An Efficient Numerical Scheme for Solving Hammerstein Integral Equation Arisen in Chemical Phenomenon

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Abstract

In Science and engineering, so many nonlinear phenomena are presented as partial differential, ordinary differential and integral equation models. So in this article, our aim is to study on Hammerstein type nonlinear integral equation

$$\mu_S(\sigma) = -RTLn\left[\int_a^b P_S(\overset{\circ}{\sigma})\exp\left\{\frac{-\varepsilon(\sigma,\overset{\circ}{\sigma}) + \mu_S(\overset{\circ}{\sigma})}{RT}\right\}d\overset{\circ}{\sigma}\right]$$

Where R is the gas constant, T the temperature, the term $\varepsilon(\sigma,\overset{\circ}{\sigma})$ denotes the interaction energy expression for the segments with screening charge density σ and $\overset{\circ}{\sigma}$ respectively, the molecular interaction in solvent is $P_S(\sigma)$ and the chemical potential of the surface segments is described by $\mu_S(\sigma)$ that should be determined. This integral equation forms the basis for the conductor-like screening model for real solvents (COSMO-RS) which is appeared in chemical phenomena. Some of numerical methods usually use techniques based on a projection in terms of some basis functions or use some quadrature formulas, and the convergence rate of these methods are usually of polynomial order with respect to N, where N represents the number of terms of the expansion or the number of points of the quadrature formula. Also, in projection methods nonlinear Hammerstein integral equation is reduced to the nonlinear algebraic equations which solving them in large scales needs high memory capacity and CPU time and because of error propagation convergence of numerical technique may be at risk. So this paper presents a powerful numerical approach based on Sinc quadrature which has exponential type convergence rate to solve conductor-like screening model for real solvents (COSMO-RS). The approach is based on preparing an iterative method to recognize the Hammerstein integral equation for the determination of the chemical potential of a surface segment as a function of screening charge density.

Keywords: Conductor-like screening model, Hammerstein integral equation, Sinc quadrature.

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1. Introduction

The conductor-like screening model for real solvents (COSMO-RS) uses a statistical thermodynamic approach based on the results of quantum chemical calculations [1-5]. This model is new approach to the description of salvation phenomena. In (COSMO-RS) calculations the solute molecules are investigated in a virtual conductor environment. In such an environment the solute molecule induces a polarization charge density σ on the interface between the molecule and the conductor. The three dimension polarization density distribution on the surface of each molecule M_i with n different types is converted to a distribution function, the so called σ-profile $(P(\sigma))$ which gives the relative amount of surface with polarity σ on the surface on the molecule.

The σ-profile for the solvent of S which might be a mixture of several compounds, $P_S(\sigma)$ can be written by adding $P^i(\sigma)$ of the components weights by their mole fraction χ_i in mixtures

$$P_S(\sigma) = \sum_{i=1}^n \chi_i P^i(\sigma)$$

The macroscopic thermodynamic properties of mixtures obtain from the microscopic molecular surface charge interactions using by statistical thermodynamic. The molecular interaction in solvent are described by $P_S(\sigma)$ and the chemical potential of the surface segments as following

$$\mu_S(\sigma) = -RTLn\left[\int_a^b P_S(\overset{\circ}{\sigma})\exp\left\{\frac{-\varepsilon(\sigma,\overset{\circ}{\sigma}) + \mu_S(\overset{\circ}{\sigma})}{RT}\right\}d\overset{\circ}{\sigma}\right] \tag{1}$$

where R is the gas constant, T the temperature and the term $\varepsilon(\sigma,\overset{\circ}{\sigma})$ denotes the interaction energy expression for the segments with screening charge density σ and $\overset{\circ}{\varpi}$, respectively where σ and $\overset{\circ}{\varpi}$ are the polarization charge of two

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interacting surface segments. The domain of integration is determined by the characteristics of the σ -profile.

We can rewrite Eq. (1) as

$$-\frac{\mu_S(\sigma)}{RT} = Ln\left[\int_a^b P_S(\overset{\circ}{\sigma})\Omega(\sigma,\overset{\circ}{\sigma})\exp\left\{\frac{\mu_S(\overset{\circ}{\sigma})}{RT}\right\}d\overset{\circ}{\sigma}\right]$$

where $\Omega(\sigma,\overset{\circ}{\sigma}) = \exp\{-\frac{\varepsilon(\sigma,\overset{\circ}{\sigma})}{RT}\}$. Now, by substituting $f(\sigma) = \exp\{-\frac{\mu_S(\sigma)}{RT}\}$ we have

$$f(\sigma) = \int_a^b P_S(\overset{\circ}{\sigma})\Omega(\sigma,\overset{\circ}{\sigma})(f(\overset{\circ}{\sigma}))^{-1}d\overset{\circ}{\sigma} \qquad (2)$$

where the above equation is well known as nonlinear Hammerstein integral equation.

In the following, let the general form of Hammerstein integral equation denoted by

$$f(x) = \int_a^b K(x,z)\psi(x,f(z))dz + g(x) \quad -\infty < a \le x \le b < \infty \qquad (3)$$

where $K(x,z), g(x)$ and $\psi(x,z)$ are known functions and $f(x)$ is an unknown function which should be determined.

Numerical methods for solving integro-differential and integral equations and investigating on existence and uniqueness of some general models such as Hammerstein type have been studied by many authors so far [6-8]. Some of them usually use techniques based on a projection in terms of some basis functions or use some quadrature formulas, and the convergence rate of these methods are usually of polynomial order with respect to N , where N represents the number of terms of the expansion or the number of points of the quadrature formula. On the other hand, in [9] it is shown that if we use the Sinc method the convergence rate is $\mathrm{d}\,(\exp(-C\sqrt{N}))$ with some $C > 0$. Although this convergence rate

is much faster than that of polynomial order.

So, in the present paper, we apply the Sinc-quadrature formula and an iterative method to estimate a numerical solution for Eq. (3). Our method dose not consist of reducing the solution of Eq. (3) to a set of algebraic equations by expanding $f(x)$ as Sinc functions with unknown coefficients, so this scheme has less computations and exponential accuracy. Also, in the following a theorem is prepared to grantee the convergence of numerical scheme.

2. Sinc Function Properties

In this section, we introduce the cardinal function and some of its properties. For this result $\sin c(x)$ definition is followed by

$$\sin c(x) = \begin{cases} \dfrac{sin(\pi x)}{\pi x}, & x \ne 0 \\ 1 & x = 0 \end{cases}$$

Now, for $h > 0$ and integer k , we define k 'th Sinc function with step size h by $S(k,h)(x) = \dfrac{\sin(\dfrac{\pi(x-kh)}{h})}{\dfrac{\pi(x-kh)}{h}}$

Definition 1. Let $H^1(D_d)$ denote the family of all functions analytic in D_d defined by $D_d = \left\{z \in \pounds : \left|\mathrm{Im}(z)\right| < d\right\}$ such that for $0 < \varepsilon < 1$, $D_d(\varepsilon)$ is defined by $D_d(\varepsilon) = \left\{z \in \pounds : \left|\mathrm{Im}(z)\right| < d(1-\varepsilon), \left|\mathrm{Re}(z)\right| < \dfrac{1}{\varepsilon}\right\}$ then $N(f,D_d) < \infty$ with

$$N(f,D_d) = \lim_{\varepsilon \to 0}(\int_{\partial D_d} |f(z)\| dz|)$$

Theorem1. Let α, β and d as positive constants, that

1- $f \in H^1(D_d)$

2- f decays exponentially on the real line such that $|f(x)| \le \alpha \exp(-\beta|x|), \quad \forall x \in \mathfrak{i}$

then we have $\displaystyle\sup_{-\infty < x < \infty}\left|f(x) - \sum_{k=-N}^{N} f(kh)S(k,h)(x)\right| \le CN^{1/2}\exp\{-(\pi d\beta N)^{1/2}\}$ for some C and step size h is taken as $h = (\dfrac{\pi d}{\beta N})^{1/2}$.

Proof. [10, 11]

Now, in order to have the Sinc approximation on a finite interval $[a,b]$ conformal map is employed as follow

$$\phi(x) = Ln(\frac{x-a}{b-x}) .$$

So, the basis function on finite interval $[a,b]$ are given by $S(k,h) o \phi(x) = \dfrac{\sin(\dfrac{\pi(\phi(x)-kh)}{h})}{\dfrac{\pi(\phi(x)-kh)}{h}}$.

3. Sinc-Quadrature Scheme

In this section, for solving equation

$$f(x) = \int_a^b K(x,z)\psi(x,f(z))dz + g(x) \quad -\infty < a \le x \le b < \infty$$

we try to discrete integral equation by quadrature formula for the above integral [12, 13] as

$$\int_a^b K(x,z)\psi(x,f(z))dz = h\sum_{k=-N}^{N} \frac{K(x,z_k)\psi(x,f(z_k))}{\phi'(z_k)} + O(\exp(-\frac{2\pi dN}{Log(\frac{2\pi dN}{\beta})}))$$

where $z_k = \dfrac{a+be^{kh}}{1+e^{kh}}$, $k = -N,...,N$ with $h = \dfrac{1}{N}\log(\dfrac{\pi dN}{\beta})$ then by substituting in the Hammerstein integral equation, we have

$$f_N(x) = h\sum_{k=-N}^{N} \frac{K(x,z_k)\psi(x,f(z_k))}{\phi'(z_k)} + g(x) .$$

Now, let

$$\begin{cases} f_1(x) = h\sum_{k=-N}^{N} \dfrac{K(x,z_k)\psi(x,g(z_k))}{\phi'(z_k)} + g(x) \\ f_{n+1}(x) = h\sum_{k=-N}^{N} \dfrac{K(x,z_k)\psi(x,f_n(z_k))}{\phi'(z_k)} + g(x), \ n = 1,2,... \end{cases} \tag{4}$$

where $\lim\limits_{n \to \infty} f_n(x) = f(x), \ -\infty < a \le x \le b < \infty$

Theorem2. Assume that $f(\phi^{-1}(x))$ and $K(x,.)$ satisfy assumptions (1) and (2) in Theorem1 with some α, β and d, and ψ satisfies Lipschitz condition respect to the second variable with Lipschitz constant L. Also, let $f_N(x)$ be the numerical solution of Eq. (3) given by

$$f_N(x) = h\sum_{k=-N}^{N} \frac{K(x,z_k)\psi(x,f(z_k))}{\phi'(z_k)} + g(x)$$

Then there exists constant C_i for $i = 1,2$ independent of N such that

$$\sup_{x \in (a,b)} |f(x) - f_N(x)| \le C_1 N^{1/2} \exp\{-(\pi d\beta N)^{1/2}\} + C_2 \exp(-\frac{2\pi dN}{Log(\frac{2\pi dN}{\beta})}) .$$

4. Numerical Examples

Example1. Let us now investigate the solution of the COSMO-RS integral equation

$$f(\sigma) = \int_a^b P_S(\overset{\circ}{\sigma})\Omega(\sigma,\overset{\circ}{\sigma})(f(\overset{\circ}{\sigma}))^{-1}d\overset{\circ}{\sigma}$$

for a particular case of the energy expression, namely the electrostatic misfit energy [5]. In this case the relevant part of the kernel of the integral equation is given by $\Omega(\sigma,\overset{\circ}{\sigma}) = \exp\{-(\sigma+\overset{\circ}{\sigma})^2\}$.
Also, we employ the following piecewise defined analytical function as synthetic σ-profile:

$$P_S(\sigma) = \begin{cases} e^{-(5\sigma+2.5)^2} + \dfrac{1}{25\sigma^2+1} + \dfrac{(\sin(5\sigma+2.5))^2}{(5\sigma-2.5)^4+1} + q(5\sigma), & -2 \le \sigma < 2 \\ 0 & otherwise \end{cases} \tag{5}$$

where $q(\sigma) = \begin{cases} -(\sigma-7)(\sigma-9), & 7 \le \sigma < 9 \\ 0 & otherwise \end{cases}$.

So, COSMO-RS integral equation will be

$$f(\sigma) = \int_{-3}^{3} P_S(\overset{\circ}{\sigma}) \exp\{-(\sigma + \overset{\circ}{\sigma})^2\}(f(\overset{\circ}{\sigma}))^{-1} d\overset{\circ}{\sigma} \text{ where } P_S(\sigma) \text{ is defined by Eq. (5).}$$

Now, applying Sinc quadrature technique and iterative formula (4) for the COSMO-RS integral equation the following numerical results are derived which are presented in Table 1.

Table1. Numerical results for COSMO-RS integral equation

n	$E(n)$
5	3.8×10^{-3}
10	3.1×10^{-4}
20	1.2×10^{-7}
40	1.5×10^{-13}

where $E(n) = \max\limits_{\sigma \in [-3,3]} \left| f_{n+1}(\sigma) - f_n(\sigma) \right|$.

Example2. Consider the integral equation (3) where $K(x,t) = e^{-10(t+x)}$ and $\psi(x, f(z)) = (f(z))^{-1}$, so by substituting the exact solution $f(x) = \dfrac{1}{x+1}$, right hand side of the equation will be $g(x) = \dfrac{21 - 11e^{10}}{100} e^{-10(1+x)} + \dfrac{1}{x+1}$. Also, let $a = 0, b = 1$, then by applying Sinc quadrature technique (4) the following numerical results are derived.

Table2. Numerical results for Example2

n	$E(n)$
5	1.3×10^{-2}
10	6.2×10^{-4}
15	1.9×10^{-5}
20	5.7×10^{-7}
30	1.8×10^{-8}

In Table2. $E(n)$ is defined as

$$E(n) = \max_j \left| f(x_j) - f_n(x_j) \right| \qquad \forall j = -N, ..., N$$

and x_j are sinc nodes which were defined in previous section.

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