# Density-functional approximations on $CO_2$@sI clathrate hydrate interactions

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**Synopsis** Clathrate hydrates have unique physical and chemical properties and considering that the stability of such systems is strongly related with its guest. In the last decades a renewed interest on these substances have grown up due to their potential industrial applications, with gas hydrate research becoming a joint field of various engineering disciplines and fundamental sciences.

So far, clathrate hydrates have attracted the interest of both experimentalists and theorists [1], focused mainly on two fundamental problems, a) at which conditions (pressure, temperature, concentration) gas hydrate may be formed or decomposed, and b) what structure type of gas hydrate could be obtained at these conditions. Although many characteristics of clathrate hydrates are well known experimentally, other relevant to microscopic aspects, such as accurate estimations through modelling is a scientific challenge. Related with this, computational simulations have been usually limited by the accuracy of the models in describing guest-host interactions, while currently first-principles and *ab initio* calculations are being used to determine molecular scale parameters (interaction force-fields, structural variables, spectra), that are essential for understanding fundamental aspects of hydrate formation, stability and thermodynamics.

Such facts, motivated us to evaluate the description of the guest-host $CO_2$@sI clathrate hydrate interactions from wave-function (WFT) and density function theory (DFT) electronic structure calculations. Computed couple-cluster or MP2 reference interaction energies for a representative set of configurations are used to assess the accuracy of modern DFT approximations (empirical and nonempirical), including the effect of semilocal approach, exact-exchange/correlation admixture, range-separation, as well as dispersion-correction terms [2]. In this work, results are presented for the T and D cages of the $CO_2$@sI clathrate hydrate (see Figure 1) obtained from twelve functionals available or recently implemented in *Gaussian* package [3]. Each density functional approximation (DFA) was evaluated following a protocol of complementary strategies [4] (see Figure 1). First, an extended benchmark dataset was introduced by performing reference explicitly correlated CCSD(T)-F12/DF-MP2 calculations, and sampling configurations in near-equilibrium and rep-

resentative stretched regions of the potential; not, as traditionally, only equilibrium configurations. In turn, error analysis was carried out for each DFA for both the minimum interaction energies, as well as the remaining set of energies, following by scans of the potential along relevant orientations, complemented by correlation plots for a complete exploration of the systems configurational space. Finally, comparisons with semiempirical, as well as *ab initio*-based effective pairwise models commonly used as a first approximation in molecular simulations, indicate that for microscopic considerations on the interactions further refinements in such analytical representations should be incorporated in these analytical representations.
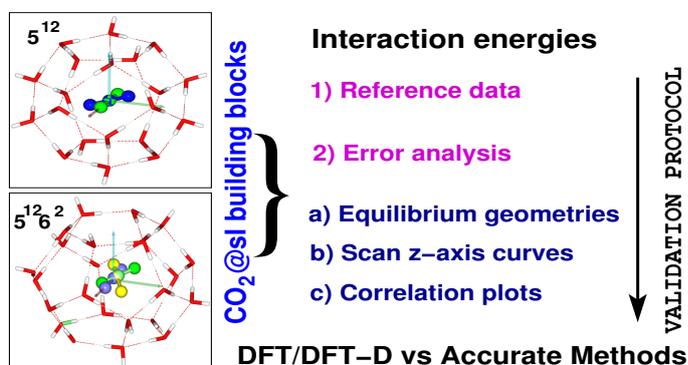


**Figure 1**. Protocol used to validate the performance of different DFAs with and without dispersion corrections for the sI building blocks, $CO_2(H_2O)_{20,24}$, interactions.

# References

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