

Development of new electronic structure methods for intermolecular interactions in multireference systems

The primary goal of modern theoretical chemistry is bringing better understanding of the results of experiments and relating them to the known laws of physics. A relevant example here is the definition of the covalent chemical bond as “a region of relatively high electron density between nuclei which arises at least partly from sharing of electrons and gives rise to an attractive force and characteristic internuclear distance”.¹ Such bonds are clearly defined and well described, both quantitatively and qualitatively, by theoretical chemistry methods.

Apart from the covalent bonds, there also exists a plethora of other types of bonds covered by a broad name “non-covalent interactions”. Albeit weaker than the covalent bonds, the non-covalent ones are just as ubiquitous in nature. They are responsible for matter’s liquid and solid phase, for the helix shape of DNA and the structure of biologically important proteins.

While it used to be very difficult to quantify those weaker than covalent interactions, the quantum chemistry methods are starting to cope with this task. However, understanding and distinguishing different types of bonds within this broad class of interactions is still challenging.

One of the most popular - and accurate - methods in this category is the Symmetry Adapted Perturbation Theory (SAPT). It allows one to compute and decompose the interaction energy between two molecules into physically meaningful terms, such as electrostatic, exchange, induction and dispersion. This allows one to e.g. identify an interaction between noble gas atoms as a van der Waals one and between water molecules as having mainly electrostatic origin. Such insight is highly valuable in interpreting and predicting the results of experiments, but also in the construction of computationally inexpensive theoretical methods.

Unfortunately, currently the applicability of SAPT is limited to the so-called single-reference systems, which means that it is not possible to describe most metallic systems and molecules that undergo a bond dissociation process. This excludes all the systems that are undergoing a chemical interaction and that in turn limits our understanding of the role that non-covalent forces play in shaping the reaction processes.

The methods we propose are free from such limitation. We hope that they will lead to an enhanced understanding of the reactivity of certain molecules, of the catalysis and adsorption processes, and that they will establish a stronger link between the chemical theory and the experiment.

¹ PAC, 1994, 66, 1077 (*Glossary of terms used in physical organic chemistry (IUPAC Recommendations 1994)*), p. 1101