Efficient Implementation of NMR Coupling Tensor Calculations

<u>F. Mack</u>[a] and F. Weigend[b]

[a]*Institute of Physical Chemistry, Karlsruhe Institute of Technology*
[b]*Institute of Nanotechnology, Karlsruhe Institute of Technology*
fabian.mack@partner.kit.edu

Nuclear spin-spin coupling constants are a quantity frequently measured in organic and inorganic chemistry for structure analysis. Quantum chemically, they are calculated as the second derivative of the energy w.r.t. the magnetic moments of the coupling nuclei. According to Ramsey's theory [1,2], four terms arise, labeled Fermi-contact (FC), spin–dipole (SD), paramagnetic spin–orbit (PSO) and diamagnetic spin–orbit (DSO). The first three terms require the iterative solving of response equations, whereas the DSO term is an expectation value over the ground state density. These terms, including the FC/SD cross term needed for anisotropic couplings, have been implemented into the program package TURBOMOLE.

Coupling constants in molecules with about 100 atoms can routinely be calculated within a few hours. Molecules with 1000 atoms are in range if one preselects certain atoms and/or employs the resolution of the identity for K (RI-K) or the seminumerical evaluation of the exchange, both of which are favorable for larger basis sets. In addition, OpenMP parallelization is available.

A further reduction of computational cost can be achieved by choosing smaller basis sets for atoms not directly involved in the couplings of interest. Findings on which atoms can be excluded are presented.

References

1. N. F. Ramsey, *Phys. Rev.* **91** (1953), 303.
2. T. Helgaker, M. Pecul in: *Calculation of NMR and EPR Parameters: Theory and Applications*, edited by M. Kaupp, M. Bühl, and V. G. Malkin (Wiley-VCH, Weinheim, 2004).