

## DESCRIPTION FOR THE GENERAL PUBLIC (IN ENGLISH)

Computational methods of quantum chemistry play an increasingly important role, while nuclear magnetic resonance (NMR) is a basic tool applied in chemistry and biochemistry to analyse molecular electronic structures and geometries. The aim of this project is to investigate the performance of different quantum chemical methods developed for the analysis of the NMR parameters in specific molecules, characterised by non-bonding interactions.

There is a variety of theoretical methods, developed over many years and now implemented in generally available computer packages, which are used to calculate the NMR parameters - shielding constants and indirect spin-spin coupling constants. However, these approaches have been formulated, tested and applied in most cases for molecules with common composition (often restricted to H, C, N and O atoms) and orthodox structure (an isolated molecule at experimental or equilibrium geometry, with standard covalent bonds). In particular, this applies to density functional theory (DFT) methods, where the choice of the exchange-correlation functional determines the accuracy of the results. In contrast to *ab initio* methods, where a hierarchy of approximations exists and the results can be systematically improved, there is no obvious way to predict *a priori* which DFT approach is to be preferred for a particular problem.

The standard procedure is to use, when available, high-level *ab initio* results to benchmark simpler *ab initio* methods (e.g. calculations with small basis sets) and DFT approximations (e.g. different functionals) against the *ab initio* values. The proposed project will involve such a comparison of different approaches, with the focus on systems characterised by non-bonding interactions.

In the studies of intramolecular through-space spin-spin coupling constants we shall focus on the applications for the determination of molecular structure. A well-known example illustrating the role of non-bonding interactions are the through-space spin-spin coupling constants. When there are various isomers of a molecule, and only in some of them there are nonbonded magnetically active nuclei relatively close to each other, huge differences of the computed coupling constants between isomers often allow for immediate identification of the isomer actually observed in experiment.

Moreover, we shall use the recently developed and programmed relativistic four-component DFT methods. To determine accurately any properties of molecules including heavy atoms one has to take into account the relativistic effects, because the presence of a heavy atom affects strongly the NMR parameters of all the nuclei in the molecule.

The existence of a well-defined hierarchy of *ab initio* methods permits an analysis of the error bars of the results. We shall analyse the accuracy of the computed NMR parameters, considering the role of different approximations. In addition to the predicted values of NMR parameters, the theory may presently provide a helpful interpretation of the results. For instance, analysing the perturbation-induced changes in the electron density one may obtain a picture showing that a large spin-spin coupling constant is due to through-space interaction.