Dependence of spin-orbit interaction constants on electron configuration of atoms and ions

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New method for evaluation of spin-orbit interaction constants was used for the systematic determination of ξ_p and ξ_d constants from the atomic spectral data of Moore for the atoms and ions from Be to Zn. The obtained results have shown the significant dependence of spin-orbit interaction constants on the electron configuration of atoms (ions). This dependence was approximated by polynomial functions of s, p, d atomic orbital electron populations. The results obtained may be used in semiempirical all valence (mainly ZDO) methods of quantum chemistry.

Был применен новый метод расчета констант спин-орбитального взаимодействия ξ_p и ξ_d по спектральным данным атомов Мура для атомов и ионов от Be до Zn. Полученные результаты показывают на отчетливую зависимость констант спин-орбитального взаимодействия от электронной структуры атомов (ионов). Полученные результаты можно использовать в полуэмпирических методах квантовой химии, беря во внимание все валентные электроны (особенно ПДП).

Detailed studies of electron structure of molecules suggest that inclusion of spin-orbit interaction (SOI) plays the important role for correct theoretical interpretation of some experimental results (magnetic phenomena, electronic spectra, photoelectron spectroscopy, *etc.*). Previous works in this field dealt preferentially with techniques permitting inclusion of SOI in the MO calculations [1—3]. As the greater part of results of those calculations is approximately linear

function of the used SOI constants, the necessity of correct parametrization of these constants becomes topical. The previous procedures of semiempirical parametrization have dealt with those cases of electron configurations obtained only from multiplet structure of the basic term. The calculation in this case is reduced to enumeration of the well-known expression [4—6]

$$\Lambda = \pm \frac{\xi}{2S} \tag{1}$$

where Λ is the Lande's parameter and S is the spin quantum number. *Dunn* [2] has evaluated by means of eqn (1) an extensive set of ξ_d constants for atoms and ions of the first two transition series with electron configurations d^α, $d^{\alpha-1}s^1$, $d^{\alpha-2}s^2$. This author has used an extrapolation for the cases in which the experimental data were not known. He has supposed that ξ_d for the given atomic number Z depends only on the number of d electrons and its change within the period is for a given electron configuration proportional to $(Z-\sigma)^4$; σ being a screening constant [7]. But one needs to include also general electron configurations $d^\alpha s^\beta p^\gamma$ in which occur both the SOI constants ξ_d and ξ_p, if one wishes to comprehend the dependence of SOI constants on the electron configuration of the atom.

Method and results

An approximative generalization of the SOI operator for the case of nonequivalent electrons in open-shell levels can be formulated [8] in the form

$$\boldsymbol{V}_{so} = \sum_i \xi(nl)_i \, \boldsymbol{l}_i \, \boldsymbol{s}_i = \sum_i \frac{\alpha^2}{2} \left\langle r^{-1} \frac{\partial V}{\partial r} \right\rangle_i \boldsymbol{l}_i \, \boldsymbol{s}_i \tag{2}$$

where α is the fine splitting constant and $V(r)$ is the averaged Coulomb potential of the nucleus and the other electrons. We understand under the term "nonequivalent electrons" the electrons with different quantum numbers n or l. The eqn (2) defines simultaneously also the effective SOI constants for the case of nonequivalent electrons.

In electron configurations $d^\alpha s^\beta p^\gamma$ these constants may be abbreviated as ξ_p and ξ_d and $\boldsymbol{V}_{so}$ may be written as a function [9]

$$\boldsymbol{V}_{so}(\xi_p, \xi_d) = \xi_p \sum_{i \in p} \boldsymbol{l}_i \, \boldsymbol{s}_i + \xi_d \sum_{i \in d} \boldsymbol{l}_i \, \boldsymbol{s}_i \tag{3}$$

We can, assuming validity of the LS scheme and knowing wave functions of the given atomic term, enumerate the actual spin-orbit splitting as a function of the effective SOI constants by numerical optimization of the criterion of maximal agreement between the calculated and the experimental spin-orbit splitting constants of the given term. The SOI constants obtained in this way depend on the

electron configuration of the atom (ion). It is advantageous to approximate these functions of discrete arguments by continuous functions dependent on the electron configuration (electron populations of individual atomic orbitals). These functions can be used as configuration dependent parameters [10—13] for a computation of some physical properties of compounds containing atoms from Be to Zn.

The proposed method of semiempirical evaluation of the effective SOI constants has several advantages [9]. A transition from configurations with equivalent electrons to configurations with nonequivalent electrons in open shells does not cause principal complications if a sufficiently general algorithm for generation of wave functions of atomic terms is used. The values, optimizing the chosen criterion of agreement between calculated and experimental splittings of the given atomic terms are taken as the best estimates of the SOI constants. Sum of squares of deviations of measured and calculated values is one of the most used criteria. The spectral energies of J levels are in our case the experimental values [14]. Because these values have normal error distribution with constant dispersion, we can use the criterion of the minimum of the sum of squares of deviations

$$F(\xi_p, \xi_d) = \sum_{i}^{N} \{E_{LS}^{calc}(J_i, \xi_p, \xi_d) - E_{LS}^{exp}(J_i, \xi_p, \xi_d)\}^2 = \min \qquad (4)$$

where N is the number of experimentally available levels J_i of the given term, $E_{LS}^{exp}(J_i, \xi_p, \xi_d)$ and $E_{LS}^{calc}(J_i, \xi_p, \xi_d)$ is spectral, resp. calculated energy of the i-th J level of the given spectral term. Solving this problem, we can reduce eqn (4) on an undetermined system of linear equations with respect to ξ_p and ξ_d, if we remember that the operator $\boldsymbol{V}_{so}(\xi_p, \xi_d)$ is additive with respect to values of ξ_p and ξ_d. A detailed description of the used method for evaluating values of $E_{LS}^{calc}(J_i, \xi_p, \xi_d)$ and for solving eqn (4) is in [9].

This problem is for configurations $s^m p^n$ or $s^m d^n$ reduced on one linear equation for one unknown, ξ_p or ξ_d, respectively. For the configurations with half-filled p levels of half-filled d levels it is possible to determine only the ξ_d/ξ_p ratio. But one needs one approximation more for the calculation of the individual SOI constants, ξ_p and ξ_d, for configurations $d^\alpha s^\beta p^\gamma$. The approximation, that all values ξ_p are equal and all values ξ_d are equal in all terms of a given electron configuration, seems to be warranted. The obtained SOI constants will be used for study of electron structure of molecules and this purpose leads to use of values of SOI constants averaged across all terms of the given electron configuration. Using the mentioned presumption, one needs for determination of the constants ξ_p and ξ_d only two terms as we get a system of two equations for two unknowns. If the given electron configuration contains more than two terms, one can solve the under-determined system of linear equations using the least-squares procedure [9].

The SOI constants were obtained using the described method for spectral accessible electron configurations of atoms from Be to Zn. The SOI constants ξ_p^{spect} for atoms and ions with electron configurations $K(2)2s^m 2p^n$ (Table 1),

$K(2)L(8)3s^m3p^n$ (Table 2), $K(2)L(8)M(18)4s^m4p^n$ (Table 3) and SOI constants ξ_p^{spect} and ξ_d^{spect} for electron configurations $K(2)L(8)3s^23p^63d^{\alpha}4s^{\beta}4p^{\gamma}$ (Table 7) were calculated as a weighted mean value from all the available spectral terms [14] in a given electron configuration. One can consider these values to be functions of discrete electron populations of individual atomic orbitals.

The electron configurations of atoms in molecules have in the framework of LCAO MO method usually noninteger values $d^vs^xp^y$, where v, x, y are nonnegative real numbers, obtained by population analysis. So, if one wishes to use the configurationally dependent values of SOI constants in LCAO MO calculation of electron structure of molecules, the mentioned discrete functions must be approximated by functions of continuous arguments v, x, y. The dependence of the effective SOI constants of atoms with electron configurations $K(2)2s^m2p^n$, $K(2)L(8)3s^m3p^n$, and $K(2)L(8)M(18)4s^m4p^n$ was approximated by polynomial functions of the type

$$\xi_p^{approx}(x,y) = \sum_{i=0}^{N_s} \sum_{j=0}^{N_p} B_{ij} x^i y^j \qquad (5)$$

where N_s, resp. N_p are maximal degrees of polynomial functions in variables x, resp. y. The dependence of the effective SOI constants of atoms of the first transition series on the electron configuration was approximated by polynomial function

$$\xi_l^{approx}(v,x,y) = \sum_{i=0}^{N_p} \sum_{j=0}^{N_d} B_{ij} v^i q^j \qquad (6)$$

where l is p or d, q is the atomic charge defined by expression

$$q = Z^{core} - v - x - y \qquad (7)$$

The values of the coefficients B_{ij} were obtained by the least-squares method and the optimal degrees of individual variables N_s, N_p, and N_d in the polynoms were obtained by maximization of correlation coefficient.

The values of coefficients B_{ij} as well as relevant statistic characteristics for individual atoms are listed in Tables 4, 5, 6, 8, and 9. In Tables 1, 2, 3, and 7 all spectral values ξ_l^{spect}, values calculated according to eqns (5) and (6) — ξ_l^{approx} and their deviations are shown. It is not possible in some cases to propose the approximative expressions because of insufficient number of spectral data.

The presented results show that the proposed regression functions sufficiently describe the dependence of SOI constants on the electron configuration of atoms (ions). Some greater deviations can be elucidated by the fact that the complete sets of spectral values for all terms of some electron configuration only once were taken for obtaining the constants of SOI (*e.g.* the terms with so-called degeneracy of name were excluded).

Table 1

Numerical values of SOI constants for atoms and ions with electron configurations $K(2)2s^m2p^n$ [meV]

Atom	m	n	q	ξ_p^{spect}	ξ_p^{approx}	Deviation
Be^x	0	1	1	0.4959		
	1	1	0	0.2479		
	0	2	0	0.2479		
B	0	1	2	2.8101	2.7353	0.0748
	1	1	1	1.8419	1.9915	-0.1495
	2	1	0	1.3224	1.2476	0.0748
	0	2	1	1.8773	1.8773	0.0000
	1	2	0	1.1689	1.1689	0.0000
C	0	1	3	8.8436	8.8436	0.0000
	1	1	2	6.6769	6.6769	0.0000
	2	1	1	5.2896	5.2896	0.0000
	0	2	2	6.3051	6.3051	0.0000
	1	2	1	4.8266	4.8266	0.0000
	2	2	0	3.6130	3.6130	0.0000
N	0	1	4	21.3238	21.3238	0.0000
	1	1	3	17.2858	17.1831	0.1027
	2	1	2	14.4638	14.4638	0.0000
	0	2	3	16.2408	16.2408	0.0000
	1	2	2	13.2553	13.4093	-0.1539
	2	2	1	10.7328	10.7328	0.0000
	1	4	0	5.9129	5.8616	0.0513
O	0	1	5	44.0527	43.1358	0.9169
	1	1	4	36.8031	37.1023	-0.2992
	2	1	3	31.9857	31.0689	0.9169
	0	2	4	34.8017	35.6753	-0.8737
	1	2	3	29.5450	30.8669	-1.3219
	2	2	2	25.1848	26.0585	-0.8737
	1	4	1	20.9519	17.8827	3.0692
	2	4	0	18.8974	18.8974	0.0000
	1	5	0	9.5993	11.1339	-1.5346
F	0	1	6	80.7495	78.3159	2.4346
	1	1	5	69.4246	67.3345	2.0919
	2	1	4	61.6572	59.7450	1.9121
	0	2	5	65.9905	69.2366	-3.2461
	1	2	4	57.2708	60.4379	-3.1672
	2	2	3	50.2987	53.1459	-2.8473
	1	4	2	47.7787	46.6449	1.1337
	2	4	1	40.8411	39.9479	0.8931
	1	5	1	39.6899	39.7484	-0.0585
	2	5	0	33.3908	33.3489	0.0419
	0	5	2	42.8129	42.0014	0.8115
Ne	2	1	5	108.7680	107.2176	1.5504
	1	2	5	101.6601	101.6601	0.0000
	2	2	4	91.1399	94.2405	-3.1007
	1	4	3	87.4804	87.4804	0.0000

Table 1 (Continued)

Atom	m	n	q	ξ_p^{spect}	ξ_p^{approx}	Deviation
Ne	2	4	2	77.1837	74.0831	3.1007
	1	5	2	75.0052	73.5659	1.4392
	2	5	1	64.6327	66.9027	-2.2700
	0	5	3	79.5097	80.2204	-0.7196

Table 2

Numerical values of SOI constants for atoms and ions with electron configurations $K(2)L(8)3s^m3p^n$ [meV]

Atom	m	n	q	ξ_p^{spect}	ξ_p^{approx}	Deviation
Na^x	0	1	0	1.4051		
Mg^x	0	1	1	7.6038		
	1	1	0	5.0475		
	0	2	0	5.0576		
Al	0	1	2	19.2575	19.6589	-0.4014
	1	1	1	15.4615	14.6586	0.8029
	0	2	1	15.1073	15.1073	0.0000
	2	1	0	9.2568	9.6583	-0.4015
	1	2	0	11.0869	11.0869	0.0000
Si	0	1	3	38.0192	38.0192	0.0000
	1	1	2	32.1805	32.1805	0.0000
	0	2	2	32.2868	32.2868	0.0000
	2	1	1	23.7206	23.7206	0.0000
	1	2	1	25.9894	25.9894	0.0000
	2	2	0	18.3803	18.3803	0.0000
P	0	1	4	65.6244	65.6244	0.0000
	1	1	3	57.5247	58.1094	-0.5847
	0	2	3	58.6582	58.6582	0.0000
	2	1	2	46.2842	46.2842	0.0000
	1	2	2	48.6204	47.7433	0.8771
	2	2	1	38.6627	38.6627	0.0000
	1	4	0	26.7188	27.0112	-0.2924
S	0	1	5	104.3870	104.3870	0.0000
	1	1	4	93.5662	93.2158	0.3504
	0	2	4	97.6397	97.6397	0.0000
	2	1	3	78.5179	78.6301	-0.1122
	1	2	3	81.0008	80.7989	0.2019
	2	2	2	68.5054	68.3371	0.1683
	1	4	1	53.9581	55.9652	-2.0071
	2	4	0	47.6952	47.7513	-0.0561
	1	5	0	45.0031	43.5483	1.4548
Cl	0	1	6	156.2090	157.0690	-0.8600
	1	1	5	142.3418	140.6218	1.7200
	0	2	5	151.4097	149.5373	1.8724

Table 2 (Continued)

Atom	m	n	q	ξ_p^{spect}	ξ_p^{approx}	Deviation
Cl	2	1	4	123.3145	124.1745	-0.8600
	1	2	4	125.1151	128.8599	-3.7448
	2	2	3	110.0550	108.1826	1.8724
	1	4	2	88.9969	88.9969	0.0000
	2	4	1	82.9043	82.9043	0.0000
	1	5	1	79.6278	79.6278	0.0000
	2	5	0	65.3110	65.3110	0.0000
Ar	0	1	7	224.6440	224.6440	0.0000
	1	1	6	205.8882	199.6261	6.2621
	0	2	6	224.6440	224.6440	0.0000
	2	1	5	182.6575	182.3968	0.2607
	1	2	5	172.9461	180.0176	-7.0715
	2	2	4	166.3930	165.9889	0.4041
	1	4	3	136.9670	140.8001	-3.8337
	2	4	2	130.9183	133.1732	-2.2540
	1	5	2	125.8353	121.1922	4.6431
	2	5	1	118.3555	116.7653	1.5902

Table 3 (Continued)

Atom	m	n	q	ξ_p^{spect}	ξ_p^{approx}	Deviation
Br	0	1	6	626.4905	626.4905	0.0000
	1	1	5	584.1912	584.1912	0.0000
	0	2	5	806.0191	806.0191	0.0000
	2	1	4	503.3413	499.2447	4.0966
	1	2	4	353.7027	353.7027	0.0000
	2	4	1	327.6323	344.0189	-16.3866
	2	5	0	304.5669	292.2769	12.2899
Kr*	1	4	3	502.1775		
	2	4	2	456.9390		
	2	5	1	443.9156		

* Number of experimental points is insufficient for regression analysis.

Table 3

Numerical values of SOI constants for atoms and ions with electron configurations $K(2)L(8)M(18)4s^m 4p^n$ [meV]

Atom	m	n	q	ξ_p^{spect}	ξ_p^{approx}	Deviation
Ga	0	1	2	141.9935	145.0516	-0.0581
	1	1	1	114.3056	108.1895	6.1161
	0	2	1	117.8832	117.8832	0.0000
	2	1	0	68.2693	71.3274	-3.0581
	1	2	0	84.0673	84.0673	0.0000
Ge	0	1	3	230.4295	234.1704	-3.7409
	1	1	2	199.4592	191.8774	7.4818
	0	2	2	220.6236	220.6236	0.0000
	2	1	1	146.0434	149.7843	-3.7409
	1	2	1	156.3283	156.3283	0.0000
As	1	1	3	305.5115	274.1471	31.3644
	0	2	3	367.7827	367.7827	0.0000
	2	1	2	242.9923	242.9923	0.0000
	1	2	2	184.3519	231.3985	-47.0466
	1	4	0	161.5836	145.9014	15.6822
Se	0	1	5	553.7581	545.4104	8.3477
	1	1	4	432.6752	449.3706	-16.6954
	0	2	4	563.7706	563.7706	0.0000
	2	1	3	361.6784	353.3307	8.3477
	1	2	3	275.2261	275.2261	0.0000
	1	4	1	239.6805	239.6805	0.0000
	2	4	0	214.7436	214.7436	0.0000

Table 4

Numerical values of coefficients B_{ij} for atoms and ions with electron configurations $K(2)2s^m 2p^n$ [meV]

Atom	i	j	B_{ij}	Standard deviation	Correlation coefficient
B	0	0	3.5933		
	1	0	-0.7793		
	0	1	-0.8580		
	1	1	0.0355	0.1832	0.9898
C	0	0	11.3820		
	1	0	-3.5019		
	2	0	0.6469		
	0	1	-2.5385		
	1	1	0.9455		
	2	1	-0.2573	0.0000	1.0000
N	0	0	26.4060		
	1	0	-6.7936		
	2	0	1.3438		
	0	1	-5.0830		
	1	1	1.9423		
	2	1	-0.6331	0.1921	0.9998
O	0	0	49.3000		
	1	0	-6.1341		
	0	1	-5.5172		
	0	2	-0.6478		
	1	1	-0.4616		
	1	2	0.5622	2.3678	0.9903
F	0	0	87.3930		
	1	0	-15.8001		
	2	0	2.6377		
	0	1	-9.0784		

Table 4 (Continued)

Atom	i	j	B_{ij}	Standard deviation	Correlation coefficient
F	1	1	3.1241		
	2	1	-0.9422	3.0127	0.9893
Ne	0	0	73.1542		
	1	0	24.4861		
	0	1	28.9942		
	0	2	-5.5158		
	1	1	-22.4348		
	1	2	3.2409	5.0438	0.9968

Table 5 (Continued)

Atom	i	j	B_{ij}	Standard deviation	Correlation coefficient
Cl	0	3	3.8142		
	1	1	-47.2981		
	1	2	19.6136		
	1	3	-2.2532	3.5689	0.9986
Ar	0	0	224.6400		
	1	0	2.1009		
	2	0	-7.5102		
	0	1	0.0000		
	1	1	-31.0130		
	2	1	11.4045	5.7732	0.9954

Table 5

Numerical values of coefficients B_{ij} for atoms and ions with electron configurations $K(2)L(8)3s^m 3p^n$ [meV]

Atom	i	j	B_{ij}	Standard deviation	Correlation coefficient
Al	0	0	24.2100		
	1	0	-5.9803		
	0	1	-4.5517		
	1	1	0.9799	0.9833	0.9922
Si	0	0	43.7510		
	1	0	-3.4146		
	2	0	-1.9654		
	0	1	-5.7324		
	1	1	-1.1135		
	2	1	0.6548	0.0000	1.0000
P	0	0	72.5900		
	1	0	1.1123		
	2	0	-5.2274		
	0	1	-6.9662		
	1	1	-6.4721		
	2	1	3.0722	1.0940	0.9994
S	0	0	111.1303		
	1	0	0.1025		
	2	0	-5.6041		
	0	1	-6.7473		
	1	1	-9.5664		
	2	1	3.8969	1.4551	0.9992
Cl	0	0	120.9505		
	1	0	13.4905		
	0	1	65.5601		
	0	2	-33.2639		

Table 6

Numerical values of coefficients B_{ij} for atoms and ions with electron configurations $K(2)L(8)M(18)4s^m 4p^n$ [meV]

Atom	i	j	B_{ij}	Standard deviation	Correlation coefficient
Ga	0	0	172.2199		
	1	0	-39.9083		
	0	1	-27.1684		
	1	1	3.0462	7.4907	0.9917
Ge	0	0	247.7172		
	1	0	-20.0908		
	0	1	-13.5468		
	1	1	-22.1023	9.1633	0.9926
As	0	0	242.8210		
	1	0	74.0746		
	0	1	62.4808		
	1	1	-105.2294	58.6774	0.9389
Se	0	0	415.0924		
	1	0	312.6704		
	0	2	-55.9789		
	1	1	-516.8131		
	1	2	108.1028	20.4476	0.9983
Br	0	0	446.9619		
	1	0	683.4233		
	2	0	-315.7055		
	0	1	179.5286		
	1	1	-704.3989		
	2	1	294.3818	20.8888	0.9989

Table 7

Numerical values of SOI constants ξ_p and ξ_d [meV]

Atom	β	γ	α	q	ξ_p^{spect}	ξ_p^{approx}	Deviation	ξ_d^{spect}	ξ_d^{approx}	Deviation
Sc	0	1	0	2	39.18	38.60	0.58	–	–	–
	0	2	0	1	28.55	29.04	-0.50	–	–	–
	1	1	0	1	28.39	29.04	-0.65	–	–	–
	0	0	1	2	–	–	–	9.82	10.21	-0.39
	0	0	2	1	–	–	–	6.54	6.54	0.00
	0	0	3	0	–	–	–	5.78	5.05	0.73
	1	0	1	1	–	–	–	8.85	9.53	-0.68
	1	0	2	0	–	–	–	6.53	6.95	-0.42
	2	0	1	0	–	–	–	8.33	8.85	-0.52
	0	1	1	1	18.35	18.35	0.00	10.99	9.53	1.46
	0	1	2	0	11.35	11.92	-0.57	5.88	6.95	-1.07
	1	1	1	0	16.84	15.70	1.14	9.71	8.85	0.86
Ti	0	1	0	3	67.61	65.88	-1.27	–	–	–
	1	1	0	2	52.75	50.85	1.90	–	–	–
	0	0	1	3	–	–	–	19.04	19.75	-0.71
	0	0	2	2	–	–	–	15.01	15.54	-0.53
	0	0	3	1	–	–	–	11.95	11.95	0.00
	0	0	4	0	–	–	–	10.68	9.55	1.13
	1	0	1	2	–	–	–	17.97	16.60	1.37
	1	0	2	1	–	–	–	14.01	14.22	-0.21
	1	0	3	0	–	–	–	11.52	12.64	-1.12
	2	0	1	1	–	–	–	11.51	13.46	-1.95
	2	0	2	0	–	–	–	13.68	12.89	0.79
	0	1	1	2	21.04	19.14	1.90	17.76	16.60	1.16
	0	1	2	1	26.72	26.72	0.00	15.49	14.22	1.27
	0	1	3	0	13.15	13.78	-0.63	10.39	12.64	-2.25
	0	2	2	0	9.15	17.87	-8.72	15.02	12.89	2.13
	1	1	1	1	17.87	21.67	-3.80	12.47	13.46	-0.99
	1	1	2	0	26.49	17.87	10.62	12.82	12.89	-0.07
V	0	1	0	4	104.97	103.95	1.02	–	–	–
	0	0	1	4	–	–	–	30.75	30.79	-0.04
	0	0	2	3	–	–	–	26.29	26.16	0.13
	0	0	3	2	–	–	–	20.37	20.37	0.00
	0	0	4	1	–	–	–	17.30	17.39	-0.09
	1	0	1	3	–	–	–	29.92	30.08	-0.16
	1	0	2	2	–	–	–	25.10	25.82	-0.72
	1	0	3	1	–	–	–	18.89	24.99	-6.10
	1	0	4	0	–	–	–	16.16	17.11	-0.95
	2	0	3	0	–	–	–	18.35	18.48	-0.13
	0	1	1	3	67.90	74.51	-6.61	30.34	30.08	0.26
	0	1	2	2	62.94	49.18	13.76	26.16	25.82	0.34
	0	1	3	1	16.22	27.95	-11.73	31.35	24.99	6.36
	0	1	4	0	14.40	10.83	3.57	18.10	17.11	0.99
	1	1	2	1	13.46	13.46	0.00	16.04	15.91	0.13
Cr	0	1	0	5	150.59	141.14	-9.45	–	–	–
	0	0	1	5	–	–	–	47.46	46.57	0.89
	0	0	2	4	–	–	–	42.05	43.33	-1.28
	0	0	3	3	–	–	–	32.52	33.88	-1.36
	0	0	4	2	–	–	–	29.45	27.55	1.90

Table 7 (Continued)

Atom	β	γ	α	q	ξ_p^{spect}	ξ_p^{approx}	Deviation	ξ_d^{spect}	ξ_d^{approx}	Deviation
Cr	0	0	6	0	–	–	–	12.05	12.20	−0.15
	1	0	1	4	–	–	–	45.72	46.99	−1.27
	1	0	2	3	–	–	–	39.51	37.95	1.56
	1	0	3	2	–	–	–	29.54	28.46	1.08
	1	0	4	1	–	–	–	27.62	22.90	4.72
	2	0	3	1	–	–	–	27.22	28.17	−0.95
	2	0	4	0	–	–	–	20.13	22.75	−2.62
	0	1	1	4	101.30	124.68	−23.38	46.46	46.99	−0.53
	0	1	2	3	114.43	101.02	13.41	40.85	37.95	2.90
	0	1	3	2	75.63	70.14	5.49	25.76	28.46	−2.70
	0	1	4	1	27.08	32.06	−4.98	17.14	22.90	−5.76
	1	1	4	0	34.47	34.47	0.00	26.32	22.75	3.57
Mn	0	1	0	6	203.73	200.90	2.83	–	–	–
	0	0	1	6	–	–	–	67.19	66.44	0.75
	0	0	2	5	–	–	–	62.33	62.78	−0.45
	0	0	3	4	–	–	–	47.81	50.22	−2.41
	0	0	4	3	–	–	–	41.92	37.14	4.78
	0	0	6	1	–	–	–	19.06	19.40	−0.34
	0	0	7	0	–	–	–	7.85	7.98	−0.13
	1	0	2	4	–	–	–	57.97	60.45	−2.68
	1	0	3	3	–	–	–	49.53	48.61	0.92
	1	0	4	2	–	–	–	42.75	38.55	4.20
	1	0	6	0	–	–	–	30.21	29.65	0.56
	2	0	4	1	–	–	–	42.15	39.96	2.19
	0	1	1	5	139.33	154.86	−15.53	66.28	67.46	−1.18
	0	1	2	4	138.13	115.10	23.03	65.17	60.65	4.52
	0	1	3	3	75.20	81.62	−6.42	48.63	48.61	0.02
	0	1	4	2	48.30	54.41	−6.11	27.81	38.55	−10.74
	0	1	6	0	21.04	18.84	2.19	29.65	29.65	0.00
Fe	0	1	0	7	277.95	272.40	5.55	–	–	–
	0	0	1	7	–	–	–	92.98	93.59	−0.63
	0	0	2	6	–	–	–	88.39	86.25	2.14
	0	0	3	5	–	–	–	66.09	69.93	−3.84
	0	0	4	4	–	–	–	59.31	56.14	3.17
	0	0	6	2	–	–	–	50.06	50.08	−0.02
	0	0	7	1	–	–	–	46.73	48.72	−1.99
	0	0	8	0	–	–	–	31.66	31.88	−0.22
	1	0	3	4	–	–	–	69.49	67.77	1.72
	1	0	6	1	–	–	–	50.46	49.30	1.16
	1	0	7	0	–	–	–	47.30	41.57	5.73
	2	0	6	0	–	–	–	49.85	51.27	−1.42
	0	1	2	5	194.38	219.38	−25.00	94.02	92.79	1.23
	0	1	3	4	207.41	185.19	22.22	64.01	67.77	−3.76
	0	1	6	1	49.17	51.94	−2.77	50.19	49.30	0.89
Co	0	0	3	6	–	–	–	87.46	87.46	0.00
	0	0	4	5	–	–	–	81.76	81.76	0.00
	0	0	7	2	–	–	–	65.65	65.65	0.00
	0	0	8	1	–	–	–	47.53	47.53	0.00
	0	0	9	0	–	–	–	48.30	48.30	0.00

Table 7 (Continued)

Atom	β	γ	α	q	ξ_p^{spect}	ξ_p^{approx}	Deviation	ξ_d^{spect}	ξ_d^{approx}	Deviation
Co	1	0	6	2	–	–	–	73.68	74.68	−1.00
	1	0	7	1	–	–	–	48.30	58.45	−10.15
	1	0	8	0	–	–	–	54.72	54.76	−0.04
	2	0	6	1	–	–	–	67.65	67.65	0.00
	2	0	7	0	–	–	–	69.37	69.10	0.27
	0	1	2	6	167.42	206.46	−39.04	197.59	197.59	0.00
	0	1	3	5	272.27	210.84	61.43	86.92	86.92	0.00
	0	1	6	2	101.61	130.24	−28.63	75.68	74.68	1.00
	0	1	7	1	56.50	72.13	−15.63	68.59	58.47	10.12
	1	1	7	0	44.99	44.99	0.00	68.84	69.10	−0.26
Ni	0	0	3	7	–	–	–	110.40	85.30	25.10
	0	0	4	6	–	–	–	108.12	145.77	−37.65
	0	0	8	2	–	–	–	70.21	61.93	8.28
	1	0	7	2	–	–	–	92.20	85.84	6.36
	1	0	8	1	–	–	–	77.50	73.81	3.69
	1	0	9	0	–	–	–	73.28	61.60	11.68
	2	0	8	0	–	–	–	64.43	85.70	−21.27
	0	1	2	7	230.60	190.86	39.74	194.74	209.08	−14.34
	0	1	3	6	106.83	164.85	−58.02	388.18	369.36	18.82
	0	1	7	2	113.95	78.31	35.64	98.29	85.84	12.46
	0	1	8	1	59.65	61.04	−1.39	78.67	73.81	4.86
	1	1	8	0	38.94	38.94	0.00	77.60	85.70	−8.10
	0	1	9	0	29.54	45.52	−15.98	76.81	61.60	15.21
Cu[*]	0	0	9	2	–	–	–	102.75	110.60	−7.85
	1	0	8	2	–	–	–	104.68	100.57	4.11
	1	0	9	1	–	–	–	100.49	106.44	−5.95
	2	0	8	1	–	–	–	84.40	84.40	0.00
	2	0	9	0	–	–	–	101.26	102.27	−1.01
	0	1	8	2	98.18			96.47	100.57	−4.10
	0	1	9	1	39.79			128.09	106.44	21.65
	1	1	9	0	61.73			95.43	102.27	−6.84
Zn[*]	1	0	9	2	–	–	–	133.48		
	2	0	9	1	–	–	–	134.79		
	0	1	9	2	69.05			199.32		
	0	1	10	1	72.15			–	–	–
	1	1	10	0	47.91			–	–	–

[*] Number of experimental points is insufficient for regression analysis.

Table 8. Numerical values of coefficients B_{ij} for ξ_p constants [meV]

Atom	i	j	B_{ij}	Standard deviation	Correlation coefficient
Sc	0	0	19.4786		
	1	0	-3.7794		
	0	1	9.5628		
	1	1	-6.9140	1.1465	0.9974
Ti	0	0	32.7850		
	1	0	-9.7059		
	2	0	1.1235		
	0	1	12.0302		
	1	1	-27.5314		
	2	1	12.9706	10.3110	0.9662
V	0	0	-55.3510		
	1	0	16.5451		
	0	1	39.8262		
	1	1	-2.0528	13.8656	0.9729
Cr	0	0	225.2308		
	1	0	-47.6912		
	0	1	-16.8197		
	1	1	3.6037	20.8681	0.9611
Mn	0	0	103.1201		
	1	0	-14.0474		
	0	1	16.2953		
	1	1	-3.1398	16.9660	0.9842
Fe	0	0	144.4909		
	1	0	-21.0278		
	0	1	18.2725		
	1	1	2.5575	34.0098	0.9867
Co	0	0	371.1809		
	1	0	-46.5987		
	0	1	-27.5423		
	1	1	7.8108	58.4831	0.9205
Ni	0	0	-13.6440		
	1	0	6.5735		
	0	1	29.0831		
	1	1	-0.8736	56.8936	0.8746

Table 9. Numerical values of coefficients B_{ij} for ξ_d constants [meV]

Atom	i	j	B_{ij}	Standard deviation	Correlation coefficient
Sc	0	0	10.7490		
	1	0	-1.9015		
	0	1	1.7730		
	1	1	-1.0915	1.0602	0.9004

Table 9 (Continued)

Atom	i	j	B_{ij}	Standard deviation	Correlation coefficient
Ti	0	0	4.9134		
	1	0	6.8200		
	2	0	-1.4151		
	0	1	4.7616		
	1	1	-1.5200		
	2	1	-0.0994	1.6055	0.8816
V	0	0	-117.9582		
	1	0	80.6180		
	2	0	-11.7131		
	0	1	76.1483		
	0	2	-10.4528		
	1	1	-35.0927		
	1	2	5.2368		
	2	1	4.5781		
	2	2	-1.2023	4.0082	0.9070
Cr	0	0	83.9462		
	1	0	-21.9859		
	2	0	1.6714		
	0	1	-1.5297		
	0	2	-1.3993		
	1	1	-7.4408		
	1	2	2.5571		
	2	1	1.8248		
	2	2	-0.4112	3.8729	0.9696
Mn	0	0	111.2124		
	1	0	-49.8767		
	2	0	12.2185		
	3	0	-1.0286		
	0	1	-9.0109		
	1	1	10.8129		
	2	1	-3.0118		
	3	1	0.1959	4.9679	0.9787
Fe	0	0	109.4429		
	1	0	-9.6955		
	0	1	-86.3113		
	0	2	32.0741		
	0	3	-2.7298		
	1	1	13.4522		
	1	2	-4.5530		
	1	3	0.2672	3.9010	0.9897
Co	0	0	390.1795		
	1	0	-73.4533		
	2	0	3.9408		
	0	1	-359.4229		
	0	2	54.2337		
	0	3	1.7778		
	1	1	77.4199		
	1	2	1.0894		
	1	3	-3.0891		

Table 9 (Continued)   Table 9 (Continued)

Atom	i	j	B_{ij}	Standard deviation	Correlation coefficient	Atom	i	j	B_{ij}	Standard deviation	Correlation coefficient
Co	2	1	-4.1650			Ni	1	1	266.9767		
	2	2	-1.0195				2	1	-33.9919		
	2	3	0.3848	7.2102	0.9944		3	1	1.6636	27.1555	0.9765
Ni	0	0	6061.9464			Cu	0	0	-204.0600		
	1	0	-1823.4321				1	0	34.0370		
	2	0	182.7496				0	1	112.1960		
	3	0	-6.0049				1	1	-12.0035	12.7195	0.6302
	0	1	-823.9808								

One must be very careful using the proposed regression functions for extrapolation of values of the SOI constants outer of the area defined by used spectral data because these functions were not tested outer of this area.

The obtained values of constants of spin-orbit interaction are the effective values because they represent the spin-orbit interaction and the other types of interactions included in the Hamiltonian. Use of these parameters in methods with configurationally dependent parameters ensures a consistency between the parametrization of the SCF calculation [10—13] and parametrization of the postprocessors.

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