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An extremum variational principle for some non-linear diffusion problems

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Abstract—An extremum variational principle for two non-linear boundary value problems is formulated. The first boundary value problem corresponds to the coupled diffusion reaction with high-order kinetics. The second boundary value problem describes zero-order chemical kinetics in a single catalyst pellet with Robin boundary conditions at the pellet's outer surface. For both problems, approximate solutions and their error estimates for several values of the parameters are obtained.

INTRODUCTION

CHEMICAL reaction and diffusion problems often lead to non-linear boundary value problems for ordinary and partial differential equations. For example, steady-state problems with a single reaction are described by a boundary value problem of the form [1]

$$x^{-s}\frac{d}{dx}\left(x^s\frac{dy}{dx}\right)-f_0(y)=0,\quad 0<x<1 \qquad (1)$$

and

$$\text{for } x=0\quad \frac{dy}{dx}=0;\quad \text{for } x=1\quad \frac{dy}{dx}=Bi(1-y). \qquad (2)$$

In equations (1) and (2) y denotes the non-dimensional concentration, x the (single) space coordinate, s depends on the problem geometry and has the values 0, 1, 2 for a slab, cylinder and sphere, respectively, and Bi is the Biot number.

The function $f_0(y)$ may have a variety of forms and in what follows we shall assume that it is given by

$$\text{(i)}\quad f_0(y)=\frac{\phi^2(1+k)y^n}{k+y^n} \qquad (3)$$

and

$$\text{(ii)}\quad f_0(y)=\phi^2y^n. \qquad (4)$$

In equations (3) and (4) ϕ^2 is the Thiele modulus, n the reaction order and k the non-dimensional parameter that measures the influence of the catalyst on the process.

Thus equations (1) and (2) with f_0 given by (i) describe the diffusion reaction with nth order kinetics inside a single catalyst pellet, while equations (1) and (2) with f_0 given by (ii) describes the diffusion reaction with nth order kinetics.

Different aspects of the boundary value problem, equations (1) and (2), with f_0 given by equation (3) were studied, for example, in refs. [1–5].

In what follows we shall treat the boundary value problems (1), (2), (3) and (1), (2), (4) by a variational procedure developed in ref. [6]. Thus we shall first construct an extremum variational principle for both problems. Then this principle will be used to obtain an approximate solution to the problem. Finally, the error in the approximate solution will be estimated. The error estimating procedure presented here is somewhat different from the procedure presented in ref. [6].

VARIATIONAL PRINCIPLE

(i) First we consider diffusion inside a single catalyst pellet. In this case $f_0(y)$ is given by (i), that is the diffusion process is described by

$$x^{-s}\frac{d}{dx}\left(x^s\frac{dy}{dx}\right)-\frac{\phi^2(1+k)y^n}{k+y^n}=0 \qquad (5)$$

$$\frac{dy}{dx}=0\ \text{ for } x=0,\quad \frac{dy}{dx}=Bi(1-y)\ \text{ for } x=1. \qquad (6)$$

The variational method developed in ref. [6], when applied to equations (5) and (6), shows certain difficulties in the error estimating procedure. Therefore, we transform equations (5) and (6) by introducing a new independent variable by the relation

$$t=x^{1+s}. \qquad (7)$$

Then equations (5) and (6) become

$$\frac{d}{dt}\left(Dt^{2s/(1+s)}\frac{dy}{dt}\right)-\frac{Ay^n}{k+y^n}=0 \qquad (8)$$

$$\lim_{t\to 0}t^{s/(1+s)}\frac{dy}{dt}=0$$

$$\frac{1}{Bi}\sqrt{D}\frac{dy(1)}{dt}=(1-y(1)) \qquad (9)$$

NOMENCLATURE

A	constant, $\phi^2(1+k)$	n	constant, order of reaction
Bi	Biot number	k	constant, measures the influence of the catalyst
C_m	constant in expression (29)	p	generalized momentum
C_0	constant in expression (A4)	t	new independent variable
D	constant, $(1+s)^2$, $s = 0, 1, 2$	x	space coordinate
$L, \mathscr{L}, G$	Lagrangian density	y	non-dimensional concentration.
I, I_1, I_2	functional in equations (11), (16) and (27), respectively		
H	Hamiltonian function	Greek symbols	
f	error of approximate solution	α	constant in equation (41)
$f_0(y)$	generating function in equation (1)	β, γ	constants in the trial solutions
dm	constant in expression (33)	ϕ^2	Thiele modulus
m	constant, $2s/(1+s)$, $s = 0, 1, 2$	ϕ_{cr}	critical value of Thiele modulus.

where $A = \phi^2(1+k)$ and $D = (1+s)^2$. Let

$$F(y) = \int^y \frac{Aq^n}{k+q^n}\,dq \tag{10}$$

then it is easy to see that equations (8) and (9) are equivalent to the stationary condition ($\delta I = 0$) for the following functional:

$$I = \int_0^1 L\,dt - \{y(1) - [y(1)^2/2]\}\sqrt{D}\,Bi \tag{11}$$

where

$$L = \frac{D}{2} t^m \left(\frac{dy}{dt}\right)^2 + F(y) \tag{12}$$

and $m = 2s/(1+s)$.

From equation (12) we can define a generalized momentum as

$$p = \frac{\partial L}{\partial \dot{y}} = Dt^m \dot{y} \tag{13}$$

where $(\dot{\ }) = d(\ )/dt$. The Hamiltonian of the problem becomes

$$H = p\dot{y} - L = \frac{p^2}{2Dt^m} - F(y) \tag{14}$$

so that the canonical equations corresponding to equation (8) read

$$\dot{y} = \frac{\partial H}{\partial p} = \frac{p}{Dt^m}$$
$$\dot{p} = -\frac{\partial H}{\partial y} = \frac{Ay^n}{k+y^n}. \tag{15}$$

We can now apply the procedure developed in ref. [6] to problem (8), (15). Let y be the exact solution to equations (8) and (9). From ref. [6] we conclude that the functional I_1 given by

$$I_1 = \int_0^1 \mathscr{L}(Y, \dot{Y}, \ddot{Y})\,dt - (Dt^m Y\dot{Y})_0^1 \tag{16}$$

with

$$\mathscr{L}(Y, \dot{Y}, \ddot{Y}) = Dt^m \dot{Y}^2 + F(Y) + \dot{P}\phi(\dot{P}) - F[y = \phi(\dot{P})] \tag{17}$$

where

$$\dot{P} = Dmt^{m-1}\dot{Y} + Dt^m \ddot{Y}$$
$$\phi(\dot{P}) = \left(\frac{k\dot{P}}{A-\dot{P}}\right)^{1/n} \tag{18}$$

is stationary ($\delta I = 0$) for $y = Y$. Also, $[\ldots]_0^1$ in equation (16) is used to denote the difference of the values of the function in brackets calculated for $t = 1$ and 0, respectively. In equation (16) Y is an admissible trial function that satisfies boundary conditions (9). Moreover, functional (16) has for $Y = y$ the value zero (see p. 206 of ref. [6]). Therefore, we have

$$I_1(y) = 0, \quad \delta I_1(y, f) = 0, \quad f = Y - y. \tag{19}$$

In the analysis that follows Y will be an approximate solution to the boundary value problem (8), (9). Then the error of the approximate solution will be expressed in terms of $f = Y - y$. Expanding $I_1(Y)$ as

$$I_1(Y) = I_1(y) + \delta I_1(y, f) + \tfrac{1}{2}\delta^2 I_1(\Psi, f) \tag{20}$$

where $\delta^2 I_1$ is the second variation of I_1 and

$$\Psi = y + \varepsilon f, \quad 0 < \varepsilon < 1 \tag{21}$$

and observing equations (19), we obtain

$$I_1(Y) = \tfrac{1}{2}\delta^2 I_1(\Psi, f). \tag{22}$$

Note that f satisfies the following boundary conditions (cf. equations (9))

$$\lim_{t\to 0} t^{s/(1+s)}\dot{f}(t) = 0$$
$$\frac{1}{Bi}\sqrt{(D)}\dot{f}(1) + f(1) = 0. \tag{23}$$

Calculating the second variation of equation (16), and using it in equation (22), we have

$$I_1(Y) = -Df(1)\dot{f}(1)+\frac{1}{2}\int_0^1\left[\frac{kAn\Psi^{n-1}}{(k+\Psi^n)^2}f^2+2Dt^m\dot{f}^2 + D^2\left(\frac{\partial\Phi}{\partial\dot{P}}\right)\bigg|_{\dot{P}=Dmt^{m-1}\Psi}+Dt^m\ddot{\Psi}(mt^{m-1}f+t^m\dot{f})^2\right]\mathrm{d}t. \quad (24)$$

From equation (24) we shall determine a bound on the L_2 norm of f.

(ii) We consider now the diffusion reaction with nth order kinetics described by

$$x^{-s}\frac{\mathrm{d}}{\mathrm{d}x}\left(x^s\frac{\mathrm{d}y}{\mathrm{d}x}\right)-\phi^2y^n = 0 \quad (25)$$

with boundary conditions (6). Introducing a new dependent variable t by equation (7), equation (25) becomes

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(Dt^{2s/(1+s)}\frac{\mathrm{d}y}{\mathrm{d}t}\right)-\phi^2y^n = 0. \quad (26)$$

The boundary conditions corresponding to equation (21) are given by equations (9). Repeating the same procedure as in case (i) we conclude that the exact solution y to equations (26) and (9) gives a stationary value to the functional

$$I_2 = \int_0^1\left[Dt^m\dot{Y}^2+\phi^2\frac{1}{n+1}Y^{n+1} + \frac{n}{n+1}\ddot{Y}\left(\frac{\ddot{Y}}{\phi^2}\right)^{1/n}\right]\mathrm{d}t-(Dt^m\dot{Y}Y)_0^1. \quad (27)$$

In equation (25) Y belongs to the same class of admissible trial functions as defined in case (i). Also, if $f = Y-y$, where y is the solution of equations (26) and (9), then by the same argument, we obtain

$$I_2(Y) = \tfrac{1}{2}\delta^2I_2(\Psi,f) = -Df(1)\dot{f}(1)+\frac{1}{2}\int_0^1\left[2Dt^m\dot{f}^2 + n\phi^2\Psi^{n-1}f^2+\frac{1}{\phi^{2n}}\frac{1}{n}(\ddot{\Psi})^{(1-n)/n}(mt^{m-1}f + t^m\dot{f})^2\right]\mathrm{d}t. \quad (28)$$

Again, equation (28) will be the basis for estimating the error of an approximate solution Y to the boundary value problem (26), (9).

ERROR ESTIMATING PROCEDURE

In this section we shall derive bounds on a certain norm of the function $f = Y-y$. The basis for our analysis are relations (24) and (28). The method presented here is slightly different from the method presented in ref. [6]. Namely, here we shall not assume that the approximate solution Y is close, in some sense, to the exact solution y. Again we consider two cases.

(i) Suppose that $(\partial\Phi/\partial\dot{P}) \geqslant 0$. Let C_m be a constant such that

$$\int_0^1\left[2Dt^m\dot{f}^2+\frac{kAn\Psi^{n-1}}{(k+\Psi^n)^2}f^2\right]\mathrm{d}t \geqslant C_m\int_0^1\dot{f}^2\,\mathrm{d}t. \quad (29)$$

In the Appendix we shall show how C_m can be determined. Then using expression (29) in equation (24), we obtain

$$-2D\dot{f}(1)f(1)+C_m\|\dot{f}\|^2 \leqslant 2I_1(Y) \quad (30)$$

where

$$\|\dot{f}\| = \left(\int_0^1\dot{f}^2\,\mathrm{d}t\right)^{1/2}.$$

From expression (30) we can, in certain cases, estimate the L_∞ norm of f. For example, if $f(1) = 0$, then the Cauchy inequality gives

$$\|f\|_{L_\infty} = \sup_{t\in[0,1]}|f(t)| \leqslant \|\dot{f}\| \quad (31)$$

so that expression (30) gives

$$\|f\|_{L_\infty} \leqslant \left[\frac{2I_1(Y)}{C_m}\right]^{1/2}. \quad (32)$$

(ii) From equation (28) we can derive an estimate similar to expression (30). Suppose that in equation (28) $\ddot{\Psi} \geqslant 0$ and let $\mathrm{d}m$ be a constant such that

$$\int_0^1[2Dt^m\dot{f}^2+n\phi^2\Psi^{n-1}f^2]\,\mathrm{d}t \geqslant \mathrm{d}m\int_0^1\dot{f}^2\,\mathrm{d}t. \quad (33)$$

Then, using expression (33) and the fact that $\ddot{\Psi} \geqslant 0$ in equation (28), we obtain

$$\mathrm{d}m\|\dot{f}\|_{L_2}^2-2D\dot{f}(1)f(1) \leqslant 2I_2(Y). \quad (34)$$

Again, if $f(1) = 0$, then the Cauchy inequality and expression (34) give

$$\|f\|_{L_\infty} \leqslant \left[\frac{2I_2(Y)}{\mathrm{d}m}\right]^{1/2}. \quad (35)$$

The value of the constant $\mathrm{d}m$ in expression (33) is determined in the Appendix.

NUMERICAL RESULTS

In this section we shall find an approximate solution to the boundary value problem (1), (2) for $f_0(y)$ given by equations (3) and (4) and for a few specific values of characteristic constants.

(i) Consider first the boundary value problem (1), (2), (3) for

$$s = 0, \quad Bi = \infty, \quad n = 1. \quad (36)$$

We assume an approximate solution in the form

Table 1. Numerical results for generating function (3)

s	Bi	n	k	ϕ^2	$I_1(Y)$	β	γ	$\|f\|_{L_\infty} \leq$
0	∞	1	3	1	1.13×10^{-3}	0.37	2.13	3.132×10^{-2}
0	∞	1	3	4	1.72×10^{-2}	0.75	2.7	9.88×10^{-2}

$$Y = (1-\beta)+\beta t^{\gamma} \tag{37}$$

where β and γ are constants to be determined. Note that equation (37) satisfies boundary conditions (9) if $\gamma > 1$. The functional (16), after using (36), becomes

$$I_1 = \int_0^1 \{k\phi^2(1+k)\ln k\phi^2(1+k)+\dot{Y}^2 + \phi^2(1+k)Y - k\dot{Y} - k\phi^2(1+k)\ln(k+Y) - k\phi^2(1+k)[\phi^2(1+k)-\dot{Y}]\}\,dt. \tag{38}$$

Constants β and γ in equation (37) are determined by substituting equation (37) into equation (38) and minimizing with respect to β and γ. The results together with error estimate (32) are given in Table 1. We also treated the case when $k \ll 1$ and ϕ has the value larger than the critical value, which in the case of slab catalyst ($s = 0$) reads [3]

$$\phi_{cr} = \left(\frac{2}{1+2/Bi}\right)^{1/2}. \tag{39}$$

For this case we assume an approximate solution in the form

$$Y(t) = 0 \quad \text{for} \quad t \in [0,\alpha]$$

$$Y(t) = \frac{t-\alpha}{1-\alpha}+\beta[\alpha-(1+\alpha)t+t^2] \quad \text{for} \quad t\in[\alpha,1] \tag{40}$$

where α defines a point, inside a catalyst pellet, from which the concentration of chemical reactant is equal to zero. Its value was determined in ref. [3] and for $Bi = \infty$ reads

$$\alpha = 1-\frac{\sqrt{2}}{\phi}. \tag{41}$$

We used α defined by equation (41) and a trial function (40) in functional (38). The constant β was determined by minimizing I_1. The values for sample calculations are presented in Table 2.

(ii) Consider now the boundary value problem (1), (2), (4) for

$$s = 0, \quad Bi = 10^6, \quad n = 2;5;10. \tag{42}$$

Functional (27) in this case becomes

$$I_2(Y) = \int_0^1 \left[\dot{Y}^2+\frac{\phi^2}{n+1}Y^{n+1}+\frac{n}{n+1}\dot{Y}\left(\frac{\dot{Y}}{\phi^2}\right)^{1/n}\right]dt - Bi[1-Y(1)]Y(1). \tag{43}$$

We used a trial function in the form

$$Y = \left(1-\beta-\frac{\beta\gamma}{Bi}\right)+\beta t^{\gamma}. \tag{44}$$

Function (44) satisfies boundary conditions (9) for all values of constants β and γ. By substituting equation (44) into equation (43) and minimizing with respect to β and γ the results shown in Table 3 were obtained.

CONCLUSION

We have shown in this paper that the variational principle formulated in ref. [6] could be successfully used for finding approximate solutions of non-linear diffusion-reaction problems of the type (1), (2), (3) and (1), (2), (4). The error estimate procedure, based on the value of the functional, is also presented.

For sample calculations we used simple one- and two-parameter trial functions which, in certain cases, showed remarkable accuracy. For approximate solutions with better error estimates one would have to use more elaborate trial functions.

Table 2. Numerical results for generating function (3) and $k \ll 1$

s	Bi	n	k	ϕ^2	$I_1(Y)$	β	$\|f\|_{L_\infty} \leq$
0	∞	1	0.001	10	1.1×10^{-2}	5	1.04×10^{-1}
0	∞	1	0.001	40	4.22×10^{-2}	20	2.04×10^{-1}

Table 3. Numerical results for generating function (4)

s	Bi	n	ϕ^2	$I_2(Y)$	β	γ	$\|\dot{f}\|^2_{L_2}+2Bi\,f^2(1) \leq$
0	10^6	2	2/3	1.09×10^{-3}	0.229	2.11	2.2×10^{-3}
0	10^6	5	1/3	3.16×10^{-4}	0.11	2.1	6.3×10^{-4}
0	10^6	10	2/11	8.71×10^{-5}	0.059	2.12	1.74×10^{-4}

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APPENDIX

(i) Let us determine a lower bound to C_m in expression (29) for

$$m = 0, \quad n = 1, \quad Bi = \infty. \tag{A1}$$

We first determine a bound on $(k+\Psi)$ in expression (29). Note that the exact solution y of equations (8) and (9) with $s = 0$ has the bound $y(t) \leqslant 1$. This follows easily from equations (8) and (9) since $y(t)$ is a convex increasing function. Now, we shall choose an approximate solution $Y(t)$ so that $Y(t) < 1$. Then, from equation (21) it follows that $\Psi \leqslant 1$. Therefore

$$\frac{kA}{(k+\Psi)^2} \geqslant \frac{kA}{(k+1)^2}. \tag{A2}$$

Then, we obtain

$$\int_0^1 \left(2\dot{f}^2 + \frac{kA}{(k+\Psi)^2} f^2\right) \mathrm{d}t \geqslant \int_0^1 \left(2\dot{f}^2 + \frac{kA}{(1+k)^2} f^2\right) \mathrm{d}t. \tag{A3}$$

We determine now a large constant C_0 so that

$$\int_0^1 \left(2\dot{f}^2 + \frac{kA}{(1+k)^2} f^2\right) \mathrm{d}t \geqslant C_0 \int_0^1 \dot{f}^2 \, \mathrm{d}t. \tag{A4}$$

From expression (A4) it follows that

$$\int_0^1 \left\{(2-C_0)\dot{f}^2 + \frac{kA}{(1+k)^2} f^2\right\} \mathrm{d}t \geqslant 0. \tag{A5}$$

Boundary conditions (23), taking into account equation $(\text{A}1)_3$, become

$$\dot{f}(0) = 0, \quad f(1) = 0. \tag{A6}$$

The best constant C_0 in expression (A5) for all $C^2([0, 1], R)$ functions f that satisfy equations (A6), can be obtained by the method described in ref. [7]. Thus, with

$$G = (2-C_0)\dot{f}^2 + \frac{kA}{(1+k)^2} f^2 \tag{A7}$$

we form the Euler–Lagrange equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial G}{\partial \dot{f}} - \frac{\partial G}{\partial f} = 2(2-C_0)\ddot{f} - \frac{2kA}{(1+k)^2} f = 0. \tag{A8}$$

The lowest mode solution to equation (A8) that satisfies equations (A6) leads to

$$C_0 = 2 + \frac{4kA}{(1+k)^2\pi^2}. \tag{A9}$$

(ii) Consider inequality (33) for $m = 0$. Let D_n be a non-negative constant such that

$$\inf_{t\in(0,1)} (n\phi^2\Psi^{n-1}) \geqslant D_n. \tag{A10}$$

Then, repeating the procedure leading to equation (A9), we obtain

$$d_0 = 2 + \frac{4D_n}{\pi^2}. \tag{A11}$$

UN PRINCIPE VARIATIONNEL EXTREMAL POUR QUELQUES PROBLEMES NON LINEAIRES DE DIFFUSION

Résumé—On formule un principe variationnel extrémal pour des problèmes non linéaires de valeurs limites. Le premier problème correspond à la diffusion couplée à une cinétique chimique d'ordre élevé. Le second problème décrit une cinétique chimique d'ordre zéro dans un boulet unique catalyseur avec des conditions de Robin sur la surface du boulet. Pour les deux problèmes, on obtient des solutions approchées avec estimation de l'erreur pour plusieurs valeurs des paramètres.

EIN EXTREMWERT-VARIATIONSPRINZIP FÜR EINIGE NICHTLINEARE DIFFUSIONSPROBLEME

Zusammenfassung—Es wird ein Extremwert-Variationsprinzip für zwei nichtlineare Randwertprobleme formuliert. Das erste Randwertproblem entspricht der gekoppelten Diffusion und Reaktion mit Kinetik höherer Ordnung. Das zweite Randwertproblem beschreibt die chemische Kinetik nullter Ordnung in einem einzelnen Katalysator-Pellet mit Randbedingungen nach Robin an der äußeren Oberfläche. Für beide Probleme werden Näherungslösungen und entsprechende Fehlerabschätzungen für einige Werte der Parameter ermittelt.

ПРИМЕНЕНИЕ ВАРИАЦИОННОГО ПРИНЦИПА ЭКСТРЕМУМОВ К НЕКОТОРЫМ НЕЛИНЕЙНЫМ ЗАДАЧАМ ДИФФУЗИИ

Аннотация—Сформулирован вариационный принцип экстремумов для двух нелинейных краевых задач. Первая краевая задача соответствует одновременному протеканию диффузионного процесса и процесса реагирования с кинетикой высокого порядка. Вторая краевая задача описывает химическую кинетику нулевого порядка в отдельной грануле катализатора с граничными условиями на внешней поверхности, охарактеризованными Робином. Для обеих задач получены приближенные решения и оценки погрешностей при нескольких значениях параметров.