

Factors Impacting the Accuracy of ^{13}C NMR Chemical Shift Predictions using Density Functional Theory – The Advantage of Long-Range Corrected Functionals

Mark A. Iron

*Computational Chemistry Unit, Department of Chemical Research Support,
Weizmann Institute of Science, Israel*

Nuclear magnetic resonance (NMR) is an indispensable tool in organic, organometallic and inorganic chemistry. Its use is key in determining structure of compounds – including stereochemistry – and in following reactions.¹ On occasion, however, it is not always definitive, and the actual structure may be debated. The use of calculated chemical shifts is becoming indispensable in helping resolve the structure,² yet sometimes the results can be either inconclusive or even incorrect.

There have been a number of studies published each looking at the impact of certain factors on the accuracy of the calculated chemical shifts. Here, an in-depth study is presented where the key factors are considered: exchange-correlation functional – where over 70 are considered, basis set, integration grids, and the NMR calculation method. For the first time (to the best of my knowledge), long-range corrected functionals were considered and are shown to be more accurate than other functionals.

Recently, Smith and Goodman proposed the DP4 probability as a reliable tool in selecting which amongst a set of potential structures is the most likely based on comparison of the calculated and experimental NMR spectra.³ This method has found significant use in the determination of the stereochemistry of natural products with several chiral centres. The parameters for DP4 were determined for the method of choice found in this study.

[1] Bagno, A.; Saielli, G., *WIREs Comput. Mol. Sci.* **2014**, *5*, 228-240.

[2] Willoughby, P. H.; Jansma, M. J.; Hoye, T. R., *Nature Protocols* **2014**, *9*, 643-660.

[3] Smith, S. G.; Goodman, J. M., *J. Am. Chem. Soc.* **2010**, *132*, 12946-12959.