VALIDATION OF META-GGA AND HYBRID EXCHANGE-CORRELATION FUNCTIONALS IN DFT CALCULATIONS OF MAGNETIC RESONANCE PARAMETERS

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The calculation and interpretation of NMR and EPR parameters by density functional methods has become one of the most valuable theoretical tools in magnetic resonance spectroscopy. The overall accuracy achievable in such DFT calculations rivals frequently that of the most sophisticated ab initio methods available, at a small fraction of the computational effort. However, a number of serious limitations remain with currently popular GGA exchange-correlation functionals, which have to be overcome to extend the range of applicability of DFT methods in this area. i) GGA functionals typically overestimate the paramagnetic contributions to linear-response properties like NMR chemical shifts or electronic g-tensors by only ca. 10% in the main group case (using UDFT approaches), but they underestimate the same properties by up to 40% in the transition metal case (e.g. Fe or Co chemical shifts, or g-tensors of 3d complexes). ii) Core-shell spin polarization effects are significantly underestimated by GGA functionals, frequently leading to appreciable errors in the calculation of EPR hyperfine coupling constants or NMR spin-spin coupling constants. As part of our ongoing efforts to improve the calculation of magnetic resonance parameters, we have now extended our program ReSpect ("**Re**lativistic **Spect**roscopy" [1]) to allow the use of a) hybrid functionals including some exact exchange, and meta-GGA functionals with either a τ-dependence (the PKZB functional [2] has been implemented), or with a dependence on $\nabla^2\rho$ (the FT98 functional [3] is implemented). Validation studies with these functionals are presented for NMR chemical shifts (including spin-orbit corrections to them), electronic g-tensors, hyperfine coupling constants, and spin-spin coupling constants.

References

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