

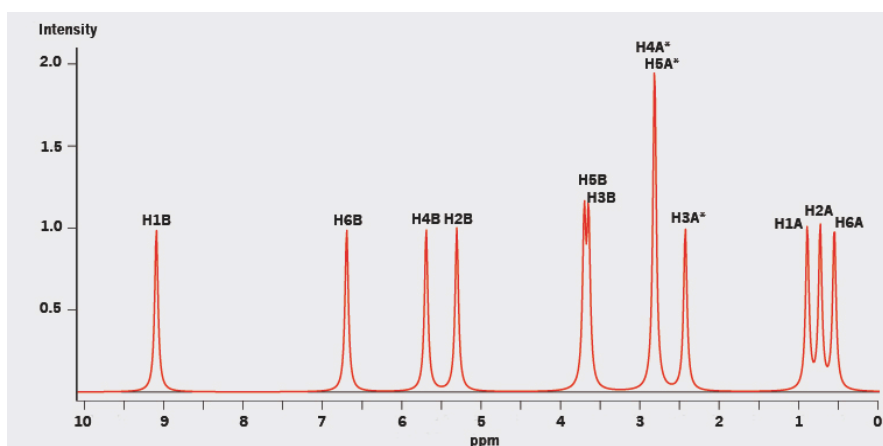
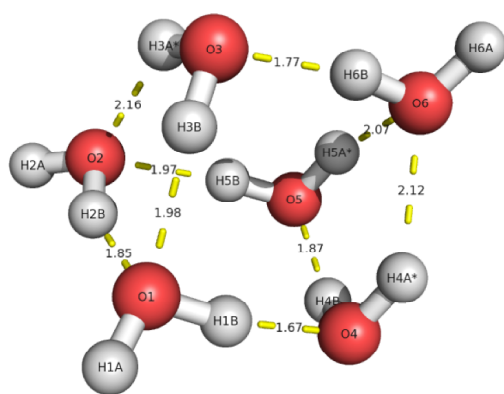
# NMR shieldings of water clusters: Is it possible to reach the complete basis set limit by extrapolation?

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The SSB-D functional has been proposed as a new all-round density functional [1] and was recently shown to perform excellently in computations of NMR shieldings [2]. In this current study, we used small water clusters in order to observe the behavior of the complete basis set (CBS) convergence of NMR shieldings constants by extrapolation. It is well known that CBS is used for calculate accurate energies with different methods which satisfy the variational principle. However, there are few studies about nuclear shielding calculations and his CBS behavior. Here, we found that for several levels of theory such as HF, MP2, CCSD, CCSD(T) or DFT (as well as SSB-D) are able to apply the Basis-Set Convergence theory for NMR Shielding by extrapolation. On the other hand, the behavior depends on how is good the exponential correlation, therefore, it is not possible to apply this method for a general case. We distinguish between Dunning, cc-pVXZ and aug-cc-pVXZ (X=D, T, Q, 5 and 6) and Jensen basis set pcS-n (n=1, 2, 3 and 4) where both are especially designed for NMR. Finally, we use our knowledge with small water hexamer conformers to obtain a theoretical CBS <sup>1</sup>H-NMR spectrum at SSB-D level of theory (see illustration for water prism).



## References

[1] M. Swart, M. Solà, F.M. Bickelhaupt, *J. Chem. Phys.* **2009**, *131*, 094103; [2] M. Swart, A.W. Ehlers, K. Lammertsma, *Mol. Phys.* **2004**, *102*, 2467; [2] Li. Armangué, M. Solà, M. Swart, *J. Phys. Chem. A* **2011**, online, DOI: 10.1021/jp108327c.