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Accurate and highly efficient approximations to the two-electron spin-orbit coupling terms

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Spin-orbit coupling (SOC), as an interaction of electronic spin with the magnetic field caused by its movement relative to other charged particles of the system, is believed to be the most important spin-dependent relativistic effect. It gives rise, or significantly contributes, to many interesting physical and chemical phenomena. Among those, we may mention for example intersystem crossing and spin-forbidden chemical reactions, phosphorescence, zero-field splitting, and electron paramagnetic and nuclear magnetic resonance spectra. It is thus evident that we may often need to include SOC in our quantum chemical calculations. However, that is generally a non-trivial task, since the evaluation of two-electron SOC integrals requires substantially, roughly by an order of magnitude, more computational effort than the evaluation of electron-electron repulsion integrals.

In this talk, we will present a new approximation to the two-electron SOC terms, which we call flexible nuclear screening spin-orbit (FNSSO). This approximation uses an effective one-electron SOC operator and accounts for the effect of two-electron SOC by screening the nuclear charges involved in the corresponding one-electron SOC integrals. Although this idea is not new (it is used for example in effective nuclear charge and screened nuclear spin-orbit approximations), our approach takes full advantage of highly flexible scheme of the screening, where

Table 1: Magnitude of SOC matrix elements (in cm^{-1}) calculated at DKH1 level with exact (SO_{full}) and various approximate treatments of two-electron SOC, using CASSCF wave functions and ANO-RCC basis set, and percentage error (PE) of used approximate approaches.

	states	SO_{full}	SO_{MF}	PE	AMFI	PE	SNSO	PE	FNSSO	PE
CH_2	S_0/T_1	10.9	11.0	0.2	11.0	0.3	14.0	28.1	11.0	1.0
GeH_2	S_0/T_1	391.9	392.0	0.0	391.6	−0.1	411.8	5.1	391.7	0.0
PbH_2	S_0/T_1	3310.4	3310.4	0.0	3309.9	0.0	3368.7	1.8	3316.5	0.2
H_2O_2	S_0/T_1	41.1	40.9	−0.5	42.0	2.1	47.2	14.7	40.9	−0.5
H_2Se_2	S_0/T_1	784.6	784.6	0.0	785.3	0.1	818.4	4.3	784.2	0.0
H_2Po_2	S_0/T_1	5225.9	5225.9	0.0	5228.7	0.1	5309.0	1.6	5235.2	0.2
CO^+	D_1/D_2	18.1	18.2	0.5	17.0	−6.3	19.9	9.7	17.8	−1.7
	D_2/D_3	60.3	60.1	−0.4	58.0	−3.8	69.8	15.7	59.7	−1.0
NO	D_1/D_2	62.6	62.9	0.4	66.4	6.0	74.7	19.3	64.1	2.3
$[Fe(H_2O)_6]^{3+}$	D_1/D_2	235.7	235.4	−0.1	228.5	−3.1	252.6	7.2	228.3	−3.2
$[Ru(H_2O)_6]^{3+}$	D_1/D_2	553.8	553.7	0.0	550.9	−0.5	595.0	7.4	551.5	−0.4
$[Os(H_2O)_6]^{3+}$	D_1/D_2	1805.1	1805.0	0.0	1799.4	−0.3	1901.9	5.4	1802.2	−0.2
NdO_2	T_1/T_2	2442.3	2468.1	1.1	2438.5	−0.2	2691.7	10.2	2459.0	0.7
UO_2	T_1/T_2	3005.1	3006.0	0.0	2977.3	−0.9	3246.9	8.0	3001.9	−0.1

basically any pair of atomic orbitals has its own screening parameter. The screening parameters come mainly from parameterization based on *ab initio* atomic SOC calculations. Additionally, we use fairly simple physical model for screening of multi-center interactions. As we will show on several practical examples (see Table 1 for brief summary of presented results), high flexibility of the screening used in FNSSO allows us to achieve mostly spectroscopic accuracy (error within 1 cm^{-1}) for SOC matrix elements in molecules composed of light atoms, and results with deviation of typically few wavenumbers for heavy-atom containing systems.

In addition to its high accuracy and general applicability, FNSSO approach is highly efficient, since only one-electron SOC integrals have to be evaluated explicitly. Moreover, it is also easy to implement, because only fairly simple modifications of existing codes for one-electron SOC calculations are needed.