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PROPOSITION I

Proposition

The stability of numerical methods which are of a stepping or iterative nature, and which are used to find approximate solutions for a wide variety of linear problems, is determined by the eigenvalues of a characteristic matrix. Specifically, if the approximate numerical method is a stepping method which can be formulated equivalent to

$$y_{n+1} = A\, y_n + f_n \qquad n \geq 0 \qquad \text{(PI-1)}$$

it is stable if an only if all the eigenvalues of the A matrix are less than one in absolute value. Under these circumstances the solution vector will converge to a vector that depends on f_n . In equation PI-1 y_{n+1}, y_n, and f_n are S-dimensional vectors, and A is a constant S x S matrix. Since the absolute value of the eigenvalues of a matrix are bounded by easily calculated norms of the matrix, a useful sufficient condition for stability of many approximate methods, including approximations for partial differential equations, can be found. In certain cases, some generalizations to non-linear equations can also be made.

Uses

Approximate methods which can be formulated equivalent to equation PI-1 include difference approximations of initial-value problems for both linear partial differential equations and systems of linear ordinary differential equations with constant coefficients, for example using Euler's method (PI. 1); and methods of iteration or successive

approximation for linear algebraic equations, for example, the Gauss-Seidel method (PI. 2). In many of such numerical methods equation PI-1 is used directly to step out the approximation. In these cases the matrix A is known explicitly, and its norms can be found using the definitions in equations III-10 and III-11. If the minimum of these norms is less than one, the stepped-out calculation must be stable. But if it is greater than one,the stepped-out calculation can be stable or unstable. For some numerical methods, although the stepping calculation is equivalent to equation PI-1, this equation is not used to carry out the approximation, and the A matrix is not known explicitly. In these cases some algebraic manipulation is required to find the relationship between the eigenvalues of matrix A and the other known matrices; however, these manipulations are often successful in giving useful stability criteria for the approximation.

In addition, a stability analysis for approximations to non-linear equations of the above type can also be made. For systems of non-linear ordinary differential equations, which could have been obtained from differencing of some variables in a non-linear partial differential equation, a difference equation for the propagation of the error based on the Jacobian matrix of the non-linear functions can be derived. In this case the constant matrix A in equation PI-1 is then related to the Jacobian evaluated at the time, and based on this linearization the stability of a method can be studied, providing elements of the y vector

do not change too much. In the same way, for a system of non-linear algebraic equations the A matrix can be taken as the Jacobian of the system evaluated close to or at the solution value of y. If then the starting estimated solution is sufficiently close to the exact solution, a method of successive approximations is stable and converges to the exact solution.

Advantages

The main advantages of using the eigenvalues of the A matrix for studying stability are:

(1) Such a study gives rigorous stability criteria which apply to all numerical approximations of a stepping nature for a wide variety of linear problems, and which apply regardless of the nature of the problem being approximated, or the origin of the system of difference equations. Further, any instability occurring in the calculation is seen to be caused by the eigenvalues of the stepping procedure, and not by round-off error. An exception is that, for some specific problems, where the initial conditions are such that all the eigenvalues with absolute values larger than one are associated with a zero weighting, round-off error can cause these weights to change slightly, and these eigenvalues become active, giving an unstable result.

(2) Stability criteria can be easily found because the absolute value of the maximum eigenvalue can be bounded by easily calculated

matrix norms. Moreover, the cause of an instability often becomes immediately obvious, and possible ways of obtaining stable solutions can sometimes be seen.

Although proofs of stability have been based on a matrix analysis of eigenvalues for methods of iteration and of approximations for ordinary differential equations, they have not been used (until recently) to derive stability criteria for approximate methods for partial differential equations. It is for this type of approximate solution that the matrix norms are particularly useful, since they reduce the problem of stability to a trivial calculation for many cases, instead of a relatively complicated Fourier analysis usually used. Further, the instability obtained in approximate solutions for partial differential solutions is shown to be caused in the same way as that which occurs in the solution of systems of ordinary differential equations or in successive approximate calculations.

Argument

The solution of the difference equation PI-1 is:

$$y_n = C\,Q^n C^{-1} y_0 + C \sum_{p=1}^{n} Q^{n-p} C^{-1} f_{p-1} \qquad \text{(PI-2)}$$

where Q is a diagonal matrix of eigenvalues q_j or Jordan boxes containing eigenvalues and C is the matrix of eigenvectors and principal vectors.

If the elements in y_n are not to go to infinity as n goes to infinity, when n is bounded, then all the eigenvalues q_j must be less than one in absolute value. Further, if the minimum norm is less than one in these circumstances, then the eigenvalues are all less than one in absolute value, and the procedure is stable.

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PROPOSITION II

Proposition

The z-transform operational calculus (PII. 1) can be used to find complete analytic solutions of systems of linear difference equations which are represented by a partial difference equation together with boundary equations and for which an initial condition is known. This solution with z-transforms follows that of Laplace transforms for partial differential equations (PII. 2).

Uses

Partial difference equations are usually obtained by a direct differencing of a partial differential equation. From this partial difference equation a system of difference equations can be generated which, together with approximations for boundary conditions, can be used to step out a numerical approximate solution to the partial differential equation. The complete analytic solution of such a partial difference equation can be compared to a corresponding solution of the partial differential equation, leading to a detailed understanding of the accuracy of difference approximations to partial differential equations.

The solution of a partial difference equation is in terms of the eigenvector and eigenvalues of the characteristic matrix of the system of difference equations. These eigenvalues and eigenvectors are obtained

from a z-transform solution of the partial difference equation which, together with boundary equations, generates the matrix. Consequently this z-transform procedure can also be used to solve some matrix eigenvector-eigenvalue problems.

Advantages

The two main advantages of z-transform solutions of partial difference equations over other methods of solution, such as separation of variables or direct matrix methods, are:

(1) The complete analytic solution which fits the initial condition and which contains the particular solution is obtained by the procedure. Thus, no additional work is necessary to find or use orthogonality relationships to fit the initial condition, or to obtain a simple expression of a finite summation for the particular solution.

(2) The z-transform technique provides a methodical procedure for solving partial difference equations which requires a minimum of ingenious and adroit manipulations. The main obstacle to carrying the solution to completion is in finding a solution for the transformed partial difference equation, which is an ordinary difference equation for problems in two variables. The reason for this difficulty, which does not occur for Laplace transforms of partial differential equations, is that solutions of ordinary difference equations are not as well known as those of differential equations.

Argument

No special analytic justification appears to be necessary for applying z-transforms to partial difference equations. The only difference between their application here, compared to their customary application, is that the transformed equation is an ordinary difference equation or a partial difference equation of one less variable than the original equation, rather than an algebraic equation. However, this does not lead to any mathematical inconsistencies in the mathematical theory of the transform or in the inversion of the transform.

This technique has been used in this thesis (Chapter IV, section D) to solve the partial difference equation of diffusion in one space dimension in Cartesian coordinates. These solutions are the same as those obtained by other methods, and also give the same numerical results as are obtained by stepping out the difference solutions. Thus, there appears to be little doubt about the applicability of this method to the partial difference equation of diffusion or to partial difference equations which result from a direct differencing of partial differential equations which can be solved with Laplace transforms. However, as with any transform technique, partial difference solutions obtained with z-transforms should be checked to be sure of their validity.

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PROPOSITION III

Proposition

The sediment by extraction test for residual fuel oils, ASTM D473-59 (PIII. 1) when applied to petroleum tars resulting from the thermal cracking of straight-run residuums and catalytic cycle oils is a measure of the compatibility of the fuel oil with benzene rather than a measure of solid material that would separate in the absence of benzene. The fact that most such thermally cracked tars are incompatible with benzene accounts for the relatively poor repeatability and reproducibility of up to about 40 per cent error reported for this test.

Argument

Many authors, as summarized in Sachanen (PIII. 2, P. III. 3), have reported incompatibility of some hydrocarbons with residual fuel oils. For example, the addition of a low-boiling paraffin hydrocarbon, such as normal pentane, to either a straight-run or cracked residuum causes organic material to be precipitated or flocculated. Such an incompatibility also can occur when two fuel oils, one of straight-run stock, the other of cracked residuum, are mixed. In this case the deposit is usually shown by rapid fouling of heater surfaces (PIII. 2).

An explanation (PIII. 3) of this behavior is that the organic material precipitated is made up of long-chain molecules with polycyclic nuclei which were originally in colloidal solution or fine

suspension in the residual. These materials are precipitated as they are lyophobic with respect to paraffins. Some of the precipitated solids can be colloidally dispersed by the addition of aromatic hydrocarbons such as benzene. Although any distinction between these materials is arbitrary, solids precipitated with normal pentane, and which can be dispersed in benzene, are referred to as asphaltenes; those that cannot be dispersed in benzene are called carbenes. Cracked residuums contain more carbenes than the straight-run residuums and they are thought to be formed by dehydrogen polymerizations and condensation reactions during the cracking operation.

Secondly, with the advent of residuum strippers and catalytic cracking units in petroleum processing in the early 1950's, the feed to thermal crackers changed drastically. Instead of having a feed of straight-run oils boiling above about 650° F, the feed now is made up of straight-run residuum boiling above 900-1050° F and a heavy cycle oil from the catalytic cracking unit usually boiling at about 650° F. This heavy cycle oil contains mostly relatively high-boiling aromatic and unsaturated hydrocarbons instead of paraffinic hydrocarbons as before. The effect of this change in feed is that the thermal crackers must have more severe cracking conditions to approach gasoline yields obtained previously and that the residual thermally cracked tar probably contains more carbenes than before. Further, the carbenes produced in thermal cracking probably contain less hydrogen than previously,

and their molecules probably have longer chains with possibly more rings. However, the cracked oils formed by thermal cracking of these feeds are high-boiling aromatic hydrocarbons which act as effective peptizers. Thus the carbenes remain peptized and do not deposit after the cracking has stopped.

However, benzene, with the lowest molecular weight of the aromatic hydrocarbons, is not as effective a peptizer for these carbenes. When it is added, it dilutes and replaces the heavy aromatic hydrocarbons that are adsorbed by the carbenes, and the carbenes precipitate. As this process takes time the amount of carbenes which are precipitated is a function of both the time of contact and the relative amount of benzene added.

Finally, in the ASTM test the volume of dilution is reasonably well controlled, but the time of contact can vary widely. The extraction is carried out by refluxing benzene into the oil sample contained in a porous thimble. Thus, the time of contact is a function of the rate of refluxing, the viscosity of the oil, and the permeability of the porous thimble. This probably accounts for the rather large range of confidence limits shown in the ASTM procedure.

Suggestions

Since sediment by extraction is a specification of No. 6 residual fuel oil (ASTM D396-62T), an effort should be made to remove the ambiguity from its meaning and to make the test more reproducible. It probably should be decided if the fuel oil compatibility with a light aromatic solvent such as benzene is related to an important fuel oil quality. Fuel oil compatibility with other fuel oils can be measured more directly using blends of the test fuel oil with two standard fuel oils of different blends in the NBTL heater tube test (PIII.3). Further, it has been pointed out that fuel oils containing aromatic stocks such as

catalytic cycle oils are compatible with most any other fuel.

If it is decided that the compatibility of the fuel with benzene is important or that this property correlates with other important qualities of fuel oil, then a better test should be devised. A possibility is that the oil could be diluted with benzene in a fixed ratio and allowed to age a certain time before filtering through a porous thimble. Filtration immediately after dilution would give a good indication of solid material originally separated in the oil. After aging for as much as 12 to 24 hours at a fixed temperature the amount of sediment would be a measure of the incompatibility of the fuel with benzene. Neither of these amounts of sediment would agree even in order of magnitude with the sediment as measured by the sediment by extraction test ASTM D473-59.

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PROPOSITION IV

Proposition

In the teaching of science and engineering, the transient and evolutionary character of all scientific theories should be emphasized. It should also be pointed out that not only are the new, more speculative theories open to question, but often even the basic concepts of accepted theories must be significantly modified, or rejected, in light of new experimental data, or because of entirely new theories better able to account for the phenomena. Moreover, theories rejected earlier are sometimes revived in a modified form. This transient nature of theories should be contrasted to the fact that accurate measurements, observations, and descriptions of physical phenomena are always valid.

Argument

Although most scientists would agree that all theories are always tentative, in the past scholars have taken the attitude that some theoretical hypotheses were unchallengeable. Such attitudes undoubtedly retarded the advance of science significantly.

One of the most glaring examples of this attitude was that of the ancient Greeks to the effect that all planetary movement is described by motion compounded from circular motion. This hypothesis was developed by Ptolemy in the second century A. D. to describe planetary motion with a fairly complicated method using epicycles. This technique, with the earth in a fixed position, gave relationships which agreed to within the accuracy of the astronomical observations then available, and lasted virtually unchanged for almost 1400 years until Copernicus simplified the theory by assuming that the

earth moved around the sun. Finally, Kepler, in the early seventeenth century, using the accurate data of Tycho Brahe, discovered the elliptical nature of the orbits.

This discovery, which in all probability helped Newton to formulate his laws of mechanics, undoubtedly was retarded because the scholars themselves considered only circular, or compounded circular, motions. The refusal to depart from one line of thought must have been due in part to limitations which they unconsciously placed on themselves. Such unconscious limitations often can prevent one from finding an obvious solution. For example, in the problem of trying to arrange six matches to form four triangles, the false assumption is often made that this must be done in two dimensions. Whereas, if the problem is expanded into three dimensions the solution becomes trivial.

Another explanation of the long time which was required for the solution of the planetary orbits is given in Astronomy , by Fred Hoyle (PIV.1). He remarks that if the sun-centered solar system with circular planetary orbits, postulated tentatively in the second century B.C. by Aristarchus, had been accepted and used, the history of astronomy and of science would have been changed radically. The reason that this theory was rejected then and for several hundred years thereafter was that it did not describe planetary motion as accurately as the developed epicycle theory. This leads Hoyle to state that, "Here we have a remarkable example to show that it does not always pay to know too much about the facts of the situation, " * and "The Greeks . . . were attempting to represent phenomena that were far too complicated for them. " *

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* Fred Hoyle, Astronomy , Doubleday and Co., Inc., Garden City, New York (1962), p. 91.

However, it was not too complicated for Kepler who had even more accurate data to work with. Indeed, Hoyle states that " . . . Kepler had a far greater respect for facts than the average scientist has . . . " * Thus, it appears that it was not wholly the accurate data that retarded the understanding of planetary motion, but a good portion of the responsibility must go to the unquestioning acceptance of the hypothesis of circular motion.

Although our understanding of both scientific phenomena and scientific theory have greatly increased since the days of Kepler, we must be watchful lest any of even our most successful theories become dogma. However, even today, one hears of data which have not been reported because of lack of agreement with current theory. Indeed, if the data are clearly in error they should be reported as such; if, however, they are accurate, it is most important that they be reported so that the theory not be used inappropriately, and so that the need for a better theory be recognized. Moreover, in many publications empirical relationships are often presented in an apologetic manner. It is rather the theorist who should apologize for not having a satisfactory theory to explain the relationship. In fact, many of our theories have been developed as explanations for such empirical relationships. Feinberg and Goldbar, writing on the conservation laws of physics (PIV.2), express the opinion that the proper relationship between theoretical and empirical results can become obscured today. They comment, " Consequently, there has been a tendency to forget that the basis of the conservation laws is, after all, empirical, . . . "

The predicament of the ancient Greeks, of trying to represent facts too complicated for them, and facts which were so accurate that partially developed theories were not satisfactory, also is the predicament of modern engineers

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* Ibid., p. 119.

and scientists. Further, Hoyle's hope that "discordant facts will not appear until worthwhile theories have had a chance to establish themselves" * is probably almost never possible, and moreover, it is only these "discordant facts" which indicate which theories are worthwhile and which allow us to use the theories intelligently.

The way to maintain scientific progress is not to suppress these facts, but for those involved in both the theory and practice of science and engineering to develop a proper perspective. This means emphasizing that too much significance can be attached to a successful theory and that " no theory ever proposed has been found ultimately to fit all the facts . . ." * With these ideas in mind no useful theory should be prematurely rejected nor should any theory, concept, or hypothesis, even though very successful, be elevated to dogma.

Suggestions

Several suggestions to bring out the tentative nature of theory are:

(1) The basic texts that first introduce students to scientific theory should give an indication of the evolution of the theories. They should not present the material in such a fashion that it appears to the student that all the answers have been found, but they should mention the discordant facts as well as the successes of the theories.

(2) On advanced levels, not only should the more complicated theories be presented, but the contradictions between these theories and empirical results should be emphasized. Further, it should be pointed out that many of these theories are almost useless in obtaining results for practical problems.

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* Ibid., p. 91.

(3) In history courses, the evolution of scientific theories and of technology should be made a part of the material covered. Not only should mention be made of the significant effect of these ideas on social, economic, and political factors, but also the effect of the evolutionary changes in science upon science itself should be brought out. In philosophy courses additional emphasis should be given to exploring proper relationships and perspectives between theory and empiricism.

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PROPOSITION V

Proposition

In a recent study of the steady state of a jacketed tubular reactor with a packed bed, in which an exothermic chemical reaction is occurring under flow conditions, Barkelew (PV.1) presents relations which show conditions which give an "unstable" reactor design. In an earlier study of both a linearized transient solution and the steady-state solution of an exothermic chemical reaction occurring in a jacketed empty tubular reactor, Bilous and Amundson (PV.2) show that a "parameter sensitivity" can occur.

The proposition is that the "instability" of Barkelew and the "parameter sensitivity" of Bilous are one and the same. Further, Barkelew's relations are suitable for empty tubes, and only under certain circumstances are they actually valid for packed-tube reactors. A brief analysis is also presented that should allow Barkelew's results to be generalized for other conditions in packed tubes and should give additional information about controlling the reaction.

Argument

In both studies, the equations are for a plug-flow reactor:

$$C_p \sigma \frac{\partial T}{\partial \theta} = - A h (T - T_j) - C_{p\,f} G \frac{\partial T}{\partial z} + Q R \qquad \text{(PV-1)}$$

$$\sigma_f \frac{\partial x}{\partial \theta} = - R - G \frac{\partial x}{\partial z} \qquad \text{(PV-2)}$$

for the first order reaction

$$A \longrightarrow B$$

where C_p = heat capacity

σ = density

A = tube surface area per unit volume

h = heat-transfer coefficient

T = temperature of fluid in cross-section

G = mass velocity

θ = time

z = distance along tube

Q = heat of reaction

R = rate of reaction

x = fraction of reactant in fluid

The difference between the equations is that the unsubscripted C_p and σ in the above equations are averaged values for both the fluid and the bed for the packed reactor; for the empty tube they are just the fluid quantities.

The expression used for the reaction rate in Barkelew's study can be applied to other than first-order reactions; but his reaction rate uses an exponential temperature dependency that is the same as the Arrhenius expression only when there is little difference between the temperature of the reactants and of the coolant. Bilous uses the conventional Arrhenius temperature dependency for the rate.

In the Bilous study the equations were solved for the steady-state temperature and concentration distributions using an analog computer. These distributions, under some conditions, showed that the maximum temperature in the reactor would increase very rapidly with small increases in the wall or jacket temperature or with small reductions in the heat-transfer coefficient.

On the basis of this behavior, Bilous defines "parametric sensitivity" as the phenomena occurring when " . . . reactor operation, without being unstable in the literal sense, will be extremely sensitive to small changes in the operating characteristics of the system." He further shows analytically that this "parametric sensitivity" is related to the transient response of the system to either a step change or a continuing sinusoidal input to the reactor. This transient response is based on a linearization of the above equations about the steady-state solution.

Barkelew numerically integrated the dimensionless equations equivalent to equations PV-1 and PV-2 with their time derivatives equal to zero for several hundred combinations of several dimensionless parameters. His steady-state temperature distributions show a behavior like that of the analog solution, and Barkelew states that " . . . there are indeed regions of extreme sensitivity to changes in parameters." His precise definition of "stability" is based on a graph that relates the maximum temperature to dimensionless ratios.

Thus, as both studies are based on the same partial differential equations, the steady-state solutions would be expected to be similar. Further, that Barkelew's "stability" is essentially the same as Bilous' "parametric sensitivity" can be seen by using Barkelew's defining graph to predict the conditions of parametric sensitivity for the problems solved by the analog. Such a numerical check does predict the parametric sensitivity of case B in Bilous. A similar calculation for Bilous' case A does not check because of the difference in Barkelew's expression for the rate of reaction mentioned above.

In both studies, the partial differential equations solved neglect several effects, including the radial temperature distribution. The temperature at each cross-section of the tube is assumed to be constant except for the drop

across a thin film at the wall. Although this is a good assumption for the empty-tube reactor with large Reynolds numbers, a significant radial temperature distribution can occur in a packed-bed reactor. As Barkelew points out, this error for the packed beds would tend to make an unstable reactor appear to be stable.

A logical extension of Barkelew's analysis that avoids this ambiguity would be to estimate a radial temperature distribution at the cross-section of maximum temperature. If we assume that at this cross-section the temperature gradient along the tube is zero, then replacing the term $-h A (T-T_j)$ with a radial energy flow term $(ke/r)(\partial/\partial r)\, r(\partial T/\partial r)$, there is obtained

$$ke\left[\frac{d^2T}{dr^2} + \frac{1}{r}\frac{d^2T}{dr}\right] + Q R = 0 \qquad (PV-3)$$

where ke = average thermal conductivity of fluid and bed

r = radial coordinate

The boundary equations for equation PV-3 are:

at the tube wall $$ke\frac{dT}{dr} = h(T-T_j) \qquad (PV-4)$$

at the center $$\frac{dT}{dr} = 0 \qquad (PV-5)$$

If one assumes that the reaction rate is either constant or a linear function of temperature, equation PV-3 can be solved analytically giving an estimated radial temperature distribution for that cross-section. In solving this equation the maximum temperature and concentration at this cross-section can be found from Barkelew's relationships and used in estimating the reaction rate. From the solution to equation PV-3 it should be apparent if a significant radial

temperature distribution does occur and if Barkelew's results wrongly predict a stable reactor design.

Conclusions

The fact that "parametric sensitivity" and "unstable" conditions are the same is important, because then Barkelew's results for a fairly wide range of kinetics and parameters are related to the transient response for empty tubular reactors. It should be pointed out that the transient response of a packed-bed reactor is expected to occur at a different rate than that of an empty reactor, even though the steady-state conditions of both might be similar. Also, a fairly simple method of estimating the radial temperature distribution at the cross-section of maximum temperature for a packed-bed reactor has been proposed to check the assumption of negligible radial temperature distribution.

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