# Benchmark Interaction Energies and Non-Additivities for Weakly Bound Non-Covalent Clusters: Beyond Dimers

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**Abstract**

Databases of benchmark interaction energies [1] have proven to be invaluable resources in the quest for efficient computational methods that can reliably describe the entire spectrum of weak interactions. However, the convergent electronic structure techniques used to generate this type of benchmark data are quite demanding and limited to fairly small systems. For example, benchmark interaction energies can easily be found for a wide range of dimers, but the same data for larger non-covalent molecular clusters (trimers, tetramers, etc.) are relatively scarce. This presentation will demonstrate the need for high quality, benchmark interaction energies and non-additivities in larger clusters as well as illustrate how the multi-centered QM:QM methods developed in our group [2,3] can extend high-accuracy benchmark procedure to such systems. In particular, we will examine the use of a 2-body:many-body multi-centered ONIOM procedure to generate CCSD(T) complete basis set limit interaction energies. If time permits, several new prototypes for $\pi$-type interactions will also be discussed. We have recently begun examining the P and Si isovalent analogues of cyanogen ($N \equiv C - C \equiv N$) and diacetylene ($H - C \equiv C - C \equiv C - H$) dimers [4] and found the effects of higher-order correlation in these systems to be significantly larger than those in aromatic systems like the benzene dimer.

[1] See, for example, Y. Zhao and D.G. Truhlar, *J. Chem. Theo. Comput.*, **1**, 415 (2005) and P. Jurečka, J. Šponer, J. Černý and P. Hobza, *Phys. Chem. Chem. Phys.*, **8**, 1985 (2006).
[2] G.S. Tschumper, *Chem. Phys. Lett.*, **427**, 185 (2006).
[3] A.M. ElSohly, C.L. Shaw, M.E. Guice, B.D. Smith and G.S. Tschumper, *Mol. Phys.*, 105, 2777 (2007).
[4] B.W. Hopkins, A.M. ElSohly and G.S. Tschumper, *Phys. Chem. Chem. Phys.*, **9**, 1550 (2007).