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Physical Properties of Many-Electron Atomic Systems Evaluated from Analytical Hartree-Fock Functions

VI. Spin-Orbit Coupling Constants*

GULZARI MALLI

Department of Chemistry, Simon Fraser University, Burnaby 2, B. C., Canada

SERAFIN FRAGA

Division of Theoretical Chemistry, Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada

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Spin-orbit coupling constants λ have been evaluated using analytical Hartree-Fock functions for a large number of atomic systems. A reasonably good agreement is found between the experimental and theoretical values of λ.

Mit Hilfe von analytischen Hartree-Fock Funktionen wurden die Spin-Bahn-Kopplungskonstanten λ für eine große Anzahl von Atomsystemen berechnet. Zwischen den experimentellen und den theoretischen Werten von λ wurde eine angemessen gute Übereinstimmung gefunden.

On a calculé les constantes d'interaction spin-orbite pour des atomes, en employant des fonctions analytiques de Hartree-Fock. L'accord entre les valeurs théoriques et expérimentales est satisfaisant.

Introduction

In the preceding papers of this series [*3, 4, 5, 6, 7*] the values for various physical properties, calculated from analytical Hartree-Fock functions, have been reported for a large number of atomic systems. The satisfactory agreement between the experimental and the theoretically calculated values has shown that Hartree-Fock functions provide a reasonable description of these systems.

This paper presents, for the same systems, the spin-orbit coupling constants, also evaluated using analytical Hartree-Fock functions.

Theoretical Considerations

For an atomic system in the absence of a field, the non-relativistic hamiltonian operator H can be written, to a good approximation, as

$$H = H_{\mathrm{fs}} + H_{\mathrm{hfs}} \, , \tag{1}$$

where

$$H_{\mathrm{fs}} = \sum_{i=1}^{n} [(p_i^2/2m) - Ze^2/r_i + \zeta(r_i)\, \boldsymbol{l}_i \cdot \boldsymbol{s}_i + \sum_{i>j} e^2/r_{ij}] \, , \tag{2}$$

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is called the fine-structure hamiltonian operator; H_{hfs} represents the hyperfine-structure hamiltonian operator.

In Eq. (2), Z is the nuclear charge of the system under consideration, r_i is the distance from the (point) nucleus to the i-th electron, (of mass m with momentum p_i), r_{ij} is the distance between the i-th and j-th electrons, and $\zeta(r_i)\, \boldsymbol{l}_i \cdot \boldsymbol{s}_i$ represents the interaction of the spin dipole moment of the i-th electron with the field produced by its own orbital motion; this term is often referred to as the "spin-orbit" interaction. The summations in Eq. (2) extend over all the electrons of the system.

There are, in addition, other contributions to H, namely, the electron spin-spin interactions, the orbit-orbit interactions, and the spin-other-orbit interactions. These contributions, included in H_{hfs}, are very small and are neglected in this work.

As the exact solutions of H_{fs} are not known, it is customary to write

$$H_{\text{fs}} = H' + V\,, \tag{3}$$

where

$$H' = \sum_i \{(p_i^2/2m) + U(r_i)\}\,,$$

$U(r_i)$ being the spherically symmetric average potential of the other electrons at the position of the i-th electron. If a good choice of $U(r_i)$ is made, the contribution of the term V is usually small and can be evaluated by perturbation theory. The eigenfunctions of H' are combinations of antisymmetrized products of single-particle functions.

For atoms of small nuclear charge, the electrostatic interaction $(\sum_{i>j} e^2/r_{ij})$ is much larger than the spin-orbit term $\sum_i \zeta(r_i)\, \boldsymbol{l}_i \cdot \boldsymbol{s}_i$, and therefore this term can be treated as a perturbation. The term e^2/r_{ij} commutes with $\boldsymbol{S}$ and $\boldsymbol{L}$ (the total spin and orbital angular momentum operators $\boldsymbol{S} = \sum_i \boldsymbol{s}_i$, $\boldsymbol{L} = \sum_i \boldsymbol{l}_i$) and so both L and S are "good" quantum numbers. The eigenvalues of H_{fs} are therefore $(2L + 1)$ $(2S + 1)$-fold degenerate and the set of these eigenstates comprises a term. The perturbation $\sum_i \zeta(r_i)\, \boldsymbol{l}_i \cdot \boldsymbol{s}_i$ does not commute with either $\boldsymbol{L}$ or $\boldsymbol{S}$. However it does commute with $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$ ($\boldsymbol{J}$ being the total angular momentum operator); and the term splits into multiplets of degeneracy $(2J + 1)$, labelled by the three quantum numbers L, S, and J (LS- or Russell-Saunders coupling).

If the spin-orbit term is much greater than the electrostatic term (usually true in heavy elements), the orbital angular momentum vector $\boldsymbol{l}$ and the spin angular momentum vector $\boldsymbol{s}$ of each electron couple to give the corresponding electron angular momentum vector $\boldsymbol{j}$, and then the $\boldsymbol{j}$ couple to a resultant $\boldsymbol{J}$ (jj-coupling scheme). In this case $\boldsymbol{J}$ also commutes with H_{fs}, and therefore J is a "good" quantum number.

The discussion in this paper is restricted, however, to the LS-coupling scheme.

The matrix elements (in the LSJ scheme) of the spin-orbit hamiltonian $H_{\text{so}} = \sum_i \zeta(r_i)\, \boldsymbol{s}_i \cdot \boldsymbol{l}_i$ for a configuration of equivalent electrons l^n, using Racah tensor

Table 1. *Values of η for various atomic configurations*[a, b]

Configuration	State	η	Configuration	State	η
p^1	${}^2P$	1	d^3	${}^4F$	1/3
p^2	${}^3P$	1/2		${}^2G$	3/10
d^1	${}^2D$	1		${}^2H$	1/5
d^2	${}^3P$	1/2	d^4	${}^3_2P$	1/6
	${}^3F$	1/2		${}^3_4P$	1/3
d^3	${}^2P$	2/3		${}^3D$	−1/12
	${}^4P$	1/3		${}^5D$	1/4
	${}^2_1D$	1/2		${}^3_2F$	1/6
	${}^2_3D$	−1/6		${}^3_4F$	−1/12
	${}^2F$	−1/6		${}^3G$	3/20
				${}^3H$	1/10

[a] For the states arising from the p^5, p^4, d^9, d^8, d^7, and d^6 configurations the corresponding values of η are the negative of those given for the corresponding states arising from the p^1, p^2, d^1, d^2, d^3, and d^4 configurations, respectively.

[b] When two or more states corresponding to the same value of S and L arise from a configuration, they can be distinguished by an additional quantum number, designated as the seniority number v, defined by RACAH [*10*]; the value of v is included here for these states, as given by RACAH [*10*], as a left subscript.

algebra [*9*, *10*], are given* by

$$W(J) = (l^n\gamma SLJ \mid \sum_i (\zeta_l)_i \, \boldsymbol{s}_i \cdot \boldsymbol{l}_i \mid l^n\gamma SLJ) = \eta\Gamma\xi_l \,, \tag{4}$$

with

$$\eta = [l(l+1)\,(2l+1)]^2\,[S(S+1)\,(2S+1)\,L(L+1)\,(2L+1)]^{-1/2}\,(l^n\gamma SL \,\|\, \boldsymbol{V}^{(11)} \,\|\, l^n\gamma SL) \,, \tag{5a}$$

$$\Gamma = \tfrac{1}{2}\,[J(J+1) - S(S+1) - L(L+1)] \,, \tag{5b}$$

$$\xi_l = \frac{\alpha^2}{2} \int R_l(r)\,[(1/r)\,\partial V/\partial r]\,R_l\,r^2\,dr \,, \tag{5c}$$

where α is the fine-structure constant and R_l denotes the radial function for the shell** l^n.

The so-called doublet separation δ is usually defined by the relation

$$\delta = W(J) - W(J-1) = J\eta\xi_l \,, \tag{6}$$

and the spin-orbit interaction constant by

$$\lambda = \xi_l/2S \,. \tag{7}$$

The evaluation of these quantities implies the calculation of η and ξ_l. The reduced matrix elements of the double tensor $\boldsymbol{V}^{(11)}$ are given by RACAH [*9*, *10*] for equivalent p and d electrons. The values of η, determined using Eq. (5a), are presented in Tab. 1 for the various terms arising from p^n and d^n configurations.

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[*] γ represents the additional quantum numbers needed to completely describe the state under consideration.

[**] This designation is not complete. The principal quantum number of the shell should be included but is omitted in order to avoid confusion with the number of electrons in the shell.

Usually one writes

$$(1/r)\,\partial V/\partial r = Z_{\text{eff}}/r^3 = [Z - q(r)]/r^3\,, \tag{8}$$

where Z_{eff} is the effective nuclear charge for the electron in the l^n shell; Z is the true nuclear charge and $q(r)$ denotes the electronic charge (excluding the electron under consideration) within a sphere of radius r. Therefore Eq. (5c) transforms into

$$\begin{aligned}\xi_l &= \frac{\alpha^2}{2}\{Z\int_0^\infty (1/r^3)\,R_l^2(r)\,r^2dr - \int_0^\infty [q(r)/r^3]\,R_l^2(r)\,r^2dr\}\\ &= \frac{\alpha^2}{2}\{Z\,\langle r^{-3}\rangle - \sum_i \int_0^\infty (1/r^3)\,R_l^2(r)\,r^2dr\int_0^r R_{l_i}^2(r_i)\,r_i^2dr_i\}\,.\end{aligned} \tag{9}$$

ξ_l has been evaluated using the analytical Hartree-Fock functions of Clementi [1] and Malli [2].

Results and Discussion

The values of the spin-orbit interaction constants for various states of positive ions, neutral atoms, and negative ions with p^n and d^n configurations are presented

Table 2. *Spin-orbit coupling constants λ (in cm^{-1}) for various states of positive ions, neutral atoms, and negative ions with p^n configurations*[a, b] *(in absolute value)*

Configuration	State	Positive ion		Neutral Atom		Negative Ion	
		System	λ	System	λ	System	λ
$2p^1$	^2P	C^+	57.9 (42.7)	B	15.3 (10.7)		
$2p^2$	^3P	N^+	60.4 (41.1)	C	21.5 (13.6)	B^-	4.5
$2p^4$	^3P	F^+	187.8 (170.9)	O	90.7 (79.3)	N^-	36.2
$2p^5$	^2P	Ne^+	597.3 (521.3)	F	316.7 (269.3)	O^-	146.6
$3p^1$	^2P	Si^+	183.8 (191.3)	Al	68.4 (74.7)		
$3p^2$	^3P	P^+	152.1 (151.9)	Si	70.7 (73.1)	Al^-	20.8
$3p^4$	^3P	Cl^+	338.2 (348.5)	S	195.3 (198.4)	P^-	97.1
$3p^5$	^2P	A^+	952.4 (954.7)	Cl	585.9 (587.3)	S^-	324.6
$4p^1$	^2P	Ge^+	1050.0 (1178.1)	Ga	479.1 (550.8)		
$4p^2$	^3P	As^+	747.1 (739.5)	Ge	412.2 (426.4)	Ga^-	143.5
$4p^4$	^3P	Br^+	1303.7 (1569.5)	Se	852.4 (994.7)	As^-	485.4
$4p^5$	^2P	Kr^+	3314.5 (3580.7)	Br	2273.0 (2456.7)	Se^-	1421.1

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[a] The theoretical values have been calculated using the Hartree-Fock functions of Clementi [1] and Malli [2].

[b] The corresponding experimental values, calculated from the data of Moore [8], are given in parentheses.

Table 3. *Spin-orbit coupling constants λ (in cm^{-1}) for various states of positive ions, neutral atoms, and negative ions with d^n configurations*[a, b] *(in absolute value)*

Configuration	State	Positive Ion		Neutral Atom		Negative Ion	
		System	λ	System	λ	System	λ
$3d^1$	^2D			Sc	96.0 (67.3)		
$3d^2$	^3F	Sc^+	39.3 (26.1)	Ti	74.1 (54.2)	Sc^-	34.8
$3d^3$	^4F	Ti^+	41.5 (28.5)	V	70.1 (51.0)	Ti^-	39.2
$3d^4$	^5D	V^+	45.1 (32.6)	Cr	71.3 (53.1)	V^-	43.7
$3d^6$	^5D	Mn^+	83.0 (67.0)	Fe	120.2 (104.0)	Mn^-	81.5
$3d^7$	^4F	Fe^+	143.5 (123.9)	Co	201.7 (181.3)	Fe^-	141.5
$3d^8$	^3F	Co^+	273.9 (237.6)	Ni	375.7 (333.0)	Co^-	271.4
$3d^9$	^2D	Ni^+	687.6 (602.8)				

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[a] The theoretical values have been calculated using the Hartree-Fock functions of CLEMENTI [*1*].

[b] The corresponding experimental values, calculated from the data of MOORE [*8*], are given in parentheses.

in Tab. 2 and 3. For comparison the corresponding experimental values are also presented. The experimental values of λ have been determined by the relation

$$\lambda J = E(J) - E(J - 1) ,$$

using the $E(J)$ values given by MOORE [*8*].

Inspection of these tables shows that the agreement is resonably good.

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Professor SERAFIN FRAGA
Division of Theoretical Chemistry
Department of Chemistry
University of Alberta
Edmonton, Canada