Relativistic unrestricted two-component calculations of electronic g-tensors and hyperfine structure

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The first two-component relativistic DFT approach for the calculation of electronic g-tensors and hyperfine structure (HFS) is reported that includes spin polarization using non-collinear spin density functionals. The method is based on the relativistic Douglas-Kroll-Hess Hamiltonian and has been implemented into the ReSpect program package. Using three SCF calculations with orthogonal orientations of total spin, the full g-matrix and HFS tensor are obtained. In contrast to previous spin-restricted two-component treatments, results for g-tensor with the new approach agree excellently with spin-polarized one-component calculations for light-atom radicals. Additionally, however, the method reproduces also successfully the negative $\Delta g_{\parallel}$ values of heavy-atom $^2\Sigma$ radicals, and the negative $\Delta g_{\perp}$ components in cysteinyl. Further validation examples include a number of organic radicals, as well as transition metal complexes. The new method removes effectively the dilemma existing up to now, regarding the simultaneous inclusion of spin polarization and higher-order spin-orbit effects in calculations of g- and HFS tensors. Moreover, it is straightforwardly applicable to higher than doublet spin multiplicities.

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