Summary of PhD thesis entitled:

Intermolecular interactions in water clusters

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This dissertation addresses the challenges of modeling intermolecular interactions in water. The primary motivation of the presented work was to find a protocol that would be accurate enough to predict the most stable isomer among water hexamers.

Traditionally, the calculation of energies for molecular clusters relies on the supermolecular method, which involves calculating energies for the entire cluster. As the system size expands, the computational cost of this approach increases rapidly. In this work, we demonstrate that the many-body expansion can be employed as an efficient alternative for calculating interaction energies. We take advantage of the rapid convergence of the many-body expansion to reproduce the results of canonical calculations with greater accuracy and reduced computational effort. By breaking down large clusters into smaller subclusters and using tailored computational methods based on the fragments' importance, we developed a protocol called the "stratified approximation" many-body approach (SAMBA). Using this approach, we achieved highly accurate benchmarks for the isomers of water hexamers and larger clusters, including 16-mers and 24-mers. Although we applied this approach only to water clusters, it can also be extended to other systems.

To model properties beyond single-point energies, an accurate intermolecular potential is required. Numerous potential energy surfaces (PESs) or force fields have been developed for water, but, as it turned out, their characterization of non-additive interaction energies, including three-body interactions, proved insufficient for accurately modeling larger water clusters. To address this issue, we developed a new three-body water potential that also incorporated improvements in the two-body part and in contributions from higher-order interactions. We conducted extensive calculations for water trimer, with more than 70 thousand trimer interaction energies computed using state-of-the-art level of theory. The resulting potential was sufficiently accurate to model the stability of water hexamers, achieving the main objective of the dissertation, and provided benchmark-quality results for larger systems.

Modeling of water is a very competitive field of research. Other groups have also proposed alternative protocols and potentials to solve the same problem. Our approaches remained competitive and gained a significant number of citations.