Solvent Effects on Chemistry with Alcohols. An Ab Initio Study
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In principle, the most fundamental laws in chemistry are known since 1926, when Schrödinger postulated his wave equation. This basic law of quantum mechanics is capable of describing all inter- and intramolecular interactions with great accuracy. Except for metals, relativistic corrections are mostly negligible and therefore the relativistic Dirac equation (1928) is of less importance. One could therefore argue that chemistry is not a science in itself. It just follows the laws of quantum mechanics and is therefore nothing but applied physics. However, as a cook does not stop when he has gathered all his ingredients, science does not stop when its basic laws are known. The 'cooking part' can still be a hell of a job. Up to now, theoretical chemists and physicists are by no means capable to replace the job of the experimentalists. If industries try to invent a new catalyst for a certain chemical process, they usually do not rely on theoretical calculations. Much more efficient are the methods of an experimentalist: a bit of intuition and a lot of trial and error. The reason for this is that theoretical calculations take enormous amounts of time when systems are complex. Mathematical analytical solutions of the Schrödinger equation only exist for the most simple systems, like the hydrogen atom. If the total number of particles is more then two, one has to rely on approximate numerical calculations. Of course, computers are an enormously powerful tool, but the number of atoms and electrons in most chemical systems is so large that even calculations on powerful supercomputers can take years.

Still, if a theoretical calculation can be performed, it can give much more insight on how the chemical process evolves and why a certain type of molecule is a good catalyst and another is not. This makes it worth studying these systems on a theoretical basis. However, the computational costs strongly limit the system size and simulation time. Gas-phase reactions containing only a small number of atoms are therefore usually the subject of these studies. Most chemical reactions in nature, in industry, or in laboratory experiments do not occur in the gas-phase, but occur in the presence
of a solvent like water. An accurate description of liquid water requires at least about 20 water molecules. In the last years an enormous progress has been made in the possibilities for theoretical calculations. This is partly due to the increase in computer power, but more important were the creative inventions of smart algorithms. Density Functional Theory and the Car-Parrinello method have, by use of minor approximations, decreased the computational costs by orders of magnitude. In combination with statistical methods to simulate rare events, the understanding of molecular behavior of more and more complex chemical reactions is in our reach.

I started my PhD four years ago and the final result is this doctoral thesis. The main question was to investigate the solvent effect on chemical reactions, in particular chemical reactions with alcohols in water. One of the conclusions of this research is that solvent dynamics is indeed very important. Molecular fluctuations in liquid water, yielding special structures between water molecules, can have an enhanced polarizing effect on solute molecules. This effect can facilitate or even initiate a chemical event. This thesis also contains a related but different subject. During the research, while studying methods for rare events, I got a new idea to improve upon the Transition Path Sampling method. In cooperation with Daniele Moroni and Peter Bolhuis we turned this idea into a completely new method for the calculation of rate constants. This new method, that we named Transition Interface Sampling, has become an important additional subject of this thesis.

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