

Benchmarking the performance of density-functional-based approaches on intermolecular interactions of Helium–water complexes

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Synopsis The He-water systems remain relatively unexplored. As only under extreme conditions, noble gases can be made to react to produce compounds, we investigated the characteristics of the interaction among He atom and water ice channels or clathrate cavities from first-principles calculations. The ability of DFT-based methods to describe such weak interactions might lead to further insights on noble-gas inclusion compounds.

In this work we studied structural properties and energetics of various water containing systems, from filled ice structures (e.g. horizontal and perpendicular I_H and I_h) to cavities of clathrate hydrates (e.g. 5^{12} , $5^{12}6$, etc) [1]. Such compounds are crystalline solids with an ice-like hydrogen bonded network that trap atoms or molecules, and in our case the "guest" atom in the clathrate cavity or in the ice channels is the He; the lightest noble gas atom. The predominant intramolecular interactions in such complexes are the hydrogen bonding between water molecules, and van der Waals (vdW) forces between the He and water molecules. Thus, *ab initio* technology have been used to investigate the guest-host interactions. Electronic structure calculations were carried out at MP2/CCSD(T) levels of theory and serve as the reference data. In turn, DFT and dispersion-corrected (DFT-D) [2] methods are then employed to describe the intermolecular interactions of such weakly bound systems. The main disadvantage of DFT-based approaches is the poorly description of hydrogen bond and vdW interactions. Therefore, we carried out calculations, choosing sets of dimers formed by one He atom and increasing number of water complexes. Given the delicate balance between the interaction energy components present on these systems, we aim to evaluate DFT and DFT-D functionals from the "simplest system" formed by one water molecule and govern exclusively by vdW forces; followed by the study of the "fundamental units" present in all ice-like frameworks (such as pentamers and hexamers), where hydrogen bonding start to have relevance on the interaction; and finally, by analyzing the interactions in the "building blocks" of ice channels and clathrate cavities.

For such purpose, we proposed [3] a protocol based on the analysis of: a) the relative error on a single optimized configuration. As we found that this is not a conclusive filter, we also calculated b) the interaction energy curve along a relevant coordinate for each type of He-water system. We found

that non-local correlation effects can be recovered only with functionals of the higher rungs of Jacob's ladder, while dispersion corrections should be included once wisely and well tested, as vdW forces are fundamentals on the description of intermediate and long range interactions. In this sense, we observed that by increasing the number of water molecules, or hydrogen bonds, the DFT functionals which keep the same interaction energy curve profile as the reference one, are: TPSS, B3LYP, B2PLYP, mPW2PLYP, CAM-B3LYP, LC-wPBE and wB97X (see Figure 1). Besides, in most of the functionals used (including GGA, meta-GGA, hybrid-GGA, hybrid-meta-GGA, double-hybrid, range-separated hybrid), the part of dispersion is better recovered by including D3BJ dispersive term. Furthermore, considering the computational cost, the functionals with best relation between computational efficiency and accuracy are: LC-wPBE and wB97XD.

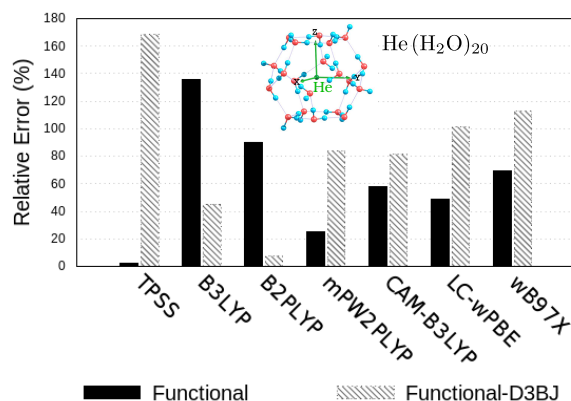


Figure 1. Performance of the indicated DFT and DFT-D functionals on a single MP2-optimized structure of 5^{12} He-clathrate-like cage (see inset panel).

References

- [1] E. D. Sloan, 2003 *Nature* **426** 353-363
- [2] S. Grimme *et al.* 2016 *Chem. Rev* **116** 5105
- [3] M. Blanco de Paz *et al.* 2017 *in preparation*

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