Model Chemistry Recommendations and Errors for Vibrational Frequency Calculations

Juan C. Zapata Trujillo, Laura K. McKemmish*
*presenting author; l.mckemmish@unsw.edu.au
University of New South Wales, Australia

Despite the widespread popularity of scaled harmonic frequency calculations to predict experimental fundamental frequencies in chemistry, prior to our recent publication[1], sparse benchmarking was available to guide users on appropriate level of theory and basis set choices (model chemistry) or deep understanding of expected errors.

In this presentation, we discuss our new benchmarking results for vibrational frequencies, highlighting our main conclusions:

1. Using model chemistry-specific scaling factors optimised for three frequency regions - low (< 1,000 cm^{-1}), mid- (1,000-2,000 cm^{-1}), and high-frequency (> 2,000 cm^{-1}) - halves the error compared to using a global scaling factor
2. Median errors are more appropriate than rmsd or mad for describing error distribution and expected performance, due to the presence of very large outliers for modes where the harmonic approximation fails
3. The highest accuracy can be obtained with double-hybrid density functional approximations with a non-Pople augmented triple zeta basis set, which can produce median frequency errors of down to 7.6 cm^{-1} (DSD-PBEP86/def2-TZVPD) which is very close to the error in the harmonic approximation, i.e., the anharmonicity error.
4. All studied hybrid functionals with non-Pople triple-zeta basis sets will produce median errors of less than 15 cm^{-1}, with the best result of 9.9 cm^{-1} with B97-1/def2-TZVPD.
5. Appropriate matching of double-zeta basis sets with hybrid functionals can produce high quality results, but the precise choice of functional and basis set is more important. The B97-1, TPSS0-D3(BJ) or ωB97X-D hybrid density functionals with 6-31G*, pc-1 or pcseg-1 are recommended for fast routine calculations, all delivering median errors of 11-12 cm^{-1}.

References:

1. Zapata Trujillo, Juan C.; McKemmish, Laura, “Model Chemistry Recommendations for Scaled Harmonic Frequency Calculations: A Benchmark Study”, Journal of Physical Chemistry A, 2023 (accepted)