Implementation and application of Hylleraas-CI method in precise computations of atoms and diatomic molecule – popular science description.

Research on atoms and diatomic molecules have a long history reaching the beginning of XIX century in case of the molecules. Most abundant element on earth, such as nitrogen, oxygen or hydrogen exist in form of diatomic molecules. Despite many years of studies diatomic molecules still hide many secrets. Thanks to the discovery of lasers it is now possible to study them with incredible precision. The most recent breakthrough in this field is connected with cooling of atoms and molecules to incredibly low temperatures. It turned out, that at temperatures near absolute zero – 0 K ($-273.15\,^{\circ}$C) – atoms and molecules behave very differently than in high temperatures. However, to study their behaviour one has to cool them down first. To cool them to such low temperatures detailed knowledge of their structure must be known. Although studies using lasers allow measuring energies of transitions between the states in the molecule, interpretation of these transitions to know how the structure of the molecule is a difficult task.

An accurate theoretical model may significantly help in this challenge. The equation which has to be solved to obtain a detailed description of chemical processes is known. It is a Schrödinger equation and it was discovered in 1926. Unfortunately finding its solution is very complicated and in almost all except few simple examples, we have to use approximations and computers (or even supercomputers) to solve it. Even then, in many cases, the solutions are not accurate enough to compete against experimental precision. The main source of difficulties is the problem of so-called electron correlation. Electron correlation is a direct effect of the fact that movement of each electron in the atoms or molecules is connected with the movement of the rest of electrons. It leads to complications in the description since when we want to calculate the movement of the first electron we have to know the behaviour of the second electron and to obtain it we need to know about the first one, whose movement we wanted to calculate.

Quantum chemists struggle with this problem for nearly a century. They found ways to solve it very accurately (with the precision that matches or even surpasses experimental measurements), but they are limited to atoms and molecules with no more than four electrons. We call these methods of solutions explicitly correlated methods, as the distance between the electrons is explicitly incorporated directly into the wave function. There are other methods that allow describing correlation of hundreds of electrons, but their accuracy is much lower than the accuracy of laser measurements. They are based on so-called orbital approximation where each electron is treated separately, so they are methods based on independent electron approximation.

In our project, we aim to develop and implement a hybrid method, that combines the strength of explicitly correlated and orbital based methods. This approach, called Hylleraas-Configuration Interaction, combines the explicitly correlated method of Hylleraas with the orbital-based configuration interaction method. We will use their combination to get the accuracy of explicitly correlated methods and extend it to a larger number of electrons. Since for the atoms and diatomic molecules precise experimental data is available we will study these two kinds of systems using computer program we will write.

It is known, that such methods are very demanding computationally, especially as the number of electrons in the systems increases it is necessary to implement the method in a parallel. It means that the structure of the program will allow hundreds of processors to work on the problem. Because of the large computer requirements, we will use some of the most powerful supercomputers in that part of Europe. Using them will allow shortening the time of computations from several years to few weeks or days. It will allow studying atomic and molecular systems with accuracy that will not be possible otherwise.