A Trip to the Density Functional Theory Zoo: Insights and Recommendations

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Research in my group comprises quantum-chemical method development and applications to both electronic ground and excited states. In this presentation, I will focus solely on our recent research on ground states, an area that has seen tremendous methodological improvements over the past years. For instance, we now have access to methods that allow the accurate treatment of systems with hundreds of atoms. Unfortunately, the large number of available approaches makes it hard for the user to understand their benefits or potential risks and, consequently, one can observe the trend to stick to a few familiar — albeit sometimes older — levels of theory. Herein, I will discuss how we can find a way through this "zoo" of methods and how we can identify reliable approaches that allow us to address chemical questions computationally. At the same time, I will also discuss problems of common approaches and our recent efforts to identify economic solutions.

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 to the general chemistry community. For this purpose, I will provide examples that touch these two main areas:

a) London-dispersion and DFT: Conventional density functional theory (DFT) approximations cannot describe the ubiquitous London-dispersion phenomenon. 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 and that their proper treatment is crucial for accurate thermochemistry.\(^1\) I will also review different strategies on how to tackle the London-dispersion problem for DFT approximations, and I will conclude by giving recommendations and insights that are useful for both users and developers.\(^2,3\)

b) Geometry optimization of polypeptides and protein fragments: This field is currently dominated by approaches that suffer from a number of problems that cause various artefacts. Herein, I will outline that one cannot hope for fortuitous error cancellation in those approaches, and I will discuss more robust alternatives that still maintain the computational efficiency of the popular strategies. Finally, I will conclude this presentation by giving a perspective on how these alternatives can advance the exciting area of Quantum Crystallography or Macromolecular Quantum Refinement.\(^4\)