Application of the Method of increments for the investigation of electron correlation effects in physisorbed systems

Carsten Müller

Freie Universität Berlin
Takustrasse 3, 14195 Berlin, Germany

Physisorption plays an important role in many different contexts of surface chemistry. In these weakly bound systems the interaction consists of two parts: electron dispersion and classical electrostatics. Dispersion is non-local electron correlation. It is neglected in Hartree-Fock (HF) theory, not included in common DFT functionals, but recovered by Møller-Plesset Perturbation (MP2) or Coupled Cluster (CC) theory. Classical electrostatic interactions are in principle well described already at the HF or DFT level, however for some molecules e.g. CO and N_2O these methods fail to reproduce the small dipole moments and consequently fail to reproduce the electrostatic interactions, too. It is therefore important to apply very accurate computational methods in order to obtain reliable data for the adsorption energy that could be compared to experiment. Due to the high computational costs of the ordinary MP2 and CC methods we here apply these theories in the framework of a local correlation scheme called The Method of Increments [1-4]. In this scheme, which can be applied for all size-consistent methods, the correlation energy is calculated as a many-body expansion in terms of localized orbital groups. Due to the local character of the electron correlation this expansion converges quite fast with much lower requirements on computational time and resources than standard implementations of post-HF methods. We have extended the method of increments to adsorption problems and investigated the systems $CO/CeO_2(110)$ [5], $CO/CeO_2(111)$ [6], $N_2O/CeO_2(111)$ [7], and $H_2S/Graphene$ [8]. We found that in all four systems electron correlation effects contribute to a large amount to the adsorption energy. On top of the large speed-up the method of increments yields some interesting insights into the nature of the molecule-surface bond in weakly bound systems.

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