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A reliable automatic simulation of singular electroanalytical transients, by the adaptive Huber method for Volterra integral equations

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ABSTRACT

In a number of transient electroanalytical experiments (such as, in particular, the potential step chronoamperometry) one expects current-time responses having a singularity at time $t = 0$. A reliable simulation of such singular responses is a difficult task. Conventional simulation techniques fail to provide accurate results close to the singularity. A recent extension [L. K. Bieniasz, J. Comput. Appl. Math. 323 (2017) 136] of the adaptive Huber method for solving Volterra integral equations (IEs) is shown to overcome this difficulty in cases when the current behaves like $t^{-1/2}$ for $t \to 0$. The method requires an availability of highly accurate approximants for computing certain integrals of the kernel functions occurring in the IEs. Relevant approximants are elaborated for several most important kernel functions specific of one-dimensional diffusion, and one kernel function for two-dimensional diffusion. The resulting algorithm is tested on two examples of single IEs describing chronoamperometry and cyclic voltammetry for a single reversible charge transfer, and one example of an IE system describing chronoamperometry for an $E_{rev}E_{rev}$ mechanism. Singular transients are simulated automatically with a prescribed accuracy, even for t arbitrarily close to the singularity.

1. Introduction

In a variety of controlled-potential transient electroanalytical experiments [1] one expects theoretically a singularity of the current-time response $i(t)$ at the initial time moment $t = 0$. Such temporal singularities typically occur in the presence of reversible (Nernstian) heterogeneous charge transfer reactions, when there is a discontinuity at $t = 0$, between initial and boundary conditions accompanying partial differential equations that describe a given experiment. Hence, the singularities are most pronounced in the case of potential step chronoamperometric experiments [1]. In other electroanalytical experiments, such as, in particular, the popular linear potential sweep or cyclic voltammetric experiments [1], the singularities are also frequently present formally, even though they tend to be ignored by modellers, in cases when they are unimportant for the analysis of experimental data.

Under conditions of purely diffusional transport in the absence of homogeneous reactions, the singular current-time responses behave asymptotically like $i(t) \sim t^{-1/2}$ when $t \to 0$. This behaviour was revealed, probably for the first time, by Cottrell, in his seminal analysis of chronoamperometry [2]. Later on, the behaviour was proven theoretically in a general way for electrodes of arbitrary geometry [3,4], and confirmed in dozens of studies devoted to particular electrode arrangements. There is also a number of theoretical papers (see, for example, Refs. [5–9]) showing an analogous behaviour for various homogeneous reaction-diffusion systems (although a general proof does not appear available). Further instances of the Cottrell-type singular transients were discovered in systems with migration-diffusion transport [10–13].

A reliable digital simulation [14] of singular current-time responses is a difficult matter. Conventional simulation methods by finite differences, finite elements, or other techniques for the direct numerical solution of partial differential equations, are widely used for this purpose. However, it is probably not commonly realised that it is mathematically not legal to use such methods at the singularity at $t = 0$. This is because most of these methods require, for convergence, an appropriate regularity of the solutions, which is absent at $t = 0$. As a consequence, such simulations are grossly inaccurate close to $t = 0$. Readers interested in the magnitudes of such errors can consult Fig. 2 in Ref. [15] or Fig. 4 in Ref. [16], from which it is seen that errors of the order of 10%, 100%, and even 1000%, are well possible. The concrete values of the initial errors depend on the simulation method, the selection of discretisation grids, and the geometry of the diffusion field (but the errors occur under all kinds of diffusion conditions). The fact that numerical results obtained in such simulations for $t > 0$ are not entirely useless, results from the relatively fast damping of the initial

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errors. However, the damping requires several (possibly many) discrete time steppings to be performed. Therefore, the use of nonuniform temporal and/or spatial grids, or adaptive grids (with temporal grid nodes concentrated near $t = 0$), can improve the simulation of the singular transients at $t > 0$ (see, for example, Refs. [17–19]), although it cannot reduce the errors at nodes closest to $t = 0$. In certain cases one can eliminate the singularities from numerical simulations by using analytical solutions for simplified systems [20,21], if only such analytical solutions are available.

In the present paper we shall demonstrate that the above difficulties can be avoided by an appropriate use of the integral equation (IE) method [22]. We shall describe a new simulation approach to singular transients, employing a specially dedicated recent extension [23] of the adaptive IE solution technique described in Refs. [24–42]. The technique is based on the Huber method [43] for one-dimensional Volterra IEs (with either nonsingular or weakly singular kernels), and it provides automatically solutions possessing a desired accuracy. The approach described here applies to one-dimensional diffusion transport without homogeneous reactions (with the exception of one example of two-dimensional diffusion). Further generalisation of the approach, to one-dimensional diffusion coupled with first order homogeneous reactions, is possible, but it requires an additional work that exceeds the scope of this study. The latter generalisation is planned to be investigated and described separately.

There have not been many former attempts to model singular transients by means of the IEs. Some examples, corresponding to the one-dimensional diffusion transport without homogeneous reactions, are available in Refs. [44–47]. In all these examples the authors tried to solve the IEs analytically, rather than numerically, possibly due in part to the lack of a suitable numerical method. However, analytical solutions may not always be obtainable. As we shall see, the present numerical method is a viable, powerful, and more general alternative to analytical solutions.

2. The adaptive Huber method for singular transients

As was described in Refs. [24–42], the adaptive Huber method is designed for solving generally nonlinear systems of Volterra IEs, that can be written in the form:

$$\boldsymbol{F}(t,\ \boldsymbol{U}(t),\ \boldsymbol{Y}(t)) = \boldsymbol{0}. \tag{1}$$

In Eq. (1) $\boldsymbol{F}(\cdot) = [F_1(\cdot), \ldots, F_M(\cdot)]^{\mathrm{T}}$ is a vector of M functions representing the individual IEs, $\boldsymbol{0}$ denotes the zero vector, $\boldsymbol{U}(t) = [U_1(t), \ldots, U_M(t)]^{\mathrm{T}}$ is a vector of M unknown functions of t, and $\boldsymbol{Y}(t) = [Y_1(t), \ldots, Y_I(t)]^{\mathrm{T}}$ is a vector of I integrals:

$$Y_j(t) = \int_0^t \mathscr{K}_\kappa(t,\ \tau)\ U_\mu(\tau)\ \mathrm{d}\tau \tag{2}$$

with $j = 1, \ldots, I$. In Eq. (2) $\mathscr{K}_\kappa(t,\ \tau)$ with $\kappa = \kappa(j) = 1, \ldots, L$ denotes one of L possible kernels, and $U_\mu(t)$ with $\mu = \mu(j) = 1, \ldots, M$ is one of the unknowns $\boldsymbol{U}(t)$ (the one associated with the jth integral).

According to the method, solutions $\boldsymbol{U}(t)$ are approximated by linear splines over a grid of dynamically selected discrete nodes t_n ($n = 0, 1, \ldots$) along the t axis, with local grid step sizes $h_n = t_n - t_{n-1}$. Consequently, integrals $\boldsymbol{Y}(t)$ are approximated by product-integration trapezium quadratures, with coefficients resulting from the integration of the splines. In this way one obtains systems of nonlinear algebraic equations, which are solved numerically for the approximations $\boldsymbol{U}_n$ to $\boldsymbol{U}(t_n)$ at every successive node t_n. Apart from determining approximate solutions, the method calculates estimates of their local errors. The estimates are used for deciding whether a discrete solution obtained possesses a requested accuracy, or has to be recalculated using a reduced step size h_n. They also serve for predicting subsequent step sizes.

In the spirit of the so-called product-integration methods for IEs, the above calculation of approximate solutions and their error estimates requires an availability of analytical formulae for the moment integrals of the kernel functions $\mathscr{K}_\kappa(t, \tau)$:

$$\int_0^t \mathscr{K}_\kappa(t,\ \tau)\ \tau^m\ \mathrm{d}\tau \tag{3}$$

with $m = 0, 1, 2$. Alternatively, in cases when such formulae do not exist, highly accurate approximants for the moment integrals must be developed (throughout this paper we use the phrase “highly accurate” to denote quantities, the relative error of which is comparable to, or even lower than the error of machine representation of double precision variables, which is about 10^{-16} according to the IEEE 754 standard [48]). This is required if we want the convergence of the method to be dependent primarily on quadrature errors and not to be affected by an inaccurate representation of the moment integrals. Relevant approximants have been elaborated for several kernel functions often encountered in electroanalytical modelling [24–42].

The local linearisation of the solutions, and error estimation based on truncated Taylor expansions, imply that the continuity of $\boldsymbol{U}(t)$ for $t \geq 0$ and the existence of at least two derivatives of $\boldsymbol{U}(t)$ with respect to t, are required by the method described in Refs. [24–42] (although the method was found to operate satisfactorily also when the solution is continuous but not differentiable at $t = 0$). However, the method of Refs. [24–42] could not calculate singular solutions. This deficiency was eliminated in the recent work [23], by assuming that $\boldsymbol{U}(t)$ can be decomposed into the sum:

$$\boldsymbol{U}(t) = \widetilde{\boldsymbol{U}}(t) + \overline{\boldsymbol{U}}(t). \tag{4}$$

In Eq. (4) $\widetilde{\boldsymbol{U}}(t) = [c_1 t^{-1/2}, \ldots, c_M t^{-1/2}]^{\mathrm{T}}$ represents singular solution components, with $\mathbf{c} = [c_1, \ldots, c_M]^{\mathrm{T}}$ denoting a vector of unknown coefficients, and $\overline{\boldsymbol{U}}(t)$ represents nonsingular solution components (possessing at least two derivatives for all $t \geq 0$, with a possible exception of $t = 0$, where $\overline{\boldsymbol{U}}(t)$ must be bounded). The decomposition (4) of $\boldsymbol{U}(t)$ implies an analogous decomposition of $\boldsymbol{Y}(t)$:

$$\boldsymbol{Y}(t) = \widetilde{\boldsymbol{Y}}(t) + \overline{\boldsymbol{Y}}(t). \tag{5}$$

The elements of $\overline{\boldsymbol{Y}}(t)$ (for $j = 1, \ldots, I$) are given by the formulae analogous to Eq. (2):

$$\overline{Y}_j(t) = \int_0^t \mathscr{K}_\kappa(t,\ \tau)\ \overline{U}_\mu(\tau)\ \mathrm{d}\tau, \tag{6}$$

whereas $\widetilde{\boldsymbol{Y}}(t)$ can be expressed as the vector

$$\widetilde{\boldsymbol{Y}}(t) = [c_{\mu(1)}\widetilde{Z}_{\kappa(1)}(t),\ \ldots,\ c_{\mu(I)}\widetilde{Z}_{\kappa(I)}(t)]^{\mathrm{T}}, \tag{7}$$

in which $\widetilde{Z}_\kappa(t)$ (for $\kappa = 1, \ldots, L$) are integrals characteristic of the various kernels:

$$\widetilde{Z}_\kappa(t) = \int_0^t \mathscr{K}_\kappa(t,\ \tau)\ \tau^{-1/2}\ \mathrm{d}\tau. \tag{8}$$

Under a number of rather straightforward assumptions [23] concerning the functions $\boldsymbol{F}(\cdot)$, one can determine coefficients $\mathbf{c}$, and discrete nonsingular solution components $\overline{\boldsymbol{u}}_n$ (together with their error estimates) numerically from the IEs. One important assumption is that the explicit dependence of $\boldsymbol{F}(\cdot)$ on $\boldsymbol{U}(t)$ must vanish in the limit of $t \to 0$. In the electrochemical context this assumption can be satisfied by requiring that quasi-reversible and irreversible heterogenous reactions do not contribute in any way to the IEs when $t \to 0$, which is consistent with the wisdom that for such reactions one does not expect temporal singularities of $\boldsymbol{U}(t)$. Coefficients $\mathbf{c}$ can be determined almost exactly, simultaneously with the initial discrete solutions $\overline{\boldsymbol{u}}_0$ and $\overline{\boldsymbol{u}}_1$ (throughout this paper, we use the phrase “almost exact” to denote quantities, the error of which consists only of machine errors resulting from the finite precision arithmetic on computers). Once $\boldsymbol{c}$ is known, the determination