Short Term Scientific Mission COST-STMS-P9-02015 Rome October 16-November 15

Topic: Modeling solvent effects during metastable anion formation in biomolecules by electron impact

Purpose of the visit

Starting a scientific collaboration to investigate the modifications on electron-induced processes in molecules under the influence of a molecular surroundings (solvent)

Scientific background

All the chemical and physical processes occurring in living bodies take place in a condensed phase, usually rather complex in composition, but in which water plays an important role. The understanding of these phenomena at the atomic and electronic level has been greatly supported by the study of the individual behaviour of the important biological molecules, either experimentally or theoretically, thanks to quantum mechanics. The quantum theoretical studies are usually done on isolated molecules and the knowledge provided by these studies has proved very useful to understand, at least qualitatively, what happens when these molecules are in a condensed phase. Nonetheless, it is also well known that some changes in the properties of interest may occur when the molecule goes from the isolated state to a condensed phase, although a detailed picture of such systems is far beyond the present computational possibilities to envisage performing the same kind of theoretical approaches as those usually developed on isolated molecules.

The necessity of being able to grasp most of the influence of a solvent on chemical systems has led theoretical chemists to develop semi-empirical models which simulate, as well as possible, the influence of the molecular surroundings in the quantum chemical computations and for more than 30 years now, a good knowledge has been accumulated on the possibilities and the limits of such models. Among them the so-called continuum models in which the liquid surrounding the molecule of interest is represented by a polarisable continuous medium have been first introduced in 1973 by the group of Nancy [1] and developed afterwards in parallel by the group of Pisa [2-4] and in Nancy [6, 7] on the basis of the same physical model but using different computational approaches. These models do not require much more computational facilities than the usual quantum chemical computations and they are now of common use by quantum chemists. They have been used in an enormous amount of studies so that the reliability of their data is now well established, especially to model the influence of a solvent on various spectroscopic phenomena [8-10]. Surprisingly, it has been shown that they can even simulate the mean effect of an aqueous surrounding although water is known to be a very special liquid which may interact with a solute by making hydrogen bonds which also

occur between water molecules themselves and explain the abnormally high dielectric constant (78 at room temperature) of this liquid. In the continuum models the polarization of the surroundings, which in return perturbs the solute molecule, depends on this dielectric constant and the fact that hydrogen bonding is mainly an electrostatic phenomenon as shown by Coulson [11] in the 1950's is probably the key of the success of these models.

The theoretical treatment of electron-induced processes in molecules is now based upon the use of the ground-state wavefunction of the molecule and the group of Rome has developed a simple and computationally attractive, purely local model potential, called the "static model exchange correlation potential" [12-15], which has been used in studying one electron resonances and fragmentation patterns of some simple molecules in the isolated state or in a solution, and some molecular clusters.

The aim of this collaboration is to initiate a systematic study of the possible effects of low energy electrons on some important components of living matter, starting from simple model systems and then increasing their complexity in order to establish to what extent the results can be extrapolated to more realistic cases. A careful study of the influence of the molecular surroundings appears to be the unavoidable first step in this endeavour.

Description of the work carried out during the visit

A preliminary approach has been devoted to the methodology used in the Laboratory to study the electron-induced processes in the molecules and the computational requirements for such studies. A detailed discussion of the recent treatment of electron scattering phenomena by the zwitterion of glycine provided us with a good introductory example.

In order to check the magnitude of the possible environment effects on electron-induced processes, we decided to analyse resonant features in a formamide target under various conditions of solvation. This molecule can be considered as the simplest model of a peptidic bond in proteins. It has been chosen as a starting case for a collaborative activity between the two groups.

The wavefuction of the fully optimized molecule, at a reasonably good level of theory (DFT B3LYP; 6-311+G**), has been computed for the isolated molecule and in two surroundings representing water and liquid formamide. The results show, as expected, an important polarization of the solute under the influence of the surrounding liquid. The scattering treatment is being performed. Some additional wavefuction computations with one or two explicit water molecules solvating the formamide molecule have been obtained at the end of the visit.

On November 8, I gave a seminar entitled: "*Liquid State Quantum Chemistry*" to the members of the laboratory. The various theoretical approaches of molecular liquids have been presented, with a special emphasis on continuum models which are, for the time being, the only ones which are computationally compatible with the methodology used in electron-induced studies.

Description of the main results obtained

The wavefunctions of the systems selected for the study have all been computed and they are under processing to study the electron-induced processes on the systems selected to start this study.

Future collaboration with the host institution

As stated above, formamide is a very simple molecule which is a model of a peptidic bond. It is envisaged to extend the study to systems of increasing complexity in order to approach the actual situation in a protein.

Confirmation by the host institute of the successful execution of the mission

The group in Rome has been very happy to have the visit of professor Rivail and the duration of the visit has been very productive in terms of establishing a specific collaborative topic and of setting up of the required tools in order to start a joint calculations between the two groups. Professor Gianturco, the coordinator of the Rome group on molecular theory and computations ,therefore very happily confirms the usefulness of the visit by professor Rivail in terms of establishing a collaborative link between the two research groups.

Signed . professor Franco A. Gianturco

References

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