

Spin-Orbit and Spin-Other-Orbit Interaction in Diatomic Molecules

L. VESETH

Institute of Physics, University of Oslo, Oslo 3, Norway

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The correct relativistic Pauli-Breit Hamiltonian for spin-orbit and spin-other-orbit interaction in atoms is adapted for use with diatomic molecules. The relation between the fundamental molecular Hamiltonian thus obtained and the phenomenological operator $AL \cdot S$ is investigated, and some theoretical considerations are made concerning Van Vleck's hypothesis of pure precession. A formula convenient for *ab initio* calculation of the spin-orbit coupling constant is derived, assuming the electronic functions to be represented by a Slater determinant of one-electron molecular orbitals. Finally a method for theoretical determination of the sign of the spin-orbit coupling constant is demonstrated by several examples.

Der korrekte Pauli-Breit-Hamiltonoperator für die verschiedenen Spin-Bahn-Wechselwirkungen in Atomen wird der Anwendung bei zweiatomigen Molekülen angepaßt. Die Beziehung zwischen den so erhaltenen molekularen Hamiltonoperator und dem phänomenologisch begründeten Operator $AL \cdot S$ wird untersucht, und einige Überlegungen zur Van Vleckschen Hypothese reiner Präzession werden dargestellt. Eine Formel für die *ab initio*-Bestimmung der Spin-Bahn-Kopplungs-Konstanten wird abgeleitet, wobei angenommen wird, daß die elektronische Wellenfunktion durch eine Slater-determinante dargestellt wird, die aus Ein-Elektronen-MO's aufgebaut ist. Schließlich wird eine Methode zur theoretischen Bestimmung des Vorzeichens der Spin-Bahn-Kopplungs-Konstanten an verschiedenen Beispielen demonstriert.

L'hamiltonien relativiste de Pauli-Breit pour l'interaction spin-orbite dans les atomes est adapté pour être utilisé dans les molécules diatomiques. La relation entre l'hamiltonien moléculaire ainsi obtenu et l'opérateur phénoménologique $AL \cdot S$ est étudiée, et l'on effectue certaines considérations théoriques sur l'hypothèse de précession pure de Van Vleck. On déduit une formule convenable pour le calcul *ab initio* de la constante de couplage spin-orbite en supposant les fonctions électroniques représentées par un déterminant de Slater. Enfin, plusieurs exemples permettent de démontrer une méthode pour la détermination théorique du signe de la constante de couplage spin-orbite.

1. Introduction

By using the simple spin-orbit coupling operator $AL \cdot S$ Hill and Van Vleck [1] and Van Vleck [2] obtained theoretical results for diatomic molecules agreeing very well with spectroscopic measurements. This is true both for the diagonal elements describing the spin-orbit splitting, and for the off-diagonal elements contributing to the A -doubling and accounting for the spin-splitting in multiplet Σ states. The justification for the operator $AL \cdot S$ is, however, rather phenomenological, and is mainly supported by the analogy with atomic systems. An investigation of the relation between this simple operator and a more fundamental expression for the spin-orbit Hamiltonian therefore seems worthwhile. It might be thought that the one-centre operator L (the total electronic angular momentum) should not be applicable to a two-centre system like a diatomic molecule. The

interesting thing is however, that molecular states often behave as if they could be ascribed a good quantum number for the operator L^2 (pure precession). This experimental fact has as yet been given very little theoretical support.

A usual starting point for calculations concerning spin-orbit interaction seems to be the Pauli approximation to the Dirac equation. This leads to a spin-orbit interaction operator of the form

$$H_{\text{SO}} = \sum_i \frac{\hbar}{(2\mu c)^2} \sigma_i (\text{grad } U_i \times p_i),$$

where σ_i denotes the Pauli matrices, U_i the potential and p_i the momentum of electron number i . This type of Hamiltonian expressed in cylindrical coordinates has for instance been used by Kovacs [3] in calculating perturbations between states of different multiplicity. Semi empirical calculations of the spin-orbit coupling constant based on a similar Hamiltonian have been carried out by Heilmann and Ballhausen [4] and by Ishiguro and Kobori [5].

An obvious shortcoming of using the operator H_{SO} for more than one electron, is the potential U_i which in this case has to be replaced by a mean potential, i.e. a one-electron operator, while a two-electron operator is of course necessary for a proper description of the interelectronic interaction.

As in the work by Blume and Watson for atoms [6] and by Fontana for the H_2 molecule [7], the starting point will therefore here be the more fundamental Pauli-Breit Hamiltonian [8] for spin-orbit and spin-other-orbit interaction. However, this atomic operator must first be adapted for use with diatomic molecules.

In the last part of this paper the emphasis will be put on deriving formulae convenient for *ab initio* calculation of the spin-orbit coupling constant for diatomic molecules. These *ab initio* expressions are then used to demonstrate by some simple examples how the sign of the spin-orbit coupling constant may be determined for a given configuration.

2. The Pauli-Breit Hamiltonian

For the spin-orbit and spin-other-orbit interactions of an atom Bethe and Salpeter [8] and Slater [9] have given the following general Hamiltonian operator (see also Blume and Watson [6])

$$H_{\text{SO}} = \frac{\alpha^2}{2} \sum_i \frac{Z}{r_i^3} l_i \cdot s_i - \frac{\alpha^2}{2} \sum_{i,j(i \neq j)} \left(\frac{r_{ij}}{r_{ij}^3} \times p_i \right) \cdot (s_i + 2s_j). \quad (1)$$

The summations are here to be extended over all electrons, p_i , l_i and s_i are respectively the momentum, the angular momentum and the spin of electron number i , the distance between electron number i and the nucleus is designated by r_i and r_{ij} is the interelectronic distance. As usual α is the fine structure constant (Hartree atomic units) and Z gives the nuclear charge. The physical interpretation of the individual terms of Eq. (1) is rather clear. The first sum represents the spin-orbit coupling of each electron in the Coulomb field of the nucleus. In the second double summation the first term with the factor s_i , is the spin-orbit

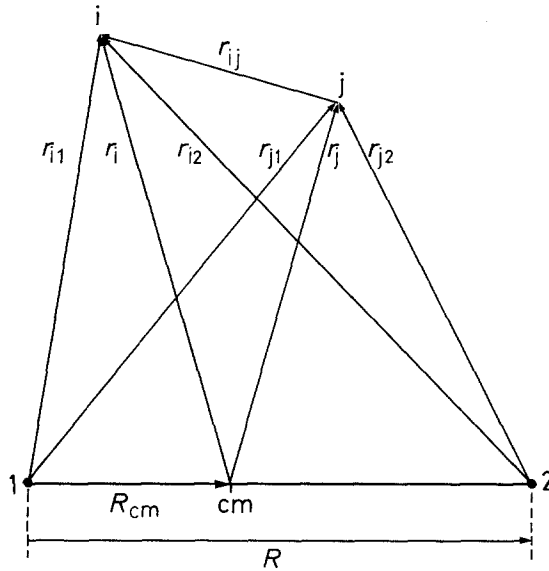


Fig. 1. Distance vectors in a diatomic molecule

coupling of electron i in the Coulomb field of electron j , and the second term with the factor s_j is due to the interaction of the spin of electron j with the orbital current of electron i .

The general formula (1) for spin-orbit and spin-other-orbit interaction may also be extended to molecules, with the one modification that all nuclei must be taken into account when calculating the first sum. The following treatment will, however, be restricted to diatomic molecules.

To derive a suitable expression for the spin-orbit and spin-other-orbit Hamiltonian for a diatomic molecule, Fig. 1, defining some distance vectors that are to be used, will be of great use. In Fig. 1 the two nuclei are numbered 1 and 2, CM denotes the centre of mass of the nuclei and two arbitrary electrons are numbered i and j . The following connections between the vectors are taken straight out of the figure

$$\begin{aligned} \mathbf{r}_{ij} &= \mathbf{r}_{i1} - \mathbf{r}_{j1} = \mathbf{r}_{i2} - \mathbf{r}_{j2}, \\ \mathbf{r}_{i1} &= \mathbf{R} + \mathbf{r}_{i2}, \\ \mathbf{r}_{j1} &= \mathbf{R} + \mathbf{r}_{j2}. \end{aligned} \quad (2)$$

By introducing the angular momenta

$$\mathbf{l}_{i1} = \mathbf{r}_{i1} \times \mathbf{p}_i, \quad \mathbf{l}_{i2} = \mathbf{r}_{i2} \times \mathbf{p}_i, \quad (3)$$

the first sum of Eq. (1) may be replaced by the two sums (one for each nucleus)

$$H_{\text{SON}} = \frac{\alpha^2}{2} \sum_i \frac{Z_1}{r_{i1}^3} (\mathbf{r}_{i1} \times \mathbf{p}_i) \cdot \mathbf{s}_i + \frac{\alpha^2}{2} \sum_i \frac{Z_2}{r_{i2}^3} (\mathbf{r}_{i2} \times \mathbf{p}_i) \cdot \mathbf{s}_i. \quad (4)$$

It will here be desirable to introduce the total angular momentum of the electrons, but this seems to be a bit complicated due to the lack of a unique origin. In a diatomic molecule only the component of the total electronic angular momentum along the molecular axis is quantized, and this component is independent of the origin as long as this is chosen on the internuclear axis. The introduction of the total electronic angular momentum in the description of the spin-orbit and spin-other-orbit coupling of a diatomic molecule, will therefore require the common origin of angular momenta to be placed somewhere on the internuclear axis, and a natural choice seems to be the centre of mass of the nuclei.

Noticing that the vector \mathbf{R}_{CM} fixes the centre of mass (CM) relative to nucleus 1, the following relations are obvious by considering Fig. 1.

$$\begin{aligned} \mathbf{r}_{i1} &= \mathbf{R}_{\text{CM}} + \mathbf{r}_i, & \mathbf{r}_{i2} &= \mathbf{R}_{\text{CM}} - \mathbf{R} + \mathbf{r}_i \\ \mathbf{r}_{j1} &= \mathbf{R}_{\text{CM}} + \mathbf{r}_j, & \mathbf{r}_{j2} &= \mathbf{R}_{\text{CM}} - \mathbf{R} + \mathbf{r}_j. \end{aligned} \quad (5)$$

The angular momentum of the electrons relative to CM will now be defined by

$$\mathbf{l}_i = \mathbf{r}_i \times \mathbf{p}_i. \quad (6)$$

This definition may look a bit artificial for electrons in the inner filled shells, which even for molecules may be considered as "belonging" to one of the nuclei. It is however, at this moment unnecessary to worry about the physical interpretation of Eq. (6); it should rather be considered as a mathematical entity to be introduced in the fundamental spin-orbit Hamiltonian. The derivation which follows will make it clear that the choice of reference point in Eq. (6) can have no influence on the results as long as it is chosen to be on the internuclear axis.

By using Eqs. (1), (4), (5), and (6) the following general expression for the spin-orbit and spin-other-orbit Hamiltonian for a diatomic molecule may be derived in terms of the electronic angular momenta referred to the centre of mass of the nuclei

$$\begin{aligned} H_{\text{SO}} &= \sum_{i,j} \xi(i,j) \mathbf{l}_i \cdot \mathbf{s}_j \\ &+ \frac{\alpha^2}{2} \left[Z_1 \sum_i \frac{\mathbf{R}_{\text{CM}} \times \mathbf{p}_i}{|\mathbf{R}_{\text{CM}} + \mathbf{r}_i|^3} \cdot \mathbf{s}_i + Z_2 \sum_i \frac{(\mathbf{R}_{\text{CM}} - \mathbf{R}) \times \mathbf{p}_i}{|\mathbf{R}_{\text{CM}} - \mathbf{R} + \mathbf{r}_i|^3} \cdot \mathbf{s}_i \right] \\ &+ \frac{\alpha^2}{2} \sum_{i,j(i \neq j)} \frac{\mathbf{r}_j \times \mathbf{p}_i}{|\mathbf{r}_{ij}|^3} (\mathbf{s}_i + 2\mathbf{s}_j). \end{aligned} \quad (7)$$

Eq. (7) has been abbreviated by using the symbol $\xi(i,j)$ which has the meaning

$$\begin{aligned} \xi(i,i) &= \frac{\alpha^2}{2} \left(\frac{Z_1}{|\mathbf{R}_{\text{CM}} + \mathbf{r}_i|^3} + \frac{Z_2}{|\mathbf{R}_{\text{CM}} - \mathbf{R} + \mathbf{r}_i|^3} - \sum_{j(j \neq i)} \frac{1}{r_{ij}^3} \right), \\ \xi(i,j) &= - \frac{\alpha^2}{r_{ij}^3} \quad (i \neq j). \end{aligned} \quad (8)$$

$\xi(i,i)$ and $\xi(i,j)$ ($i \neq j$) are evidently independent of the choice of origin for the angular momenta as the only relevant distances are the distance between electron and nucleus and the interelectronic distance.

The last three sums of Eq. (7) are of special interest. By taking the mean value over the electronic state, the first two of these sums will obviously vanish because the mean value of the momentum of an electron in a bound state is zero. The same argument may also be applied to show that even the last sum in Eq. (7) will vanish in the mean (see also Fontana [7]).

The only part of the Hamiltonian (7) that "survives" when taking the mean value over the electronic state is therefore

$$H'_{so} = \sum_{i,j} \xi(i,j) \mathbf{l}_i \cdot \mathbf{s}_j. \quad (9)$$

Even in this operator (9) only the components of \mathbf{l}_i and \mathbf{s}_j along the molecular axis (z -components) will on an average give a contribution different from zero. Since these components, just as $\xi(i,j)$, are independent of where on the internuclear axis the origin of angular momenta is situated, it follows that the operator (9) too is independent of this choice. The conclusion is therefore that the Hamiltonian (9), which corresponds to the experimental spin-orbit splitting, may be given in terms of the angular momenta of the electrons referred to a common arbitrary origin on the internuclear axis.

The contribution to the Hamiltonian (9) due solely to the electronic charges is given by

$$H'_{soe} = -\frac{\alpha^2}{2} \sum_i \left(\sum_{j(j \neq i)} \frac{1}{r_{ij}^3} \right) \mathbf{l}_i \cdot \mathbf{s}_i - \alpha^2 \sum_{i,j(i \neq j)} \frac{1}{r_{ij}^3} \mathbf{l}_i \cdot \mathbf{s}_j. \quad (10)$$

The first of these sums represents the contribution to the spin-orbit interaction due to the Coulomb field of the electrons, while the second sum is the spin-other-orbit interaction.

An expression of the type $\sum_i \xi(r_i) \mathbf{l}_i \cdot \mathbf{s}_i$ is often taken as a fundamental form of the spin-orbit Hamiltonian (for instance Kovacs [3], Heilmann and Ballhausen [4]), with the underlying assumption that each electron moves in a field axially symmetric about the internuclear axis. The simple and general Hamiltonian (9) is, however, derived without this symmetry assumption, and in addition the spin-other-orbit interaction is included by the terms $\xi(i,j) \mathbf{l}_i \cdot \mathbf{s}_j$ for $i \neq j$.

3. Matrix Elements of the Spin-Orbit and Spin-Other-Orbit Hamiltonian

In connection with perturbation calculations, both diagonal and off-diagonal matrix elements of the spin-orbit and spin-other-orbit Hamiltonian will be needed. Off-diagonal elements enter particularly in the calculation of Λ -doubling and spin-splitting (Σ states), while the diagonal elements are responsible for the spin-orbit splitting. Calculations in this field have hitherto been carried out by assuming the rather phenomenological form $A \mathbf{L} \cdot \mathbf{S}$ for the spin-orbit coupling operator (Hill and Van Vleck [1], Van Vleck [2]). \mathbf{L} and \mathbf{S} denote here the total electronic angular momentum and the total electronic spin respectively, A is usually called the spin-orbit coupling constant. It should be of some interest to see how these matrix elements come out if one takes the general Hamiltonian (7) as the starting point. The electronic eigenfunctions will further be specified to be Hund's case (a)

functions, as this is the type of function used by Van Vleck [2]. Hund's case (a) functions may be written symbolically in the form

$$\Psi_a = |qA\Sigma S\rangle, \quad (11)$$

where A is the quantized component along the internuclear axis of the total electronic angular momentum, S denotes the total electronic spin with component Σ along the molecular axis, and q represents the other quantum numbers necessary to specify the electronic state.

As a first approximation only the first sum of the operator (7) (i.e. Eq. (9)) will be considered, as the treatment of this part can serve as a demonstration of the method of calculation. An off-diagonal element of this operator is given by

$$M_1 = \langle qA\Sigma S | \sum_{i,j} \xi(i,j) l_i \cdot s_j | q'A'\Sigma'S' \rangle, \quad (12)$$

which may be rewritten as

$$M_1 = \langle qA\Sigma S | \sum_{i,j} \xi(i,j) [\frac{1}{2}l_{i+}s_{j-} + \frac{1}{2}l_{i-}s_{j+} + l_{iz}s_{jz}] | q'A'\Sigma'S' \rangle. \quad (13)$$

Using the Wigner-Eckart theorem (see for instance Tinkham [10]) this expression is further transformed into

$$\begin{aligned} M_1 = & \langle qA | \sum_{i,j} \frac{1}{2} \xi(i,j) (qS \| s_j \| q'S) l_{i+} | q'A' \rangle \langle \Sigma S | S_- | \Sigma'S' \rangle \\ & + \langle qA | \sum_{i,j} \frac{1}{2} \xi(i,j) (qS \| s_j \| q'S) l_{i-} | q'A' \rangle \langle \Sigma S | S_+ | \Sigma'S' \rangle \\ & + \langle qA | \sum_{i,j} \xi(i,j) (qS \| s_j \| q'S) l_{iz} | q'A' \rangle \langle \Sigma S | S_z | \Sigma'S' \rangle. \end{aligned} \quad (14)$$

In Eq. (14) the reduced matrix element $(qS \| s_j \| q'S)$ has been introduced (see Tinkham [10]) by the relation $\langle q\Sigma S | s_{j+} | q'\Sigma'S' \rangle = (qS \| s_j \| q'S) \langle \Sigma S | S_+ | \Sigma'S' \rangle$. l_{i+} , l_{i-} , s_{j+} and s_{j-} denote the usual step up and step down operators. The electronic functions have further been simplified by writing $|qA\rangle$ (q orbital quantum numbers only) and $|q\Sigma S\rangle$ (q spin quantum numbers only) depending on the type of quantum numbers of importance for the actual matrix element.

The rather complicated Eq. (14) may be written in a more compact form by defining the components of a vector operator A in the following way

$$\begin{aligned} A_+ &= \sum_{i,j} \xi(i,j) (qS \| s_j \| q'S) l_{i+}, \\ A_- &= \sum_{i,j} \xi(i,j) (qS \| s_j \| q'S) l_{i-}, \\ A_z &= \sum_{i,j} \xi(i,j) (qS \| s_j \| q'S) l_{iz}. \end{aligned} \quad (15)$$

According to the usual rules for matrix multiplication Eq. (14) is transformed into

$$\begin{aligned} M_1 = & \langle qA\Sigma S | \frac{1}{2} A_+ S_- | q'A'\Sigma'S' \rangle \\ & + \langle qA\Sigma S | \frac{1}{2} A_- S_+ | q'A'\Sigma'S' \rangle \\ & + \langle qA\Sigma S | A_z S_z | q'A'\Sigma'S' \rangle. \end{aligned} \quad (16)$$

Returning to the general Hamiltonian (7), it is easily seen that the last three sums hitherto neglected may be treated in exactly the same way as the term $\sum_{i,j} \xi(i,j) \mathbf{l}_i \cdot \mathbf{s}_j$. Since these sums only contain scalar products between orbital- and spin vectors, they may be transformed into an analogue of Eq. (16), the only difference lies in a redefinition of the operator A . Therefore, if the vector operator A is chosen in the prescribed way, Eq. (16) will give the most general expression for the matrix elements (for $\Delta S = 0$) of the general spin-orbit and spin-other-orbit Hamiltonian (7).

The matrix element of the phenomenological operator $AL \cdot S$ corresponding to Eq. (16) will be

$$\begin{aligned} & \langle qA\Sigma S | AL \cdot S | q'A'\Sigma'S \rangle \\ &= \langle qA\Sigma S | \frac{1}{2} AL_+ S_- | q'A'\Sigma'S \rangle \\ &+ \langle qA\Sigma S | \frac{1}{2} AL_- S_+ | q'A'\Sigma'S \rangle \\ &+ \langle qA\Sigma S | AL_z S_z | q'A'\Sigma'S \rangle. \end{aligned} \quad (17)$$

A comparison between Eq. (16) and Eq. (17) now shows that these expressions are formally identical. It is thereby proved that the simple replacement operator $AL \cdot S$ in the perturbation calculation (assuming $\Delta S = 0$) will give energy formulae of exactly the same form as the general Hamiltonian (7). The only difference will appear in the definition and meaning of the usually experimentally determined parameters entering into these formulae.

The results given by Van Vleck [2] are simplified by noticing that the operators AL_x and AL_y are equivalent in all respects. This simplification is also possible for the matrix element (16) since the operators A_x and A_y are equivalent in the same way as AL_x and AL_y .

4. Considerations Concerning the Hypothesis of Pure Precession

The derivation leading up to Eq. (16) gives a definition of the operator A that will be too complicated for quantitative computations of for instance the spin-orbit coupling constant. In what follows the calculations therefore will be of a less general kind, i.e. some restrictions will be put on the electronic eigenfunctions $|qA\Sigma S\rangle$, while still retaining Hund's case (a) structure.

As is well-known, the square of the total electronic angular momentum L^2 will generally not be quantized in a diatomic molecule, but what is equally well-known, is that molecular states often behave as if their total electronic angular momentum could be ascribed a good quantum number (pure precession). A natural procedure would therefore be to try to replace the orbital electronic function $|qA\rangle$ by a series expansion in eigenfunctions of L^2 , i.e. functions of the type $|qAL\rangle$. With reference to Mustelin [11] the following starting point will be adopted

$$|qA\rangle = \sum_L a_{qAL} |qAL\rangle (L \geq A). \quad (18)$$

Let R be the operator reflecting the electrons in a plane containing the molecular axis. R operating on the function $|qA\rangle$ gives the result

$$R|qA\rangle = f|q-A\rangle, \quad (19)$$

where f is a phase factor. Since the operation of reflecting the electrons is the same as changing the coordinate system from a right handed to a left handed or vice versa, the expansion coefficients for $|q-A\rangle$ must be the same as those for $|qA\rangle$, i.e.

$$|q-A\rangle = \sum_L a_{qAL} |q-AL\rangle. \quad (20)$$

According to Mustelin [11] the following relation holds true

$$R|qAL\rangle = (-1)^{-L+A} w |q-AL\rangle, \quad (21)$$

where w is a phase factor depending only on quantum numbers contained in the symbol q . Applying R to Eq. (18) and taking into account Eqs. (19), (20) and (21), it follows that in the series expansion (18) the values of L must be either all even or all odd. Otherwise an alternating sign would occur in the expansion of the function $|q-A\rangle$, disagreeing with Eq. (20).

Reintroducing the spin quantum numbers into the function designation, the functions that from now on will be used are obtained

$$|qA\Sigma S\rangle = \sum_L a_{qAL} |qAL\Sigma S\rangle \quad (L \geq A). \quad (22)$$

It should here be restated that L is to run over even numbers only or odd numbers only.

Rather than using the functions (22) to calculate matrix elements of the general Hamiltonian (7), the procedure will here be simplified by taking instead the operator (9) as the starting point. This is correct for diagonal elements, and is in fact no restriction for off-diagonal elements ($\Delta S = 0$) because the treatment could easily be extended to the Hamiltonian (7), just as in the derivation of Eq. (16).

The matrix element to be calculated is the following

$$\begin{aligned} M_2 &= \langle qA\Sigma S | \sum_{i,j} \xi(i,j) \mathbf{l}_i \cdot \mathbf{s}_j | q'A'\Sigma'S \rangle \\ &= \sum_{L,L'} a_{qAL}^* a_{q'A'L} \langle qAL\Sigma S | \sum_{i,j} \xi(i,j) \mathbf{l}_i \cdot \mathbf{s}_j | q'A'L\Sigma'S \rangle. \end{aligned} \quad (23)$$

It is now assumed that L and L' both are to run over even values only or both over odd values only. This must obviously be the case if a relation of pure precession (or approximate pure precession) exists between the states $|qA\Sigma S\rangle$ and $|q'A'\Sigma'S\rangle$. Due to this restriction the only possible values of L' in Eq. (23) are $L' = L$, $L \pm 2$, $L \pm 4$, etc., and as the operator involved in the matrix element (23) consists of vector operators, only $L' = L$ can give a non-vanishing contribution to the matrix element. According to this statement Eq. (23) is transformed into

$$M_2 = \sum_L a_{qAL}^* a_{q'A'L} \langle qAL\Sigma S | \sum_{i,j} \xi(i,j) \mathbf{l}_i \cdot \mathbf{s}_j | q'A'L\Sigma'S \rangle. \quad (24)$$

The Wigner-Eckart theorem may now be used both for the orbital- and spin part of the operator, and the result is

$$M_2 = \sum_L \langle AL\Sigma S | L \cdot S | A' L \Sigma' S \rangle a_{qAL}^* a_{q'A'L} \cdot \sum_{i,j} (qL \parallel \xi(i,j) l_i \parallel q' L) \cdot (qS \parallel s_j \parallel q' S). \quad (25)$$

$(qL \parallel \xi(i,j) l_i \parallel q' L)$ and $(qS \parallel s_j \parallel q' S)$ are the reduced matrix elements of the orbital- and spin parts of the operator.

It is convenient to make Eq. (25) more compact by writing

$$M_2 = \sum_L \langle AL\Sigma S | A(L) L \cdot S | A' L \Sigma' S \rangle \quad (26)$$

and

$$A(L) = a_{qAL}^* a_{q'A'L} \sum_{i,j} (qL \parallel \xi(i,j) l_i \parallel q' L) (qS \parallel s_j \parallel q' S). \quad (27)$$

It should now be pointed out that the general Hamiltonian (7) would lead to a result differing from Eq. (25) or Eq. (26) only by some additional orbital reduced matrix elements coming from the last three sums of Eq. (7), and this would only alter the definition of the parameter $A(L)$. The matrix element (26) may therefore be ascribed to the general Hamiltonian (7), however, with attention called to the assumption immediately following Eq. (23). Comparing Eq. (26) with the corresponding matrix element of the simple operator $AL \cdot S$, the close similarity is easily recognized. The only difference is the summation over the quantum number L in Eq. (26), and that the parameter $A(L)$ corresponding to the spin-orbit coupling constant A , is now a function of L .

Because of their correspondence to the experimental spin-orbit splitting, the diagonal elements are of special interest. These elements are obtained by putting $q' = q$, $A = A'$ and $\Sigma = \Sigma'$ into Eqs. (26) and (27). It is further recognized that in this case $\langle AL\Sigma S | L \cdot S | AL\Sigma S \rangle = \langle A\Sigma | L_z S_z | A\Sigma \rangle$, i.e. the diagonal elements are independent of the quantum number L , and therefore the diagonal matrix element (26) may be written

$$M_3 = \langle A\Sigma | L_z S_z | A\Sigma \rangle \cdot \sum_L A(L). \quad (28)$$

All that is now needed to bring the diagonal matrix element (28) of the Hamiltonian (7) into agreement with the corresponding element of the operator $AL \cdot S$, is the replacement of the spin-orbit coupling constant A by $\sum_L A(L)$, i.e. $A = \sum_L A(L)$.

The united atom eigenfunctions corresponding to a Hamiltonian H_0 will also be of the form $|qAL\rangle$. If the molecule is to be formed by separating the nuclei, a perturbation operator V must be added to the united atom Hamiltonian H_0 , and a particular united atom function (zero order) $|qAL_0\rangle$ may be mixed with functions of other L -values, i.e. $|qAL_0\rangle' = \sum_L a_{qAL} |qAL\rangle$. The coefficients a_{qAL} ($L \neq L_0$) are determined by matrix elements of the type $\langle qAL_0 | V | qAL \rangle$.

The perturbation operator V may be expanded in a series of spherical tensors of increasing rank. Due to the restriction $L = L_0, L_0 \pm 2$, etc. the first rank tensor

gives no contribution to the off-diagonal coefficients mixing states of unequal L . In a domain where the convergence of the series for V is rapid, good quantum numbers L are therefore to be expected. As the convergence for V is assumed to be rapid especially for small internuclear distances, this gives theoretical support for the experimental fact that the pure precession relation is as a rule best fulfilled for molecules of small internuclear distance, for instance for the hydrides.

As an illustration of this convergence, consider the perturbing operator V for a diatomic molecule composed of atoms of very unequal nuclear charges (for instance hydrides). Placing the origin in the nucleus of highest charge number, the first and second rank contributions to V are obtained by a Taylor series expansion to the second order,

$$V \sim - \sum_i \frac{1}{r_i} \left(\frac{Rz_i}{r_i^2} + \frac{3}{2} \frac{R^2 z_i^2}{r_i^4} \right).$$

In this case it is thus easily seen that a small internuclear distance R (i.e. $R \ll r_i$) leads to a rapid convergence of the series.

For large internuclear distances the configuration interaction hitherto neglected, may also lead to a mixing of states of unequal L . This is due to the phase factor w in Eq. (21) which may differ for different configurations, allowing some configurations with odd values of L and other with even values. If however, the included configurations contain all even values of L or all odd values, nothing concerning the quantization of L will be altered. The derivation of the formulae (26) and (28) could even be generalized by taking this type of configuration interaction into account, and the only alteration of the formulae would be an additional sum running over q and q' .

5. Formulae for *ab initio* Calculation of the Spin-Orbit Coupling Constant

So far the purpose of this paper has been to investigate the relations between the phenomenological spin-orbit coupling operator $AL \cdot S$ and the fundamental Pauli-Breit Hamiltonian (1). This investigation has also made possible some considerations concerning the theoretical basis of the hypothesis of pure precession.

In the treatment to follow the emphasis will be put on obtaining "practical" formulae for the spin-orbit coupling constant, i.e. formulae convenient for qualitative as well as quantitative considerations. As the formulae (27) and (28) don't look very useful for this purpose, a fresh start will be made from the Hamiltonian (9). Since only diagonal elements now need to be considered, this is a proper Hamiltonian. Only the components of l_i and s_j along the molecular axis (z -components) contribute to the diagonal elements, and the treatment will therefore be restricted to these components. The electronic eigenfunctions will from now on be designated by $|q\Lambda\Sigma S\rangle$, and this implies that no quantization of the total electronic angular momentum is assumed. The derivation of the desired formulae requires a further specification of these functions.

As a first starting point electronic functions in the form of a simple product of one-electron molecular orbitals (Hartree-product) will be assumed, each MO being an eigenfunction for l_{iz} and s_{jz} with eigenvalues m_i and s_j respectively.

The diagonal element of the Hamiltonian (9) may then be written

$$M_4 = \frac{\langle \Lambda \Sigma | L_z S_z | \Lambda \Sigma \rangle}{\Lambda \Sigma} \sum_{i,j} \langle q \Lambda \Sigma S | \xi(i,j) l_{iz} s_{jz} | q \Lambda \Sigma S \rangle. \quad (29)$$

The factor $\frac{\langle \Lambda \Sigma | L_z S_z | \Lambda \Sigma \rangle}{\Lambda \Sigma} = 1$ has been included for a simple identification of the spin-orbit coupling constant which, with reference to Eq. (28), is now given by

$$A = \frac{1}{\Lambda \Sigma} \sum_{i,j} \langle q \Lambda \Sigma S | \xi(i,j) l_{iz} s_{jz} | q \Lambda \Sigma S \rangle. \quad (30)$$

Eq. (30) is easily transformed into

$$A = \frac{1}{\Lambda \Sigma} \sum_{i,j} \langle q \Lambda \Sigma S | \xi(i,j) | q \Lambda \Sigma S \rangle m_i \sigma_j. \quad (31)$$

As will be seen later it is convenient to rewrite Eq. (8) as follows

$$\begin{aligned} \xi(i, i) &= \eta(i) + \frac{1}{2} \sum_{j(j \neq i)} \xi(i, j), \\ \eta(i) &= \frac{\alpha^2}{2} \left(\frac{Z_1}{|\mathbf{R}_{cm} + \mathbf{r}_i|^3} + \frac{Z_2}{|\mathbf{R}_{cm} - \mathbf{R} + \mathbf{r}_i|^3} \right). \end{aligned} \quad (32)$$

If the molecular orbital for electron number i with quantum numbers m_i and σ_i is denoted by $\phi_i(i)$, the following result is obtained

$$\langle q \Lambda \Sigma S | \xi(i, i) | q \Lambda \Sigma S \rangle = \alpha_i + \frac{1}{2} \sum_{j(j \neq i)} \gamma_{ij}, \quad (33)$$

where α_i and γ_{ij} are to be replaced by

$$\begin{aligned} \alpha_i &= (\phi_i(i), \eta(i) \phi_i(i)) \\ \gamma_{ij} &= (\phi_i(i) \phi_j(j), \xi(i, j) \phi_i(i) \phi_j(j)) \quad (i \neq j). \end{aligned} \quad (34)$$

The following final expression for the spin-orbit coupling constant given by Eq. (31) is then obtained

$$A = \frac{1}{\Lambda \Sigma} \left[\sum_i \left(\alpha_i + \frac{1}{2} \sum_{j(j \neq i)} \gamma_{ij} \right) m_i \sigma_i + \sum_{i,j(i \neq j)} \gamma_{ij} m_i \sigma_j \right]. \quad (35)$$

Remembering that the formulae (30) and (31) contain two-electron operators, the formula (35) obtained by using Hartree-functions is expected to be a rather rough approximation. However, it turns out that the one-electron contributions, since they are due to the nuclear charges, outweigh the two-electron terms. So the rather simple formula (35) ought to be of some value for qualitative considerations or rough quantitative calculations. If a higher degree of accuracy is required, the electronic functions should be replaced by an antisymmetric product of one-electron molecular orbitals (Hartree-Fock functions), i.e. a Slater determinant. To obtain eigenfunctions of the squared total electronic spin S^2 , linear combinations of Slater determinants corresponding to the same value of Λ and Σ will generally

be required. Quite often, however, it happens that Λ and Σ have the maximum value possible according to the assumed configuration, and in this case only one Slater determinant is available for the construction of the proper electronic function.

Assuming the electronic function to be given by just one Slater determinant, a formula for the spin-orbit coupling constant A will now be derived by calculating the diagonal matrix elements of the Hamiltonian (9). The treatment of this matrix element may be simplified by first considering the case $i=j$, giving the result

$$\langle q\Lambda\Sigma S | \sum_i \xi(i, i) l_{iz} s_{iz} | q\Lambda\Sigma S \rangle = \sum_k \beta_k m_k \sigma_k. \quad (36)$$

β_k is here to be replaced by

$$\beta_k = \alpha_k + \frac{1}{2} \sum_{l(l \neq k)} (\gamma_{kl} - \gamma'_{kl} \delta_{\sigma_k \sigma_l}). \quad (37)$$

α_k and γ_{kl} are defined as indicated by Eq. (34), while the exchange integral γ'_{kl} is defined by

$$\gamma'_{kl} = (\phi_k(i) \phi_l(j), \xi(i, j) \phi_l(i) \phi_k(j)) \quad (i \neq j), \quad (38)$$

$\phi_k(i)$ being the one-electron molecular orbital corresponding to the eigenvalues m_k and σ_k of the operators l_{iz} and s_{iz} .

The case $i \neq j$ leads in the same way to

$$\langle q\Lambda\Sigma S | \sum_{i, j(i \neq j)} \xi(i, j) l_{iz} s_{jz} | q\Lambda\Sigma S \rangle = \sum_{k, l(k \neq l)} (\gamma_{kl} - \gamma'_{kl} \delta_{\sigma_k \sigma_l}) m_k \sigma_l, \quad (39)$$

γ_{kl} and γ'_{kl} being defined by Eqs. (34) and (38). Again including the factor $\frac{\langle \Lambda\Sigma | L_z S_z | \Lambda\Sigma \rangle}{\Lambda\Sigma} = 1$, the following result is obtained

$$\begin{aligned} & \langle q\Lambda\Sigma S | \sum_{i, j} \xi(i, j) l_{iz} s_{jz} | q\Lambda\Sigma S \rangle \\ &= \frac{\langle \Lambda\Sigma | L_z S_z | \Lambda\Sigma \rangle}{\Lambda\Sigma} \left[\sum_k \beta_k m_k \sigma_k + \sum_{k, l(k \neq l)} (\gamma_{kl} - \gamma'_{kl} \delta_{\sigma_k \sigma_l}) m_k \sigma_l \right]. \end{aligned} \quad (40)$$

The spin-orbit coupling constant A is accordingly given by

$$A = \frac{1}{\Lambda\Sigma} \left[\sum_k \beta_k m_k \sigma_k + \sum_{k, l(k \neq l)} (\gamma_{kl} - \gamma'_{kl} \delta_{\sigma_k \sigma_l}) m_k \sigma_l \right]. \quad (41)$$

Some conclusions concerning the contribution to the spin-orbit coupling constant from electrons in filled shells are implicit in the formula (41). First consider the summation

$$\sum_k \beta_k m_k \sigma_k = \sum_k \alpha_k m_k \sigma_k + \frac{1}{2} \sum_k \sum_{l(l \neq k)} (\gamma_{kl} - \gamma'_{kl} \delta_{\sigma_k \sigma_l}) m_k \sigma_k.$$

Noticing that the parameters α_k , γ_{kl} and γ'_{kl} all are independent of spin, it follows that in the summations $\sum_k \alpha_k m_k \sigma_k$ and $\sum_k \sum_{l(l \neq k)} \gamma_{kl} m_k \sigma_k$ it will be sufficient to let k run over unfilled shells only. This means that the interaction between the nuclear charges and electrons in filled shells gives no contribution to the spin-orbit

coupling constant, since the nuclear contribution is represented by the sum $\sum_k \alpha_k m_k \sigma_k$.

In the summation $\sum_k \left(\sum_{l(l \neq k)} \gamma'_{kl} \delta_{\sigma_k \sigma_l} \right) m_k \sigma_k$, however, k must be extended also to filled shells if there are electrons in unfilled shells. This is due to the spin dependency introduced by the factor $\delta_{\sigma_k \sigma_l}$, and is closely analogous to a similar result in the Hartree-Fock theory (spin-polarized Hartree-Fock).

In Eq. (41) there now remains the sum $\sum_{k, l(k \neq l)} (\gamma_{kl} - \gamma'_{kl} \delta_{\sigma_k \sigma_l}) m_k \sigma_l$. Here it is easily verified that the sum of all terms where both k and l refer to filled shells, will vanish. This is, however, not the case when one of the indices k or l refers to an unfilled shell. The interaction between electrons in filled shells and electrons in unfilled shells therefore can contribute to the spin-orbit coupling constant via these terms.

A comparison between Eqs. (35) and (41) shows that Eq. (35) obtained by using Hartree-functions, differs from Eq. (41) mainly in that it lacks the exchange integrals. The terms containing the parameters γ_{kl} and γ'_{kl} represent the electronic screening of the nuclear charges, and must therefore be assumed to give a very significant contribution to the spin-orbit coupling constant. Another result is that the exchange integral γ'_{kl} tends to be of the same order of magnitude as the direct integral γ_{kl} (see Walker and Richards [12]). Thus the approximation obtained by neglecting the exchange terms will be rather poor.

The formula (41) should be convenient for *ab initio* calculations of the spin-orbit coupling constant. The problems involved in these calculations will lie mainly in carrying out the integrations necessary to determine the parameters α_k , γ_{kl} and γ'_{kl} . A strict determination of the parameters γ_{kl} and γ'_{kl} requires that some hard two-centre integrals of an operator of the type $\frac{1}{r_{12}^3}$ be carried out, but it has turned out it is often a fairly good approximation to neglect these integrals (see Walker and Richards [12]). With this approximation the remaining integrals are taken care of by standard procedures. An extensive treatment of two-electron spin-orbit integrals have been given by Matcha *et al.* [14].

The one-electron molecular orbitals $\phi_k(i)$ may for instance be replaced by self consistent LCAO-MO's (Roothaan functions). Hitherto self consistent LCAO-MO's have only been calculated for electronic states representable by one Slater determinant. So at present the fact that one is restricted to using one Slater determinant by formula (41) gives rise to no practical limitations.

6. The Sign of the Spin-Orbit Coupling Constant

In fact very little material concerning the theoretical determination of the sign of the spin-orbit coupling constant in diatomic molecules has been published. The only discussion of the subject found by the present author is in one of Mulliken's early papers [13]. But as the latter relies upon a rather intuitive model of the coupling, a renewed discussion based on a more fundamental model seems worthwhile. The inspiration for this investigation is that the sign of the coupling constant can usually be unambiguously determined experimentally.

Therefore the existence of a clear theoretical relation between sign and configuration will help a great deal in the determination of the latter.

The investigation will be based on Eq. (41) for the spin-orbit coupling constant. As the task is now to study a qualitative feature, there is no point in retaining all the terms of Eq. (41), and some approximations in the remaining terms will also be convenient. The last summation in Eq. (41) representing the spin-other-orbit coupling, will be neglected since it is found in practice that the spin-orbit coupling (the first summation) outweighs the spin-other-orbit coupling, and thereby determines the sign of the coupling constant. So the starting point will be

$$A = \frac{1}{\Lambda\Sigma} \sum_k \beta_k m_k \sigma_k, \quad (42)$$

where the summation is assumed to run over unfilled shells only. As a final reasonable approximation the values of β_k are assumed to be the same for equivalent electrons.

By introducing the new symbols a_k and b_k defined by $a_k = m_k/\Lambda$ and $b_k = \sigma_k/\Sigma$, Eq. (42) can be rewritten

$$A = \sum_k \beta_k a_k b_k. \quad (43)$$

The point in introducing the symbols a_k and b_k is that the following simple relations

$$\sum_k a_k = 1, \sum_k b_k = 1, \quad (44)$$

are valid even when the summations are restricted to unfilled shells only. Of course it is assumed here that Λ and Σ are both different from zero, otherwise there would be no spin-orbit splitting.

To illustrate how the sign of the coupling constant may be determined from Eqs. (43) and (44) and the Pauli principle, it is best to consider some examples.

Assume first that there is only one electron outside closed shells, and that this electron has a quantum number $m_k = m_1$ different from zero. Formula (43) gives directly $A = \beta_1 a_1 b_1$, and the relation (44) leads to $a_1 b_1 > 0$, i.e. the result is $A > 0$ if the parameter β_1 is positive.

Two equivalent electrons outside closed shells lead either to $\Lambda = 0$ or $\Sigma = 0$, or both $\Lambda = 0$ and $\Sigma = 0$, and thereby no spin-orbit splitting.

The case of three equivalent electrons in addition to filled shells is a more interesting example. With a suitable choice of indices the following relations must exist according to the Pauli principle, $a_1 = a_2 = -a_3$ and $b_1 = -b_2$. By relation (44) it then follows that $a_3 < 0$ and $b_3 > 0$, and Eq. (43) gives $A = \beta_3 a_3 b_3$, i.e. $A < 0$ for positive value of β_3 .

Assuming a positive value of the parameter β (the value of β will of course depend on the configuration) it is thus proved that the value of the spin-orbit coupling constant will be positive when there is one electron outside closed shells, i.e. when a shell is less than half full. Similarly it is also proved that a negative value of the coupling constant is obtained when there are three equivalent electrons outside closed shells, i.e. when a shell is more than half full. This result

is easily seen to be in close agreement with the corresponding one for atoms (Hund's third rule), the difference is, however, that in atoms this rule is restricted to the ground state.

For the sake of completeness it should be pointed out that the electronic states so far treated, are all correctly described by just one Slater determinant.

Some important configurations with more than one unfilled shell will also be included among the examples.

The configuration $\sigma\pi$ implies $a_1 = 0$ and $a_2 = 1$. The possibility $b_1 = -b_2$ leads to $\Sigma = 0$ and is therefore uninteresting, while $b_1 = b_2 > 0$ gives $A = \beta_2 a_2 b_2 > 0$ for $\beta_2 > 0$. For a positive value of β_2 the ${}^3\Pi$ state derivable from the configuration $\sigma\pi$ therefore must be regular (i.e. positive value of A), and similarly the configuration $\sigma\delta$ leads to a regular 3A state, etc.

The configuration $\sigma\pi^3$ may be treated in just the same way as the configuration π^3 , leading to a negative value of the coupling constant, and the same applies to the configuration $\sigma\delta^3$, etc.

The configuration $\pi^2\pi$ yields a more complicated example. A division into two cases is here convenient

- | | |
|-----------------------------------|--------------------------------------|
| 1) $a_1 = a_2,$ | 2) $a_1 = -a_2 \rightarrow a_3 > 0,$ |
| $b_1 = -b_2 \rightarrow b_3 > 0,$ | a) $b_1 = b_2,$ |
| a) $a_3 > 0,$ | b) $b_1 = -b_2 \rightarrow b_3 > 0.$ |
| b) $a_3 < 0,$ | |

The fact that some of the states derivable from the configuration $\pi^2\pi$ must be represented by a linear combination of several Slater determinants, prohibits a straightforward determination of the sign of the coupling constant by means of the relations (43) and (44). The case 1a) above leads to just one ${}^2\Phi$ state, while the case 2a) gives a ${}^4\Pi$ state among others. However, each of these two states can be represented by just one Slater determinant (for the ${}^4\Pi$ state $\Sigma = \frac{3}{2}$ is assumed), and for both states Eq. (43) gives $A = \beta_3 a_3 b_3$. In view of 1a) and 2a) above this leads to $A > 0$ for positive values of β_3 .

The other states derivable from the configuration $\pi^2\pi$ are all of the ${}^2\Pi$ type. To obtain eigenfunctions for the operator S^2 these ${}^2\Pi$ states must be represented by a linear combination of four Slater determinants (three functions for $S = \frac{1}{2}$ and one for $S = \frac{3}{2}$). It is therefore impossible to make any conclusions regarding the sign of the coupling constant until the proper linear combinations are determined.

For a three-electron system Kovács [3] has given eigenfunctions for S^2 , and he concludes that for the $\pi^2\pi$ configuration two of the ${}^2\Pi$ states are inverted and the third regular. The simple considerations of Mulliken [13] in this case lead to the same result, but as eigenfunctions for S^2 are not taken into account, this method should be viewed with suspicion in the general case.

An example of another character is formed by the 2A states derived from the configuration $\sigma\pi^2$. In this case $a_1 = 0$, $a_2 = a_3 > 0$, $b_2 = -b_3$ and $b_1 > 0$, leading to $A = 0$ by use of Eq. (43). However, a small negative value of A is usually observed for this type of 2A states (Lefebvre-Brion and Bessis [16]), especially in light diatomic molecules. This non-zero value of A is assumed to be caused

by the terms neglected in Eq. (43), i.e. the last sum in Eq. (41) representing the spin-other-orbit coupling (Mulliken [13]). Neglecting the contributions from filled shell electrons, the result is $A = (2\gamma_{21} - \gamma'_{21})a_2b_1$. The negative value of $2\gamma_{21}$ (see Eqs. (8), (34) and (38)) is assumed to outweigh the exchange integral γ'_{21} , and remembering that a_2b_1 is positive as stated above, this leads to a negative value of the coupling constant.

In the formula (37) for β_k the positive parameter α_k represents the contribution from the nuclear charges, while the summation represents the electronic contribution. The assumption of a positive value for β_k is now based on another assumption, namely that the nuclear contribution outweighs the electronic. This assumption is mainly backed up by the fact that in atoms the spin-orbit splitting is usually very well described by the operator $\sum_i \frac{1}{2\mu^2 c^2} \frac{1}{r_i} \frac{\partial U(r_i)}{\partial r_i} \mathbf{l}_i \cdot \mathbf{s}_i$ (see Condon and Shortley [15]). For all reasonable potentials $\frac{\partial U(r_i)}{\partial r_i}$ will be positive, reflecting the domination of the nuclear charges.

7. Conclusion

As pointed out in the introduction, a main purpose of this paper has been to investigate the relations between the simple phenomenological operator $AL \cdot S$ and a more fundamental expression for the spin-orbit Hamiltonian. This fundamental Hamiltonian is taken to be the Pauli-Breit operator (1) for spin-orbit and spin-other-orbit coupling.

Considering diagonal elements only (electronic mean values), the operator (9) has been derived from the Hamiltonian (1) without any approximations. The formula (9) shows that for mean values the "intuitive" operator $\sum_{i,j} \xi(i,j) \mathbf{l}_i \cdot \mathbf{s}_j$ for spin-orbit and spin-other-orbit coupling is a strict consequence of the Pauli-Breit operator.

For diagonal as well as off-diagonal elements ($\Delta S = 0$) the formula (16) implies the interesting conclusion that the fundamental Pauli-Breit operator leads formally to exactly the same results as the simple operator $AL \cdot S$. However, some of the parameters entering the calculation need to be redefined.

In view of the experimentally well-verified hypothesis of pure precession, a further approach towards the operator $AL \cdot S$ seems interesting. The point is then to introduce the total electronic angular momentum L , and this is obtained by the series expansions (18) and (22). By noticing that in these series expansions the values for L must be either all even or all odd, theoretical support has been given to the hypothesis of pure precession for molecules of small internuclear distance.

It should be further pointed out that even if the pure precession relation is fulfilled, since the value of the entering parameter $A(L)$ is determined by the off-diagonal element (27), it will differ from the corresponding experimentally determined value of the spin-orbit coupling constant. This distinction should be taken into account when disagreements between experimental values and pure precession values are considered, for instance in the A -doubling parameters.

The other main purpose of this paper has been the derivation of formulae convenient for *ab initio* calculations of the spin-orbit coupling constant. The most significant result here is given by Eq. (41). By the derivation of Eq. (41) the electronic functions are assumed to be properly represented by just one Slater determinant of molecular orbitals. Since this is a correct assumption for most of the actual molecular states, and since the actual electronic functions (Roothaan functions) hitherto calculated are of this form, the possibility of taking linear combinations of Slater determinants into account is not considered.

As a by-product of Eq. (41) a discussion of the sign of the spin-orbit coupling constant has been included. This discussion verifies the main results of Mulliken's simple considerations [13], and leads to an analogy to Hund's third rule for atoms. For states that must be represented by a linear combination of more than one Slater determinant, Mulliken's results, however, seem to be doubtful.

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Professor Leif Veseth
Institute of Physics
Universitetet I Oslo
P.O. Box 1048, Blindern
Oslo 3, Norway