Molecular Simulation and Environmental Effects - A Mathematical and Numerical Perspective

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This thesis draws together various mathematical and numerical contributions to Quantum Chemistry.

Chapter 1 is devoted to a presentation of the spirit and models of Molecular Simulation with a specific attention for Quantum Chemistry.

Chapter 2 deals with questions of convergence for some algorithms for solving the Hartree-Fock equations. On the one hand, we prove that the "natural" Roothaan algorithm may lead to oscillations, and on the other hand that the so-called level-shifting algorithm does converge provided the shift parameter is large enough.

The following chapters investigate specific problems related to molecular systems *in situ*, that is to say in interaction with an external environment.

A first approach to simulating environmental effects consists in treating the interaction between the molecular system and the external medium as a perturbation. In chapter 3, the perturbation theory for linear operators is extended to the nonlinear setting of the Hartree-Fock model.

The interaction of a molecular system with an environment is often a dynamic process. This is obviously the case when a chemical reaction is studied. Chapter 4 presents the mathematical analysis of one of the approximations of the time-dependent Schödinger equation which describes the dynamics of the system, namely the non-adiabatic Hartree-Fock model. We prove in particular that the evolution problem is well-posed (global existence and uniqueness of the solution) when the molecular system is subjected to a time-dependent uniform electric field, which is a first step towards the theoretical study of laser control of chemical reactions.

Most of the chemical reactions of interest in industry or in life sciences take place in the liquid phase, where solvant effects play a crucial role. In view of applications, it is therefore important to be able to perform Quantum Chemistry calculations on solvated molecules. Continuum models, in which the solvant molecules are represented by a dielectric continuous medium that modifies the electrostatic interactions between the charges supported by the solute molecule, are the solvation models which offer at the present time the best compromise between accuracy and computational effort.

Our contribution to the numerical study of continuum models took place within a collaboration with the Laboratory of Chemistry of the University of Pisa (Italy) and the Institut de Protection et de Sûreté Nucléaire. Two aspects were concerned:

1. the extension of the standard continuum model to new physical settings such as anisotropic solvants (liquid crystals, cristalline matrices), and ionic solvants (physiological liquids);

2. the implementation of new formulae for the total energy derivatives with respect to nuclear coordinates in view of geometry optimization and vibration spectra calculation for solvated molecules.

Key-words. Quantum Chemistry; Schrödinger equation; Hartree-Fock model; Continuum models; Nonlinear analysis; Integral methods; Convergence of algorithms.