(Un)Chemical Bonding: Surprises in Non-Covalent Interactions in Molecular Systems

Alexandre Tkatchenko[1]

[1] Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Non-covalent van der Waals (vdW) interactions are ubiquitous in molecules and condensed matter, and play a crucial role in determining the structure, stability, and function for a wide variety of systems. The accurate prediction of these interactions from first principles is a substantial challenge because they are inherently quantum mechanical phenomena that arise from correlations between many electrons within a given system. We discuss the recently developed efficient method [1,2] that combines quantum and classical electrodynamics and accurately describes the nonadditive many-body vdW energy contributions arising from interactions that cannot be modeled by an effective pairwise approach. It is demonstrated that such contributions can significantly affect the behavior of biological (DNA), chemical (molecular crystals), and condensed (bulk, hybrid interfaces) systems. In most of these cases it is found that collective vdW interactions play a noticeable, if not crucial role, not just for quantitative values but also for the qualitative behavior [3,4,5,6].

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