DENSITY FUNCTIONAL CALCULATIONS OF EPR PARAMETERS

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Density functional methods allow the calculation and interpretation of both hyperfine tensors and electronic g-tensors of EPR spectroscopy. While studies of hyperfine couplings for organic radicals today are routine, more recently significant interest has also been directed to attempts of quantitative calculations of hyperfine tensors for transition metal complexes. A systematic validation of different exchange-correlation functionals for 21 3*d* transition metal complexes has revealed both scope and limitations of present DFT approaches [1]. The major problem is the proper description of both core-shell and valence-shell spin polarization, without introducing exceedingly large spin contamination. This has motivated a detailed examination of the mechanisms of spin polarization in transition metal complexes [2]. These studies have also provided new qualitative insights into the interpretation of hyperfine couplings in such systems. A recently developed second-order perturbation DFT approach for the calculation of electronic g-tensors, based on accurate yet efficient approximations to the full molecular spin-orbit operators [3], has meanwhile been validated. It has now been applied to various chemical problems, ranging from biologically relevant vanadium complexes to bioradicals relevant in photosynthesis.

References

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