

Density Functional Calibration for Indirect Spin-Spin Coupling Constant Calculations

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Abstract: The use of computational methods in order to determine NMR parameters can be challenging. Although Coupled Cluster and MCSCF calculations are the most accurate methods to evaluate magnetic properties, due to high computational cost they can be applied only for small molecular systems. On the other hand, DFT methods are the only ones that can treat properly "real systems" regularly, so that there is an interest to improve approximations to calculate coupling constants [1-3]. There is no "universal DFT" to evaluate all types of NMR coupling constants. Therefore, some benchmark studies have been reported in order to find the DFT with best accuracy for NMR properties – one of most recent evaluated the precision for 39 DFTs and compared with SOPPA *ab initio* methods [4]. In this work 26 DFTs are initially evaluated, changing the percentage of Hartree-Fock orbital exchange (E_x^{HF}) in order to obtain the best possible accuracy. The calibration set contains HF, CO, H₂O, NH₃, BF₃, BHF₂, F₂O, PH₃, PF₃, CH₄, C_2H_2 , C_2H_4 and C_2H_6 , and all systems are described by aug-pcJ-2 basis set. BHandH, B1B95 50% E_x^{HF} , B971 50% E_x^{HF} , B972 40% E_x^{HF} and B98 50% E_x^{HF} provided accurate results, so further investigation is done by optimizing geometries and performing vibrational corrections, and they are compared with SOPPA(CCSD) and SOPPA(CC2) levels of theory. New DFTs generated by combination of exchange and correlation potentials, changing E_x^{HF} , are evaluated to determine which approaches are better. Accurate ones are performed for geometries optimization, and compared with accuracy for every single coupling constant. Tests will be done to ensure if these functionals are good to describe spin-spin coupling in a variety of systems.

Key-words: DFT, NMR, Indirect Spin-Spin Coupling Constant

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