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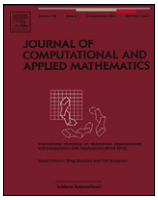

Sinc approximation for numerical solution of integral equation arising in conductor-like screening model for real solvent

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ABSTRACT

In this study, we present the existence of solutions for some nonlinear integral equations known as Hammerstein type which forms the basis for the conductor-like screening model for real solvents (COSMO-RS). By using the techniques of noncompactness measures, we employ the basic fixed point theorems such as Darbo's theorem to obtain the mentioned aim in Banach algebra. Then this paper presents a powerful numerical approach based on the Sinc approximation to solve the equation which forms the basis for the conductor-like screening model for real solvents (COSMO-RS). The approach is based on the recognition of the Hammerstein integral equation for the determination of the chemical potential of a surface segment as a function of screening charge density. Then convergence of this technique is discussed by preparing a theorem which shows an exponential type convergence rate and guarantees the applicability of that.

1. Introduction

The conductor-like screening model for real solvents (COSMO-RS) is an important method for thermodynamic equilibria investigation in fluid and liquid mixtures. This model uses a statistical thermodynamic approach based on the results of quantum chemical calculations. This model is a new approach to the description of solvation phenomena. (COSMO-RS) calculates the dielectric screening charges and energies on a van der Waals-like molecular surface in the approximation of a conductor. This model is available in MOPAC 7 and MOPAC 93 [1,2]. The previous studies show that dielectric continuum models are applicable to hydration phenomena. Although continuum solvation models are used for other solvents than water [3], none of these solvents are considered nearly as intensively as water, because water can offer the opposite ideal surface charge densities for all faces of a solute as good as a conductor. Therefore, this is the reason for the conductor-like screening of most solutes in water.

The proper investigation and theoretical study of molecules in solution is one of the most important actual challenges for computational chemistry. The proper description of a solute molecule in a solvent on a molecular scale is a very hard task, because the solute is interacting with several surrounding solvent molecules and these interact with others and so on. The experimental behavior and the thermodynamic properties of solute–solvent systems based on COSMO are investigated. This model is used for a description of boiling point and surface tension of a solvent in the presence of solute molecules. As an example, this model explains why acetone has a considerably lower boiling point than water, although it has the same polarity as water. On the basis of this model, we find the well-known fact that water is not able to screen small ions as perfectly as larger ones [4]. Also, this model is used for determining the critical micelle concentration in ionic surfactants [5]. We can investigate the effect of electrolytes or organic solvents on the CMC of surfactants by this model.

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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 dimensional 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 of 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 are obtained from the microscopic molecular surface charge interactions using statistical thermodynamics. The molecular interactions in solvents are described by $P_S(\sigma)$ and the chemical potential of the surface segments as follows

$$\mu_S(\sigma) = -RT \ln\left[\int_a^b P_S(\tilde{\sigma}) \exp\left\{\frac{-\epsilon(\sigma,\tilde{\sigma}) + \mu_S(\tilde{\sigma})}{RT}\right\} d\tilde{\sigma}\right], \tag{1}$$

where R is the gas constant, T the temperature and the term $\epsilon(\sigma,\tilde{\sigma})$ in Eq. (1) denotes the interaction energy expression for the segments with screening charge density σ and $\tilde{\sigma}$, respectively where σ and $\tilde{\sigma}$ are the polarization charge of two interacting surface segments. The domain of integration is determined by the characteristics of the σ-profile.

We can rewrite Eq. (1) as

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

where

$$\Omega(\sigma,\tilde{\sigma}) = \exp\left\{-\frac{\epsilon(\sigma,\tilde{\sigma})}{RT}\right\}.$$

Now, by substituting

$$f(\sigma) = \exp\left\{-\frac{\mu_S(\sigma)}{RT}\right\}$$

we have

$$f(\sigma) = \int_a^b P_S(\tilde{\sigma})\Omega(\sigma,\tilde{\sigma})(f(\tilde{\sigma}))^{-1} d\tilde{\sigma}, \tag{2}$$

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

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

$$f(x) = \int_a^b K(x,z)\Psi(x,f(z))dz + g(x); \quad x \in [a,b] \tag{3}$$

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

Investigation on existence theorems for some nonlinear functional–integral equations has been presented in other references such as [6,7]. First of all, we try to prove the existence of the solution for a Hammerstein type integral equation. To get these results, we employ the fixed point theorem and Darbo condition with respect to a measure of noncompactness in the Banach algebra.

Regarding the fact that we cannot solve the nonlinear Hammerstein integral equation defined by Eq. (3) to find an exact solution, numerical techniques are employed to estimate an approximated solution. Numerical methods for solving integro-differential and integral equations and investigating the existence and uniqueness of some general models such as Hammerstein type have been studied by many authors so far [5–16]. Some of them usually use techniques based on a projection in terms of some basis functions or use some quadrature formulas, and the convergence rates 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 [17] it is shown that if we use the Sinc method the convergence rate is $O(\exp(-c\sqrt{N}))$ for 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 does not consist of reducing the solution of Eq. (3) to a set of algebraic equations by expanding $f(t)$ as Sinc functions with unknown coefficients, so this scheme has less computations and exponential accuracy. Also, in the following a theorem is prepared to guarantee the convergence of the numerical scheme.

This paper is organized as follows. In Section 2, we introduce some preliminaries and use them to prove the existence of a solution for a general form of integral equation. In Section 3, we state basic theorems and properties of the Sinc function