Fully relativistic calculations of NMR and EPR parameters in the framework of the matrix Dirac-Kohn-Sham equation

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During the last two decades it has become clear that, when going down the periodical table, NMR and EPR parameters are much earlier affected by relativistic effects than the geometry of molecules. This is due to a well-known strong sensitivity of those parameters to the details of the electronic structure in the core area. While some systems and problems could be safely treated by more approximate relativistic approaches, there is still a need for fully relativistic calculations of NMR and EPR parameters. In this context, an overview of recent progress made in our group in fully relativistic Dirac-Kohn-Sham calculations of NMR and EPR parameters will be reported. In particular, we will present the working equations for calculation of NMR parameters (shielding tensor [1] and spin-spin coupling tensor [2]) within the matrix Dirac-Kohn-Sham (mDKS) equation. Our approach uses a restricted magnetically balanced (RMB) basis that allows one to solve efficiently the DKS equation in the presence of a magnetic field [1]. First pilot applications to calculation of chemical shifts using GIAO approach will be shown. Importance of variational treatment of spin-orbit operators in calculations of g-tensor for large transition metal complexes will be demonstrated.

1. S. Komorovsky, M. Repisky, O. L. Malkina, V. G. Malkin, I. Malkin Ondik, M. Kaupp, J. Chem. Phys. **128**, (2008) 104101.
2. M. Repisky, S. Komorovsky, O. L. Malkina, V. G. Malkin, Chemical Physics **356** (2009) 236–242.