Theoret. Chim. Acta (Berl.) 33, 347—349 (1974)
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Atomic Spin-Orbit Interaction Parameters from Spectral Data for 19 Elements

Klaus Wittel* and Rolf Manne

Department of Chemistry, University of Bergen, Bergen, Norway

Received October 9, 1973

The spin-orbit coupling constants ζ_{nl} and the Slater-Condon parameters F_2 and G_1 are determined from spectral data for several neutral atoms and monopositive ions.

Key words: Intermediate coupling – Spin-orbit coupling constants – Slater-Condon parameters

As part of a project aimed at calculating the effects of spin-orbit interaction in molecular photoelectron spectra we have calculated the atomic spin-orbit interaction parameters for 19 elements in the right part of the periodic table, i.e. in general with partly filled valence p shells. The calculations are based upon the intermediate coupling scheme [1] and have comprised a least-squares fitting of spin-orbit interaction parameters ζ_{nl} as well as of the relevant Slater-Condon parameters F_k and G_k to atomic energy levels as given in Moore's tables [2]. The calculations have been made for neutral atoms and for monopositive ions in their ground state configurations. Where the ground state configuration is s^2 the calculation was instead made for the sp configuration. The spin-orbit interaction parameters obtained are given in Table 1. The values are all given positive sign which agrees with the definition of ζ_{nl} as a one-electron integral. In this way we deviate from the tables of matrix elements for configurations with more than half-filled shells where the sign is reversed [3]. Table 2 gives the Slater-Condon parameters. The values of the spin-orbit interaction parameters for monopositive ions are being used in a semi-empirical molecular orbital scheme where the spin-orbit interaction is treated as the effective one-electron operator (summation over atoms A)

$$H_{\text{eff}}^{\text{S.O.}} = \sum_A \xi(r_{A1})\, \boldsymbol{l}_{A1} \cdot \boldsymbol{s}_{A1} ,$$

and where the non-relativistic part of the effective hamiltonian is approximated according to the Extended Hückel Method [4]. The molecular spin orbitals and their energy eigenvalues are used for the identification of molecular ionization energies in photoelectron spectra according to Koopmans' theorem. The results of these calculations are being published elsewhere [5, 6].

* Present and permanent address: Institut für Anorganische Chemie II, Universität Frankfurt, Federal Republic of Germany.

Table 1. Spin-orbit coupling constants for neutral atoms and monopositive ions (eV)

Element	Neutral atom		Monopositive ion	
16 S	$3p^4$	0.05	$3p^3$	
17 Cl	$3p^5$	0.07	$3p^4$	0.08
18 Ar	$3p^6$	—	$3p^5$	0.12
31 Ga	$4s^2p$	0.07	$4sp$	0.11
32 Ge	$4p^2$	0.11	$4p$	0.15
33 As	$4p^3$	0.19	$4p^2$	0.20
34 Se	$4p^4$	0.22	$4p^3$	0.29
35 Br	$4p^5$	0.30	$4p^4$	0.35
36 Kr	$4p^6$	—	$4p^5$	0.44
48 Cd	$4d^{10}\,5sp$	0.14	$4d^{10}\,5p$	0.21
			$4d^9\,5s^2$	0.28
49 In	$5s^2p$	0.18	$5sp$	0.29
50 Sn	$5p^2$	0.27	$5p$	0.35
51 Sb	$5p^3$	0.40	$5p^2$	0.44
52 Te	$5p^4$	0.49	$5p^3$	0.60
53 J	$5p^5$	0.63	$5p^4$	0.73
80 Hg	$5d^{10}\,6sp$	0.52	$5d^{10}\,6p$	0.75
			$5d^9\,6s^2$	0.75
81 Tl	$6s^2p$	0.64	$6sp$	1.00
82 Pb	$6p^2$	0.91	$6p$	1.16
83 Bi	$6p^3$	1.25		

Table 2. Slater-Condon parameters F_2 and G_1 (eV)

Element	Configuration	F_2	G_1
16 S	$3p^4$	0.18	
17 Cl^+	$3p^4$	0.23	
31 Ga^+	$4sp$		1.39
32 Ge	$4p^2$	0.13	
33 As	$4p^3$	0.15	
33 As^+	$4p^2$	0.17	
34 Se	$4p^4$	0.17	
35 Br^+	$4p^4$	0.19	
48 Cd	$5sp$		0.77
49 In^+	$5sp$		1.13
50 Sn	$5p^2$	0.11	
51 Sb	$5p^3$	0.13	
52 Te	$5p^4$	0.15	
52 Te^+	$5p^3$	0.16	
53 J^+	$5p^4$	0.21	
80 Hg	$6sp$		0.71
81 Tl^+	$6sp$		1.02
82 Pb	$6p^2$	0.11	
83 Bi	$6p^3$	0.12	

This work was partly supported by a travel grant from Deutsche Forschungsgemeinschaft to K. Wittel.

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Prof. Rolf Manne
Department of Chemistry
University of Bergen
N-5014 Bergen, Norway