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# Complete Spin-Orbit Interaction in Many-Electron Atoms*

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The complete spin-orbit coupling constants have been evaluated, including both the spin-own orbit and the spin-other orbit terms, for all the positive ions, neutral systems, and negative ions from He to Kr, as well as for various isoelectronic series.

Für alle positiven und negativen Ionen und für die neutralen Atome von He bis Kr sowie für verschiedene isoelektronische Serien werden die kompletten Spin-Bahn-Kopplungskonstanten einschließlich der Spin-Bahn-Wechselwirkung verschiedener Elektronen berechnet.

## Introduction

Because of its importance, as the main contributor to the splitting of the terms of a multiplet, the spin-orbit interaction in many-electron atoms has received great attention.

The *complete* spin-orbit interaction consists of one-body spin-orbit couplings and two-body, mutual spin-orbit interactions, the latter including both direct and exchange terms. Horie [8] developed the formulation for the two-body, mutual spin-orbit interactions between the open-shell electrons; in the literature this contribution is known under the designation of *spin-other-orbit* interaction. Blume and Watson [2], on the other hand, treated the one-body couplings and the remaining two-body, mutual interactions, which behave (including both the direct and exchange terms) as an effective one-body spin-orbit coupling; in the literature this contribution is known under the designation of *spin-own-orbit* interaction. The most extensive calculations have been carried out by Fraga and co-workers [6, 11, 14], but unfortunately only the spin-own-orbit interaction (without the exchange terms) was considered in that work. On the other hand, Blume and Watson [3], Froese-Fischer [7], and Malli [10] have evaluated the complete spin-orbit interaction for a limited number of systems, using Hartree-Fock functions.

The purpose of the present work is to report now the values of the complete spin-orbit interaction for all the positive ions, neutral atoms, and negative ions from He to Kr, as well as for a number of isoelectronic series.

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## Theoretical Considerations

The spin-orbit hamiltonian for a many-electron atom is

$$\mathscr{H}_{so} = \tfrac{1}{2}\alpha^2 \sum_i \left\{ Z r_i^{-3} (\boldsymbol{l}_i \;\; \boldsymbol{s}_i) - \sum_{j \neq i} r_{ij}^{-3} (\boldsymbol{r}_{ij} \times \boldsymbol{p}_i) \;\; (\boldsymbol{s}_i + 2\boldsymbol{s}_j) \right\},$$

where the summations extend to all the electrons in the system, characterized by the momentum ($\boldsymbol{p}$), angular momentum ($\boldsymbol{l}$), and spin angular momentum ($\boldsymbol{s}$) vector operators; $r_i$ defines the position of electron $i$ with respect to the nucleus (with charge $Z$) and $r_{ij}$ is the interelectronic distance between electrons $i$ and $j$. The fine structure constant is represented by $\alpha$.

The spin-orbit interaction for a given state may be expressed,

$$(vSLJ|\mathscr{H}_{so}|vSLJ) = (-1)^{S+L+J} \begin{Bmatrix} S & S & 1 \\ L & L & J \end{Bmatrix} (vSL\|\mathscr{H}_{so}\|vSL),$$

in terms of 6-$j$ symbols and double-barred matrix elements. The state under consideration is labelled by the total quantum numbers $S$, $L$, $J$, and the seniority number, $v$.

The spin-orbit coupling constant, $\lambda$, is defined by the relation

$$(vSLJ|\mathscr{H}_{so}|vSLJ) = \lambda\Gamma,$$

with

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

so that

$$\lambda = [S(S+1)(2S+1)L(L+1)(2L+1)]^{-\frac{1}{2}} (vSL\|\mathscr{H}_{so}\|vSL),$$

which can be transformed into

$$\lambda = \eta_1 \zeta_c + \eta_2 M^{(0)} + \eta_3 M^{(2)}$$

(for configurations involving up to $d$ electrons). The spin-own-orbit parameter, $\zeta_c$, defined by Blume and Watson [2], includes the spin-orbit coupling of the electrons in the nuclear coulombic field and the direct and exchange terms of the effective one-body couplings arising from the two-body interactions not included in the spin-other-orbit contribution of Horie [8]; the latter is given by the last two terms in the above expression. The radial integrals, $M^{(k)}$, have been defined by Marvin [12].

The values of the coefficients $\eta(vSL)$ can be determined from the formulas obtained by Horie [8] for the double-barred matrix elements. The corresponding values for up to half-filled shells are presented in Table 1. The values for the conjugated configurations can be obtained by the relations.

$$\begin{aligned} \eta_1(l^m) &= -\eta_1(l^n), \\ \eta_2(l^m) &= \eta_2(l^n) + [2(m+n) - 6]\,\eta_1(l^n), \\ \eta_3(d^m) &= \eta_3(d^n) - \tfrac{12}{7}\,\eta_1(d^n), \end{aligned}$$

with $m+n = 2(2l+1)$, where $l$ is the orbital angular momentum quantum number of the shell under consideration. These expressions are valid only for $p^n$ and $d^n$ configurations. (The values in Table 1 might also be obtained from the coefficients given by Barnes *et al.* [1].)

Table 1. Values of the parameters $\eta(l^n vSL)$ for some important configurations[a]

| Configuration | State[b] | $\eta_1$ | $\eta_2$ | $\eta_3$ |
|---|---|---|---|---|
| $p^1$ | ${}^2_1P$ | $1$ | | |
| $p^2$ | ${}^3_2P$ | $\frac{1}{2}$ | $-6$ | |
| $p^3$ | ${}^2_3D$ | $0$ | $-\frac{37}{5}$ | |
| | ${}^2_1P$ | $0$ | $-5$ | |
| $d^1$ | ${}^2_1D$ | $1$ | | |
| $d^2$ | ${}^3_2F$ | $\frac{1}{2}$ | $-\frac{27}{7}$ | $\frac{51}{49}$ |
| $d^3$ | ${}^4_3F$ | $\frac{1}{3}$ | $-\frac{38}{7}$ | $-\frac{6}{49}$ |
| $d^4$ | ${}^5_4D$ | $\frac{1}{4}$ | $-6$ | $\frac{3}{7}$ |

[a] These parameters vanish for the states ${}^1D(p^2)$, ${}^1S(p^2)$, ${}^4S(p^3)$, and ${}^6S(d^5)$.

[b] The seniority number, $v$, is given as a left subscript.

## Results and Discussion

Tables 2–5 collect all the values of $\lambda$ for the systems under consideration, with comparison to the experimental values obtained from the data of Moore [13], as given by Fraga and co-workers [5, 14]; the latter are given in brackets. The values[1] of $\zeta_c$ and $M^{(k)}$ have been obtained from the analytical Hartree-Fock functions of Clementi [4] and Malli [9].

Calculations have also been carried out for the first positive ion of the configurations $K(2)\,L(8)\,3s^2\,3p^6\,3d^n\,4s^2$. The corresponding absolute values are: Ti, $3d^1\ {}^2D$, 147 (93); V, $3d^2\ {}^3F$, 101; Cr, $3d^3\ {}^4F$, 88 (84); Mn, $3d^4\ {}^5D$, 85 (87); Co, $3d^6\ {}^5D$, 158 (144); and Ni, $3d^7\ {}^4F$, 256. (The experimental values are given in parentheses.)

The agreement with the experimental values, excellent for the light elements, deteriorates as one progresses along the periodic system, reflecting the fact that the LS coupling is not appropriate for the heavy elements.

For simplicity, no comparison is made here with the results of Blume and Watson [3], but it must be mentioned that the agreement is excellent, better for the light elements than for the heavy atoms: the largest difference is 4 cm$^{-1}$ for Cl, Ga, and Se. The exception, however, is Br, where the present value is 2211 cm$^{-1}$ while Blume and Watson [3] predict a value of 2194 cm$^{-1}$; it is evident that the difference (17 cm$^{-1}$) between both theoretical results is negligible relative to the difference (well over 200 cm$^{-1}$) with the experimental result of 2454 cm$^{-1}$.

In addition, it should be pointed out that the relative weights of the direct and exchange terms within the spin-own-orbit contribution are similar to those observed by Blume and Watson [3]; for that reason the discussion is not repeated here. It should be sufficient to mention that a simple comparison (for systems with the open shell occupied by only one electron, where the spin-other-orbit interaction vanishes) with the values of Malli and Fraga [11], that included only the direct terms, reveals that the exchange contribution may be as high as 30% (relative to the uncorrected value) for B, decreasing to about 3% for heavier atoms.

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[1] The values of all the radial integrals needed have been collected in the Technical Report TC-7105, Department of Chemistry, University of Alberta. This Technical Report has been placed at the Depository of Unpublished Data, National Science Library, National Research Council, Ottawa 7, Canada K1A OR6. A limited number of copies is available upon request.

Table 2. Absolute values[a] (in cm$^{-1}$) of the spin-orbit coupling constant, $\lambda$, for positive ions, neutral atoms, and negative ions

| Configuration[b] | State | Positive ions | | Neutral atoms | | Negative ions | |
|---|---|---|---|---|---|---|---|
| | | System | $\lambda$ | System | $\lambda$ | System | $\lambda$ |
| $2p^1$ | $^2P$ | C | 43 | B | 10 | | |
| | | | [43] | | [11] | | |
| $2p^2$ | $^3P$ | N | 42 | C | 14 | B | 2 |
| | | | [45] | | [15] | | |
| $2p^3$ | $^2D$ | O | 11 | N | 5 | C | 2 |
| | $^2P$ | | 7 | | 3 | | 1 |
| $2p^4$ | $^3P$ | F | 171 | O | 81 | N | 31 |
| | | | [160] | | [74] | | |
| $2p^5$ | $^2P$ | Ne | 517 | F | 268 | O | 120 |
| | | | [521] | | [269] | | |
| $3p^1$ | $^2P$ | Si | 169 | Al | 62 | | |
| | | | [191] | | [75] | | |
| $3p^2$ | $^3P$ | P | 140 | Si | 65 | Al | 19 |
| | | | [159] | | [75] | | |
| $3p^3$ | $^2D$ | S | 2 | P | 1 | Si | 0.4 |
| | $^2P$ | | 1 | | 0.7 | | 0.3 |
| $3p^4$ | $^3P$ | Cl | 319 | S | 183 | P | 90 |
| | | | [324] | | [188] | | |
| $3p^5$ | $^2P$ | A | 896 | Cl | 549 | S | 302 |
| | | | [955] | | [587] | | |
| $3d^1$ | $^2D$ | | | Sc | 77 | | |
| | | | | | [67] | | |
| $3d^2$ | $^3F$ | Sc | 31 | Ti | 59 | Sc | 27 |
| | | | [27] | | [54] | | |
| $3d^3$ | $^4F$ | Ti | 32 | V | 55 | Ti | 30 |
| | | | [30] | | [51] | | |
| $3d^4$ | $^5D$ | V | 35 | Cr | 56 | V | 33 |
| | | | [36] | | [53] | | |
| $3d^6$ | $^5D$ | Mn | 77 | Fe | 112 | Mn | 75 |
| | | | [62] | | [104] | | |
| $3d^7$ | $^4F$ | Fe | 131 | Co | 186 | Fe | 129 |
| | | | [117] | | [181] | | |
| $3d^8$ | $^3F$ | Co | 244 | Ni | 338 | Co | 242 |
| | | | [227] | | [333] | | |
| $3d^9$ | $^2D$ | Ni | 608 | Cu | 821 | | |
| | | | [603] | | | | |
| $4p^1$ | $^2P$ | Ge | 1018 | Ga | 464 | | |
| | | | [1178] | | [551] | | |
| $4p^2$ | $^3P$ | As | 725 | Ge | 399 | Ga | 139 |
| | | | [740] | | [426] | | |
| $4p^3$ | $^2D$ | Se | 1 | As | 0.7 | Ge | 0.3 |
| | $^2P$ | | 0.8 | | 0.5 | | 0.2 |
| $4p^4$ | $^3P$ | Br | 1269 | Se | 829 | As | 472 |
| | | | [1570] | | [995] | | |
| $4p^5$ | $^2P$ | Kr | 3226 | Br | 2211 | Se | 1381 |
| | | | [3581] | | [2457] | | |

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[a] The values for $p^n$, with $n > 3$, and $d^n$, with $n > 5$, are negative.

[b] The positive ions of the transition elements (from Sc through Ni) have configurations $4s^0\,3d^n$.

Table 3. Absolute values[a] (in cm$^{-1}$) of the spin-orbit coupling constant, $\lambda$, for the isoelectronic series[b] $2p^n$

| System | $2p^1$, $^2P$ | $2p^2$, $^3P$ | $2p^4$, $^3P$ | $2p^5$, $^2P$ |
|---|---|---|---|---|
| B | 10 | | | |
| | [11] | | | |
| C | 43 | 14 | | |
| | [43] | [15] | | |
| N | 118 | 42 | | |
| | [116] | [45] | | |
| O | 263 | 100 | 81 | |
| | [258] | [105] | [74] | |
| F | 507 | 202 | 171 | 268 |
| | [497] | [210] | [160] | [269] |
| Ne | | 365 | 318 | 517 |
| | | [382] | [301] | [521] |
| Na | | | 543 | 906 |
| | | | [512] | [909] |
| Mg | | | 869 | 1477 |
| | | | [185] | [1484] |
| Al | | | | 2281 |
| | | | | [2293] |

[a] The values are negative for $n > 3$.
[b] With configurations $K(2)\ 2s^2\ 2p^n$.

Table 4. Absolute values[a] (in cm$^{-1}$) of the spin-orbit coupling constant, $\lambda$, for the isoelectronic series[b] $3p^n$

| System | $3p^1$, $^2P$ | $3p^2$, $^3P$ | $3p^4$, $^3P$ | $3p^5$, $^2P$ |
|---|---|---|---|---|
| Al | 62 | | | |
| | [75] | | | |
| Si | 169 | 65 | | |
| | [191] | [75] | | |
| P | 338 | 140 | | |
| | [373] | [159] | | |
| S | 586 | 252 | 183 | |
| | [633] | [284] | [188] | |
| Cl | 930 | 411 | 319 | 549 |
| | [995] | [458] | [324] | [587] |
| A | | 625 | 506 | 896 |
| | | [699] | [507] | [955] |
| K | | | 756 | 1362 |
| | | | [744] | [1441] |
| Ca | | | 1079 | 1969 |
| | | | [1037] | [2077] |
| Sc | | | | 2741 |
| | | | | [2885] |

[a] The values are negative for $n > 3$.
[b] With configurations $K(2)\ L(8)\ 3s^2\ 3p^n$.

Table 5. Absolute values[a] (in $\mathrm{cm}^{-1}$) of the spin-orbit coupling constant, $\lambda$, for the isoelectronic series[b] $3d^n$

| System | $3d^1$, $^2D$ | $3d^2$, $^3F$ | $3d^3$, $^4F$ | $3d^4$, $^5D$ | $3d^6$, $^5D$ | $3d^7$, $^4F$ | $3d^8$, $^3F$ | $3d^9$, $^2D$ |
|---|---|---|---|---|---|---|---|---|
| Sc | 86 | 31 | | | | | | |
| | [79] | [27] | | | | | | |
| Ti | 158 | 63 | 32 | | | | | |
| | [154] | [60] | [30] | | | | | |
| V | 253 | 106 | 57 | 35 | | | | |
| | [248] | [105] | [56] | [36] | | | | |
| Cr | 377 | 163 | 91 | 57 | | | | |
| | [383] | [165] | [92] | [58] | | | | |
| Mn | 535 | 236 | 135 | 87 | 76 | | | |
| | [542] | [240] | [135] | [90] | [62] | | | |
| Fe | | | 189 | 125 | 115 | 131 | | |
| | | | [192] | [133] | [100] | [117] | | |
| Co | | | | 172 | 162 | 189 | 244 | |
| | | | | [186] | | [176] | [227] | |
| Ni | | | | | 221 | 262 | 344 | 608 |
| | | | | | | | [322] | [603] |
| Cu | | | | | 292 | 349 | 465 | 833 |
| | | | | | | | | [829] |
| Zn | | | | | | 455 | 612 | 1107 |

[a] The values are negative for $n > 5$.

[b] With configurations $K(2)\,L(8)\,3s^2\,3p^6\,3d^n$.

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