Spin-orbit matrix elements for a combined spin-flip and IP/EA approach

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We present a practical approach for computing the Breit-Pauli spin-orbit matrix elements of multiconfigurational systems with both spin and spatial degeneracies using our recently developed RAS-nSF-IP/EA method (JCTC, 15, 2278, 2019). The spin-orbit matrix elements of all the multiplet components are obtained from a single reduced one-particle density matrix as a result of the Wigner-Eckart theorem. The two-electron contributions to the spin-orbit interactions are accounted by means of a mean field spin-orbit approach. Basis set dependence and the effect of correlating the core and semi-core orbitals are examined. Surprisingly good accuracies are obtained despite the fact that the efficient wavefunction approximations we explore neglect the bulk of dynamical correlation. The approach is validated by comparison to experimental data and the application range of the approach is illustrated by calculating spin-orbit splitting in metal complexes through the state-interaction procedure.