2017 RACI Physical Chemistry Division Lecture

An Excursion to the Density Functional Theory Zoo: Insights for Electronic Ground and Excited States

Lars Goerigk

School of Chemistry, The University of Melbourne, VIC 3010

Abstract: Over the past years, we have seen tremendous improvements in the development of quantum-chemical procedures and we now have access to methods that allow the accurate treatment of systems with even hundreds of atoms. However, the large number of available methods also makes it hard for the user to understand their benefits or potential risks. As a consequence one can therefore observe the trend to stick to a few familiar — albeit sometimes older — levels of theory.

This presentation aims to provide a better understanding of how quantum-chemical method developers think and how their efforts can lead to insights that are also significant for the general chemistry community. Herein, I will discuss problems of common approaches and my group's recent efforts to identify better alternatives. I will cover two of our main research areas, viz. method development for electronic ground and excited states:

1) London dispersion and DFT:
Conventional density functional theory (DFT) approximations cannot describe the ubiquitous London-dispersion phenomenon (van-der-Waals forces). Despite the fact that this has been known for more than two decades, the importance of dispersion is still often underestimated in common computational applications. I will outline that London-dispersion effects can in fact be sizeable, that they can determine the outcome of chemical reactions and that their proper treatment is crucial for accurate thermochemistry.

2) Treatment of Molecular Electronic Excited States:
In the form of a time-dependent (TD) formalism, DFT is also regularly applied to obtain electronic excitation energies and transition dipole moments for (mostly) organic dyes. Also in this field the user is faced with the same "zoo" of density functional approximations as in the case of ground-state applications. Herein, I will present our successful efforts in the development of new TD-DFT approaches that surpass popular methods — including the omnipresent TD-B3LYP approach — not only in accuracy, but also in robustness and reliability.

Biography

Lars Goerigk is a lecturer at the School of Chemistry at The University of Melbourne. In 2011, he obtained his PhD in the group of Prof. Stefan Grimme at the University of Münster, Germany. He then relocated to The University of Sydney on a postdoctoral scholarship funded by the Germany Academy of Sciences “Leopoldina”, where he worked in the group of Prof. Jeffrey R. Reimers. In 2014, Lars joined the School of Chemistry at The University of Melbourne as an ARC DECRA Fellow, where he transitioned to a continuing role as a lecturer in June 2016. Lars’ area of expertise is Theoretical and Computational Quantum Chemistry with special emphasis on density functional theory (DFT) method development, the treatment of electronic excited states, and applications to bio-, inorganic-, and organic-chemical problems. He has made decisive contributions towards the development of one of the most accurate density functionals currently available (PWPB95), and his work also contributed towards a better understanding of the role of London-dispersion in chemical reactions and molecular structures. One of his research passions is to close the gap between method developers and method users by promoting a better understanding of DFT methods, of what they can and — more importantly — of what they cannot achieve. Lars’ work has been acknowledged with several awards, including the 2011 IBM-Zerner Award, the 2014 Selby Award and the 2017 RACI Physical Chemistry Division Lectureship.