-3i/2)\exp(-it)+i\exp(it)/4-174i/108].$$

which reveals that the amplitude of chemical oscillation will be increased with time because of the presence of the power terms of t.

When $\omega\neq\pm 1$, $\pm 1/2$, and ± 2, the zeroth order solution is

$$\eta_o(t)=\xi(s^{-1}-i)[(1-\exp(-\omega_-t))/\omega_- -(1-\exp(-\omega_+t))/\omega_+]/4, \tag{42}$$

$$\begin{aligned}\beta_o(t)=&-(s+i)\{\xi(s^{-1}-i)4\}^2[\omega_d^2\{1-\exp(-3it)\}/3i\\&+\{1-\exp(-(1-2\omega)it)\}/(i\omega_+^2(1-2\omega))\\&+\{1-\exp(-(1+2\omega)it)\}/(i\omega_-^2(1+2\omega))\\&+2\omega_d\{1-\exp(-(2-\omega)it)\}/(i\omega_+(2-\omega))\\&-2\omega_d\{1-\exp(-(2-\omega)it)\}/(i\omega_-(2+\omega))\\&-2\{1-\exp(-it)\}/(i\omega_-\omega_+)]/2\end{aligned}$$

with

$$\omega_-\equiv i(1-\omega),\ \omega_+\equiv i(1+\omega),\ \text{and}\ \omega_d\equiv\omega_-^{-1}-\omega_+^{-1}.$$

We notice that there is no power terms of t in the zeroth order solution. Hence we can expect the response to be quasi-periodic in the transient time region.

When the frequency of the external input is quite different from the internal frequency, as shown in Figure 4, the oscillation in the case of weak input is regular with multiple alternating peaks. As the input becomes stronger, the oscillations become more distorted as shown in Figure 5. As the value of ω approaches that of the internal frequency, the phenomena of "beats" oscillation occurs as shown in Figure 6.

We have discussed the responses of the Lotka-Volterra model to the constant, exponentially decaying, and periodic external inputs with the aid of star expansion method. We now summarize the important results obtained in the present work.

(1) For oscillating systems perturbed by a constant input, the temporal oscillation is relatively simple. The frequency of oscillation is the same as internal frequency. The system approaches a focal point regardless of the system parameters.

(2) When an exponentially decaying input is supplied to the system, the responses are simple, too. They transit from a quasi-periodic to periodic oscillation cycling around the steady state.

(3) For a periodic input, the entrainment severely depends on the difference in the frequencies of the unperturbed system and of the external input.

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Appendix

We will consider the system under a constant input. In section III, we discuss the stability of a steady state attained under a constant input and showed that the stability of the model system which we consider depends only on the sign of $tr(J)$. There are five kinds of behavior available in our model system:

1) $tr(J)<0$, $\Delta\geq 0$: stable node (monotonic approach)
2) $tr(J)<0$, $\Delta<0$: stable focus (damped oscillatory approach)
3) $tr(J)=0$: Hopf bifurcation (oscillatory behavior)
4) $tr(J)>0$, $\Delta\geq 0$: unstable node (monotonic divergence)
5) $tr(J)>0$, $\Delta<0$: unstable focus (oscillatory divergence)

If there exists a curve satisfying $tr(J)=0$ in $\xi-s$ parameter plane, then the system subjected to the parameters on the curve will show the Hopf bifurcation[9]. When the system crosses over the curve, stability of the system is changed. We will show below that there doesn't exist the Hopf bifurcation curve for the physically acceptable values of parameters. From Eq. (33).

$$\begin{aligned}tr(J)&=sx_1^s-s^{-1}x_2^s\\&=[\{(1+\xi\Theta)^2+4\xi^2\}^{1/2}\Theta-\xi(\Theta^2+4)-\Theta]/2\end{aligned} \tag{A1}$$

where $\Theta\equiv s-1/s$ and $\Theta\in(-\infty,\infty)$. $Tr(J)$ is a continuous function of ξ and Θ. On the Hopf bifurcation curve which satisfies that $tr(J)=0$, Eq. (A1) becomes

$$\Theta_c[(1+\xi_c\Theta_c)^2+4\xi_c^2]^{1/2}=\xi_c(\Theta_c^2+4)+\Theta_c. \tag{A2}$$

Subscript c denotes the values of parameters in the critical curve (the Hopf bifurcation curve). To obtain the explicit expression of ξ_c in terms of Θ_c, each side of Eq. (A2) is squared to yield a quadratic equation for ξ_c

$$\xi_c[2\Theta_c+\xi_c(\Theta_c^2+4)]=0. \tag{A3}$$

The two roots are

$$\xi_c=0\ (\text{independent of}\ \Theta_c) \tag{A4}$$

and

$$\xi_c = -2\Theta_c/(\Theta_c^2+4). \qquad \text{(A5)}$$

Eq. (A4) is a trivial solution with no external input. If Eq. (A5) is substituted into Eq. (A2), we obtain

$$[(1+\xi_c\Theta_c)^2+4\xi_c^2]^{1/2} = -1. \qquad \text{(A6)}$$

Since ξ_c and Θ_c are both real, Eq. (A6) is physically meaningless. Therefore, we conclude that Eq. (A5) is not a physically acceptable solution. Hence, there is no Hopf bifurcation curve in the parameter plane because $tr(J)=0$ is not satisfied physically. Since $tr(J)[\neq 0]$ is a continuous function with respect to ξ and Θ, $tr(J)$ has the same sign on the whole plane of physically acceptable parameter values. Therefore, we can easily determine the sign of $tr(J)$ by arbitrarily taking the parameter values. For example, $tr(J)<0$ when $\Theta=0$ and $\xi=1.0$. It is, therefore, concluded that the steady state attained under a constant input is locally stable.

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Theoretical Studies of 1,5-Sigmatropic Rearrangements Involving Group Transfer[1]

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The 1,5-sigmatropic rearrangements involving group (X) migration in ω-(X)-substituted 1,3-pentadiene, $C^1H_2=C^2H$-$C^3H=C^4H$-C^5H_2-X, where X=H, CH_3, BH_2, NH_2, OH or F, are investigated MO theoretically using the AM1 method. For the migrating groups without lone pair electrons, X=H, CH_3, or BH_2, the suprafacial pathway is favored, whereas for the migrating groups with lone pair electrons participating in the TS, X=NH_2, OH, or F, the antarafacial pathway is favored electronically. However excessive steric inhibition in the antarafacial TS for X=NH_2 leads to subjacent orbital controlled suprafacial process. The antarafacial shift of F is relatively disfavored compared to that of OH due to smaller orbital overlap and larger interfrontier energy gap in the TS.

Introduction

The [*i, j*] sigmatropic rearrangements[2] involve variety of processes and have been widely studied experimentally and theoretically. The unifying features of all these reactions are that they are concerted, uncatalyzed and involve a bond migration through a cyclic transition state (TS) in which an atom or a group is simultaneously joined to both termini of a π electron system.[3] In the 1,5-sigmatropic rearrangement involving group transfer, a terminal group, X, at C_1 shifts to C_5 in a neutral 1,3-pentadiene system, (I), with σ-π bond interchanges occurring at the both termini, C_1 and C_5.

$$C^5H_2=C^4H-C^3H=C^2H-C^1H_2-X$$

(I)

However the number of electrons, not the number of atoms, participating in the cyclic TS determines the selection rules[4]; when $4n+2$ electrons participate, suprafacial migration in thermally allowed, whereas for $4n$ electron systems antarafacial migration is allowed. For example, suprafacial migration of a group X is normally allowed for 6 electron systems involving [1,5]-neutral, [1,6]-cation and [1,4]-anionic rearrangements. In a previous work on the role of lone paois in 1,3-sigmatropic group rearrangements[5,6], however, we have shown that for a migrating group with lone pair electrons (X), the participation of lone pairs in the TS causes an alteration of the selection rule; normally antarafacial-allowed [1,3]-group shift becomes suprafacially allowed [1,5]-group shift when lone pair electrons on the migrating group participate in the TS. In this work, we report on the AM1-MO[7,8] theoretical studies of sigmatropic rearrangements involving group (X) migrations in the 1,3-pentadiene system, I, using various migrating groups without (X=H, BH_2 or CH_3) and with (X=NH_2, OH, or F) lone pair electrons. Here