Stefan Grimme

Efficient and accurate theoretical treatment of dispersion interactions

Long-range electron correlation, commonly referred to as (London) dispersion and usually identified as the attractive part of a van der Waals interatomic potential, has become a research topic of general interest in chemistry. Dispersion is the driving force for molecular aggregation, influences the thermodynamic stability of molecules, and is relevant to many important chemical phenomena such as molecular recognition, reaction selectivity, protein folding, catalysis, and many more [1]. The growing interest in such phenomena with a special focus on their theoretical description is reflected in the DFG-funded priority program "Control of London dispersion interactions in molecular chemistry" lasting for 6 years until 2020. A primary goal of this program was the development of chemical design principles that utilize dispersion interactions in the construction of novel molecular structures and chemical reactions. The key points and the progress achieved were now presented as the main topic at the Bunsen-Tagung 2022.

Because dispersion effects mainly occur in larger systems and condensed matter, their importance has been overlooked by the majority of theoretical chemistry for decades [2]. However, triggered by the dramatic failure of popular density functional approximations such as B3LYP for non-covalent interactions, various correction schemes as well as better density functionals have been developed in the last 15-20 years. The problem is rather general, i.e., well established mean-field electronic structure methods like Hartree-Fock, almost all common semi-local density functional approximations, and semi-empirical molecular orbital theories do not account for long-range electron correlation effects. The most prominent approaches to solve this problem can be classified into three groups: (i) non-local, density-based functionals, (ii) semi-classical C₆-dispersion coefficient based, and (iii) highly parameterized density functionals like M06-2X. Note that for large molecules (and condensed matter systems) the correct interatomic R⁻⁶ asymptotic distance behavior of the dispersion energy is important which is only fulfilled by methods in group i) and ii). In any case, for non-metallic systems the electronic part of the problem is relatively well understood and modern dispersion-corrected Kohn-Sham DFT is able to provide quantitative results for many of the problems mentioned above. The efficient and widely used D3/D4 dispersion methods nowadays define the standard

Prof. Dr. Stefan Grimme

Clausius-Institut für Physikalische und Theoretische Chemie Mulliken Center for Theoretical Chemistry Universität Bonn Beringstr. 4, D-53115 Bonn grimme@thch.uni-bonn.de in the field and can be applied routinely in combination with various theoretical models including also force-fields or machine learning techniques. Actual theoretical research considers large Pl-conjugated systems for which different reference wave function theory based methods provide relatively large differences on the order of 10-20 % of the interaction energy [3]. Other topics of future research are the relevance of many-body effects (usually an atom-pair wise treatment covers about 95 % of the dispersion energy), dispersion in metallic (low-gap) systems and the partial quenching effects occurring in solution.

Regarding the use of dispersion in chemistry as a new design principle, e.g., by so-called "dispersion energy donors"[4] which are large, polarizable functional groups like tBut or tri-methylsilyl, the future seems bright. Synthetically oriented chemists could already thermodynamically stabilize rather unusual bonding situations with this technique [5] that also enables new possibilities in targeted catalyst [6] and compound design. Applying the D3/D4-models, energetically stabilizing effects of various donor groups can easily be decomposed into common electronic and the interesting dispersion contributions even in the theoretically difficult intramolecular situation present in manifold organicand organometallic compounds [7]. Eventually, in many complex systems under typical conditions, a subtle balance of inter- and intramolecular dispersion, solvation as well as entropic effects determine the observed chemical and physical properties. For a recent general overview of modern computational chemistry with some emphasis on DFT and a robust and efficient theoretical treatment of dispersion interactions, see Ref. [8].

References

- J. P. Wagner, P. R. Schreiner, Angew. Chem. Int. Ed. 2015 54, 12274 - 12296.
- [2] S. Grimme, A. Hansen, J. G. Brandenburg, C. Bannwarth, Chem. Rev. 2016 **116**, 5105 – 5154.
- [3] C. Villot, F. Ballesteros, D. Wang, and K. U. Lao, J. Phys. Chem. A, 2022 126, 4326 - 4341.
- [4] S. Grimme, R. Huenerbein, S. Ehrlich, *ChemPhysChem.* 2011 12, 1258 – 1261.
- [5] D. J. Liprot, P. P. Power, Nat. Rev. Chem. 2017, 1, 0004.
- [6] T. H. Meyer, W. Liu, M. Feldt, W. Wuttke, R. A. Mata, L. Ackermann, Chem. Eur. J. 2017 23, 5443 – 5447.
- [7] M. Bursch, E. Caldeweyher, A. Hansen, H. Neugebauer, S. Ehlert, S. Grimme, Acc. Chem. Res. 2019 52, 258 – 266.
- [8] M. Bursch, J.-M. Mewes, A. Hansen, S. Grimme, Angew. Chem. Int. Ed. 2022, e202205735.

UNDERSTANDING DISPERSION INTERACTIONS IN MOLECULAR CHEMISTRY

Prof. Dr. Stefan Grimme

Stefan Grimme studied Chemistry and finished his PhD in 1991 in Physical Chemistry. He habilitated in Theoretical Chemistry in the group of Sigrid Peyerimhoff. In 2000, he



got the C4 chair for Theoretical Organic Chemistry at the University of Münster. In 2011, he accepted an offer as the head of the Mulliken Center for Theoretical Chemistry at the University of Bonn. He is the recipient of the Schrödinger medal and the "Gottfried Wilhelm Leibniz-Preis". His main research interests are the development and application of quantum chemical methods for large molecules, density functional theory, and noncovalent interactions. News

CRC 1333 "Molecular Heterogeneous Catalysis in Confined Geometries"- 2nd Funding Period Granted





Final preparations before the opening of the 121st Bunsen-Tagung. © DBG/ Jan Will



Biocatalysts use 3D confined geometries of defined size, polarity and tortuosity to promote desired reactions, e.g. by destabilizing the ground state or stabilizing preferred transition states. In chemical catalysis, confinement has been successfully used to accomplish improved enantioselectivity. However, confinement effects remain poorly understood, barely quantified and successful applications are still very much hit-and-miss. Within the CRC 1333, we set out to understand and exploit confinement effects so they can be used as a design principle in a wide range of catalytic reactions.

In the first funding period (2018-2022), materials with tailored surfaces and unprecedented sub-nanometer precision in terms of pore size were prepared. By targeted variation of pore size, we could significantly increase the selectivity in olefin meta-thesis and in several addition reactions. In the second funding period (2022-2026), we will now develop methods to quantify the effects of the confined geometric cavities and exploit them to optimize a wide range of catalytic reactions, ranging from organocatalytic alkylations to carbon dioxide reduction.

The CRC 1333 links 19 research groups at the University of Stuttgart with partners at the Max Planck Institute for Solid State Research in Stuttgart and the Universities of Paderborn, Marburg and Bochum. Our members contribute expertise in materials development, catalysis, analytical chemistry, theory and simulations.

More details about the individual projects and the scope of the CRC can be found at: https://www.crc1333.de/

Contact: **Michael R. Buchmeiser** (michael.buchmeiser@ipoc. uni-stuttgart.de)