

MAGNETIC COUPLINGS AND RELATIVISTIC EFFECTS IN THE CHEMICAL SHIFT OF PARAMAGNETIC MOLECULES: A FIRST-PRINCIPLES STUDY

S. A. Rouf, J. Mareš and J. Vaara

NMR Research Group, Centre for Molecular Materials, University of Oulu, Finland
email: awais.physicist@gmail.com

We applied the Kurland-McGarvey [1] theory to calculate the nuclear shielding and shielding anisotropies in paramagnetic molecules. It has been found that for the special case of the zero-field-split ground multiplet, it is important to include the so-called magnetic (Zeeman and hyperfine) couplings [2-5] between the sublevels. This method is applied in the context of first-principles calculations on example systems like Co(II) [4], Ni(II) [6], Cr(III) [2,7], and metallocenes [7] shown in the Figure. We applied the complete active space self-consistent field (CASSCF) wave function theory and N-electron valence-state perturbation theory (NEVPT2) [8] on these systems to calculate g and ZFS tensors with SVP and TZVP locally dense basis (LDBS). To calculate the hyperfine coupling tensor A, DFT (both PBE and the hybrid PBE0) were used with the SVP and TZVP basis sets. The relativistic effects are included at the second-order Douglas-Kroll-Hess (DKH) level for the g and ZFS tensors, and for the A tensor at the fully relativistic four-component matrix-Dirac Kohn-Sham (mDKS) level. The quantum chemistry packages used for chemical shift were ORCA, GAUSSIAN, and ReSpect [9] while the molecular geometries were optimised by Turbomole. The results obtained from these calculations are in a good agreement with the experimental. This work provides a straightforward platform for further development of pNMR shielding theory in terms of first-principles wavefunctions, as well as for applications in current problems in bio- and materials sciences, including low-temperature experiments.

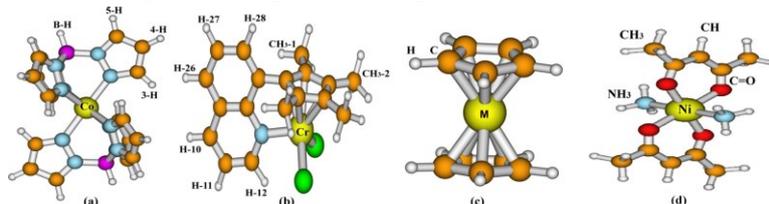


Figure: Geometrical structures of the studied paramagnetic molecules

- [1] R. J. Kurland, B. R. McGarvey, [J. Magn. Reson. 2, 286 \(1970\)](#).
- [2] T. O. Pennanen and J. Vaara, [Phys. Rev. Lett. 100, 133002 \(2008\)](#).
- [3] A. Soncini, W. Van den Heuvel, [J. Chem. Phys. 138, 021103 \(2013\)](#).
- [4] S. A. Rouf, J. Mareš, and J. Vaara, [JCTC 11, 1683 \(2015\)](#) and references therein.
- [5] J. Vaara, S. A. Rouf, and J. Mareš, [JCTC 11, 4840 \(2015\)](#) and references therein.
- [6] S. A. Rouf, V. B. Jakobsen, J. Mareš, N. D. Jensen, C. J. McKenzie, J. Vaara, and U. Gro. Nielsen, manuscript in preparation.
- [7] S. A. Rouf, J. Mareš, and J. Vaara, manuscript in preparation.
- [8] F. Neese, [J. Chem. Phys. 127, 164112 \(2007\)](#) and references therein
- [9] M. Repisky, S. Komorovsky, V. G. Malkin, O. L. Malkina, M. Kaupp, K. Ruud, and co-authors [Relativistic Spectroscopy DFT program, version 3.3.0 \(beta\), 2013](#).