

## A nonlinear Study for the Schlögl Models with some Kinds of External Input. I.

Moon H. Ryu, Dong J. Lee\*, and Il D. Kim

*Department of Chemistry, Chosun University, Kwang-Ju 501-759*

*\*Department of Chemistry, National Fisheries University of Pusan, Pusan 608-023. Received February 21, 1991*

A new perturbation theory called as star expansion method is used to obtain the nonlinear retarded solution of the Schlögl models with some kinds of external input. The approximate nonlinear solutions are compared with the exact solution, linear solutions, and those obtained by the Feynman method.

### Introduction

The motions of dynamical systems subjected to external excitations are governed by differential equations involving a forcing term (or source term). When the source function is considered as an arbitrary datum, the corresponding solutions are functionals of this source. As is well known, in the case of linear equations each of these functionals is expressed with the help of an integral involving a Green function. For nonlinear equations this notion is generalized into that on  $n$ -point functions defined as the kernels of the functional Taylor expansion of the solutions with respect to the source. These  $n$ -point functions are, in particular, currently used in field theory, where they are related to the vacuum expectation values of the fields.<sup>1</sup>

The purpose of the present paper is to obtain a nonlinear solution for the one component chemical reaction models (the Schlögl models<sup>2,3</sup>) under various kinds of external input with the aid of a new expansion technique (called as the star expansion method) originally proposed by Houard and coworker.<sup>4-6</sup>

In section II. A, B we briefly discuss the star expansion method for the retarded Green function of nonlinear equation with a time dependent external input and compare it with the well-known Feynman method. In section II. C, D we obtain approximate nonlinear solutions for the Schlögl models with some kinds of external input. In the final section the approximate nonlinear results are compared with the linear solutions, exact one (if it exists) and those obtained by the Feynman expansion method.

### Theory

In this section we shall discuss the difference between the Feynman and star expansion method. Let us consider the following general nonlinear differential equation

$$\frac{dX(t)}{dt} = \xi(t) + P_r(X) \quad (1)$$

with

$$P_r(X) = \sum_{v \geq 1} \alpha_v(t) X^v, \quad (2)$$

where  $\xi(t)$  is an arbitrary external input and  $\alpha_v$ 's are the parameters. In general, the retarded solution of Eq. (1) is written as

$$X(t) = \int_0^t d\tau \left[ \prod_{v \geq 1} G_v(t, \tau) \right] \xi(\tau) \quad (3)$$

where  $\prod_{v \geq 1} G_v(t, \tau)$  is the functionals of  $\xi$  defined by

$$G_v(t, \tau) = \exp \left[ \int_{\tau}^t \alpha_v(\tau') X^{v-1}(\tau') d\tau' \right] \quad (4)$$

The product of unit step function  $\theta(t-\tau)$  by  $\prod_{v \geq 1} G_v(t, \tau)$  is the retarded Green function of Eq. (1) which is in fact equivalent to the set constituted by Eq. (3) and the equations

$$\frac{d}{dt} G_v(t, \tau) = \alpha_v(t) X(t)^{v-1} G_v(t, \tau), \quad G_v(\tau, \tau) = 1 \quad (5)$$

The latter, or the equivalent expression Eq. (4), implies the composition relation

$$G_v(t_1, t_2) G_v(t_2, t_3) = G_v(t_1, t_3), \quad \forall t_1, t_2, t_3, v \quad (6)$$

The basic equations (4) and (5) will be taken as the starting point of perturbation theory. At first, let us consider the Feynman expansion method.

**Feynman Expansion Method.** For the product

$$K(t, \tau) = \prod_{v \geq 1} G_v(t, \tau) \quad (7)$$

Eq. (5) gives

$$\frac{d}{dt} K(t, \tau) = \left[ \sum_{v \geq 1} \alpha_v(t) X(t)^{v-1} \right] K(t, \tau), \quad K(\tau, \tau) = 1 \quad (8)$$

and, therefore,

$$K(t, \tau) = 1 + \int_{\tau}^t d\tau' \left[ \sum_{v \geq 1} \alpha_v(\tau') X(\tau')^{v-1} \right] K(\tau', \tau) \quad (9)$$

The solution is

$$X(t) = \int_0^t d\tau \xi(\tau) + \int_0^t d\tau \sum_{v \geq 1} \alpha_v(\tau) X(\tau)^v \quad (10)$$

This is nothing but the integral form of Eq. (1). The iteration method leads to the well-known Feynman expansion.

Now, we will explain the star expansion method, that is, another version of a perturbation theory which, in some cases, furnishes an expression for Green function  $G$  completely explicitly, that is to say free from integrations.

**Star Expansion Method.** Instead of solving the equation for the product  $K = \prod G_v$ , we consider separately the equations for the  $G_v$ 's. The solution now developed needs, at first, the elimination of the linear term of  $P_r(X)$ ; this is

easily done by replacing the function  $X(t)$  by  $y(t)\exp[-\int d\tau\alpha_v(\tau)]$ , which satisfies an equation of the type (1), without the linear term, and with modified function  $\eta(t)$  and  $\alpha_v(t)$ ,  $v=1$ . From now we thus assume that  $P_i$  does not contain a linear term. With the aid of Eq. (6), we transform Eq. (5) into

$$\frac{d}{d\tau}G_v(t, \tau) = -\alpha_v(\tau)y(\tau)^{v-1}G_v(t, \tau) \quad (11)$$

then

$$\frac{d}{d\tau}G_v(t, \tau)^{v-1} = -(v-1)\alpha_v(\tau)y(\tau)^{v-1}[G_v(t, \tau)]^{v-1} \quad (12)$$

and, introducing the expression (3) and the composition law (6), we get

$$\begin{aligned} \frac{d}{d\tau}G_v(t, \tau)^{v-1} &= -(v-1)\alpha_v(\tau) \int_0^\tau d\tau_1 \cdots d\tau_{v-1} \eta(\tau_1) \cdots \eta(\tau_{v-1}) \\ &\quad \times \prod [G_v(\tau, \tau_1) \cdots G_v(\tau, \tau_{v-1})] [G_v(t, \tau)]^{v-1} \\ &= -(v-1)\alpha_v(\tau) \int_0^\tau d\tau_1 \cdots d\tau_{v-1} \eta(\tau_1) \cdots \eta(\tau_{v-1}) \\ &\quad \times \prod [G_v(t, \tau_1) \cdots G_v(t, \tau_{v-1})] \prod_{q=v}^{\infty} [G_q(\tau, t)]^{v-1} \end{aligned} \quad (13)$$

By integration on  $\tau$  between  $\tau$  and  $t$ , this gives

$$\begin{aligned} G_v(t, \tau)^{v-1} &= 1 + (v-1) \int_\tau^t d\tau' \alpha_v(\tau') \int_0^{\tau'} d\tau_1 \cdots d\tau_{v-1} \eta(\tau_1) \cdots \eta(\tau_{v-1}) \\ &\quad \times \prod [G_v(t, \tau_1) \cdots G_v(t, \tau_{v-1})] \prod_{q=v}^{\infty} [G_q(\tau', t)]^{v-1} \end{aligned} \quad (14)$$

Multiplying by  $\theta(t-\tau)$  and permuting the integrations, (14) becomes

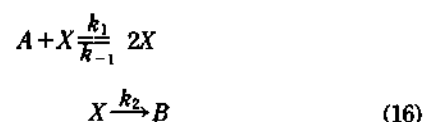
$$\begin{aligned} \theta(t-\tau)G_v(t, \tau) &= \theta(t-\tau) \left\{ 1 + (v-1) \int_0^t d\tau_1 \cdots d\tau_{v-1} \eta(\tau_1) \cdots \eta(\tau_{v-1}) \right. \\ &\quad \times \left[ \prod_{i=1}^{v-1} \theta(t-\tau_i) G_v(t, \tau_i) \right] \\ &\quad \times \int_{\sup(\tau_1, \dots, \tau_{v-1}, \tau)}^t d\tau' \alpha_v(\tau') \prod_{q=v}^{\infty} [\theta(t-\tau) G_q \\ &\quad \left. (\tau', t)]^{v-1} \right\}^{1/v-1} \end{aligned} \quad (15)$$

With the use of Eq. (15), we may easily obtain the nonlinear retarded solution of nonlinear differential equation under consideration.

The Feynman expansion and the star expansion lead to different physical interpretations. In any term of the first one, some of the given source  $\eta(\tau_1), \eta(\tau_2), \dots$  distribute amongst disjointed bundles; each of them has a number  $v$  of elements equal to one of the exponents appearing in polynomials  $P_i(X)$  and creates a new source  $\alpha_v(\tau)\eta(\tau_1)\cdots\eta(\tau_v)$  at a subsequent time  $\tau$ . This process repeats itself with the remaining  $\eta$ -sources and new ones, and so on, until the time  $t$  to give a contribution to  $X(t)$ . On the contrary, in terms of the star expansion, when  $P_i(X) = \alpha X^v$ , all the  $\eta$ -sources gather in a single stage into bundles having  $v$  elements; these bundles are jointed so that each source can belong to different ones, and the resulting contribution to  $X(t)$  is factorized. When  $P_i$  is an arbitrary polynomial, a similar description holds for each step of a more complicated process,

in which each bundle eventually creates a new source acting in the next step. In the next section we apply this method to chemical reaction systems which have been known as the Schlögl models.

**Application to the Schlögl Model I.** This model describes the derivative of the concentration of the intermediate  $X$  with respect to time in the following chemical reaction scheme with concentrations of other species being held constant.



The rate equation of this scheme is the Schlögl model I exhibiting a second order phase transition. When the system is disturbed by an exponential input, it may be written as

$$\frac{dX}{dt} = P_i(X) + \xi \exp(-\gamma t) \quad (17)$$

with

$$P_i(X) = \beta X - \alpha X^2 \quad (18)$$

Here,  $\alpha = k_{-1}$ ,  $\beta = Ak_1 - k_2$ , and  $\gamma$  is arbitrary number to be given by the form of an external input.

It follows from the theory in section II. B that the retarded Green function of Eq. (17) is given as

$$\begin{aligned} \theta(t-\tau)G(t, \tau) &= \theta(t-\tau) \left[ 1 \times \int_0^t d\tau_1 \eta(\tau_1) [\theta(t-\tau_1)G(t, \tau_1)] \int_{\sup(\tau_1, \tau)}^t d\tau' \alpha(\tau') \right. \\ &\quad \left. \right] \end{aligned} \quad (19)$$

where  $\eta(t) = \xi \exp[-(\beta + \gamma)t]$  and  $\alpha(t) = -\alpha \exp(\beta t)$ . With the use of Eq. (19), we obtain the nonlinear retarded solution of Eq. (17), which is written as

$$X(t) = a(t)[1 + b(t)]^{-1}, \quad |b(t)| < 1 \quad (20)$$

where

$$a(t) = \frac{\xi}{(\beta + \gamma)} [\exp(\beta t) - \exp(-\gamma t)],$$

$$b(t) = \frac{\alpha \xi}{\beta} \left\{ \frac{1}{(\beta + \gamma)} [\exp(\beta t) - \exp(-\gamma t)] + \frac{1}{\gamma} [\exp(-\gamma t) - 1] \right\} \quad (21)$$

The results of  $X(t)$  for the explicit forms of external input are given in Table 1. The  $\exp(-\gamma t)$  in Table 1 can be neglected for long time.

**Application to the Schlögl Model II.** This model is provided by the following sequence of reactions scheme with concentrations of other species being held constant.



The rate equation of this scheme is a Schlögl model II exhibiting a first order phase transition, which can be represented by Eq. (7) with

**Table 1.** The Approximation Solution for the Schlögl Model I with /sme Kinds of External Input

$\eta(t)$	$a(t)$	$b(t)$
$\xi\theta(t)$	$\frac{\xi}{\beta} [\exp(\beta t) - 1]$	$-\frac{\alpha\xi}{\beta} \{t + \frac{1}{\beta} [\exp(\beta t)]\}$
$\xi \exp(-\gamma t)$ ( $\gamma > 0$ )	$\frac{\xi}{(\beta + \gamma)} [\exp(\beta t) - \exp(-\gamma t)]$	$\frac{\alpha\xi}{\beta} \{ \frac{1}{(\beta + \gamma)} [\exp(\beta t) - \exp(-\gamma t)] + \frac{1}{\gamma} [\exp(-\gamma t) - 1] \}$
$\xi \sin(\omega t)$	$\frac{\xi}{(\beta^2 + \omega^2)} \{ [-\beta \sin(\omega t) - \omega \cos(\omega t)] + \omega \exp(\beta t) \}$	$\frac{\alpha\xi}{\beta} \{ \frac{1}{(\beta^2 + \omega^2)} [-\beta \sin(\omega t) - \omega \cos(\omega t)] + \omega \exp(\beta t) \}$ $-\frac{1}{\omega} [1 - \cos(\omega t)]$

**Table 2.** The Approximation Solution for the Schlögl Model II with Some Kinds of External Input

$\eta(t)$	$a(t)$	$b_k$	$c(t)$
$\xi\theta(t)$	$\frac{\xi}{\beta} [\exp(\beta t) - 1]$	$b_0 = 1, b_1 = \frac{1}{2}$ $b_{k>1} = \frac{(2k-1)}{2^{k+1}}$	$\frac{\alpha\xi^2}{\beta^3} [\exp(-\beta t) - 1] [\exp(\beta_0) - 1]^2$
$\xi \exp(-\gamma t)$ ( $\gamma > 0$ )	$\frac{\xi}{(\beta + \gamma)} [\exp(\beta t) \exp(-\gamma t)]$	$b_0 = 1, b_1 = \frac{1}{2}$ $b_{k>1} = \frac{(2k-1)}{2^{k+1}}$	$\frac{\alpha\xi^2}{\beta(\beta + \gamma)} [\exp(-\beta + \gamma t) - 1] \{ \frac{1}{(\beta + \gamma)} [\exp(2\beta t) - \exp[(\beta - \gamma)t]] - \frac{1}{(\beta - \gamma)} [\exp[(\beta - \gamma)t] - 1] \}$
$\xi \sin(\omega t)$	$\frac{\xi}{(\beta^2 + \omega^2)} \{ [-\beta \sin(\omega t) \omega \cos(\omega t)] + \omega \exp(\beta t) \}$	$b_0 = 1, b_1 = \frac{1}{2}$ $b_{k>1} = \frac{(2k-1)}{2^{k+1}}$	$-\frac{\alpha\xi^2}{\beta(\beta^2 + \omega^2)^2} \{ [\exp(-\beta t) [-\beta \sin(\omega t) - \omega \cos(\omega t) + \omega] [-2\beta \exp(\beta t) \sin(\omega t) + \omega [\exp(2\beta t) - 1]] \}$

$$P(X) = \beta X - \alpha X^3 \tag{23}$$

where  $\alpha = k_2$ ,  $\beta = Ak_1$  and  $\gamma$  is arbitrary number. Then with the aid of Eq. (15), we easily obtain the retarded Green function

$$\theta(t - \tau) G_2(t, \tau) = \theta(t - \tau) [1 + 2 \int_0^t d\tau_1 d\tau_2 \eta(\tau_1) \eta(\tau_2) [\theta(t - \tau_1) G_2(t, \tau_1) \times [\theta(t - \tau_2) G_2(t, \tau_2) \int_{\sup(\tau_1, \tau_2, \tau)}^t d\tau' \alpha(\tau')]^{1/2}]] \tag{24}$$

where  $\gamma(t) = \xi \exp[-(\beta + \gamma)t]$  and  $\alpha(t) = -\alpha \exp(2\beta t)$ . Using Eq. (24), the nonlinear solution of the rate equation with Eq. (23) is obtained as

$$X(t) = a(t) \sum_{k=0}^{\infty} b_k c(t)^k \tag{25}$$

where

$$a(t) = \frac{\xi}{(\beta + \gamma)} [\exp(\beta t) - \exp(-\gamma t)]$$

$$b_k : b_0 = 1, b_1 = \frac{1}{2}, b_{k>1} = \frac{(2k-1)}{2^{k+1}}$$

$$c(t) = \frac{\alpha\xi^2}{\beta(\beta + \gamma)} \{ \exp[-(\beta + \gamma)t] - 1 \} \{ \frac{1}{(\beta + \gamma)} [\exp(2\beta t) - \exp[(\beta - \gamma)t]] - \frac{1}{(\beta - \gamma)} [\exp[(\beta - \gamma)t] - 1] \} \tag{26}$$

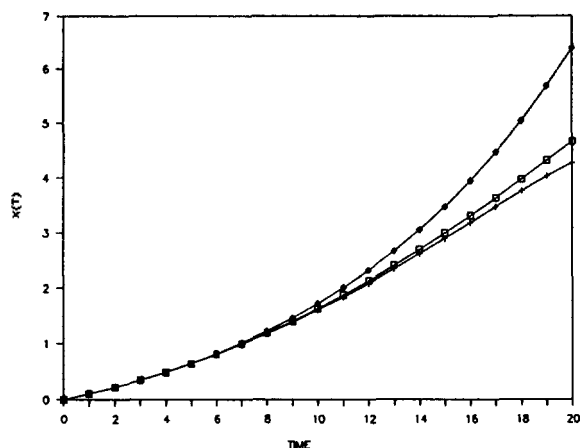
The results of  $X(t)$  for the explicit forms of some kinds of external input are given in Table 2. As was explained in model I, the  $\exp(-\gamma t)$  can be neglected for long time. In the next section, we shall discuss approximate results in Table 1 and 2 by a comparison of the linear solution, exact solution and those obtained by the Feynman expansion method.

### Discussion and Conclusion

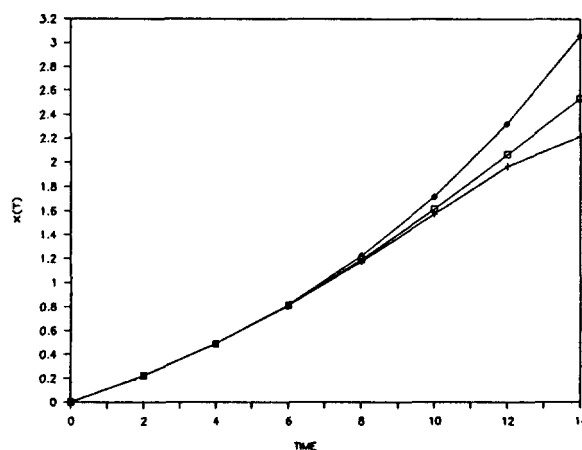
At first let us discuss the Schlögl model, In the case of a constant external input, the exact solution is

$$X(t) = \frac{2\xi[1 - \exp(\delta t)]}{\beta[\exp(\delta t) - 1] - \delta[1 + \exp(\delta t)]}, \delta = (\beta^2 + 4\alpha\xi)^{1/2}$$

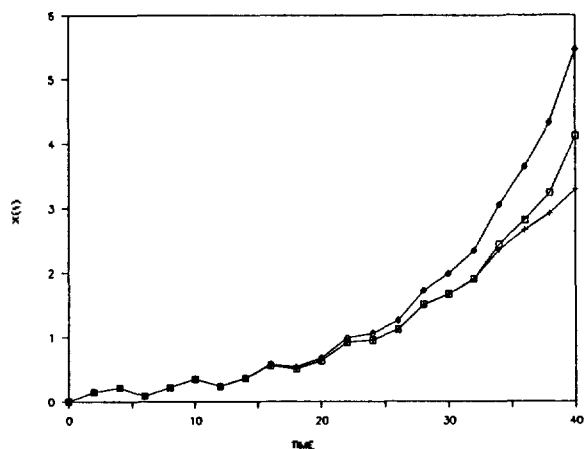
The approximate nonlinear result in Table 1 can be compared with the exact solution, the Feynman's result and linear result by taking specific value of the parameter. For the case of  $\alpha = 0.01$  and  $\beta = \xi = 0.1^2$ , the comparison is in Figure 1 shows that the present result obtained by the star method is in very good agreement with the exact one and Feynman result in time region  $|b(t)| < 1$ , where the approximation is satisfied.<sup>9</sup> In this case the result of the Feynman method



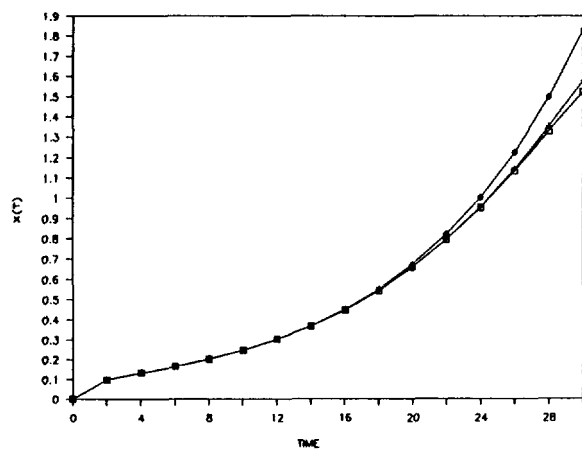
**Figure 1.** A comparison of the present result with the exact solution, the Feynman result and the linear result for  $\eta(t) = \xi\theta(t)$  in Table 1.  $\square$ : Exact solution,  $+$ : Present result,  $\diamond$ : Feynman's result,  $\triangle$ : Linear result.



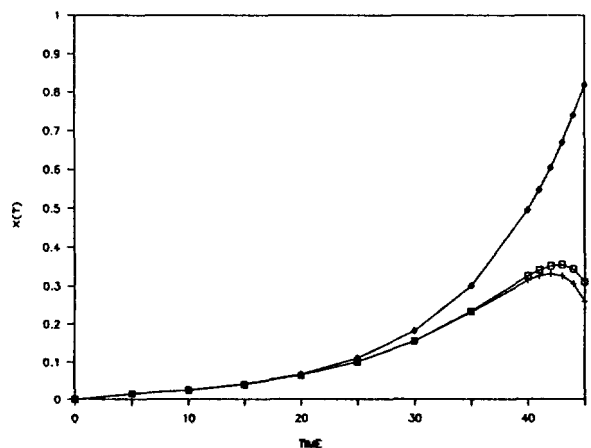
**Figure 4.** A comparison of the present result with the linear result and result obtained by the Feynman method for  $\eta(t) = \xi\theta(t)$  in Table 2.  $\square$ : Feynman's result,  $+$ : Present result,  $\diamond$ : Linear result.



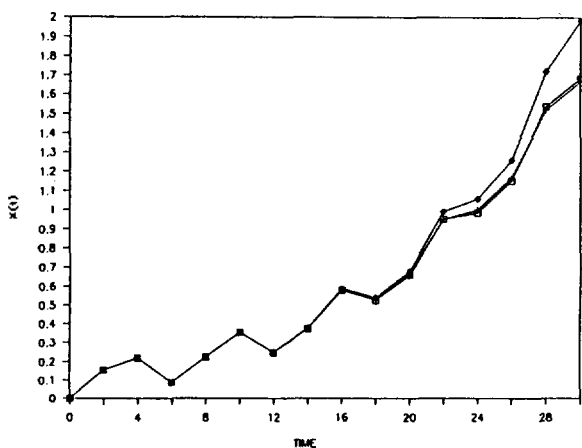
**Figure 2.** A comparison of the present result with the linear result and result obtained by the Feynman method for  $\eta(t) = \xi \exp(-\gamma t)$  in Table 1.  $\square$ : Feynman's result,  $+$ : Present result,  $\diamond$ : Linear result.



**Figure 5.** A comparison of the present result with the linear result and result obtained by the Feynman method for  $\eta(t) = \xi \exp(-\gamma t)$  in Table 2.  $\square$ : Feynman's result,  $+$ : Present result,  $\diamond$ : Linear result.



**Figure 3.** A comparison of the present result with the linear result and result obtained by the Feynman method for  $\eta(t) = \xi \sin(\omega t)$  in Table 1.  $\square$ : Feynman's result,  $+$ : Present result,  $\diamond$ : Linear result.



**Figure 6.** A comparison of the present result with the linear result and result obtained by the Feynman method for  $\eta(t) = \xi \sin(\omega t)$  in Table 2.  $\square$ : Feynman's result,  $+$ : Present result,  $\diamond$ : Linear result.

is better than the present result, as time approaches to the time limit. For an example, at the  $t=20$ , the deviation of both results from the exact value are about 2% and 8%, respectively. From the results the Feynman method in the Schlögl model I is more accurate than the star expansion. However, for other systems it can not be said that the solution of the Feynman expansion is better than that of the star expansion, since these two methods have quite different physical meaning as follows: In the Feynman expansion the sources distribute amongst disjointed bundles. Each of them has 2 elements and creates a new source at a subsequent time. This process repeats itself with the remaining sources and new ones, until the time  $t$  to give a contribution to the solution. However, in star method all the sources gather in a single stage into bundles. These bundles are jointed so that each source can belong to different ones and the resulting contribution to the solution is factorized. It should be mentioned that we may easily obtain an almost exact solution as possible by including the higher order terms in the star expansion, since the star expansion is systematic and simple, as shown in Section (C). Of course, the smaller the ratio  $\alpha\xi/\beta$  is, the longer the time region  $|b(t)|$  is. In the long time region the linear result deviates from the exact one. This confirms that the multitime scaling method is very useful tool to study nonlinear dynamics.<sup>9,10</sup> The present results in the cases are compared with those obtained by the Feynman method.<sup>8</sup> In the time region where both the approximation are satisfied they agree well each other. For examples the comparisons are shown in Figure 2-6 by choosing  $\alpha=0.01$ ,  $\beta=\xi=0.1$ , and  $\gamma=\omega=1$ .

It can be stated that for most cases the linear approxima-

tion is quite reasonable only in the short time region.<sup>11</sup> Although the present method agrees well with the Feynman method, the former is more systematic and simpler than the latter especially in the multicomponent system.<sup>12</sup> Thus, it may be concluded that the star expansion method is a very powerful tool to discuss the nonlinear phenomena in chemical reaction dynamics.

## References

1. C. Itzykson and J. B. Zuber, *Quantum Field Theory* (McGraw-Hill, New York, 1980).
2. F. Schlögl, *Z. Physik*, **253**, 147 (1972).
3. A. Nitzan, P. Ortholeva, J. Deutch, and J. Ross, *J. Chem. Phys.*, **61**, 1058 (1972).
4. J. C. Houard, *Lett. Nuovo Cimento*, **33**, 519 (1982).
5. J. C. Houard and M. Irac-Astaud, *J. Math. Phys.*, **24**, 1997 (1983).
6. J. C. Houard and M. Irac-Astaud, *J. Math. Phys.*, **25**, 3451 (1984).
7. The Dimension of  $\beta$ ,  $\gamma$  and  $\omega$  is  $\text{time}^{-1}$  and that  $\alpha$  and  $\xi$  is  $(\text{concentration time})^{-1}$ . For simplicity the dimensionality is neglected.
8. In the actual comparison the third order expansion terms have been used in both cases.
9. K. O. Han, D. J. Lee, J. M. Lee, K. J. Shin, and S. B. Ko, *Bull. Kor. Chem. Soc.*, **7**, 224 (1986).
10. M. Suzuki, *J. Stat. Phys.*, **16**, 11 (1977).
11. M. H. Ryu, Ph. D. thesis, Chosun University, (1990).
12. In subsequent papers the present method is extended to multicomponent system.

## A Theoretical Study of Gas-Surface Phonon Scattering: Model He-Si(100) Bulk and Reconstructed Surfaces

Seung Chul Park\*, Chang Hwan Rhee  
Woong Lin Hwang†, Yoon Sup Lee‡, and Myung Soo Kim‡

Department of Chemistry and Institute of Basic Science,  
Kangweon National University, Chuncheon 200-701

\*Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 130-650

‡Department of Chemistry, Seoul National University, Seoul 151-742. Received February 28, 1991

We present a theoretical investigation of the inelastic atom-surface phonon scattering for a model He-Si(100) system by the classical trajectory-quantum forced oscillator(DECENT) method. Single and multi-phonon transition probabilities of normal modes are calculated for several initial beam orientations and several initial kinetic energies. In order to understand surface structure effects, the calculation has been done on both reconstructed and unreconstructed surfaces of the He/Si(100) system. The origin of mode specificity for energy transfer is discussed. The contribution of one, two, and multi-phonon events to the total energy transfer between 0 and 600 K is also given.

## Introduction

The study of gas-surface collision dynamics on silicon solid surfaces has become a topic of major interest in surface sci-

ences. There are several reasons for this study. Reactions of gases with the silicon solid surfaces are widely used in micro-fabrications of very-large-scale-integrated (VLSI) circuits.<sup>1</sup> Energy transfer from atoms and molecules to surface