ANISOTROPIC SPIN-ORBIT COUPLING FOR l^N CONFIGURATION IN A CRYSTAL FIELD

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Anisotropic spin-orbit coupling in a crystal field for N electron systems is treated within the framework of quasirelativistic quantum mechanics. The Hamiltonian of this interaction is expressed by certain irreducible tensor operators, and its matrix elements are calculated as known functions of independent radial parameters. Numerical values of appropriate coefficients for p, d, f and g shells are given. Formulas for radial parameters are derived in terms of multipole charge distribution producing the crystal field. Evaluation of these parameters in the point charge model leads to the conclusion that the effect is 10^4 times less than the electrostatic effect of the crystal field. Hence, in general, the effect of anisotropic spin-orbit coupling in a crystal field can be neglected. An important exception is that of orbitally nondegenerate terms, where the considered effect could cause appreciable splitting.

1. *Introduction*

In an earlier paper [1], we considered in a quasirelativistic approximation the spin-orbit interaction for a single electron moving in an electric field having symmetry of any point group, and derived general formulas for the Hamiltonian of this interaction and its matrix elements in a basis of atomic states. We pointed out that such an interaction gives a contribution to the splitting of energy levels of an ion placed in the crystal field. We moreover derived independent radial parameters describing this contribution. In the present paper, we generalize these results for the N-electron case and evaluate the range of magnitude of the radial parameters.

2. *Hamiltonian, and its matrix elements*

a) General form of the one-particle spin-orbit coupling Hamiltonian for an N-electron system

The Hamiltonian of one-particle spin-orbit interaction for an N-electron system in a quasirelativistic approximation, *i.e.* with accuracy up to v^2/c^2, can be written as

$$H_{SO} = \frac{\hbar}{2m^2c^2} \sum_{j=1}^{N} \mathbf{s}_j \cdot [\mathrm{grad}_j V(\mathbf{r}_j) \wedge \mathbf{p}_j] \tag{1}$$

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with $\hbar$ — Planck's constant, m — electron mass, c — velocity of light in vacuum, $\boldsymbol{s}_j$, $\boldsymbol{r}_j$ and $\boldsymbol{p}_j$ — spin, position and momentum operators for the j-th electron, respectively, $V(\boldsymbol{r}_j)$ — the potential energy for a single electron. In the case of an ion in a crystal field

$$V(\boldsymbol{r}_j) = \frac{Ze^2}{r_j} + V_H(r_j) + V_c(\boldsymbol{r}_j^{\mathrm{I}}), \qquad r_j = |\boldsymbol{r}_j| \tag{2}$$

where the first, second and third term describes respectively the Coulomb attraction energy of the nucleus of the central ion, the self-consistent energy which replaces the influence of the other electrons of the central ion, and the crystal field. The first two terms have spherical symmetry, so that they contribute to isotropic spin-orbit coupling only [2]. The third term has only symmetry of a point group and leads to anisotropic spin-orbit interaction.

As it is known from quantum electrodynamics, the Hamiltonian (1) for $N = 1$ is, in the quasirelativistic approximation, the most general form of the spin-dependent part of the energy of a single electron interacting with the external electrostatic field produced by an arbitrary distribution of charges [3]. In the case $N > 1$, one has moreover to take into account relativistic two-body effects, namely spin-spin and spin-other orbit coupling [4], which, as was shown by Blume and Watson [2], contribute to the isotropic spin-orbit coupling parameter. The role of two-body effects in determining the anisotropic spin-orbit parameters will be briefly discussed in Chapter 4.

In considering the role of spin-orbit coupling in determining the energy level structure of paramagnetic ions in diamagnetic host crystals, it is convenient to express the Hamiltonian (1) as a series of irreducible spherical tensor operators. Let us rewrite Eq. (2)in the form

$$V(\boldsymbol{r}_j) = \sum_{k=0}^{\infty} \sum_{q=-k}^{k} V_{kq}(r_j)\, Y_q^{(k)}(\vartheta_j \varphi_j), \tag{3}$$

where the $V_{kq}(r_j)$ describe the radial distribution of potential energy for the j-th electron; $Y_q^{(k)} = i^k Y_{kq}$, where Y_{kq} are spherical harmonics defined by Condon and Shortley [5]. According to Ref. [1], the Hamiltonian (1) can be written in the form

$$H_{SO} = \sum_{j=1}^{N} \sum_{k=0}^{\infty} \sum_{q=-k}^{k} \sum_{A=\mathrm{I}}^{\mathrm{II}} \sum_{a=1}^{2} Q_{kq}^{Aa}(r_j)\, \Gamma_{Aaq}^{(k)}(j), \tag{4}$$

where

$$Q_{kq}^{\mathrm{I1}}(r_j) = \alpha \left(\frac{2(k+1)}{2k+1}\right)^{1/2} \left(\frac{dV_{kq}(r_j)}{dr_j} \frac{\partial}{\partial r_j} - k \frac{V_{kq}(r_j)}{r_j} \frac{\partial}{\partial r_j}\right)$$

$$Q_{kq}^{\mathrm{I2}}(r_j) = \alpha \left(\frac{2(k+1)}{2k+1}\right)^{1/2} \left(\frac{1}{r_j} \frac{dV_{kq}(r_j)}{dr_j} - k \frac{V_{kq}(r_j)}{r_j^2}\right)$$

$$Q_{kq}^{\mathrm{III}}(r_j) = \alpha \left(\frac{2k}{2k+1}\right)^{1/2} \left(\frac{dV_{kq}(r_j)}{dr_j} \frac{\partial}{\partial r_j} + (k+1) \frac{V_{kq}(r_j)}{r_j} \frac{\partial}{\partial r_j}\right)$$

$$Q_{kq}^{\mathrm{II2}}(r_j) = \alpha \left(\frac{2k}{2k+1}\right)^{1/2} \left(\frac{1}{r_j} \frac{dV_{kq}(r_j)}{dr_j} + (k+1) \frac{V_{kq}(r_j)}{r_j^2}\right) \tag{5}$$

$$\alpha = \frac{-i\hbar^2}{2m^2c^2}, \tag{6}$$

whereas

$$\Gamma^{(k)}_{Aa\,q}(j) = [Y^{(k_A)}(j) \times [\boldsymbol{w}^{(1)}_a(j) \times \boldsymbol{s}^{(1)}_j]^{(1)}]^{(k)}_q, \tag{7}$$

where

$$\boldsymbol{w}_a(j) = \begin{cases} \boldsymbol{n}_j = \boldsymbol{r}_j / r_j & \text{for} \quad a = 1 \\ \nabla^*_j = \boldsymbol{t}_{\vartheta} \partial / \partial_{\vartheta_j} + (1/\sin\vartheta_j) \boldsymbol{t}_{\varphi_j} \partial / \partial \varphi_j & \text{for} \quad a = 2 \end{cases} \tag{8}$$

and

$$k_A = \begin{cases} k+1 & \text{for} \quad A = \text{I} \\ k-1 & \text{for} \quad A = \text{II} \end{cases} \tag{9}$$

The radial operators Q^{Aa}_{kq} and angular operators $\Gamma^{(k)}_{Aa\,q}$ satisfy the hermitian adjoint relations derived in Chapter 4 of [1].

It is convenient to separate the orbital and spin variables in the operators (7) in order to carry out calculations in the LS basis of states. To this aim, we perform a recoupling according to the formula

$$\Gamma^{(k)}_{Aa\,q} = \sum_{k'=k_A-1}^{k_A+1} [k_A 1_a(k') 1_s k | k_A, 1_a 1_s(1) k] \times$$

$$\times [[Y^{k_A} \times \boldsymbol{w}^{(1)}_a]^{(k')} \times \boldsymbol{s}^{(1)}]^{(k)}_q = \sum_{k'} [\Theta(A, a, k)^{(k')} \times \boldsymbol{s}^{(1)}]^{(k)}_q, \tag{10}$$

where

$$\Theta(A, a, k)^{(k')}_{q'} = (-1)^{k+k_A} (3(2k'+1))^{1/2} \begin{Bmatrix} 1 & 1 & 1 \\ k & k_A & k' \end{Bmatrix} [Y^{(k_A)} \times \boldsymbol{w}^{(1)}_a]^{(k')}_{q'} \tag{11}$$

the tensor operators and their products satisfy the conventions stated in Appendix A of [1]. The appropriate Yutsis–Bandsaitis diagram [6], corresponding to Eq. (10), is shown in Fig. 1.

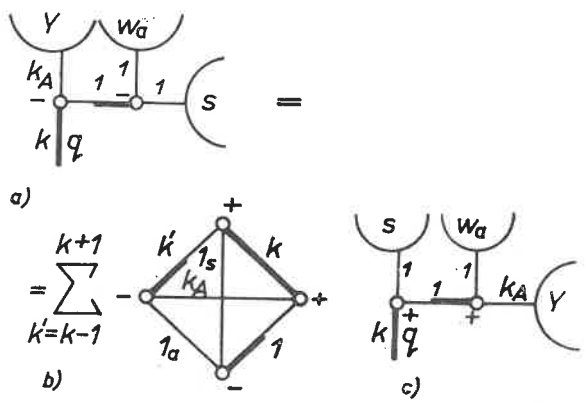

Fig. 1. Diagram of Eq. (10). a — diagram of $\Gamma^{(k)}_{Aa\,q}$, b — diagram of transformation matrix $[k_A\, 1_a(k') 1_s k | k_A, 1_a 1_s(1) k]$, c — diagram of the tensor product $[[Y^{(k_A)} \times \boldsymbol{w}^{(1)}_a]^{(k')} \times s^{(1)'}]^{(k)}_q$

From (11), we easily obtain (see Fig. 2)

$$(l||\Theta(A,\,a,\,k)^{(k')}||l') = (-1)^{l+l'+k+k_A+k'}\,(2k'+1)\{3(2k_A+1)/4\pi\}^{1/2}\times$$
$$\times \begin{Bmatrix} 1 & 1 & 1 \\ k & k_A & k' \end{Bmatrix} \sum_{l''} (l||C^{(k_A)}||l'')(l''||\boldsymbol{w}_a^{(1)}||l) \begin{Bmatrix} 1 & k_A & k' \\ l & l' & l'' \end{Bmatrix} \tag{12}$$

where

$$C^{(k_A)} = \{4\pi/(2k_A+1)\}^{1/2} Y^{(k_A)}.$$

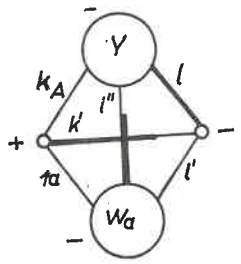

Fig. 2. Subsidiary diagram to evaluate $(l\,||\,[Y^{(k_A)}\times \boldsymbol{w}_a^{(1)}]\,||\,l')$

The matrix elements of the Hamiltonian (4) can be calculated as well-defined functions of the radial parameters $\langle nl|Q_{kq}^{Aa}|n'l'\rangle$ for any N electron state in a central field. We now consider in detail the l^N configuration case. The anisotropic spin-orbit coupling is described, here, by a relatively small number of parameters. Notably, the energy level structure of l^N configurations is perhaps the most important in explaining experimental EPR and optical data.

b) Effective Hamiltonian within the framework of l^N configuration states

Restricting our considerations to l^N configuration states, we can average the Hamiltonian (4) over radial wave functions, the same for all electrons. An effective Hamiltonian for l^N configurations can be constructed in terms of unit tensor operators $U_q^{(k)}$ and $V_{q\ \sigma}^{(k)(1)}$, introduced by Racah (see *e.g.* Karasiya *et al.* [7] and references therein) and given by

$$U_q^{(k)} = \sum_{j=1}^{N} u_q^{(k)}(j),$$

$$V_{q\ \sigma}^{(k)(1)} = \sum_{j=1}^{N} u_q^{(k)}(j) S_\sigma^{(1)}(j) = \sum_{j=1}^{N} v_{q\ \sigma}^{(k)(1)}(j) \tag{13}$$

where $u_q^{(k)}(j)$ and $S_\sigma^{(1)}(j)$ are unit one-electron tensor operators acting on the orbital and spin variables, respectively, and determined by their reduced matrix elements as

$$(l||u^{(k)}||l') = i^k \delta_{ll'}\delta(l,\,k,\,l') \qquad \text{for } k = 1,\,2,\,\ldots,\,2l$$
$$(l||u^{(0)}||l') = (2l+1)^{1/2}\delta_{ll'}$$
$$(\tfrac{1}{2}||S^{(0)}||\tfrac{1}{2}) = 2^{1/2},\quad (\tfrac{1}{2}||S^{(1)}||\tfrac{1}{2}) = i(3/2)^{1/2}, \tag{14}$$

where

$$\delta(l, k, l') = \begin{cases} 1 & \text{where } |l-l'| \leqslant k \leqslant l+l' \\ 0 & \text{in other cases.} \end{cases} \tag{15}$$

According to (10), the one-electron operator $\Gamma_{Aa\,q}^{(k)}$ can be replaced within the framework of l^N states by

$$\Gamma_{Aa\,q}^{(k)}(j)_{\text{eff}} = \sum_{k'} (-i)^{k'} (l||\Theta(A, a, k)^{(k')}||l)\, [u^{(k')}(j) \times S^{(1)}(j)]_q^{(k)} \tag{16}$$

where

$$[u^{(k')}(j) \times S^{(1)}(j)]_q^{(k)} = \sum_{q'+\sigma=q} (-1)^{k'+1-q} (2k+1)^{-1/2} \begin{pmatrix} k' & 1 & k \\ q' & \sigma & -q \end{pmatrix} v_{q'}^{(k')(1)}{}_{\sigma}(j). \tag{17}$$

We can now replace (4) by the equivalent Hamiltonian

$$H_{SO}^{\text{eff}} = \sum_{kq} \sum_{A,a} \bar{Q}_{kq}^{Aa} \sum_{k'} (-i)^{k'} (l||\Theta(A, a, k)^{(k')}||l) [V^{(k')\times(1)}]_q^{(k)} \tag{18}$$

where

$$\bar{Q}_{kq}^{Aa} = \langle nl|Q_{kq}^{Aa}|nl\rangle = \int_0^\infty r^2 R_{nl}(r) Q_{kq}^{Aa} R_{nl}(r) dr, \tag{19}$$

being the radial part of the one-electron wave function, and

$$[V^{(k')\times(1)}]_q^{(k)} = \sum_{q'+\sigma=q} (-1)^{k'+1-q} (2k+1)^{-1/2} \begin{pmatrix} k' & 1 & k \\ q' & \sigma & -q \end{pmatrix} V_{q'}^{(k')(1)}{}_{\sigma}. \tag{20}$$

The matrix elements of the equivalent Hamiltonian (18) in the basis of l^N states are the same as those of "true" Hamiltonian (4).

Eq. (19) defines the radial parameters describing the magnitude of anisotropic spin-orbit coupling. According to the results of Ref. [1], only two of the four parameters corresponding to averaging of the operators (5) over radial wave functions are independent (in the l^N configuration case). As independent parameters, we choose

$$\bar{Q}_{kq}^{n} = \frac{\hbar^2}{2m^2c^2} \left\langle nl \left| \frac{1}{r} \frac{dV_{kq}}{dr} \right| nl \right\rangle \tag{21}$$

$$\bar{Q}_{kq}^{\omega} = \frac{\hbar^2}{2m^2c^2} \left\langle nl \left| \frac{V_{kq}}{r^2} \right| nl \right\rangle \tag{22}$$

(these parameters are real for even q). According to (5) and Eqs (42) and (51) of [1], we can write the equivalent Hamiltonian in the form

$$H_{SO}^{\text{eff}} = \sum_{k,q} \sum_{k'} \{\bar{Q}_{kq}^{n} G_n(k, k', l) + \bar{Q}_{kq}^{\omega} G_{\omega}(k, k', l)\} [V^{(k')\times(1)}]_q^{(k)} \tag{23}$$

where G_n and G_ω are coefficients invariant with respect to rotations, and given by

$$G_n(k, k', l) = (-i)^{k'+1}[(k+1)/2(2k+1)]^{1/2}[k(l||\Theta(\text{I}, 1, k)^{(k')}||l) + 2(l||\Theta(\text{I}, 2, k)^{(k')}||l)] +$$
$$+ (-i)^{k'+1}[k/2(2k+1)]^{1/2}[-(k+1)\,(l||\Theta(\text{II}, 1, k)^{(k')}||l) + 2(l||\Theta(\text{II}, 2, k)^{(k')}||l)] \tag{24}$$

$$G_\omega(k, k', l) = (-i)^{k'+1}k[(k+1)/2(2k+1)]^{1/2}[(l||\Theta(\mathrm{I}, 1, k)^{(k')}||l) - 2(l||\Theta(\mathrm{I}, 2, k)^{(k')}||l)] +$$
$$+(-i)^{k'+1}(k+1)[k/2(2k+1)]^{1/2}[-(l||\Theta(\mathrm{II}, 1, k)^{(k')}||l) + 2(l||\Theta(\mathrm{II}, 2, k)^{(k')}||l)]. \quad (25)$$

From the triangle rule $\Delta(1, k, k')$ resulting from the Wigner $6j$ symbol occurring in (11), it is obvious that $k' = k-1, k, k+1$. We show in Appendix A that

$$G_n(k, k, l) = G_\omega(k, k, l) = 0 \quad (26)$$

$$G_n(k, k+1, l) = (-1)^{1+k/2}[(k+2)/(2k+1)]^{1/2}(l||[Y^{(k+1)} \times V^{*(1)}]^{(k+1)}||l) \quad (27)$$

$$G_n(k, k-1, l) = (-1)^{1+k/2}[(k-1)/(2k+1)]^{1/2}(l||[Y^{(k-1)}V) \times {}^{*(1)}]^{(k-1)}||l) \quad (28)$$

$$G_\omega(k, k+1, l) = -KG_n(k, k+1, l) \quad (29)$$

$$G_\omega(k, k-1, l) = (k+1)G_n(k, k-1, l). \quad (30)$$

In Appendix B we derive some relations between the coefficients G_n, G_ω and one-electron coefficients defined in Ref. [1]. In Table I we give numerical values of $G_n(k, k', l)$ for p, d, f and g configurations (for $l = 0$, we have $G_n = G_\omega = 0$). The $G_\omega(k, k', l)$ can now easily be obtained from (29) and (30).

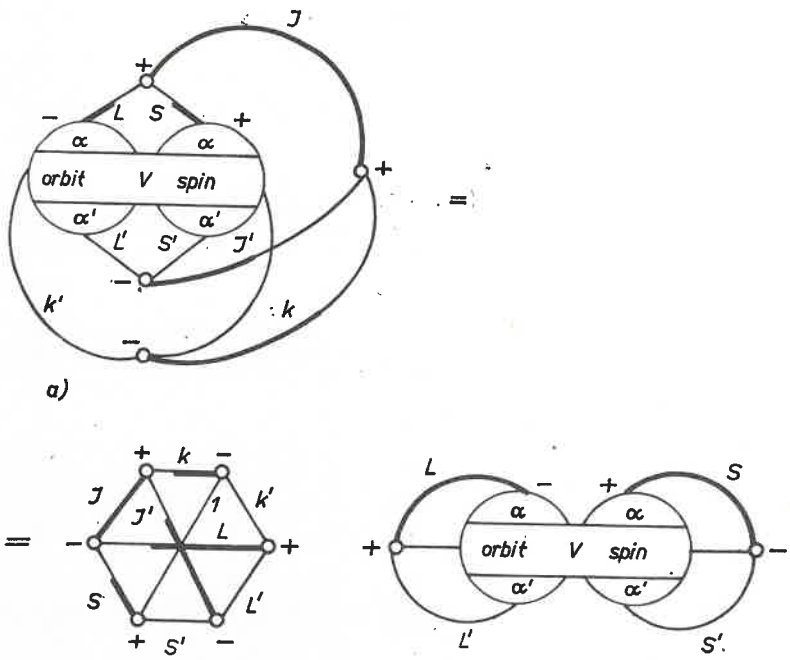

Fig. 3. Matrix elements of the double tensor operator: a — diagram of $(l^N\alpha LSJ||[V^{(k')\times(1)}]^{(k)}||l^N\alpha'L'S'J')$; the bridge connecting the spin and orbital parts of operator V indicates that for $N > 2$ the operator $V^{(k')(1)}$ cannot be separated into a product of two operators, one of which acts on the orbital variables only and the other on spins, b — diagram proportional to the $9j$ Wigner coefficient occuring in (31), c — diagram of $(l^N\alpha LS||V^{(k')(1)}||l^N\alpha'L'S')$

The evaluation of matrix elements of the Hamiltonian (23) reduces to computing the matrix elements of the unit Racah operator (20). Using the graphical methods of the angular momentum theory [6], we find

$$(l^N\alpha LSJ||[V^{(k')\times(1)}]^{(k)}||l^N\alpha' L'S'J')$$

$$= [(2J+1)\,(2J'+1)\,(2k+1)]^{1/2} \begin{Bmatrix} L & S & J \\ L' & S' & J' \\ k' & 1 & k \end{Bmatrix} (l^N\alpha LS||V^{(k')(1)}||l^N\alpha' L'S'). \tag{31}$$

The reduced matrix elements $(l^N\alpha LS||V^{(k')(1)}||l^N\alpha' L'S')$ are tabulated in Ref. [7] or elsewhere (see references given in [7]). The graphical representation of Eq. (31) is given in Fig. 3.

Thus, by means of Eqs (26)–(31), we can derive the matrix elements of the equivalent Hamiltonian H_{SO}^{eff} (23) for arbitrary l^N configuration states as functions of the independent radial parameters $\overline{Q}_{kq}^{n}$ and $\overline{Q}_{kq}^{\omega}$ given by (21) and (22), respectively.

TABLE I

Numerical values of coefficients $\pi^{1/2}G_n(k, k', l)$ for p, d, f and g shells (all non-zero values are adduced)

k	k'	$l=1$	$l=2$	$l=3$	$l=4$
0	1	$-3/\sqrt{2}$	$-3\sqrt{5}/\sqrt{2}$	$-3\sqrt{7}$	$-3\sqrt{3.5}$
2	1	$-3/2\sqrt{5}$	$3/2$	$3\sqrt{7}/\sqrt{2.5}$	$3\sqrt{3}/\sqrt{2}$
	3	—	$\sqrt{2.3}$	$7\sqrt{2}/\sqrt{5}$	$3^2\sqrt{2.3}/\sqrt{11}$
4	3	—	$-\sqrt{5}/\sqrt{2}$	$-7/\sqrt{2.3}$	$-3^2\sqrt{5}/\sqrt{2.11}$
	5	—	—	$-\sqrt{5.7}/\sqrt{3}$	$-3^2\sqrt{5}/\sqrt{13}$
6	5	—	—	$5\sqrt{7}/\sqrt{2.13}$	$3^2.5\sqrt{3}/13\sqrt{2}$
	7	—	—	—	$2.3.5\sqrt{2.3.7}/13\sqrt{11}$
8	7	—	—	—	$-3.5.7\sqrt{3}/\sqrt{11.13.17}$

3. Evaluation of radial parameters

The radial parameters, $\overline{Q}_{kq}^{Aa}$, determining the anisotropic spin-orbit energy, depend according to (19) and (5) on the shape of the radial wave function of electrons of the central ion and on the electric field distribution (3). The radial wave function for an ion placed in a crystal is different from that of a free ion (the former is more extended than the latter) for reason of the nephelauxetic effect resulting from ligand charge penetration into the region occupied by electrons of the central ion (see *e.g.* [8] p. 192 and references therein). This effect is obviously dependent on the host crystal. Similarly, the electric field distribution also depends on the crystal.

The electric charge density producing the field (3) can be written in the form

$$\varrho(\boldsymbol{r}') = \sum_{k=0}^{\infty} \sum_{q=-k}^{k} \varrho_{kq}(r')\, Y_q^{(k)}(\vartheta', \varphi'), \tag{32}$$

where the $\varrho_{kq}(r')$ describe the distribution of multipole charges. On inserting (32) into the expression:

$$V(\boldsymbol{r}) = -e \int \frac{\varrho(\boldsymbol{r}')}{|\boldsymbol{r}'-\boldsymbol{r}|} d^3\boldsymbol{r}' \tag{33}$$

well-known from electrostatic theory, and using the expression:

$$\frac{1}{|\boldsymbol{r}'-\boldsymbol{r}|} = \sum_{k=0}^{\infty} \frac{4\pi}{2k+1} \left[\frac{r'^k}{r^{k+1}} \Theta(r-r') + \frac{r_k}{r'^{k+1}} \Theta(r'-r) \right] \sum_{q=-k}^{k} (-1)^{k-q} Y_q^{(k)}(\vartheta, \varphi) Y_{-q}^{(k)}(\vartheta', \varphi') \tag{34}$$

where

$$\Theta(x) = \begin{cases} 1 & \text{for} \quad x > 0 \\ 0 & \text{for} \quad x < 0 \end{cases} \tag{35}$$

is the Heaveside function, and on performing integrations over ϑ', φ' we obtain, by confrontation with (3):

$$V_{kq}(r) = \frac{-4\pi e}{2k+1} \int_0^{\infty} \varrho_{kq}(r') \left[\frac{r'^{k+2}}{r^{k+1}} \theta(r-r') + \frac{r_k}{r'^{k-1}} \theta(r'-r) \right] dr'. \tag{36}$$

Introducing two radial functions

$$A_{kq}(r) = -\frac{4\pi e}{2k+1} \int_r^{\infty} \varrho_{kq}(r') r'^{-k+1} dr' \tag{37}$$

$$B_{kq}(r) = -\frac{4\pi e}{2k+1} \int_0^{r} \varrho_{kq}(r') r'^{k+2} dr' \tag{38}$$

we can rewrite (36) in the form

$$V_{kq}(r) = A_{kq}(r) r^k + B_{kq}(r) r^{-k-1}. \tag{39}$$

This formula relates the radial distribution of potential with the distribution of appropriate multipole charge $\varrho_{kq}(r')$.

Anisotropic spin-orbit coupling in a crystalline field for the case of l^N configuration is described by independent parameters $\overline{Q}_{kq}^n$ and $\overline{Q}_{kq}^{\omega}$, given by (21) and (22), respectively. These parameters are associated with functions

$$\frac{2m^2c^2}{\hbar^2} Q_{kq}^n(r) \equiv \frac{1}{r} \frac{dV_{kq}(r)}{dr} = kr^{k-2} A_{kq}(r) - (k+1) r^{-k-3} B_{kq}(r) \tag{40}$$

$$\frac{2m^2c^2}{\hbar^2} Q_{kq}^{\omega}(r) \equiv \frac{V_{kq}(r)}{r^2} = r^{k-2} A_{kq}(r) + r^{-k-3} B_{kq}(r). \tag{41}$$

By insertion of (40) and (41) into (21) and (22), respectively, we can in principle compute the independent parameters $\overline{Q}_{kq}^n$ and Q_{kq}^{ω}, provided we know the multipole charge distribution $\varrho_{kq}(r')$ and the radial wave function $R_{nl}(r)$. According to (37), we can interpret the terms

containing $A_{kq}(r)$ as an effect arising from charges beyond electrons of the unfilled l^N shell of the central ion, *i.e.* charges of surrounding ligands and, possibly, external closed shells of the central ion (*e.g.* $5s^25p^6$ shells in the case of rare earth ions). Similarly, the terms containing $B_{kq}(r)$ can be interpreted as an effect of internal charges, *i.e.* of that part of the ligand charge which penetrates into the region occupied by the l^N electrons as well as of the charge of the nucleus and internal closed shells (these shells contribute to $B_{kq}(r)$ for $k > 0$ also, by way of the polarization induced by ligands).

It is well known that, in crystal field theory, one cannot use the purely electrostatic model based on formula (33) (see *e.g.* [8], p. 213), because the interaction of central ion electrons with ligands cannot be fully replaced by an electric field as given by (3). It is necessary to account for electrostatic exchange interactions between the electrons of the central ion and those of the ligands. Hence, the crystal field parameters $\overline{V}_{kq}^{\text{expt}}$, computed from experimentally known optical spectra, cannot be identified with the quantities

$$\overline{V}_{kq} = \langle nl|V_{kq}(r)|nl\rangle \tag{42}$$

but should be considered as effective parameters which describe not only purely electrostatic effects but also covalency and overlapping effects (*e.g.* in the rare earth salts V_{kq}^{expt} can differ from $\overline{V}_{kq}$ even by one order of magnitude). It is noteworthy that these limitations connected with crystal field theory do not concern the spin-orbit coupling considered in the present paper. This follows from the obvious statement that, by Eq. (1), the spin-orbit interaction depends only on the electrostatic influence of neighbourhood on a moving electron, but does not depend — as a one-particle interaction — on any exchange effects. Relativistic exchange effects could be related with magnetic two-particle interactions, which we shall discuss briefly in the following Section.

Let us now consider the simplest, though often used model of a crystal field, namely the point charge model. For this case we can obtain the parameters $\overline{Q}_{kq}^n$ and $\overline{Q}_{kq}^{\omega}$ as simple functions of quantities whose numerical values are well known.

The point charge model assumes that the crystal field is produced by point charges placed at the centres of ligand ions, outside the region occupied by l^N electrons. Hence the charge density can be written as

$$\varrho(\boldsymbol{r}') = \varrho_0(r') + \sum_i \tilde{q}_i \delta(\boldsymbol{r}' - \boldsymbol{r}_i), \tag{43}$$

where $\varrho_0(r')$ is the density of the central ion charge (having spherical symmetry), $\tilde{q}_i$ — an effective charge of the i-th ligand at $\boldsymbol{r}_i$. Moreover, it assumes that, for every i,

$$r_i > r_{nl} \tag{44}$$

where r_{nl} denotes the radius of the region at l^N electrons. The multipole charges corresponding to the distribution (43) are given by

$$\varrho_{kq}(r') \equiv (-1)^{k-q} \int_0^{2\pi} d\varphi \int_0^{\pi} \varrho(r') Y_{-q}^{(k)}(\vartheta', \varphi') \sin \vartheta' d\vartheta'$$

$$= 2\pi^{1/2} \varrho_0(r') \delta_{k,0} + (-1)^{k-q} \sum_i \frac{2\tilde{q}_i}{r_i^2} (r' - r_i) Y_{-q}^{(k)}(\vartheta_i, \varphi_i). \tag{45}$$

Substituting (45) into (37) and (38), we obtain (for $r < r_{nl}$)

$$A_{kq}(r) = \frac{-8\pi^{3/2}e}{2k+1}\,\delta_{k,0}\int_r^\infty \varrho_0(r')r'dr' + (-1)^{k-q+1}\,\frac{8\pi e}{2k+1}\sum_i \frac{\tilde{q}_i}{r_i^{k+1}}\,Y_{-q}^{(k)}(\vartheta_i,\varphi_i) \tag{46}$$

and

$$B_{kq}(r) = \frac{-8\pi^{3/2}e}{2k+1}\,\delta_{k,0}\int_0^r \varrho_0(r')\,r'dr'. \tag{47}$$

Hence, for $k > 0$, the coefficients A_{kq} do not depend on r, and the B_{kq} vanish. Inserting (46) and (47) into (39) and then (39) into (42), we obtain the well-known relation

$$\overline{V}_{kq} = A_{kq}\langle nl|r^k|nl\rangle. \tag{48}$$

Similarly, inserting (40) and (41) into (21) and (22), respectively, we obtain

$$\overline{Q}_{kq}^n = \frac{\hbar^2}{2m^2c^2}\,kA_{kq}\,\langle nl\,|r^{k-2}|\,nl\rangle \tag{49}$$

$$\overline{Q}_{kq}^\omega = \frac{\hbar^2}{2m^2c^2}\,A_{kq}\,\langle nl|r^{k-2}|\,nl\rangle. \tag{50}$$

Thus, we can evaluate the parameters $\overline{Q}_{kq}^n$ and $\overline{Q}_{kq}^\omega$ which determine the anisotropic spin--orbit coupling in a crystal field, provided we know the coefficients A_{kq} and the quantum--mechanical averages $\langle r^k\rangle_{nl}$.

By (48), (49) and (50), we obtain

$$\frac{\overline{Q}_{kq}^\omega}{\overline{V}_{kq}} = \frac{\overline{Q}_{kq}^n}{k\overline{V}_{kq}} = \frac{\hbar^2}{2m^2c^2}\,\frac{\langle nl\,|r^{k-2}|\,nl\rangle}{\langle nl\,|r^k|\,nl\rangle}. \tag{51}$$

Since, according to Ref. [9], the $\langle nl|r^k|nl\rangle$ expressed in units of a_B^k (a_B — the Bohr radius) are of the order of unity, the ratio (51) can be evaluated as

$$\frac{\overline{Q}_{kq}^\omega}{\overline{V}_{kq}} \sim \frac{A_c^2}{8\pi^2 a_B^2} \approx 0.2661\cdot 10^{-4}. \tag{52}$$

Hence one can anticipate the effect of anisotropic spin-orbit coupling in a crystal field to be about 10^4 times smaller than the electrostatic effect of this crystal field. The influence of this interaction on the observed splitting of free ion energy levels in a crystal field is very small compared with the electrostatic interaction, and is thus very difficult to detect experimentally. Nevertheless, there is one interesting exception, namely the S terms, which are not split by (3) in the first order of perturbation theory. We shall discuss this case in detail in a subsequent paper [10].

4. *Two-body spin-dependent interactions*

In the quasirelativistic description of a system of N electrons, it is necessary to take into account, in addition to one-body spin-orbit coupling, the so-called magnetic two-body interactions [2, 4]. Among these, spin-dependent are only the spin-spin and spin-other orbit interactions, the energies of which are given by:

$$H_{SS} = \frac{e^2\hbar^2}{2m^2c^2} \sum_{i\neq j}^{N} r_{ij}^{-3} \{\boldsymbol{s}_i \cdot \boldsymbol{s}_j - 3r_{ij}^{-2}) (\boldsymbol{s}_i \cdot \boldsymbol{r}_{ij}) (\boldsymbol{s}_j \cdot \boldsymbol{r}_{ij})\} \tag{53}$$

$$H_{SOO} = \frac{e^2\hbar^2}{2m^2c^2} \sum_{i\neq j}^{N} r_{ij}^{-3} (\boldsymbol{r}_{ij} \wedge \boldsymbol{p}_i) \cdot (\boldsymbol{s}_i + 2\boldsymbol{s}_j) \tag{54}$$

where $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$ is the vector operator of mutual position of the i-th and j-th electrons. Blume and Watson [2] have shown that these interactions contribute strongly to the isotropic spin-orbit coupling constant (this constant corresponds to $\bar{Q}^n_{00}$ in our notation). Simple symmetry considerations indicate, however, that neither H_{SS} nor H_{SOO} can contribute to $\bar{Q}^n_{kq}$, $\bar{Q}^\omega_{kq}$ for $k > 0$. Namely, it is easily checked that both Hamiltonians commute with the total angular momentum operator $\boldsymbol{J}$ for the considered system of N electrons:

$$[H_{SS}, \boldsymbol{J}^2] = [H_{SOO}, \boldsymbol{J}^2] = 0 \tag{55}$$

$$[H_{SS}, J^z] = [H_{SOO}, J^z] = 0 \tag{56}$$

though they do not commute with $\boldsymbol{L}$ and $\boldsymbol{S}$ separately; hence, they exhibit spherical symmetry, whereas the one-particle operator H_{SO} given by (4) has a symmetry lower than spherical when any $k > 0$ term is non-zero. Consequently, two-body interaction does not alone split the free ion energy levels in crystals and does not lead to the above-mentioned contribution. These interaction can, however, lead to a contribution to general splitting by interfering with the crystal field in the second and higher orders of perturbation theory.

A stricter theory of interaction of the l^N central ion electrons with ligands should take into account two-body relativistic effects, such as interaction of the spin a central ion electron with the orbit of a ligand electron, *etc.* Such interactions, after appropriate averaging over states of ligands, can also lead to contributions to the parameters of anisotropic spin-orbit coupling for $k > 0$. Such contributions are a counterpart of those to V_{kq} mentioned in the preceding Section, which are related with electrostatic exchange effects with ligand electrons. In the present paper, we neglect such effects and restrict ourselves to crystal field theory, where interaction with ligands is replaced by a purely electrostatic field.

5. *Final remarks and conclusions*

In the present paper, we derived the one-particle anisotropic spin-orbit interaction Hamiltonian for an N-electron system in a crystal field having any point group symmetry. We moreover expressed the matrix elements of this Hamiltonian in the basis of arbitrary l^N configuration states as known functions of independent radial parameters. As shown here,

such an interaction leads to a splitting of free ion energy levels, similar to splitting by the crystal field. Evaluation of the radial parameters in the point charge model of the crystal field leads to the conclusion that the contribution of these interaction to the total splitting is, in general, negligibly small. One can, however, expect the role of this interaction to increase considerably in the case of orbitally non-degenerate levels, since such levels are not split by the crystal field in the first order of perturbation theory.

According to the general formulas of Section 3, it can be concluded that the radial parameters describing the anisotropic spin-orbit coupling depend in a complicated way on the distribution of multipole charges and that this dependence is other than that of the usual crystal field parameters.

We use the concept of spin-orbit coupling in the so-called quasirelativistic approximation, where the states of an individual electron, as well as those of a system of N electrons are obtained by non-relativistic quantum-mechanical methods, replacing relativistic effects by additional terms in the Schrödinger Hamiltonian, such as spin-orbit, spin-spin coupling *etc.* According to Refs [2, 3, 4], such an approximation differs from a strictly relativistic description by quantities of order $(v/c)^2$, where v is the mean velocity of an electron. A different approach is due to Wybourne [11], who considered a relativistic electron *i.e.* one whose wave function obeys Dirac's rather than Schrödinger's equation in a central field perturbed by a crystal field, and showed that the crystal field leads to spin-dependent effects. Wybourne formally generalized the results for one electron by using the concept of the so-called "relativistic LS states" introduced by Sandars and Beck [12]. In this formalism, the matrix elements of spin-dependent interactions are functions of relativistic radial parameters. In our opinion, both Wybourne's and our approach describe the same physical phenomenon. A detailed comparison of the assumptions and results of two approaches will be the subject of a separate paper.

APPENDIX A

Derivation of formulas for the invariants $G_n(k, k', l)$, $G_\omega(k, k', l)$

In order to derive Eqs (26)–(30) from (24) and (25), it is convenient to compute the matrix elements $(l||\Theta(A, a, k)^{(k')}||l)$ given by (12), as well-defined functions of l and k. Using the well-known formulas for the matrix elements of $\boldsymbol{w}_a^{(1)}$ (see Eqs (31) and (32) of Ref. [1]), the formulas appropriate for the $6j$ Wigner symbols [13], and the relation

$$\frac{(l \,||\, C^{(k_A)} \,||\, l-1)}{(l \,||\, C^{(k_A)} \,||\, l+1)} = \left(\frac{(2l-1)\,(2l-k_A+1)\,(2l+k_A+2)}{(2l+3)\,(2l+k_A+1)(2l-k_A)} \right)^{1/2} \tag{A1}$$

which can be easily obtained from the formula for a reduced matrix element of spherical harmonics (see *e.g.* [6]), we can perform analytically the summation in (12) and express $(l||\Theta(A, a, k)^{(k')}||l)$ by $(l||C^{(k_A)}||l+1)$ (l'' in (12) runs over $l-1$, $l+1$ only). The results are assembled in Table II. For the case $k' = k$, on substitution of the appropriate quantities from this Table into (24) and (25) and using the relation

$$\frac{(l \,||\, C^{(k+1)} \,||\, l+1)}{(l \,||\, C^{(k-1)} \,||\, l+1)} = \left(\frac{(k-1)\,(k+1)\,(2l-k+2)\,(2l+k+2)}{k(k+2)\,(2l-k+1)\,(2l+k+3)} \right)^{1/2} \tag{A2}$$

which can be derived similarly to (A1), we immediately obtain (26). Similarly, for $k' = k+1$, we obtain

$$G_n(k, k+1, l) = -\left(\frac{2\cdot 3\,(k+1)\,(2k+3)}{2k+1}\right)^{1/2}\begin{Bmatrix}1 & 1 & 1\\ k & k+1 & k+1\end{Bmatrix}(l\,||\,[Y^{(k+1)}\times\nabla^{*(1)}]^{(k+1)}||\,l) \tag{A3}$$

and for $k' = k-1$

$$G_n(k, k-1, l) = -\left(\frac{2\cdot 3(2k-1)}{2k+1}\right)^{1/2}\begin{Bmatrix}1 & 1 & 1\\ k & k-1 & k-1\end{Bmatrix}(l\,||\,[Y^{(k-1)}\times\nabla^{*(1)}]^{(k-1)}||\,l). \tag{A4}$$

The expressions for G_ω for these two cases are given by (29) and (30), respectively. Introducing the appropriate formulas for the $6j$ Wigner symbols from [13] into (A3) and (A4), we obtain (27) and (28), respectively.

TABLE II

Expressions for $(l||[Y^{k_A}\times \boldsymbol{w}_a^{(1)}]^{(k')}||l)/(l||Y^{k_A}||l+1)$ as functions of l, k

k	k'	$\boldsymbol{w}_a = \boldsymbol{n}$	$\boldsymbol{w}_a = \nabla^*$
$k+1$	k	$\left(\frac{(2l+1)(k+2)(2l+k+3)}{(2l+3)(2k+3)(2l+k+2)}\right)^{1/2}$	$-\frac{k}{2}\left(\frac{(2l+1)(k+2)(2l+k+3)}{(2l+3)(2k+3)(2l+k+2)}\right)^{1/2}$
	$k+1$	0	$\frac{1}{2}\left(\frac{(2l+1)(2l-k)(2l+k+3)}{(2l+3)}\right)^{1/2}$
$k-1$	$k-1$	0	$\frac{1}{2}\left(\frac{(2l+1)(2l-k+2)(2l+k+1)}{2l+3}\right)^{1/2}$
	k	$\left(\frac{(2l+1)(k-1)(2l-k+2)}{(2l+3)(2k-1)\,(2l-k+1)}\right)^{1/2}$	$\frac{k+1}{2}\left(\frac{(2l+1)(k-1)(2l-k+2)}{(2l+3)(2k-1)(2l-k+1)}\right)^{1/2}$

APPENDIX B

Relations between the invariants G_n, G_ω and the one-electron coefficients of Ref. [1]

In order to check the numerical computations related to the evaluation of matrix elements of $\hat{H}_{SO}$ (4), it is convenient to derive certain relations between the coefficients of this paper and those of the preceding one [1]. In particular, these relations enable us to verify anew the Tables of both papers. Since the coefficients $G_n(k, k', l)$ and $G_\omega(k, k', l)$ are, according to (27)–(30), proportional to $(l||\Theta(A, a, k)^{(k')}||l)$, and the coefficients $g_{n\omega}(j, j', k)$, $g_{\omega\omega}(j, j', k)$ of [1] are expressed* by $S(j, j', k, A, a)$ see (53) and (54) of [1], we give here only the relation between $(l||\Theta(A, a, k)^{(k')}||l)$ and $S(j, j', k, A, a)$.

* In the right-hand term of formula (50) of Ref. [1] (which provides the definition of $S(j, j', k, A, a)$) an additional factor $2^{-1}\pi^{-1/2}$ should appear. Moreover, in Tables II and III of [1], the constant $\pi^{-1/2}$ is omitted everywhere.

The reduced matrix element of $\Gamma^{(k)}_{Aa\,q}$ in the basis of one-electron $|l_j m_j\rangle$ states is, according to (10), equal to

$$(lj||\Gamma^{(k)}_{Aa\,q}||l'j') = [(2j+1)(2j'+1)(2k+1)]^{1/2}\times$$
$$\times\sum (l||\Theta(A,a,k)^{(k')}||l')(\tfrac{1}{2}||\mathbf{s}^{(1)}||\tfrac{1}{2}) \begin{Bmatrix} l & \frac{1}{2} & j \\ l' & \frac{1}{2} & j' \\ k' & 1 & k \end{Bmatrix}. \tag{B1}$$

Comparing (B1) with (49) of [1], we obtain for $l = l' = 3$ (the f^1 case)

$$\sum_{k'} (3||\Theta(A,a,k)^{(k')}||3) \begin{Bmatrix} 3 & \frac{1}{2} & j \\ 3 & \frac{1}{2} & j' \\ k' & 1 & k \end{Bmatrix} = (-1)^{j+j'}\cdot 2(3\cdot 7)^{1/2} S(j,j',k,A,a). \tag{B2}$$

By means of this formula, the Tables of [1] and the column $l = 3$ of Table I of the present paper have been checked.

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