

The Infinite Basis Set Limit for the Hydrogen Sulfide Dimer; the Role of D-Functions¹

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Recently, we developed new methodology to greatly decrease the cost of infinite basis set evaluations for hydrogen-bonded systems such as water or hydrogen fluoride clusters. Clearly basis set demands for weakly bound clusters are even greater than in covalently bonded systems of the same size, since a diffuse region of the wavefunction must well represented in the former case. We were able to greatly reduce the cost of evaluations of the complete basis set limit by carefully and systematically eliminating functions from the correlation consistent family of basis sets that may not be contributing to the long-range interactions.

A natural step to follow up for those studies was to consider periodic trends and to examine similar molecules, where the central atom is heavier. Obviously the nature of the interaction changes with the change in central atom, and here we show that in the case of hydrogen sulfide clusters (the second-row analog of water), where dispersion plays a more significant role, the basis set demands for the evaluation of the infinite basis set limit are different from those systems where hydrogen bonding occurs. Two findings in particular are consistent with previous observations for the evaluation of thermochemical and cluster properties involving H₂S: 1) unlike H₂O, HF, or NH₃ clusters, counterpoise correction does not improve convergence to the asymptotic limit, and 2) d-functions are crucial to these weak interactions (as they are for thermochemical properties), so a good representation of these functions is crucial to avoid erratic behavior in a sequence of otherwise well tempered basis sets. Even the excellent series of augmented correlation consistent bases require an improvement of the d-functions. On the other hand the basis set reductions that worked well for systems with hydrogen bonds also work well for H₂S clusters.

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