Quadratic spin-orbit mechanism of electronic g-tensor

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For accurate interpretation of electron paramagnetic resonance (EPR) spectra of heavy elements, it is essential to understand how the electronic g-tensor in linked to the electronic structure, and the assistance of quantum-chemical calculations is desirable. In this work, we investigate the contribution of quadratic spin-orbit (SO) effect to the g-shift matrix utilizing third-order perturbation theory. We show that the dominant quadratic SO term – spin-Zeeman (SO^2/SZ) consistently makes a negative contribution to the g-shift, regardless of the particular electronic configuration. Additionally, we explore how the SO^2/SZ term interplays with the linear orbital-Zeeman (SO/OZ) contribution giving rise to the individual principal values of the g-tensor, and demonstrate our conclusions on selected Ir and Rh pincer complexes.