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Cyclic Successive First-Order Reactions, Oscillations, Resonance and Spectra

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Two classes of cyclic, successive first-order linear, irreversible chemical reactions are found to exhibit chemical oscillations, and we elucidate how they show up. Furthermore, these are applied to stationary open systems where a starting chemical species is pumped in as a sinuasoidal function of time and an intermediate species is pumped out as the same function, and spectra for the rates of participating species are obtained which show sharp resonance peaks that are missing in nonoscillating systems. Hence, the present cyclic model suggests that even such simple reactions can undergo resonance motion which can produce strong harmonic activities similar to the usual ones of under damped harmonic oscillators.

It has been known for a quite sometime that nonlinear chemical reactions lead to oscillations.[1] However, these have not been accounted for linear systems such as successive first-order chemical reactions until quite recently. Suzuki and Morita[2] showed that ordinary cyclic successive first-order chemical reactions in fact exhibit oscillations. In this paper, we shall present more examples showing stronger linear chemical oscillations than the previous case[2] and clarify how this can be explained.

As stated previously,[2] a cyclic condition plays a pivotal role for a successive reaction to oscillate. A restoring force has been obtained from the cycle. Hence, we shall confine ourselves to the cyclic reaction in this paper. Moreover, to gain the maximum strength of the restoring force, we neglect the backward reactions for a while. This also makes theoretical treatments much easier. Thus, let us first consider the irreversible reaction in Figure 1for which the rate equations are given by

$$\frac{\mathrm{d}a_0(t)}{\mathrm{d}t} = -k_1 a_0(t) + k_N a_{N-1}(t)$$

$$\frac{\mathrm{d}a_{\mathrm{j}}(t)}{\mathrm{d}t} = -k_{j+1} a_j(t) + k_j a_{j-1}(t); \quad j = 1, 2, 3, ..., N - 1 \quad (1)$$

To treat these equations, we find it convenient to introduce the method of the Laplace transform. By setting the initial condition in the following

$$a_j(0) = a_0(0)\delta_{0,j} \quad (2)$$

where $\delta_{0,j}$ is the Knonecker delta, we immediately find the expressions

$$a_0(s) = \frac{(s + k_2)(s + k_3)...(s + k_N)}{f(s)} a_0(0) \quad (3)$$

where

$$f(s) = (s + k_1)(s + k_2)...(s + k_N) - k_1 k_2 ... k_N \quad (4)$$

$$a_j(s) = \frac{k_1 k_2 ... k_j (s + k_{j+2})(s + k_{j+3})...(s + k_N)}{f(s)} a_0(0); \quad j = 1, 2, ..., N - 1 \quad (5)$$

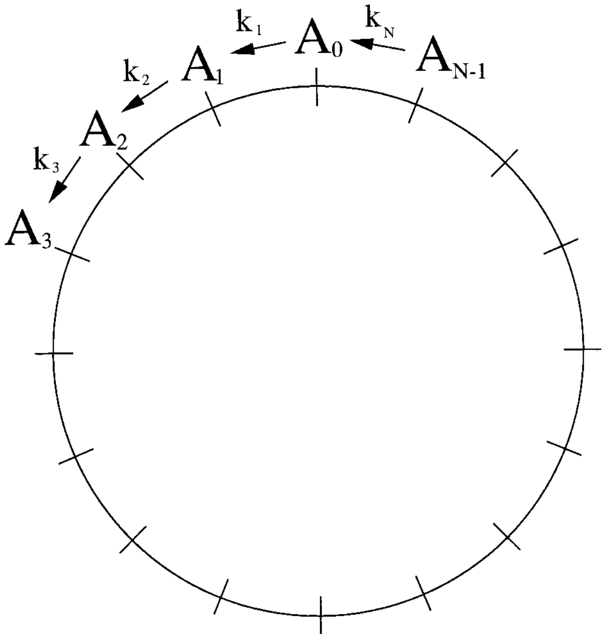

Figure 1. Irreversible successive cyclic first-order reaction.

and the Laplace transform of a function, $g(t)$ has been written through the expression $g(s) = \int_0^\infty g(t)\mathrm{e}^{-st}\,\mathrm{d}t$. It is immediately seen from eq 3 that the dynamic behavior of $a_0(t)$ is determined irrespective of how each site other than site 0 is arranged as far as the cycle is constructed with k_1, k_2, k_3, ..., k_N. Furthermore, we note that the second term on the right-hand side in eq 4 arises from the cyclic condition. Without this term, $f(s)$ becomes the ordinary successive irreversible reaction with both ends at sites 0 and $N - 1$. Hence, we see the cyclic condition shifts from $f\,(s) = (s + k_1)(s + k_2)...(s + k_N)$ to $f(s) = (s + k_1)(s + k_2)...(s + k_N) - k_1k_2...k_N$, which can change the dynamic behavior drastically from nonoscillatory to oscillatory.

In view of the cyclic property of the present reaction, we can express $a_j(s)$ for the more general case where the initial concentration is $a_j(0) = a_L(0)\delta_{L,j}$ with $L = 0, 1, 2, ..., N - 1$ instead of $a_j(0) = a_0(0)\delta_{0,j}$ based on the above results as follows:

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$$a_j(s) = a_L(0)\frac{k_1k_2...k_j(s+k_{j+2})(s+k_{j+3})...(s+k_L)k_{L+1}...k_N}{f(s)}; \quad j = 0, 1, 2, ..., L \qquad (6)$$

$$a_j(s) = a_L(0)\frac{(s+k_1)(s+k_2)...(s+k_L)k_{L+1}...k_j(s+k_{j+2})(s+k_{j+3})...(s+k_N)}{f(s)}; \quad j = L+1, L+2, ..., N-1 \qquad (7)$$

For the present linear case, we can use the usual superposition principle when $a_L(0)$ is more than one and less than or equal to $N - 1$.

To get explicit time-behavior of $a_j(t)$, we have to solve the equation of $f(s) = 0$ which cannot be performed in general except for small N and simple cases such as the previous one[2], but numerically, it does not give difficulties. One obvious solution is $s = 0$ that leads to the $a_j(\infty)$

$$a_j(\infty) = \frac{1}{k_{j+1}\left(\frac{1}{k_1} + \frac{1}{k_2} + ... + \frac{1}{k_N}\right)} \qquad (8)$$

Suppose each solution, $s = -\alpha_m$, is not identical one another, then we can express

$$a_j(t) = a_j(\infty) + \sum_{m=1}^{N-1} C_{j,m}e^{-\alpha_m t} \qquad (9)$$

where

$$C_{j,m} = \frac{k_1k_2...k_j}{(k_1-\alpha_m)(k_2-\alpha_m)...(k_{j+1}-\alpha_m)\left(\frac{1}{k_1-\alpha_m} + \frac{1}{k_2-\alpha_m} + ... + \frac{1}{k_N-\alpha_m}\right)} \qquad (10)$$

For the case where the solution is not this type, we still can express $a_j(t)$ with the help of the residue theorem in complex algebra. Because $k_j > 0$, we see that the real part of α_m must be positive. Hence, in order for $a_j(t)$ to oscillate, we require α_m to have a large value of nonzero imaginary part in comparison with that of the real part, which physically corresponds to a small damping for an oscillator.

To establish a general procedure to find such a solution seems to be difficult, if not impossible. In this paper, let us consider three cases a−c for $k_j = (j)^{1/2}$, $k_j = j$ and $k_j = j^2$, respectively. These have been chosen with a view that faster feeds through the cycle increase the strength of oscillations while keeping the same decaying transition rate of k_1. In Figures 2 and 3, $a_0(t)$ is shown for various values of N for cases a and b, where oscillations occur. However, unexpectedly, we found no oscillations for the case of c. This makes us believe there will be an upper limit for K smaller than 2 where $k_j = j^K$ for oscillations to occur. To understand this, we have calculated α_m and $C_{0,m}$ for $N = 20$ and for cases a−c, and results are plotted in Figure 4. Obviously, we see the significant difference for (c) in comparison with (a) and (b). Numbers of real roots for (c) at smaller s are greater, and the absolute values are bigger. We see that $f(s)$ as s decreases oscillates strongly, which results in intersecting with the real axis of s that leads to the real roots quite close to $-k_j$ with large absolute values. These are why $C_{0,m}$ becomes extremely small for small real roots for case c. Whereas profiles for cases a and b are roughly similar, which is the case of appearance of oscillations. This should be remembered with the previous simple case of $k_j = 1$ where $s = -1 + \exp(2\pi m/N)$ and $C_{0,m} = 1/N^2$. Hence, to get oscillations from the cyclic reactions, we should have as few as the real roots on the real negative axis of s apart from $s = 0$ for odd N and from $s = 0$ and another one at the smallest s for even N. Ideally greater absolute values of $C_{0,m}$ with the greater values of the imaginary parts of the roots at small absolute values of the real parts for $f(s) = 0$ will be just fit for the oscillations. Note from the upper curves in Figure 4 that as the power K increases, they gradually deform from the simple circle for $K = 0$.

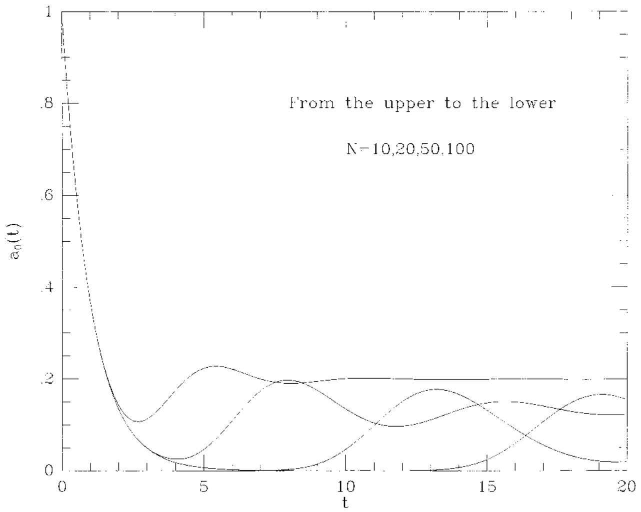

Figure 2. Time profiles of $a_0(t)$ for case a where $k_j = (j)^{1/2}$ for several values of N.

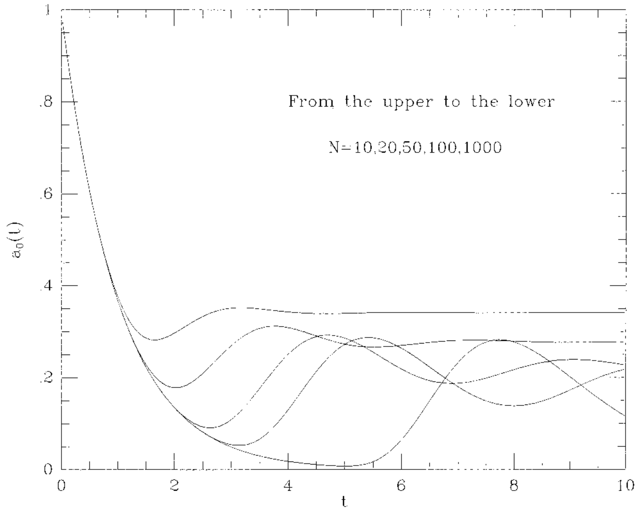

Figure 3. Time profiles of $a_0(t)$ for case b where $k_j = j$ for several values of N.

So far, we have been discussing the linear chemical oscillation for a closed system where material exchange between the chemical system and the external surroundings is prohibited so that the system would stop oscillating eventually. Let us now extend our considerations on open systems by bearing in mind that our system is a beautifully simple linear case where profound results must be found without carrying out elaborate complex calculations. To this end, we can use some significant conclusions from linear response theory.

The first example is a transient response of the system when we inject a flux, $p(t) = da_0(t)/dt$ so that the first equation in eq 1 leads to

$$k_1a_0(t) = k_Na_{N-1}(t) - p(t)$$

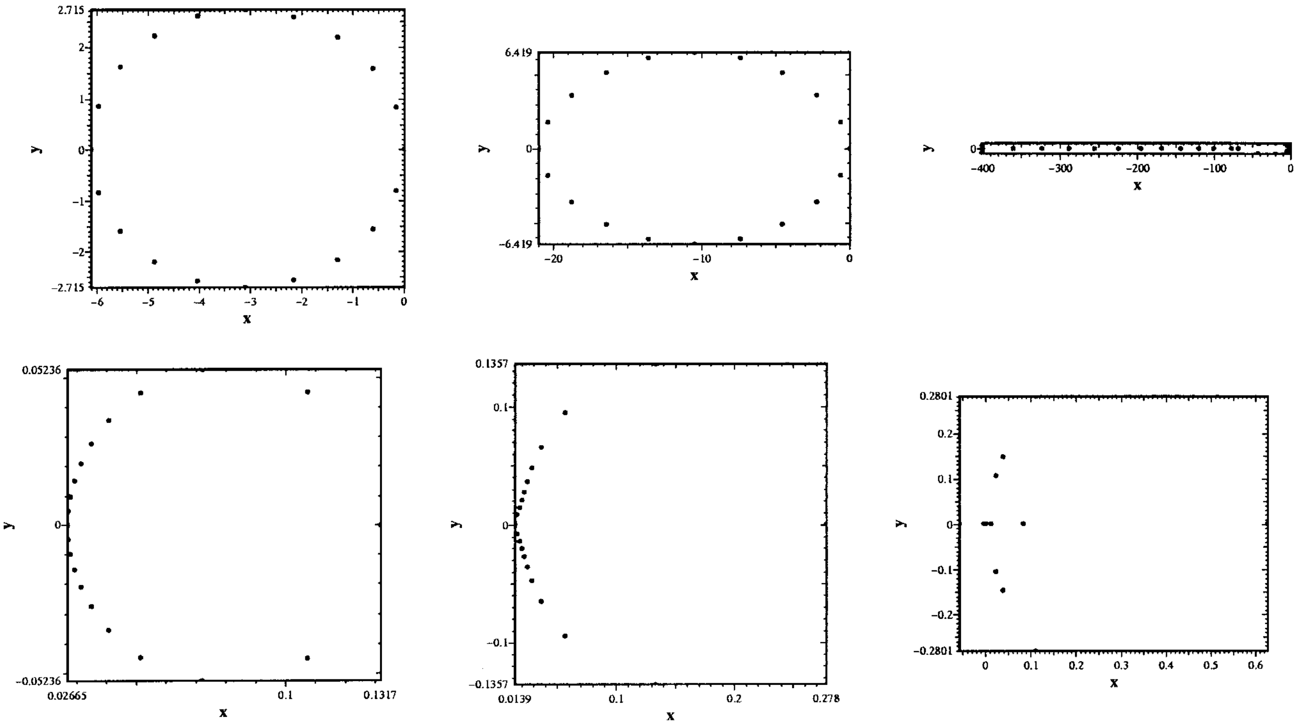

Figure 4. Complex plane plots for α_m (upper plots) and for $C_{0,m}$ (lower plots) for cases a−c from the left to the right.

Substitution of this expression into that for $da_1(t)/dt$ in eq 1 gives a set of simultaneous rate equations whose homogeneous terms are similar to those in eq 1 for the $N - 1$ system where $a_0(t)$ and k_1 are missing with a single inhomogeneous term, $-p(t)$ for the rate equation for $a_1(t)$. Namely, apart from the inhomogeneous term, the resulting system is regarded as if the 0 site is absent from the cycle in Figure 1 where the $N - 1$ site is directly connected to the 1 site with k_N skipping the 0 site. With this in mind and the linear character of the system, the Laplace transforms for $a_j(s)$ with $j = 1, 2,..., N - 1$ can be readily written down from eqs 3 and 5 as follows:

$$a_1(s) = -p(s)\frac{(s + k_3)(s + k_4)...(s + k_N)}{f_1(s)} \tag{11}$$

where

$$f_1(s) = (s + k_2)(s + k_3)...(s + k_N) - k_2...k_N \tag{12}$$

$$a_j(s) = -p(s)\frac{k_2k_3...k_j(s + k_{j+2})(s + k_{j+3})...(s + k_N)}{f_1(s)}; \quad j = 2, 3, ..., N - 1 \tag{13}$$

Note that if $p(t)$ is regarded as a simple pumping-in term in addition to $da_0(t)/dt$, the final expression for $a_j(s)$ in eqs 3 and 5 is obtained just after replacing $a_0(0)$ by $p(s)$. Hence its mathematical structure is identical to the previous case without this additional term so that we will not consider this case any further. By using the convolution theorem for the Laplace transform and the fact that $f_1(s)$ can be written as $f_1(s) = sg_1(s)$, we can express

$$\frac{da_j(t)}{dt} = -\int_0^t (t - u)B_j(u)\, du = -\int_0^t B_j(t - u)p(u)\, du; \quad j = 1, 2, ..., N - 1 \tag{14}$$

where $B_j(t)$ is a function obtained by taking the inverse Laplace transform of the coefficient of $-p(s)$ for $a_j(s)$ in eqs 11 and 13 after replacing $f_1(s)$ by $g_1(s)$. This is a typical result from linear response theory where an after-effect, $da_j(t)/dt$, takes place after injection of $p(t)$ with a system function, $B_j(t)$. Typically, if we choose an infinitively sharp spike like pulse for $p(t) = D\delta(t - \tau)$, we see that

$$da_j(t)/dt = -DB_j(t - \tau); \quad t \geq \tau$$

so that the observed signal, $da_j(t)/dt$, is solely determined by the system function, $B_j(t)$, apart from the $-D$ term. This is based on a similar usual technique for cardiac testing.

The above is for the transient effect which is related to the stationary motion in view of the linear response theory. To get this stationary motion where oscillations persist, we have to make the system open by feeding the starting chemical species at the rate of $p(t) = da_0(t)/dt$ as in the previous case and by pumping out the same amount, $-q(t) = -\, da_L(t)/dt$, from the system where $p(t) = -q(t)$. In this way, we can keep the total concentration of $a_j(t)$ with $j = 1, 2, 3, ..., L - 1, L + 1, ..., N - 1$ independent of time. By using considerations on deriving eqs 6, 7, 11, and 13, we find by assuming $a_j(0) = 0$ for $j = 0, 1, 2, ..., N - 1$ that

$$a_j(s) = -p(s)\frac{k_2k_3...k_j(s + k_{j+2})(s + k_{j+3})...(s + k_L)(s + k_{L+2})...(s + k_N)}{f_2(s)} - q(s)\frac{k_2...k_j(s + k_{j+2})(s + k_{j+3})...(s + k_L)k_{L+2}...k_N}{f_2(s)}; \quad j = 1, 2, ..., L \tag{15}$$

$$a_j(s) = -p(s)\frac{k_2k_3...k_Lk_{L+2}...k_j(s + k_{j+2})(s + k_{j+3})...(s + k_N)}{f_2(s)} - q(s)\frac{(s + k_2)...(s + k_L)k_{L+2}...k_j(s + k_{j+2})(s + k_{j+3})...(s + k_N)}{f_2(s)}; \quad j = L + 1, L + 2, ..., N - 1 \tag{16}$$

where

$$f_2(s) = (s + k_2)(s + k_3)...(s + k_L)(s + k_{L+2})...(s + k_N) - k_2k_3...k_Lk_{L+2}...k_N \quad (17)$$

Now, if we set

$$p(t) = P + Q \cos\omega t \quad (18)$$

substitute this in the above equations by noting the relation similar to eq 14, and put $s = i\omega$, we find expressions for chemical spectra, $S_j(\omega) = S_j'(\omega) - iS_j''(\omega)$

$$S_j(\omega) = \int_0^\infty \frac{\mathrm{d}a_j(t)}{\mathrm{d}t}\, \mathrm{e}^{-i\omega t}\, \mathrm{d}t \quad (19)$$

for $\mathrm{d}a_j(t)/\mathrm{d}t$ which lead to the frequency dependent amplitudes, $S_j'(\omega)$ and $S_j''(\omega)$, for alternating functions, cos ωt and sin ωt, respectively. Because we know that the integrants for $S_j(\omega)$ except for $\mathrm{e}^{-i\omega t}$ can be decomposed into a series such as in eq 9 where each term with $1/[x_m + i(\omega - y_m)]$ in which $\alpha_m = x_m + iy_m$, we will find a resonance term where $\omega = y_m$ with small x_m which gives a strong value for $S_\mathrm{j}(\omega)$. It must be emphasized that, because the poles are determined solely from $f_2(s) = 0$, α_m must appear for all $\mathrm{d}a_j(t)/\mathrm{d}t$ with different $C_{j,m}$, which leads to the resonance for all $\mathrm{d}a_j(t)/\mathrm{d}t$, unless $C_{j,m}$ is different enormously for the active mode. Hence, the present linear cycle model suggests that all of the chemical species become excited at the same frequency. These resonances are missing for the overdamped case where all x_m are large such as for small N and case c. In other words, α_m specifies whether each oscillator is an under- or over-damped one. The smaller x_m except for $x_m = 0$ is, the more chance the system will oscillate. These spectra could show up sharply even for small oscillations in the time domain where $C_{j,m}$ are dominant, whereas for the spectra, x_m are decisive. In Figure 5, we show $|S_j(\omega)|$ for the special case of $k_j = 1$ with $N = 100$ and $L = 75$. It is seen that the sharp peaks at the lowest ω do not depend sensitively on values of j, whereas those at higher frequencies do.

If we are allowed to suppose each chemical site is an active part in a biological system, the feed is implied to be a food, and it is consumed in a body at site L, we will understand how the system is stationary and cyclic and each site can resonate with a dominant frequency. However, if at least one of k_i becomes zero because of a fatal nature, the system suddenly becomes nonresonance so that the system will never be able to recover.

The present model can also be applied to a catalytic reaction which must be cyclic, and this study suggests the reaction is oscillatory.

Now let us discuss the linear chemical oscillation for the previous closed systems again in connection with the principle of detailed balancing[3,4] that is valid in equilibrium. To this end, we introduce reversible cyclic reactions. First, we consider the case in ref 2 where

$$\cdots \underset{k}{\overset{k'}{\rightleftharpoons}} A_{j+2} \underset{k}{\overset{k'}{\rightleftharpoons}} A_{j+1} \underset{k}{\overset{k'}{\rightleftharpoons}} A_j \underset{k}{\overset{k'}{\rightleftharpoons}} A_{j-1} \underset{k}{\overset{k'}{\rightleftharpoons}} \cdots$$

$$\text{with } j = 0, 1, 2, ..., N - 1;\ A_N = A_0; \text{ and } A_{-1} = A_{N-1} \quad (\mathrm{A})$$

Here we must distinguish between the end of the reaction and equilibrium, whose concentrations of a chemical species at the j site are represented by $a_j(\infty)$ and a_j^e, respectively. We imagine that the system reaches equilibrium after a long time following the end of the reaction. The principle of detailed balancing requires the condition of

$$ka_j^e = k'a_{j+1}^e \quad (20)$$

if the system maintains the same reaction scheme in A as that in the reaction dynamics. Scheme A gives rise to

$$a_j(\infty) = 1/N \quad (21)$$

by assuming $\sum_j^{N-1} a_j(0) = 1$ at time $t = 0$. Hence, if we put

$$a_j(\infty) = a_j^e \quad (22)$$

we see that this does not allow eq 20 to hold except for the case of $k = k'$ where no oscillations are possible. This is due to the introduction of the cyclic boundary conditions in A where each A_j must be identical after "forgetting" the initial values.

We did not suppose that our reaction in A did persist until equilibrium. Rather, the end of the reaction is far from equilibrium, so that it can change state before equilibrium where our system can reorganize the state so as to satisfy properties at equilibrium including the principle (see ref 5 for a nice example to understand the point). We think of an interesting case where

$$\cdots \underset{k}{\overset{k}{\rightleftharpoons}} A_{j+2} \underset{k'}{\overset{k'}{\rightleftharpoons}} A_{j+1} \underset{k}{\overset{k}{\rightleftharpoons}} A_j \underset{k'}{\overset{k'}{\rightleftharpoons}} A_{j-1} \underset{k}{\overset{k'}{\rightleftharpoons}} \cdots$$

$$\text{for even } N \text{ with } j = 0, 1, 2, ..., N - 1;\ A_N = A_0; \text{ and } A_{-1} = A_{N-1} \quad (\mathrm{B})$$

which satisfies the principle up to equilibrium without changing in state. Note that the equilibrium concentration, a_j^e, happens to give the same value as $a_j(\infty)$ in A in eq 21. If our system switches to this system after the end of the reaction by equilibrium, we see that, without changing the concentration at all, we can in fact change the state that satisfies the principle. The solution for scheme B is expressed in terms of the generating function $G(m, t)$ (see ref 2)

$$G(m, t) = \mathrm{e}^{-(k+k')t}\left\{G(m, 0) \cosh \Delta t + \frac{\sinh \Delta t}{\Delta}[(k + k') \cos \beta_m G(m, 0) + i \sin \beta_m (k - k')F(m, 0)]\right\} \quad (23)$$

where

$$\beta_m = \frac{2\pi m}{N} \qquad \Delta = \sqrt{(k - k')^2 + 4kk' \cos^2 \beta_m}$$

$$F(m, 0) = \sum_{j=0}^{N-1} (-1)^j \beta_m^j a_j(0)$$

Another interesting reaction which also satisfies the principle without switching states is

$$\cdots \underset{k'}{\overset{k}{\rightleftharpoons}} A_{j+2} \underset{k}{\overset{k'}{\rightleftharpoons}} A_{j+1} \underset{k'}{\overset{k}{\rightleftharpoons}} A_j \underset{k}{\overset{k'}{\rightleftharpoons}} A_{j-1} \underset{k'}{\overset{k}{\rightleftharpoons}} \cdots$$

$$\text{for even } N \text{ with } j = 0, 1, 2,..., N - 1,\ \mathrm{A_N} = \mathrm{A_0} \text{ and } \mathrm{A_{-1}} = \mathrm{A_{N-1}} \quad (\mathrm{C})$$

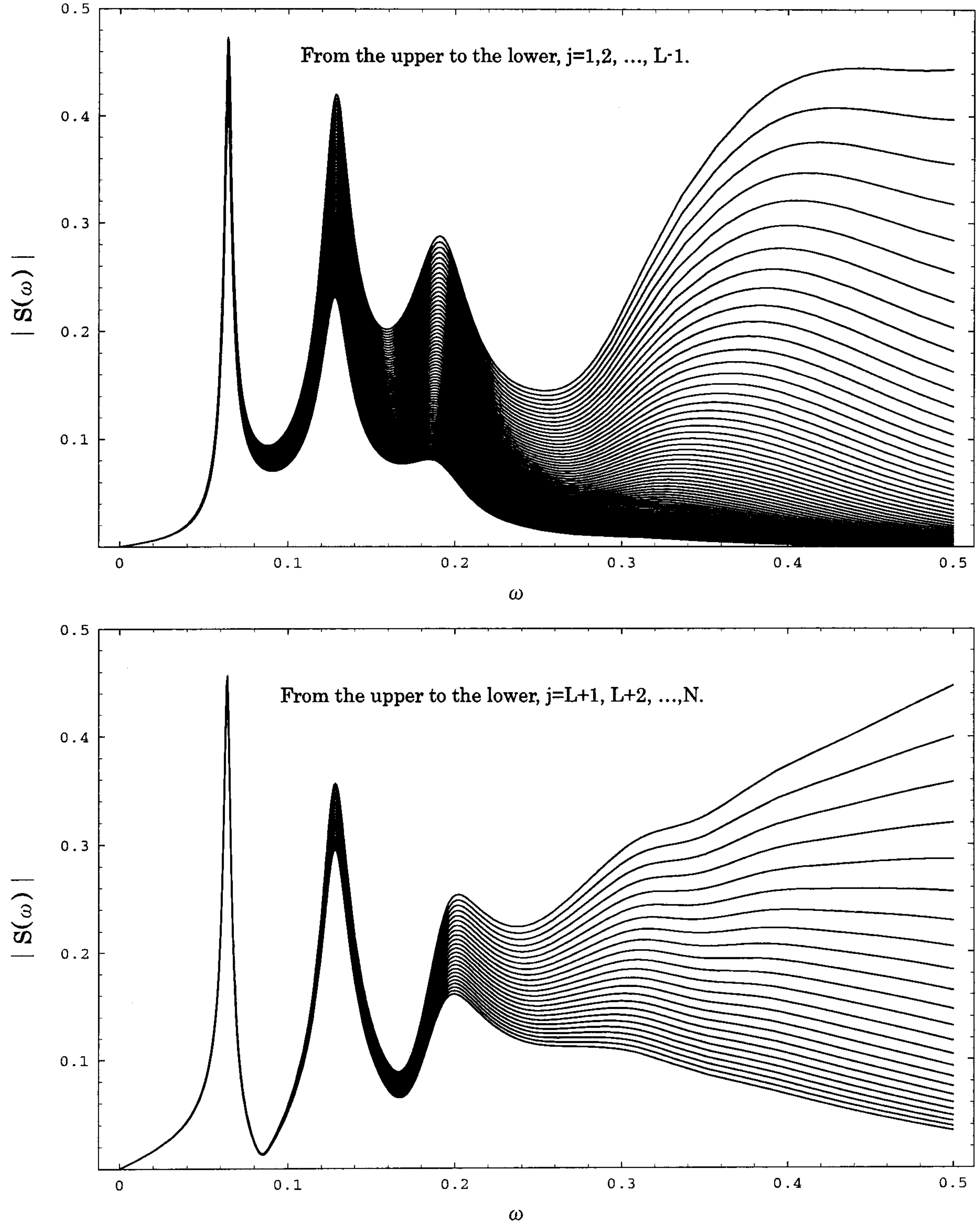

Figure 5. Plots of $|S_j(\omega)|$ for the special case of $P = 0$, $Q = 1$, $k_j = 1$, $N = 100$, and $L = 75$. Values of j are 1, 2, ..., $L - 1$ (the top figure) and $j = L + 1, L + 2, ..., N - 1$ (the bottom figure) viewed from the right-hand side from the upper to the lower curves, respectively.

This leads to

$$G(m, t) = \mathrm{e}^{-(k+k')t}\Big\{G(m, 0)\cosh \Delta t + \frac{\sinh \Delta t}{\Delta}[\cos \beta_m(k + k')G(m, 0) + (\cos \beta_m - 1)(k - k')F(m, 0)]\Big\} \quad (24)$$

and the equilibrium concentrations

$$a_j^e = \frac{2\quad k'}{Nk + k'} \quad (25a)$$

for even j with even N and

$$a_j^e = \frac{2\quad k}{Nk + k'} \quad (25b)$$

for odd j with even N. Even though we tried to obtain $a_j(t)$ for reactions B and C, we have not found oscillations.

Hence, our system in A is valid to reaction dynamics far from equilibrium (see ref 6 for various examples of nonlinear systems), which is not quite in harmony with the principle of the detailed balance. In fact, it is quite an unbalanced system, whereas reactions B and C are balanced ones similar to reaction A when $k = k'$ which does not lead to oscillations. This gives rise to imaginary values of α_m for Scheme A and real ones for Schemes B and C. In other words, the systems satisfying the principle of detailed balancing lead to real values of α_m, whereas the oscillating ones yield imaginary α_m.

Finally, we emphasize that examples of oscillating linear cyclic reactions are not only restricted to those in ref 2 and the present paper, but they can be found in many other cyclic systems where the above guidance will be useful.

References and Notes

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