Unified approach to spin-dependent operators for configuration state functions

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Configuration interaction (CI) methods based on spin-adapted configuration state functions (CSFs) have the ability to target specific spin states and lead to a compact representation of the wave function for some open-shell molecules like exchange-coupled systems. In this contribution, we demonstrate how angular momentum diagrams can be used to arrive at a unified approach for treating one-electron mean-field spin–orbit coupling (SOC) and two-electron spin–spin coupling (SSC) operators in a CSF basis.[1] A new graphical representation of the SSC operator leads to a significantly reduced number of different segment factors compared to previous work, as well as the sharing of identical segment factors in both SOC and SSC. This results in very concise working equations. Applications will be presented on zero-field splitting and electron paramagnetic resonance g-tensors within the CSF-based iterative configuration expansion (ICE)[2,3] selected CI method.
Furthermore, we will point out how the presented ideas can be generalized to arbitrary operators in a two-component relativistic framework.[4] In our unified treatment, the calculation of different operators requires in part shared information, leading to potentially big computational savings when these operators are treated simultaneously.

[1] L. Lang, V. G. Chilkuri, F. Neese, in preparation.
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[4] L. Lang, in preparation.