Dynamic Padé approximants in the theory of periodic and chaotic chemical center waves[a)]

P. Ortoleva

Department of Chemistry, Indiana University, Bloomington, Indiana 47401
(Received 20 February 1978)

A Padé approximant scheme is introduced to analyze chemical composition center waves. The theory shows how the outer plane wavelike nature of these phenomena, such as spiral or circular waves, couples to the core dynamics. Since the latter may have an autonomous frequency different from that of the plane wave outer behavior, it is shown that all the richness of phenomena found for forced nonlinear oscillations are in principle possible. These include periodic and aperiodic centers, multiple centers compatible with a given outer wavelength, and centers which oscillate at a fraction of the outer plane wave frequency, e.g., subharmonic resonance. The theory provides a simple self-consistent approximate stability analysis for the center waves.

I. INTRODUCTION

Beautiful time-dependent patterns of chemical concentrations have been observed in far from equilibrium reacting media.[1,2] The geometries observed include outwardly propagating periodic circular and rotating spiral waves and aperiodic circular waves which seem to appear and disappear and rotating waves whose spiral core has an apparently chaotic meandering evolution.

The theoretical approach to this problem has included computer simulation of model kinetic systems showing periodic circular and rotating waves[3] and aperiodic spiral waves,[4] all in bounded media.

Analytical treatments of these phenomena have only met with modest success. Using bifurcation analysis it was shown that in an infinite medium one could construct propagating solutions with well-behaved plane wavelike geometry far from the center for circular and spiral waves.[5] Unfortunately, near the core of the wave the bifurcation analysis broke down because the leading term had a divergence at the center of the wave.

This nonuniformity of the approximate solutions due to core divergences was also found in the application of oscillator perturbation methods.[5] In this approach one assumes that the system has a homogeneous limit cycle in the chemical kinetics. Then one seeks solutions which may be viewed as a weak distortion of this homogeneous temporal cycle due to local changes of phase and frequency renormalization due to diffusion. Again, as in the case of the bifurcation analysis, the strained coordinate[8] or multiple time scales[7] methods of extending limit cycle dynamics yielded divergences in the core of the wave. In the cycle perturbation theory the divergence occurred in the local phase of oscillation for periodic circular waves. For periodic spiral waves it is easy to understand why the cycle perturbation theory is "doomed" from the beginning since in these phenomena there exists a point at the spiral core which is independent of time[5]—a condition never well approximated by a limit cycle oscillation.

In the theory of plane waves both the bifurcation and limit cycle theories have met with great success.[5,8] Thus, in light of the fact that both spiral and circular waves look like plane waves when viewed along a ray far from the core of the pattern, one would like to at least retain some features of these theories. Furthermore, if one in fact knows the form of the plane waves then one would like to incorporate this information in constructing approximate solutions to describe center waves. However, as for the weakly perturbed oscillator theory one may show (see the Appendix) that assuming the center wave is a weak distortion of a plane wave leads to core nonuniformities (in this case divergencies in the phase of the wave).

The behavior of center waves in their inner core has been studied using an expansion in the radial coordinate measuring the distance from the geometrical center.[5] Thus if the column vector of concentrations $\Psi(\mathbf{r},t)$ is written as a function of the radial coordinate r and the unit directional vector $\hat{n}$ we assume the existence of a Taylor expansion of the form

$$\Psi(r,\hat{n},t)=\sum_{l=0}^{\infty}\Psi_l(\hat{n},t)r^l\,. \qquad (I.1)$$

Inserting such an expansion into the reaction–diffusion equations, one obtains a hierarchy of differential equations for the Ψ_l. The problem arises in closing the hierarchy, however, since the rate of change $\partial\Psi_l/\partial t$ depends not only on Ψ_m for $m\leq l$ but also on Ψ_{l+2}. Despite this fact, some geometrical properties of circular and spiral waves near their cores were determined.[5]

Thus the theoretical situation has been that center waves could be understood far from the core and that a small r expansion for the core behavior required some information about the solution just outside the core truncation of (I.1) to order N_T requires knowledge of Ψ_{N_T+2}. What is thus needed is an orderly procedure for incorporating the outer, plane wavelike information into the inner core equations.

Padé approximants[9] present themselves as a technique for carrying out the inner–outer matching. Indeed, this powerful technique has been successful in many problems in phase transition and molecular physics. In these applications a straightforward perturbation expansion [the analogues of (I.1)] have convergence and other

[a)]Work supported in part by a grant from the National Science Foundation.

 0021-9606/78/6901-0300$01.00

difficulties. The Pade approximants allow one both to extend the validity of the perturbation series and furthermore to naturally incorporate information well beyond the radius of convergence of that series (the analogue of the plane wave behavior far from the center wave core). In the present paper we carry out a Padé approximant procedure to describe center waves of chemical composition.

We shall show that the Padé approximant effectively provide a way of fixing the coefficient Ψ_{N_T+2} needed to close the hierarchy generated by the core expansion (I.1). For example, with circular waves the coefficients Ψ_l are independent of the $d-1$ angular variables (for a d dimensional medium) and only depend on time t. They obey a set of differential equations of the form

$$\frac{d\Psi_l}{dt} - \mathfrak{F}_l(\Psi_0, \Psi_2, \ldots \Psi_l, \Psi_{l+2}) . \qquad (I.2)$$

If we truncate this sequence at N_T then the last function Ψ_{N_T} couples to Ψ_{N_T+2}, the latter being determined through the Padé procedure from the properties of plane waves, valid far from the core. Denoting the column vector of coefficients Ψ_l, $0 \le l \le N_T$ as W, we may rewrite (I.2) in the form

$$dW/dt = \mathfrak{F}(W, \Psi_{N_T+2}(t)) , \qquad (I.3)$$

where $\Psi_{N_T+2}(t)$ is fixed by the plane wave behavior through the Padé scheme we shall introduce in the next section. Equations of this form are called nonautonomous because the term $\mathfrak{F}$ depends explicitly on time [through $\Psi_{N_T+2}(t)$].[10] We note that the solutions of (I.3) with Ψ_{N_T+2} held constant may have autonomous oscillatory solutions with frequency ω_c, the "core frequency." Furthermore, the term Ψ_{N_T+2} being generated by the plane wave solution has frequency $\omega(k^2)$ for outer plane wave structure with wave vector k. Thus the solutions to (I.3) can have all the richness that has been found in the theory of forced oscillations as follows.[10]

(1) *Synchrony*. The center dynamics is entrained by the outer wave frequency. This typically occurs if the frequency mismatch $|\omega(k^2) - \omega_c|$ does not exceed a critical level.

(2) *Subharmonic Resonance*. The center dynamics becomes locked into a frequency less than that of the outer frequency $\omega(k^2)$.

(3) *Aperiodic Centers*. The center dynamics is not entrained by the outer frequency $\omega(k^2)$ but evolves according to multiply periodic motion. Since the periods are generally not commensurate the evolution is not periodic.

(4) *Asynchronous Quenching*. The outer frequency is so much in excess of the center frequency ω_c that the inherent core oscillation is frozen out.

(5) *Amplitude Jumping*. The amplitude $a(\omega(k^2))$ of the synchronized center oscillation [case (1)] may depend on the outer frequency $\omega(k^2)$ with an S-shaped (hysteritic) bahavior. Thus there can exist a range of k^2 over which there is more than one core solution compatible with a given outer (plane wave) structure.

In the theory presented here we shall demonstrate some of these phenomena in a reacting–diffusing system with center waves.

Note that the language of entrainment of the core by the plane wave dynamics is not to be taken literally. Indeed, the entire system is autonous so that the overall center wave dynamics is more accurately described as a mutual entrainment/resonance interaction of the core and the outer plane wave domain.

Spiral waves have been found in systems without anutonomous oscillation.[1,3] Apparently, for these systems the core dynamics is perturbed because of diffusion in such a way as to lead to oscillatory (or chaotic) behavior. The possibility of such effects is naturally built into the present approach. Indeed, the core dynamics generated by neglecting Ψ_l for $l>0$ will be excitable in this case and the coupling to higher order terms, either autonomous or driven by the outer plane wave dynamics, can lead to continuous jumping over excitation thresholds for the lowest order kinetics $d\Psi_0/dt = R(\Psi_0)$, where $R(\Psi)$ is the rate of reaction.

II. DYNAMIC PADÉ APPROXIMANTS FOR CENTER WAVES

We shall now outline our program for constructing Padé approximants for the description of center waves. The parameters of the Padé approximants are determined dynamically, as solutions to sets of coupled partial differential equations, a fact distinguishing the present method from the usual Padé scheme.

The center waves are disturbances in the concentrations $\Psi(\mathbf{r}, t)$ which we take to obey the continuity equations

$$\partial\Psi/\partial t = D\nabla^2\Psi + R(\Psi) , \qquad (II.1)$$

where D is a matrix of diffusion coefficients and R is a function of concentrations fixing the rate of reaction. (Modifications of this equation to include charge neutrality coupling due to the presence of the charge on ionic species have also been considered in the theory of chemical waves.)[11]

The solutions to (II.1) that we seek—center waves—essentially are plane waves far from the center at $\mathbf{r}=0$. Let us consider briefly the plane wave solutions to (II.1). A periodic plane wave solution Ψ^∞ of wave vector k and frequency $\omega(k^2)$ is of the form $\Psi^\infty(\mathbf{k}\cdot\mathbf{r} + \omega t)$. Introducing the wave coordinate ϕ given by

$$\phi \equiv \mathbf{k} \cdot \mathbf{r} + \omega t \qquad (II.2)$$

the plane wave $\Psi^\infty(\phi)$ is seen to obey the ordinary differential equation

$$k^2 D \frac{d^2\Psi^\infty}{d\phi^2} - \omega \frac{d\Psi^\infty}{d\phi} + R(\Psi^\infty) = 0 . \qquad (II.3)$$

We seek solutions $\Psi(\mathbf{r}, t)$ to (II.1) which have the asymptotic behavior

$$\Psi(\mathbf{r}, t) \underset{r\to\infty}{\sim} \Psi^\infty(\phi^\infty) , \qquad (II.4)$$

and where the modified phase ϕ^∞ differs from that for plane waves in ways that depend on the geometry of the center wave. For example,

$$\phi^\infty = \begin{cases} \omega t \pm kr, & \text{circular waves} \\ \omega t \pm kr + n\theta, & n \text{ arm spiral waves}. \end{cases} \qquad \text{(II.5)}$$

In (II.5), θ is the angular variable in circular coordinates.

As mentioned in Sec. I, we introduce an expansion in the distance r ($\equiv |\mathbf{r}|$) from the center of the wave to describe the core [see (I.1)]. The problem still remains as to how to incorporate the outer plane wave behavior (II.4), (II.5) into the core expansion (I.1) and consequent core hierarchy [analogous to that given in (I.2) for circular waves] of differential equations for the coefficients $\Psi_l(\hat{n}, t)$ of r^l.

Strictly speaking, a Padé approximant $[N, M]$ is a ratio of polynomials (in r here) of degree N and M which when expanded is term by term equal to a given power series to some specified order. In addition, the degrees N, M can be chosen in accordance with known asymptotic behavior. The theory of Padé approximant shows that certain classes of functions can be approximated arbitrarily closely over a given range of r if the polynomials are of sufficiently high order. We shall now use an extension of such a philosophy to construct an approximate solution for $\Psi(r, \hat{n}, t)$ using the core expansion and the outer plane wave behavior to fix the properties of the approximants at small and large r, respectively.

Consider the following sequence of functions $\Psi^{(L)}$:

$$\psi_{(i)}^{(L)} = \left(\sum_{m=0}^{L} b_{(i)m} r^m\right)^{-1} \left(a_{(i)L} r^L \psi_{(i)}^\infty(\varphi^\infty) + \sum_{m'=0}^{L-1} a_{(i)m'} r^{m'}\right), \qquad \text{(II.6)}$$

where $a_{(i)m}$ and $b_{(i)m}$ depend on $\hat{n}$ and t and where the subscript (i) labels the chemical species. Clearly $\Psi^{(L)}[\equiv (\psi_{(1)}^L, \psi_{(2)}^L \cdots)]$ has the correct outer wave behavior as long as $a_{(i)L} = b_{(i)L}$. We note that ϕ^∞ depends on r and hence (II.6) is not strictly a Padé approximant. It is this modification of the Padé scheme which allows us to insure that the oscillatory character of the solution at large r is retained. Furthermore, we may fix the coefficients a_m, b_m, and L so that to any desired order the small r behavior is determined exactly as follows. Expanding (II.6) in powers of r we obtain

$$\psi_{(i)}^{(L)} = \frac{a_{(i)0}}{b_{(i)0}} + \left(\frac{a_{(i)1}}{b_{(i)0}} - \frac{a_{(i)0}}{(b_{(i)0})^2} b_{(i)1}\right) r + \cdots, \qquad \text{(II.7)}$$

and hence upon comparison with (I.1) we have

$$\psi_{(i)0} = a_{(i)0}/b_{(i)0}, \qquad \psi_{(i)1} = \left(\frac{a_{(i)1}}{b_{(i)0}} - \frac{a_{(i)0} b_{(i)1}}{b_{(i)0})^2}\right), \qquad \cdots. \qquad \text{(II.8)}$$

Note that we also have the identification

$$\psi_{(i)L} \to \frac{a_{(i)L}}{b_{(i)0}} \Psi^\infty(\tilde{\phi}^\infty) + \cdots, \qquad \text{(II.9)}$$

where $\tilde{\phi}^\infty = \phi^\infty(r = 0, \hat{n}, t)$. This identification, *generated by the Padé approximant*, serves to fix the Lth order coefficient of the core expansion and hence truncate the core expansion by incorporating information from the plane wave domain. This in broadest outline is the essence of the technique. The differential equations of the type (I.2) generated by substituting the core expansion (I.1) into the reaction diffusion equation (II.1) serve to fix the coefficients of the Padé approximant *dynamically* as solutions of time evolution equations [such as (I.2)].

One subtlety has not surfaced in the above presentation. As we shall show by example in the next section the core expansion for circular waves is only in *even* powers of r while the distribution of phase ϕ^∞ for the plane wave domain is an *odd* function of r. This change of analyticity as we go from the core to the outer domain will be shown to be associated with a branch point of the appropriate extension of the phase function ϕ^∞ from the outer to the core domain. This branch point behavior can, as we shall show by example in the next section, be incorporated into a modfied Padé approximant scheme for the extension of ϕ^∞.

The theory is shown by example to provide a simple stability analysis for the center waves within the Padé approximant scheme.

Although the theory is explicitly applied to a model system the methods presented may be directly extended to general reaction diffusion systems.

III. CIRCULAR WAVES IN A MODEL SYSTEM

A. The model

We now carry out the Padé approximant procedure for a model system known to have plane wave solutions. Consider the variables X and Y to "react" and diffuse according to the model equation

$$\frac{\partial}{\partial t}\begin{bmatrix} X \\ Y \end{bmatrix} = D\nabla^2 \begin{bmatrix} X \\ Y \end{bmatrix} + \begin{bmatrix} B & -A \\ A & B \end{bmatrix}\begin{bmatrix} X \\ Y \end{bmatrix}. \qquad \text{(III.1)}$$

Both "species" X and Y are taken to have the same diffusion coefficient D, and the quantities A and B are functions of the radial variable R given by

$$R^2 = X^2 + Y^2. \qquad \text{(III.2)}$$

It is convenient to introduce the set of variables R, Φ defined by

$$X = R\cos\Phi,$$
$$Y = R\sin\Phi. \qquad \text{(III.3)}$$

In terms of these variables the continuity equation (III.1) takes the form

$$\partial R/\partial t = RB(R) + D\{\nabla^2 R - R|\nabla\Phi|^2\}, \qquad \text{(III.4)}$$

$$\partial\Phi/\partial t = A(R) + D\{\nabla^2\Phi + 2\nabla R \cdot \nabla\Phi/R\}. \qquad \text{(III.5)}$$

These equations will provide the basis of our analysis.

B. Plane waves

Plane wave solutions of (III.4) and (III.5) have been discussed by several authors.[5,8,12] It is easy to see that

$$\Phi^\infty = A(R^\infty)t + \mathbf{k}\cdot\mathbf{r}, \qquad \text{(III.6)}$$

where $R^\infty(k^2)$ is a constant satisfying

$$B(R^\infty) - k^2 D = 0\,, \qquad \text{(III. 7)}$$

is a solution to (III. 4) and (III. 5). Furthermore, this solution represents a plane wave of wave vector k with frequency $A(R^\infty(k^2))$ and velocity $-A(R^\infty)/|k|$ parallel to k.

C. Circular geometry

We now consider a two dimensional medium with points r specified by the polar coordinates r, θ. For circular centers R and Φ are independent of the angular variable θ. Thus for this geometry (III. 4) and (III. 5) become

$$\frac{\partial R}{\partial t} = RB(R) + D\left\{\frac{\partial^2 R}{\partial r^2} + \frac{1}{r}\frac{\partial R}{\partial r} - R\left(\frac{\partial \Phi}{\partial r}\right)^2\right\}, \qquad \text{(III. 8)}$$

$$\frac{\partial \Phi}{\partial t} = A(R) + D\left\{\frac{\partial^2 \Phi}{\partial r^2} + \frac{1}{r}\frac{\partial \Phi}{\partial r} + \frac{2}{r}\left(\frac{\partial R}{\partial r}\right)\left(\frac{\partial \Phi}{\partial r}\right)\right\}. \qquad \text{(III. 9)}$$

We now seek solutions via the Padé approximant matching scheme, which will map onto the plane wave solutions far from the center at $r = 0$.

D. Core expansion

First we consider the behavior of the center waves in the core, e.g., r near 0. We assume the existence of an expansion of R and Φ in r in the form

$$\begin{Bmatrix} R \\ \Phi \end{Bmatrix} = \sum_{n=0}^{\infty} \begin{Bmatrix} R_n \\ \Phi_n \end{Bmatrix} r^n\,. \qquad \text{(III. 10)}$$

Substituting these expansions into (III. 8) and (III. 9) we see that the R_n, Φ_n vanish for odd powers of n. For the first two even powers we obtain

$$dR_0/dt = R_0 B(R_0) + 4DR_2\,, \qquad \text{(III. 11)}$$

$$d\Phi_0/dt = A(R_0) + 4D\Phi_2\,, \qquad \text{(III. 12)}$$

$$dR_2/dt = (RB(R))_0' R_2 - 4DR_0\Phi_2^2 + 16DR_4\,, \qquad \text{(III. 13)}$$

$$d\Phi_2/dt = A_0' R_2 + 8DR_2\Phi_2/R_0 + 16D\Phi_4\,, \qquad \text{(III. 14)}$$

where $(RB)_0'$ is $d(RB)/dR$ evaluated at R_0 and similarly for A_0'. It is clear from the structure of the equations that the general equation for R_n takes the form

$$dR_n/dt = \mathfrak{F}_n(R_0, R_2, \ldots R_n : \Phi_0, \Phi_2, \ldots \Phi_n) + c_n R_{n+2}\,, \qquad \text{(III. 15)}$$

and similarly for Φ_n (where $\mathfrak{F}_n$ is a function of its arguments and c_n is a constant). Thus this sequence never closes as discussed for the general case in the previous sections.

E. Outer behavior

Far from the core of circular waves the waves are essentially planar and hence we have the following limiting behavior

$$R \underset{r \to \infty}{\simeq} R^\infty(k^2)\,, \qquad \text{(III. 16)}$$

$$\Phi \underset{r \to \infty}{\simeq} A(R^\infty)t \pm kr\,. \qquad \text{(III. 17)}$$

F. The Padé approximant

In the spirit of the general discussion of the previous section we shall now construct Padé approximants for R and Φ. To keep our calculation simple we limit ourselves to the lowest order approximant scheme that will be capable of performing the desired matching.

The simplest polynomial ratio which yields the proper limiting behavior for R is given by

$$R^p \sim \frac{a_0 + a_2 k^\infty r^2}{1 + a_2 r^2}\,. \qquad \text{(III. 18)}$$

The function a_2 has the dimensions of an inverse length squared and roughly speaking characterizes the dimensions of the core. As shall become clear below, if we wish to construct a simple theory, involving only closed equations in the two zeroth order quantities R_0 and Φ_0, we must pick a value for a_2. The core diameter is typically of order of the wavelength of the outer plane wave. Thus we take $a_2 = \tilde{k}^2$ and we have

$$R^p = \frac{a_0 + R^\infty(\tilde{k}r)^2}{1 + (\tilde{k}r)^2}\,, \qquad \text{(III. 19)}$$

where $\tilde{k} \approx k = 2\pi/\lambda$. However we retain the distinction between $\tilde{k}$ and k to emphasize that some caution should be shown in interpreting our detailed conclusions later in the analysis. In higher order theories a_2 is picked by the equations (as will be presented elsewhere). For example, in the next higher order scheme R_2 and R_4 are determined by expanding (III. 18) for order r^4 and expressing them in terms of a_0, a_2, and R^∞. Then a_2 is determined as a solution of (III. 13) (rewritten in terms of a_0, a_2, and R^∞ as in Sec. G below).

Construction of an approximant for Φ is not quite so straightforward. An apparent paradox arises because for small r, Φ contains only even powers of r [see (III. 12) and (III. 14)], whereas for large r, Φ is linear in r (see (III. 17)]. Apparently Φ as a function of r has a branch point as follows. Consider the simple choice

$$\Phi^p \sim A(R^\infty)t \pm [\alpha_0^2 + (kr)^2]^{1/2}\,. \qquad \text{(III. 20)}$$

Clearly, this *ansatz* has the correct outer behavior and furthermore is expressible as a series only in even powers in r in the core. Also, one may write fractional powers of more general polynomial ratios which would generate "higher order" approximants. The interesting point is that functional forms such as (III. 20) have branch points (because of the square root function) which allows for the apparent change of behavior in the core ($kr \ll 1$) and in the plane wave region ($kr \gg 1$).

In the following paragraphs we shall adopt the simple Padé approximant scheme (III. 19) and (III. 20) to generate the desired matching.

G. Matching the core and outer solutions

We now use the core (small r) expansions of the Padé approximant to truncate the core equations (III. 11)–(III. 14). Expanding the Padé approximant R^p in (III. 14) for small r we obtain

$$R^p \sim a_0 + [R^\infty - a_0](\tilde{k}r)^2 + \cdots\,. \qquad \text{(III. 21)}$$

With this we see that $a_0 = R_0$ and that furthermore we may approximate R_2 by

$$R_2 \approx [R^\infty - R_0]\tilde{k}^2\,. \qquad \text{(III. 22)}$$

Thus we may obtain a closed equation for R_0 by combining (III.22) and (III.11) to obtain

$$dR_0/dt = R_0 B(R_0) + 4D\tilde{k}^2[R^\infty - R_0]. \qquad \text{(III.23)}$$

Similarly, we expand Φ^p to obtain

$$\Phi^p = A(R^\infty)t \pm \alpha_0 \pm (kr)^2/2\alpha_0 + \cdots \qquad \text{(III.24)}$$

and hence

$$\Phi_2 = \pm k^2/2\alpha_0, \qquad \text{(III.25)}$$

$$\alpha_0 = \pm[\Phi_0 - A(R^\infty)t]. \qquad \text{(III.26)}$$

With this and (III.12) we obtain a closed equation for Φ_0 in the form

$$\frac{d\Phi_0}{dt} = A(R_0) + \frac{2Dk^2}{[\Phi_0 - A(R^\infty)t]}. \qquad \text{(III.27)}$$

Thus (III.23) and (III.27) are a closed set of coupled ordinary differential equations that provide an approximate description of circular waves. In the remainder of this section we shall analyze these equations.

H. Analysis of the matched truncated dynamics

The R_0 dynamics decouples from the Φ_0 dynamics in this approximation. Since the R_0 equation (III.23) is a single first order equation its asymptotic ($t \to \infty$) solutions are either unbounded or steady states. Thus we first seek steady solutions $\overline{R}_0$ satisfying

$$\overline{R}_0 B(\overline{R}_0) + 4Dk^2[R^\infty - \overline{R}_0] = 0. \qquad \text{(III.28)}$$

To proceed further we must make a specific assumption on the form of B. For simplicity of analysis we take

$$B = 1 - |R| \qquad \text{(III.29)}$$

for which

$$|R^\infty| = 1 - k^2 D. \qquad \text{(III.30)}$$

Thus there are plane wave solutions for

$$0 < k^2 < k_c^2 \equiv D^{-1}. \qquad \text{(III.31)}$$

With this $\overline{R}_0$ obeys the quadratic (assuming $R_0 \geq 0$)

$$\overline{R}_0^2 + (4D-1)\overline{R}_0 - 4D\tilde{k}^2(1 - k^2D) = 0, \qquad \overline{R}_0 \geq 0 \qquad \text{(III.32)}$$

and hence

$$\overline{R}_0 = \tfrac{1}{2}(1-4D) + \tfrac{1}{2}\sqrt{(1-4D)^2 + 16D\tilde{k}^2(1-k^2D)}, \qquad \overline{R}_0 \geq 0. \qquad \text{(III.33)}$$

We expect that $\tilde{k}$ will vary with k, $\tilde{k} = \tilde{k}(k)$ and in fact that $\tilde{k}$ is a monotonically increasing function of and on the order of magnitude of k. To simplify our analysis we take

$$\tilde{k} = k, \qquad \text{(III.34)}$$

keeping in mind that this is only a rough estimate. It does have the essential features of monotonicity and that for homogeneous evolution, $k=0$, we have $\tilde{k}(0)=0$. Again these "claims" can only be put on a reasonably rigorous basis when a higher order Padé scheme is used such that $\tilde{k}$ is picked by the equations in the manner discussed above using (III.13) and (III.18) to determine a_2.

To insure real values for $\overline{R}_0$ the quantity inside the square root must be positive. Hence

$$K_-^2 < k^2 < K_+^2, \qquad \text{(III.35)}$$
$$K_\pm^2 = \frac{1}{2D}[1 \pm \sqrt{1 + 4(1/4 - D)^2}].$$

Since $K_-^2 < 0$ the minimum value of k^2 is zero (since k is real). Furthermore we note that

$$K_+ > k_c = D^{-1/2}, \qquad \text{(III.36)}$$

e.g., there exist circular waves at shorter wavelengths than can be possible for plane waves. However, the outer solution we have assumed is not valid for $k > k_c$ since in that case $|R^\infty(k)| < 0$, which is impossible. Thus for

$$0 < k < k_c \qquad \text{(III.37)}$$

this model has circular waves with plane waves as outer solutions, and for

$$k_c < k < K_+ \qquad \text{(III.38)}$$

we conjecture the possibility that the system supports localized centers which decay within a few multiples of k^{-1} beyond the center. For example, when $k = k_c$ we have $R^\infty(k_c) = D$ and hence

$$\overline{R}^p(r) \sim \frac{(1-4D)D}{D + r^2}, \qquad k = k_c. \qquad \text{(III.39)}$$

Since we have assumed $\overline{R} \geq 0$ we see that the solutions (III.33) are valid only for $D < 1/4$.

If we now assume $\overline{R}_0 < 0$ then the first term in (III.32) changes sign and we obtain (again taking $\tilde{k} = k$)

$$\overline{R}_0 = \tfrac{1}{2}[4D - 1 \pm \sqrt{(4D-1)^2 - 16Dk^2(1-k^2D)}]. \qquad \text{(III.40)}$$

These solutions are valid (i.e., real) for

$$Q_-^2 < k^2 < Q_+^2, \qquad \text{(III.41)}$$

$$Q_\pm^2 = \frac{1}{2D}[1 \pm \sqrt{1 - 4(1/4 - D)^2}]. \qquad \text{(III.42)}$$

The cutoff wave vectors are real only if

$$(1-4D)^2 < 4, \qquad \text{(III.43)}$$

e.g., $0 < D < 3/4$. For this case both the lower and upper cutoff vectors are real so that the range (in k) of these phenomena is bounded away from the origin, e.g., these are strictly inhomogeneous phenomena and cannot be considered as a small k extension of a homogeneous oscillation. Furthermore, both solutions (±) given in (III.40) are negative as long as

$$0 < D < 1/4, \qquad \text{(III.44)}$$

which falls in the range of D values for which there are real cutoff wave vectors $Q_\pm$. Note, however, from (III.42) that $Q_\pm^2 < k_c^2$ and hence these waves exist over a narrower range bounded from below and above by the range of plane waves ($0 < k^2 < k_c^2$).

In Figs. 1 and 2 we show schematically both the case $\overline{R}_0 > 0$ and $\overline{R}_0 < 0$ for $R^\infty > 0$. Note that for the case $\overline{R}_0 < 0$ there is a node at a value of r, r_n, given by

$$(kr_n)^2 = -\overline{R}_0. \qquad \text{(III.45)}$$

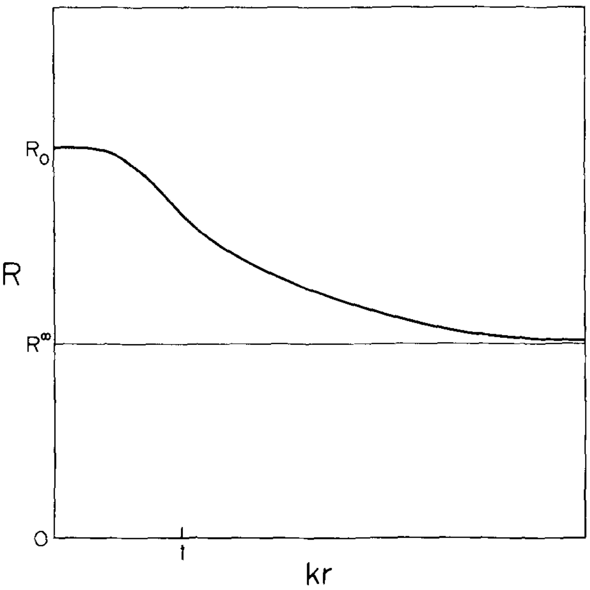

FIG. 1. Wave amplitude R for a circular wave as calculated for the lowest order dynamic Padé scheme presented in Sec. III for the model (III. 29). R is plotted as a function of the dimensionless length kr, where k is the wave vector of the wave in the plane wave domain at long distance r from the circular wave center at $r=0$. The quantity $R^\infty = R(k^2)$ is the amplitude of plane waves. Note that in the core there is a maximum of the disturbance for the case $R_0 > 0$ where R_0 is the value of $R(kr=0, t)$ as calculated from the lowest order dynamic Padé.

I. Stability

The stability of the above phenomena can be determined within the present theory. Letting

$$R_0 = \overline{R}_0 + \delta R_0 \tag{III.46}$$

and linearizing (III. 23) in δR_0 we obtain

$$d\delta R/dt = [(RB)_0' - 4Dk^2]\delta R\,, \tag{III.47}$$

and hence stability is indicated when

$$(RB)_0' - 4Dk^2 < 0\,. \tag{III.48}$$

Limiting our discussion to the case $\overline{R}_0 > 0$ within the specific model (III. 29) we obtain

$$\overline{R}_0 > \tfrac{1}{2}(1 - Dk^2)\,,\ \text{stable}\,.$$

From (III. 33) we thus obtain

$$\sqrt{(1-4D)^2 + 16Dk^2(1-k^2D)} > 4D(1-k^2)\,. \tag{III.49}$$

From this one may derive a range of k for stability. In particular a range of k around zero is stable as long as $(1-4D) > 4D$, e.g., $D < 1/16$. The full stability analysis for this and the case $\overline{R}_0 < 0$ will be presented elsewhere.

J. Properties of the phase Φ

Thus far we have not analyzed the Φ_0 equation. Let

$$\beta \equiv \Phi_0 - A(R^\infty)t\,. \tag{III.50}$$

Then (III. 27) becomes

$$d\beta/dt = A(R_0) - A(R^\infty) + 2Dk^2/\beta\,. \tag{III.51}$$

This has a time independent solution $\overline{\beta}$ given by

$$\overline{\beta} = \frac{2Dk^2}{A(R^\infty) - A(\overline{R}_0)}\,. \tag{III.52}$$

Letting $\beta = \overline{\beta} + \delta\beta$ and similarly for R_0 we obtain

$$\frac{d\delta\beta}{dt} = A_0'\delta R - \frac{2Dk^2}{\overline{\beta}^2}\,\delta\beta\,. \tag{III.53}$$

Coupling this equation to (III. 47), one may carry out the full stability analysis for $(\overline{R}_0, \overline{\Phi}_0)$. Assuming that δR regresses, e.g., (III. 48) holds, then perturbations in Φ_0, e.g., in β, also regress since $-Dk^2/\overline{\beta}^2 < 0$. Thus the phase at the center, β, attains the value $\overline{\beta}$ asymptotically as long as $\overline{R}_0$ is stable.

Note that these conclusions are not valid if A is a constant. In this case β obeys the equation

$$d\beta/dt = 2Dk^2/\beta, \quad A\ \text{const}\,. \tag{III.54}$$

Thus we obtain

$$\beta(t) = \pm\sqrt{\beta(0)^2 + 4Dk^2t} \tag{III.55}$$

and hence

$$\Phi^p = At \pm [\beta(0)^2 + 4Dk^2t + k^2r^2]^{1/2}\,. \tag{III.56}$$

Such systems can apparently not sustain periodic center waves unlike those with A that can vary with R. These latter systems attain a constant, stable value of the center phase, $\overline{\beta}$, because the center frequency can adjust to that of the outer solution $A(R^\infty)$. A center (III. 56) is a chaotic (or at least aperiodic) center.

IV. REMARKS

The dyanmic Padé analysis of the model system in the previous section shows that the scheme can be con-

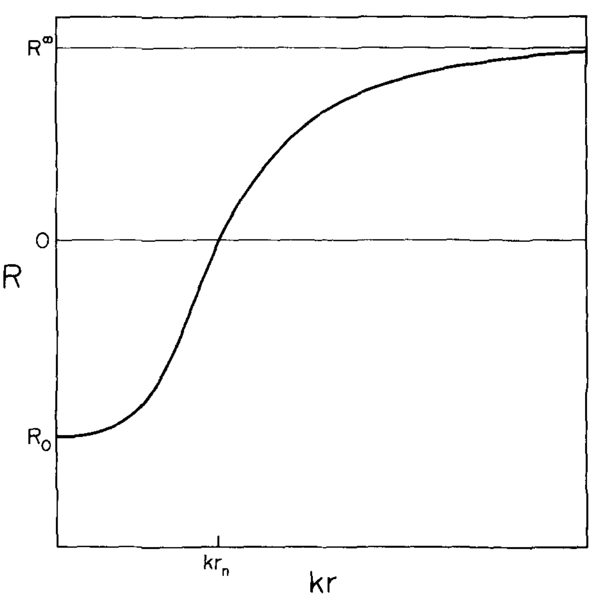

FIG. 2. Same as Fig. 1 except for the case $\overline{R}_0 < 0$. These circular waves are found to exist over a more restrictive range of wave vectors of the outer plane wave wave vector values. Note that since $R=0$ at r_n these circular wave phenomena have a node at r_n and furthermore the core, $r < r_n$, has a phase shift of π from that of the plane wave since R changes sign as r passes through r_n.

sistently carried out to obtain center waves. A variety of interesting possibilities present themselves even for the simple case studied. These include multiple centers ($R_0 \gtrsim 0$), periodic and aperiodic centers, and spatially localized centers.

Caution is advised in interpreting the low order Padé approximant results. One should test convergence of the scheme by analyzing higher order approximant schemes.

In future reports we shall present results on spiral waves and the convergence of sequences of Padé approximants of higher order. We are also applying the theory to an analysis of the Field, Noyes, Koros kinetic model of the "Belousov–Zhabotinsky–Zaikin–Winfree" reaction.

The technique may even be applicable to multiple time scale systems wherein sharply propagating "discontinuities" in composition are known to propagate.[13] Also it is interesting to note that the scheme presented here may be used to study the stability of the complex patterns—a problem of great interest in determining the physical realizability of given solutions. Finally, the theory may be applied to a variety of systems with inhomogeneous kinetics and for matching outer solutions to boundary layers at catalytic surfaces or membranes.

ACKNOWLEDGMENTS

The author thanks Professor P. Langhoff (Department of Chemistry, Indiana University) for several valuable suggestions and a critical reading of the manuscript. Many thanks are due to Professor Dale Larsen (Department of Mathematics, Indiana University) for his critical reading of the manuscript and sage remarks.

APPENDIX: WEAKLY DISTORTED PLANE WAVE THEORY

We expect that far from the core the wave form depends only weakly on the explicit space variable r and similarly for the phase function ϕ of the wave. Thus we introduce a scaling hypothesis of the form

$$\Psi(r,t)=\chi(\rho,\phi)\,, \tag{A1}$$

$$\phi \equiv \omega t+\beta(\rho)+kr\,, \tag{A2}$$

where

$$\rho=\epsilon r \tag{A3}$$

assuming that χ and β are well behaved as $\epsilon \to 0$. With this (II.1) becomes for spherical waves in $\delta+1$ dimensions

$$\omega\frac{\partial\chi}{\partial\phi}=D\left\{\epsilon^2\frac{\partial^2\chi}{\partial\rho^2}+2\epsilon\frac{\partial^2\chi}{d\rho d\phi}\left(k+\epsilon\frac{d\beta}{d\rho}\right)+\epsilon^2\frac{\partial\chi}{\partial\phi}\frac{d^2\beta}{d\rho^2}+\frac{\partial^2\chi}{\partial\phi^2}\times\left(k+\epsilon\frac{d\beta}{d\rho}\right)^2+\epsilon\frac{\delta}{\rho}\left[\epsilon\frac{\partial\chi}{\partial\rho}+\frac{\partial\chi}{\partial\phi}\left(k+\epsilon\frac{d\beta}{d\rho}\right)\right]\right\}+R(\chi)\,. \tag{A4}$$

Now we assume the existence of the expansions

$$\chi=\sum_{n=0}^{\infty}\chi^{(n)}\epsilon^n\,,$$

$$\beta=\sum_{n=0}^{\infty}\beta^{(n)}\epsilon^n \tag{A5}$$

and collect terms. To order zero

$$\omega\frac{\partial\chi^{(0)}}{\partial\phi}=k^2D\frac{\partial^2\chi^{(0)}}{\partial\phi^2}+R(\chi^{(0)})\,, \tag{A6}$$

and hence to lowest order the profile is plane wave like (Ψ^{∞}),

$$\chi^{(0)}=\chi^{\infty}(\phi)\,. \tag{A7}$$

The first order equation becomes

$$\omega\frac{\partial\chi^{(1)}}{\partial\phi}=D\left[2k\frac{\partial^2\chi^{(0)}}{\partial\phi^2}\frac{d\beta^{(0)}}{d\rho}+\frac{\delta k}{\rho}\frac{\partial\chi^{(0)}}{\partial\phi}\right]+\Omega\chi^{(1)}+k^2D\frac{\partial^2}{\partial\phi^2}\chi^{(1)}\,, \tag{A8}$$

where

$$\Omega\equiv\left(\frac{\partial R}{\partial\chi}\right)\bigg|_{\chi=\chi^{(0)}}\,. \tag{A9}$$

We rewrite this in the form

$$\mathcal{L}\chi^{(1)}=kD\left\{\frac{2d\beta^{(0)}}{d\rho}\frac{\partial^2\chi^{(0)}}{\partial\phi^2}+\frac{\delta}{\rho}\frac{\partial\chi^{(0)}}{\partial\rho}\right\}, \tag{A10}$$

$$\mathcal{L}\equiv\omega\frac{\partial}{\partial\phi}-k^2D\frac{\partial^2}{\partial\phi^2}-\Omega(\phi)\,. \tag{A11}$$

Note that taking the derivative of (A6) one obtains

$$\mathcal{L}\frac{\partial\chi^{(0)}}{\partial\phi}=0\,, \tag{A12}$$

and hence $\mathcal{L}$ has (at least) one zero eigenvalue. Thus we cannot solve (A10) for $\chi^{(1)}$ unless the rhs is orthogonal to the null space of the adjoint of $\mathcal{L}$. Denoting this (assumed unique) null eigen function by $\lambda_0(\phi)$ and introducing an inner product $(A,B)=(1/2\pi)\int_0^{2\pi}ABd\phi$ we obtain from the solubility condition

$$\frac{d\beta^{(0)}}{d\rho}=\frac{\delta M}{\rho}\,, \tag{A13}$$

where

$$M\equiv\frac{-2(\lambda_0, D\partial^2\chi^{(0)}/\partial\phi^2)}{(\lambda_0, D\partial\chi^{(0)}/\partial\phi)}\,. \tag{A14}$$

Hence

$$\beta^{(0)}=\delta M\ln\rho+\text{const.} \tag{A15}$$

Thus for two or higher dimensions ($\delta\geq 1$) there is a persistent (logarithmic) contribution to the phase.

The scaling parameter ϵ arose in a rather unnatural way and not from any dimensionless combination of physical parameters. Thus if we set $\epsilon=1$ we should come up with consistent results with the natural smallness parameter and slow functional dependence manifesting themselves. Indeed the logarithmic dependence of $\beta^{(0)}$ seems to bear out our hypothesis of slow variations of β.

The plane wave distortion formula clearly breaks down in the core since $\ln r \to -\infty$ as $r \to 0$. This is the type of breakdown that required the invocation of the Padé procedure.

[1]A. T. Winfree, Scientific American **230**, 82 (1974).
[2]N. Kopell and L. Howard, Science **180**, 1171 (1973).
[3](a) A. T. Winfree, in *Advances in Theoretical Chemistry*, edited by H. Eyring (1978); (b) T. Erneux and M. Herschkowitz-Kaufman, J. Chem. Phys. **66**, 248 (1977); (c) T. Yamada and Y. Kuramoto, Prog. Theor. Phys. **55**, 2035 (1976).
[4]F. B. Gulk and A. A. Petrov, Biofizika **17**, 261 (1972); and Ref. 3.
[5]P. Ortoleva and J. Ross, J. Chem. Phys. **60**, 5090 (1974).
[6]P. Ortoleva and J. Ross, J. Chem. Phys. **58**, 5673 (1973); P. Ortoleva, J. Chem. Phys. **64**, 1395 (1975).
[7]P. Ortoleva, in *Advances in Theoretical Chemistry*, edited by H. Eyring (1978).
[8]N. Kopell and L. Howard, Studies Appl. Math. **52**, 291 (1973).
[9]*The Padé Approximants in Theoretical Physics*, edited by G. A. Baker and J. L. Gammel (Academic, New York, 1970).
[10]A. Andronov and A. Witt, Arch. Elektrotech. (Berlin) **24** (1930); J. Stoker, *Nonlinear Vibrations* (Interscience, New York, 1950); N. Minorsky, *Nonlinear Oscillations* Krieger, Huntington, NY, 1974).
[11]S. Schmidt and P. Ortoleva, J. Chem. Phys. **67**, 3771 (1977).
[12]J. Dreitlein and M.-L. Smoes, J. Theor. Biol. **46**, 559 (1974).
[13]D. Feinn and P. Ortoleva, J. Chem. Phys. **67**, 2119 (1977), and references cited.