COMMON THEORETICAL FRAMEWORK FOR QUANTUM CHEMICAL SOLVENT EFFECT THEORIES

János G. ÁNGYÁN*
Institut für Physikalische und Theoretische Chemie der Universität Bonn, Wegelerstrasse 12, 5300 Bonn 1, Germany

Abstract

Quantum chemical solvent effect theories deal with the description of the electronic structure of a molecular subsystem embedded in a solvent or other molecular environment. The average reaction field theories, which describe electrostatic and polarization interactions between solute and solvent, can be formulated in terms of a nonlinear reaction potential operator. This operator depends on the one hand on the reaction potential function of the solvent, and on the other hand on the charge density operators, which appear in the solute-solvent interaction. The former quantity is determined by the physical model of the solvent (e.g. dielectric continuum, discrete model, crystal lattice, etc.). The charge density operator can be approximated at different levels, like exact, one-centered and multicentered multipolar forms. These two ingredients of the theory, the reaction potential response function and the specific charge density operator, define unequivocally different solvent effect models. Various versions of average reaction field models are critically reviewed on the basis of this common theoretical framework.

1. Introduction

Recently, a great deal of effort has been devoted to the modeling of physicochemical processes in condensed phases, e.g. solids, liquids, solutions, or biological environments. The progress in various fields, like in the theory of intermolecular forces, in computer simulation techniques and in solid-state physical methods, enabled us to have a better understanding of many of these important phenomena. It became evident that, at least in certain cases, the influence of the intermolecular interactions on the electronic structure of the constituents is essential.

In particular, the electronic structure of solute molecules can be strongly coupled to the solvent structure and conversely. This effect can be the key element, for example, in the understanding of the microscopic mechanism of certain reactions in solution [1].

*On leave from Quantum Theory Group, Institute of Physics, Technical University of Budapest, Budafoki út 8, H-1521 Budapest, Hungary. Present address: Laboratoire de Chimie Théorique, Université de Nancy I, P.B. 239, Vandœuvre-lès-Nancy, F-54506, France.

© J.C. Baltzer AG, Scientific Publishing Company
Quantum chemical solvent effect theories [2, 3] provide a self-consistent description of the solute electronic structure, which is strongly coupled to a polarizable environment. Such calculations are indispensable to get an insight into molecular properties [4–6] and reactivity [7–10] in condensed phases. This goal is usually achieved by means of a solute-only model Schrödinger equation, corresponding to some simplified representation of the solvent.

Many semi-empirical and ab initio models have been proposed in the past twenty-five years, beginning with the heuristic solvation model of Klopman in 1967 [11] and the reaction field models of Rinaldi and Rivail [12], Newton [13] in 1973, and of Tapia and Goscinski [14] in 1975. These models and later developments [8, 15–26] sometimes seem to be very different although it is widely accepted that the underlying basic physical model in all the cases is the reaction field idea, attached to the name of Onsager [27]. This model assumes that the polar solute system, which is embedded in a solvent, polarizes its surroundings. The polarized environment creates a field, the reaction (or polarization) field which, in turn, acts back on the solute subsystem.

This simple picture has been originally formulated for a point dipole, embedded in a dielectric continuum, and many quantum chemical adaptations of the continuum model followed this line. Later, refinements improved the representation of both the solute charge distribution and the solvent, and led to various forms of the corresponding effective quantum chemical solute operator. Unfortunately, the differences of the mathematical formulations were an obstacle to having a direct comparison of different models, which is badly lacking in this field.

In the present contribution, it is attempted to formulate the most important quantum chemical solvent effect models within a relatively simple, common mathematical framework. By doing this, we extend in some sense earlier efforts of Tapia, outlined in some of his review papers [2, 28].

Why is it important to get a kind of unified view of the various quantum chemical solvent effect models? We think that this can be rewarding from several different aspects. First, a unified view may render it easier to appreciate the physical significance of the models, which are quite often of rather different origin, and makes it easier to analyse their scope of validity. Secondly, the application of various perturbational schemes to the solute-only effective Schrödinger equation can be done directly on the generally formulated case, thus avoiding eventual pitfalls due to specific aspects of certain simplified models and reducing considerably the analytical effort [29]. Thirdly, the computational implementation of the various solvent effect models can be greatly simplified. In particular, the very same quantum chemical code can be used to take into account the effect of very different solvent (or environmental) models. Such a computer program system is under development in our laboratories [30].

The solvent effect models are based on the assumption that there exists a free energy functional (or at zero absolute temperature, a total energy functional) $J(\psi, X)$ which depends on the solute wave function $\psi$ and on some generalized