A Comparative Study of DFT Methods for the Evaluation of Hydrogen-Bonded Molecular Clusters

Sotheavy Chhin, Steven Morgan, Ryan McNulty and Glênisson de Oliveira

Rhode Island College, Physical Sciences Department
600 Mt. Pleasant Ave., Providence, RI 02908

In recent years, methodology for the evaluation weakly bound complexes has evolved to the point that accuracy has increased and the cost of calculations has been reduced greatly, while hardware has become much faster and more powerful. In our group for instance, in the last two and a half years methods have been developed to decrease the cost of high-level *ab initio* calculations so that the infinite basis set limit can be evaluated at a lower cost without loss of accuracy – the time for calculations is now reduced by more than two orders of magnitude. However, it is unlikely that any developments in the foreseeable future will allow for evaluations of very large clusters, as long as formal theoretical formulations depend on system size (N) by factors of N^5 to N^9. One possible solution is to use methods that are not quantum mechanical per se. Some specialized force fields have been successfully used in the past, but DFT can be used more promptly since these methods do not depend on molecular parameters that take a long time to develop, and functionals are widely available in commercial software.

Unlike *ab initio* calculations, there is no hierarchy of methods in density functional theory; methods have to be tested for specific purposes. In this work we examine what may be the most extensive list of functionals yet reported for the evaluation of hydrogen bonded complexes. Over 80 functionals were tested, and results were compared with high-level *ab initio* calculations for clusters of hydrogen sulfide and water. Both structure and energetics were considered, and ultimately six methods consistently produced results closest to our target values. Larger basis sets than the initial auc-cc-pVDZ were tested with these selected functionals, and only two showed slight improvement with a balanced increase in basis set size. Further augmentations in the diffuse region did not lead to the same improvements as in ab initio methods. Clearly, the limit in accuracy for DFT methods is reached with moderately sized basis sets. Besides basis set effects, many-body effects were studied by progressively increasing cluster size, and unlike coordination complexes, the accuracy of methods remained consistent for smaller or larger systems.

* This work was supported by NSF grant CHE 0116435, as part of the MERCURY supercomputer consortium, a Title II grant from the US Department of Education, and by the Rhode Island College Faculty Research Funds and Faculty Development Funds