Visualization of nuclear spin-spin coupling pathways by real-space functions

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Indirect nuclear spin-spin coupling constants are amongst the most important magnetic resonance parameters, invaluable in establishing molecular structure from NMR spectroscopy. Their detailed understanding in terms of molecular and electronic structure is thus of central importance in many fields of research and has been pursued since the beginnings of NMR spectroscopy more than 50 years ago. For example, questions of "through-space" versus "through-bond" mechanisms, the coupling pathways in polycyclic systems and, most recently, spin-spin couplings through hydrogen bonds have stimulated intensive discussions. Today, the quantum-chemical calculation of coupling constants has in many cases reached predictive accuracy. This has in turn enhanced the interest in interpretation, i.e. to go from accurate *numbers* to deeper *insight*.

Different types of analyses were used to obtain further information about different contributions to spin-spin coupling in terms of localized or canonical molecular orbitals (MOs). While these approaches can provide very useful insight, their conclusions depend on MO transformations and are thus strongly *model-dependent*: different MO schemes may lead to conflicting interpretation.

Here we will show that a model-independent description of spin-spin coupling is possible, based on real-space functions in three-dimensional space, which is appropriate for both localized and delocalized bonding situations [1,2]. The newly proposed and implemented real-space functions allow unprecedented insights into the pathways of indirect nuclear spin-spin couplings. In particular, this method allows one to distinguish through-space and through-bond interactions.

1. O.L. Malkina, V.G. Malkin: Visualization of nuclear spin-spin coupling pathways by real-space functions, Chemie Int. Ed., **42**, 4335-4338, 2003.
2. O.L. Malkina, "Interpretation of indirect nuclear spin-spin coupling constants", in "Calculation of NMR and EPR Parameters: Theory and Applications", Eds. M. Kaupp, M. Bühl, V.G. Malkin, Wiley, Weinheim, 2004.