On the Investigation of Pseudoscalar Molecular Properties and Polynomial Approximations According to Ruch and Schönhofer

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Analytic chirality functions in one or more ligand parameters representing pseudoscalar molecular properties are shown to decompose as linear combinations in the elementary chirality functions of a suitable module basis. The implications of this decomposition for an approximation ansatz are considered.

Key words: Chirality functions – Theory of invariants – Homochirality

1. Introduction

When one seeks to employ chirality functions F (comp. [1, 2]) in one or more ligand parameters in investigations of pseudoscalar molecular properties, two types of problems occur.

1) By working out a classical or quantum-mechanical theory of the chiral property under consideration, the analytic form of the desired chirality function is obtained – usually a power series in one or more independent parameters $\lambda, \mu, \ldots$. By a suitable definition of the molecular frame and attached ligands the parameters $\lambda, \mu, \ldots$ may be taken as ligand parameters if one restricts the investigation to molecules of an identical molecular frame. One may then choose a suitable centre $\lambda^0, \mu^0, \ldots$ of the expansion such that an abitrary order of the expansion represents, by itself, a chirality function with respect to the group of symmetry transformations of the molecular frame. When the symmetry of each contribution in the expansion is taken into consideration, the actual computation of the function F is greatly eased (comp. [3, 4]).

2) If a suitable amount of measurements of a chiral property have been performed without an available theoretical description of that property [5–7], one may tentatively make the hypothesis that only one "semi-empirical" ligand parameter λ needs to be considered – while having no accurate idea of the physical meaning of λ. Then one may try to find an approximation of the chirality function F by basing

the analysis on a polynomial of suitable symmetry in λ. But from the lack of knowledge as to the physical quality of λ one is not able to choose with certainty a centre of reference (centre of expansion in λ) such that the λ-polynomial is a good approximation and carries the highest possible symmetry. That is, one cannot be sure from the outset that the required λ-polynomial will turn out to be a chirality function with respect to the group of symmetry transformations of the molecular frame.

2. Chirality Functions in a Single Parameter

Let there be given a class of molecules with the class defining property of a common achiral molecular frame with n sites for ligands. The group G of the symmetry transformations of the frame consists of the rotations and reflections which leave the frame invariant. Further, let there be given a set of "structureless" ligands characterized by a single parameter λ such that an arbitrary point $\lambda = (\lambda_1, \ldots, \lambda_n)$ of an n-dimensional parameter space defines a molecule of the class by a suitable numbering of the n sites of the molecular frame. Thus, the symmetry operations of the frame applied to an actual molecule can be represented by some permutations of the ligands, i.e. by some permutations of the n coordinates $\lambda_1, \ldots, \lambda_n$ representing the ligands. The permutations form a group S which is a homomorphic image of G (comp. [1]).

Now, if F is a pseudoscalar property of the molecules of the class, a measurement of F furnishes an identical result for molecules which differ only in a rotation of the frame, whereas a measurement of enantiomers (molecules which differ in a reflection of the frame) furnishes a result which is identical in absolute value but differs as to the sign.

Let $F(\lambda) = F(\lambda_1, \ldots, \lambda_n)$ be an analytic function on the n-dimensional parameter space such that F represents the pseudoscalar property F:

$$F \longrightarrow F(\lambda) = F(\lambda_1, \ldots, \lambda_n) \tag{1}$$

Then F is a chirality function. The symmetry operations of the molecular frame applied to an actual molecule then become permutations of the arguments of F. Particularly, permutations which represent a rotation of the frame leave F invariant whereas F changes sign under permutations which represent a reflection of the molecular frame.

Because of its analyticity, one can expand F about a point $\lambda^0 = (\lambda_1^0, \ldots, \lambda_n^0)$ of the parameter space in an n-fold Taylor series. One gets in the usual notation:

$$F(\lambda^0 + \lambda) = F(\lambda^0) + \sum_q^{1, \infty} \frac{1}{q!} (\lambda, \mathrm{grad})^q F(\lambda) \big|_{\lambda = \lambda^0}$$

$$= F(\lambda^0) + \sum_q^{1, \infty} \frac{1}{q!} (\lambda, \mathrm{grad}_0)^q F(\lambda^0) \tag{2}$$

with

$$(\lambda, \text{grad})^q = \left(\lambda_1 \frac{\partial}{\partial \lambda_1} + \cdots + \lambda_n \frac{\partial}{\partial \lambda_n} \right)^q \tag{3}$$

$$(\lambda, \text{grad}_0)^q = \left(\lambda_1 \frac{\partial}{\partial \lambda_1^0} + \cdots + \lambda_n \frac{\partial}{\partial \lambda_n^0} \right)^q \tag{4}$$

The equation

$$F(\lambda) = F(\lambda_1, \ldots, \lambda_n) = 0 \tag{5}$$

defines the hypersurface of the zeros of F in the n-dimensional parameter space. On this hypersurface one finds zeros of F which represent achiral molecules and one may find zeros which represent chiral molecules. Achiral zeros of a chirality function – in contrast to chiral zeros – are a necessary consequence of the symmetry of the molecule as, for achiral molecules, a reflection of the frame represents a symmetry operation. Thus, all chirality functions of the class of molecules have in common the set of achiral zeros (taken as points in the parameter space). If λ^0 is an achiral zero, then for any analytic chirality function F:

$$F(\lambda^0 + \lambda) = \sum_q^{1, \infty} \frac{1}{q!} (\lambda, \text{grad}_0)^q F(\lambda^0) \tag{6}$$

For any order q of the Taylor expansion (6) the operator

$$(\lambda, \text{grad})^q \tag{7}$$

is totally symmetric with respect to permutations of the $\lambda_1, \ldots, \lambda_n$. Thus, the expression

$$(\lambda, \text{grad})^q F(\lambda) \tag{8}$$

represents a chirality function with respect to the molecular class under consideraation.

The symmetry of the particular molecule defined by the point $\lambda^0 = (\lambda_1^0, \ldots, \lambda_n^0)$ defines a certain subgroup G_0 $(G_0 \subset G)$ of the group G of symmetry operations of the frame and, in consequence, a certain subgroup S_0 $(S_0 \subset S)$ of the group S of permutations which represent the symmetry operations of the frame. Thus, the function:

$$F(\lambda^0 + \lambda) = F(\lambda_1^0 + \lambda^1, \ldots, \lambda_n^0 + \lambda_n) \tag{9}$$

is totally symmetric under the permutations of S_0 applied to $\lambda_1^0, \ldots, \lambda_n^0$. In consequence, $F(\lambda^0 + \lambda)$ is a chirality function of S_0 with respect to $\lambda_1, \ldots, \lambda_n$, that is, if the permutations of S_0 are applied to the increments $\lambda_1, \ldots, \lambda_n$. Thus, for any order q of the series expansion (6) the expression

$$(\lambda, \text{grad}_0)^q F(\lambda^0) \tag{10}$$

represents a rational integral chirality function in the increments $\lambda_1, \ldots, \lambda_n$ with respect to the permutation group S_0. The particular case when the actual molecule

given by $\lambda^0 = (\lambda_1^0, \ldots, \lambda_n^0)$ possesses the highest possible symmetry, namely the symmetry of the molecule frame, deserves special interest, as under these circumstances one obtains $S_0 = S$ and, in consequence, for any order q of the series expansion (6) the expression (10) represents by itself a rational integral chirality function with respect to the group S of permutations applied to the increments $\lambda_1, \ldots, \lambda_n$.
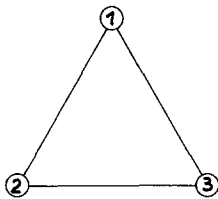
Example: Symmetry group C_{3v}.

Fig. 1.

The function

$$F(\lambda) = (\lambda_1 - \lambda_2)(\lambda_2 - \lambda_3)(\lambda_3 - \lambda_1) \tag{11}$$

is a chirality function for this molecular class. A Taylor series expansion about the achiral point

$$\lambda_1^0 = \lambda_2^0 \neq \lambda_3^0$$

leads to:

$$
\begin{aligned}
F(\lambda^0 + \lambda) =\ & (\lambda_2 - \lambda_1)(\lambda_1^0 - \lambda_3^0)^2 \\
& + (\lambda_2 - \lambda_1)(2\lambda_3 - \lambda_1 - \lambda_2)(\lambda_3^0 - \lambda_1^0) \\
& + (\lambda_2 - \lambda_1)(\lambda_3 - \lambda_2)(\lambda_3 - \lambda_1)
\end{aligned} \tag{12}
$$

Each order of the series expansion (12) represents a chirality function with respect to the symmetry group C_s of the molecules defined by $\lambda_1^0 = \lambda_2^0 \neq \lambda_3^0$. Only the achiral molecules given by $\lambda_1^0 = \lambda_2^0 = \lambda_3^0$ possess the full symmetry of the frame and in this case one simply gets in the above example:

$$F(\lambda^0 + \lambda) = (\lambda_2 - \lambda_1)(\lambda_3 - \lambda_2)(\lambda_3 - \lambda_1) \tag{13}$$

Chirality functions of polynomial form can be considered as relative invariants with the factor system $\{+1, -1\}$, with respect to the group S (or S_0) of permutations of the n independent parameters $\lambda_1, \ldots, \lambda_n$ (comp. [8]). Particularly, the factor $(+1)$ obtains for a permutation which represents a rotation, whereas the factor (-1) obtains for a permutation which represents a reflection. Totally symmetric polynomials are called "absolute invariants", with a factor system consisting of $(+1)$ only. The relative invariants (of a given factor system) form a so-called "R-module" [12] with respect to the ring of absolute invariants. By a theorem taken from the theory of invariants [8], the R-module of the relative invariants of any given factor system is "finitely generated" [12], i.e., there exists a finite module basis such that any relative invariant of the factor system may be represented by a linear combination in the elements of the basis with coefficients which are elements of the set of absolute invariants. Let $\{\chi_1, \ldots, \chi_m\}$ be the module basis of the rational integral chirality functions (with respect to S or S_0), then for any arbitrary rational integral chirality function $f = f(\lambda)$, one obtains:

$$f = t_1 \chi_1 + \cdots + t_m \chi_m \tag{14}$$

where $t_1, \ldots, t_m$ represent rational integral functions in the parameters $\lambda_1, \ldots, \lambda_n$, which are totally symmetric with respect to the permutations of S (or S_0). For a

chirality function $F(\lambda) = F(\lambda_1, \ldots, \lambda_n)$ which is analytic in the independent parameters $\lambda_1, \ldots, \lambda_n$, one therefore obtains:

$$F(\lambda) = T_1 \chi_1 + \cdots + T_m \chi_m \tag{15}$$

where $T_1, \ldots, T_m$ represent analytic functions in the parameters $\lambda_1, \ldots, \lambda_n$, which are totally symmetric with respect to the permutations of S (or S_0).

By a treatment which is generally applicable (comp. [8], p. 111), one can construct a finite module basis for the rational integral chirality functions of a permutation group S (or S_0). In general, though, a basis is obtained which is strongly redundant. In the individual case it thus seems more advisable to construct a module basis by starting from the chirality polynomials of lowest degree [1, 2] in λ and then to show completeness by complete induction.

As has been mentioned earlier, among the points of the hypersurface in the parameter space given by the relation

$$F(\lambda) = F(\lambda_1, \ldots, \lambda_n) = 0 \tag{16}$$

one finds achiral and, in general, chiral molecules. That is, the set of zeros of F contains a subset of those zeros which – representing achiral molecules – are completely determined by symmetry such that the set of common zeros of any system of chirality functions defined on the parameter space must necessarily contain the set of achiral zeros.

For a module basis $\{\chi_1, \ldots, \chi_m\}$ the set of the common zeros of the basis elements is called the "algebraic set" ("Nullstellengebilde") of the basis. The algebraic set is obtained by the intersection of the m-hypersurfaces

$$\chi_1 = 0, \ldots, \chi_m = 0 \tag{17}$$

in parameter space. Obviously, the algebraic set of $\chi_1, \ldots, \chi_m$ contains the minimal algebraic set which is just the set of the achiral zeros.

Let $\{\chi_1, \ldots, \chi_r\}$ be a selection of elements from a module basis where the algebraic set of the $\chi_1, \ldots, \chi_r$ is the set of the achiral zeros of the molecular class. Then, any chirality function χ vanishes in any of the points of the algebraic set of the $\{\chi_1, \ldots, \chi_r\}$. By Hilbert's Nullstellensatz [9] there exists a positive integer p so that for any rational integral chirality function χ one obtains:

$$\chi^p = h_1 \chi_1 + \cdots + h_r \chi_r \tag{18}$$

where $h_1, \ldots, h_r$ are some polynomials.

If P is the projection operator on the chiral representation, Q the projection operator on the symmetric representation of the permutation group S (resp. S_0), then one obtains:

$$P h_i \chi_i = \chi_i Q h_i = I_i \chi_i \tag{19}$$

where $I_i = Q h_i$, $i = 1, \ldots, r$, was introduced.

Putting

$$I_0 = -Q\chi^{p-1} = \begin{cases} 0 & \text{if } p \text{ is even} \\ -\chi^{p-1} & \text{if } p \text{ is odd} \end{cases} \tag{20}$$

one gets:

$$I_0\chi + I_1\chi_1 + \cdots + I_r\chi_r = 0 \tag{21}$$

In the case of $\{\chi_1, \ldots, \chi_r\}$ already representing a complete module basis, one may take $p = 1$ and $I_0 = -1$. Otherwise, the basis may permit so-called "syzygies", i.e. there may be rational integral absolute invariants $T_0, T_1, \ldots, T_r$, so that one obtains for the module basis $\{\chi_0, \chi_1, \ldots \chi_r, \ldots\}$:

$$T_0\chi_0 + T_1\chi_1 + \cdots + T_r\chi_r = 0 \tag{22}$$

The relation (22) is valid identically in the parameters $\lambda_1, \ldots, \lambda_n$. If syzygies exist, the decomposition of an arbitrary rational integral chirality function χ into a linear combination of basis elements is not unique.

From now on it is assumed that the algebraic set of the module basis $\{\chi_1, \ldots, \chi_m\}$ of the rational integral chirality functions is equal to the set of achiral zeros of the molecular class. Then, for any chiral molecule as a point λ in the parameter space, there exists a chirality function for which λ represents a chiral zero and there exist other chirality functions for which λ does not represent a chiral zero. For any analytic chirality function F decomposed according to (15)

$$F = T_1\chi_1 + \cdots + T_m\chi_m \tag{23}$$

the achiral zeros of F are fixed by the algebraic set of the elements $\chi_1, \ldots, \chi_m$ of the module basis, whereas the chiral zeros of F are determined by the analytic functions $T_1, \ldots, T_m$ which are totally symmetric with respect to the permutations of S (or S_0). There are, in other words, no chiral zeros of F predetermined by the algebraic set of the elements of the module basis. Two cases may now be considered:

a) The module basis of the chirality functions consists of a single element χ_1 only.
b) The module basis of the chirality functions consists of at least two elements χ_1, χ_2.

According to the assumption made above, the function χ_1 in case (a) can only have achiral zeros. A nontrivial chirality function χ changes sign on the (real) parameter space. Thus, in the n-dimensional real space the algebraic set is the hypersurface given by $\chi_1 = 0$, which divides the parameter space into open regions containing the chiral points, with boundaries consisting of the achiral points (comp. the classification of molecules according to the concept of homochirality [10, 11]). Case (a) is characteristic of molecular classes of category a in [10].

In case (b) the set of achiral zeros is the algebraic set of at least two polynomials, i.e. the intersection of at least two hypersurfaces in the (real) parameter space. Thus, the set of achiral zeros – being of a dimension of less than $(n-1)$ – does not divide the parameter space into open regions. In contrast to case (a), any continuous

chirality function necessarily possesses chiral zeros the position of which cannot be determined by symmetry arguments. Case (b) is characteristic of molecular classes of category b in [10].

Example: Symmetry group C_{2v}, molecular class of cat. (b).

Module basis $\{\chi_1, \chi_2)$ with

$$\chi_1 = \lambda_1 - \lambda_2 + \lambda_3 - \lambda_4 \tag{24}$$

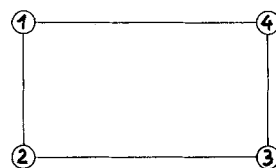$$\chi_2 = \lambda_1\lambda_3 - \lambda_2\lambda_4 \tag{25}$$

Fig. 2.

For the achiral points $\lambda_1 = \lambda_2 \neq \lambda_3 = \lambda_4$ one has:

$$\lim_{\lambda_3 \to \lambda_4} \left(\lim_{\lambda_1 \to \lambda_2} \frac{\chi_2}{\chi_1} \right) = \lambda_1 \tag{26}$$

$$\lim_{\lambda_1 \to \lambda_2} \left(\lim_{\lambda_3 \to \lambda_4} \frac{\chi_2}{\chi_1} \right) = \lambda_3 \tag{27}$$

Thus, the totally symmetric function χ_2/χ_1 is discontinuous at the achiral points $\lambda_1 = \lambda_2 \neq \lambda_3 = \lambda_4$ and a continuous transformation

$$\chi_2 = \frac{\chi_2}{\chi_1}\chi_1 \tag{28}$$

does not exist.

By complete induction it is shown that $\{\chi_1, \chi_2\}$ is a complete module basis.

To determine the common zeros of χ_1, χ_2, the following algebraic system of equations has to be investigated:

$$\chi_1 = \lambda_1 - \lambda_2 + \lambda_3 - \lambda_4 = 0 \tag{29}$$

$$\chi_2 = \lambda_1\lambda_3 - \lambda_2\lambda_4 = 0 \tag{30}$$

The resultant $R(\chi_1, \chi_2)$ of χ_1, χ_2 with respect to the parameter λ_1 vanishes on the algebraic set of χ_1, χ_2 [12]. One obtains:

$$R_{\lambda_1}(\chi_1, \chi_2) = \begin{vmatrix} 1 & -\lambda_2 + \lambda_3 - \lambda_4 \\ \lambda_3 & -\lambda_2\lambda_4 \end{vmatrix} = (\lambda_2 - \lambda_3)(\lambda_3 - \lambda_4) = 0 \tag{31}$$

From $\chi_1 = 0$ one gets:

$$\lambda_2 - \lambda_3 = 0 \longrightarrow \lambda_1 - \lambda_4 = 0 \tag{32}$$

resp. $\quad \lambda_3 - \lambda_4 = 0 \longrightarrow \lambda_1 - \lambda_2 = 0 \tag{33}$

Thus, the algebraic set of $\{\chi_1, \chi_2\}$ consists of the achiral zeros (achiral points) of the parameter space.

An arbitrary chirality function

$$F = T_1\chi_1 + T_2\chi_2 \tag{34}$$

necessarily possesses chiral zeros which are in no way predetermined by the algebraic set of the module basis $\{\chi_1, \chi_2\}$ but which depend on the properties of the totally symmetric functions T_1, T_2.

If one sets about interpreting the measurements of a chirality observation F with the aid of an "ansatz" in a suitable polynomial in λ, then, obviously, such an ansatz must comprise all elements of the module basis of S (resp. S_0), so that no chiral zero of the chiral property under investigation is predetermined. For molecular classes of category (a) an approximation

$$F \simeq \rho\chi_1 \tag{35}$$

with a constant ρ might be suitable (comp. [5–7]). (35) implies an open neighbourhood about a reference point (centre of expansion) in parameter space in which no chiral zeros of F are to be found.

For molecular classes of category (b) no continuous chirality function exists without chiral zeros. The achiral zeros are imbedded in the set of chiral zeros for any continuous chirality function F so that chiral zeros of F exist in any neighbourhood of an achiral zero in parameter space. Obviously, an ansatz in the "chirality polynomial" alone, i.e. in the basis element of the lowest degree (approximation of the first kind in [1, 2]), suffices only in the case of chirality functions F having the same set of chiral zeros as the chirality polynomial in a neighbourhood of an achiral zero. The simplest general ansatz for molecular classes of category (b) obtains as:

$$F \simeq \rho_1\chi_1 + \cdots + \rho_m\chi_m, \quad (m > 1) \tag{36}$$

with constants $\rho_1, \ldots, \rho_m$ to be determined from experiment.

The following theorem proves to be useful (comp. [1]):

Theorem: A rational integral function $g(\lambda_1, \ldots, \lambda_n)$ depends exclusively on the differences $(\lambda_i - \lambda_j)$ of the independent variables $\lambda_1, \ldots, \lambda_n$, if and only if the following holds:

$$\sum_i^{1,n} \frac{\partial}{\partial \lambda_i} (g(\lambda_1, \ldots, \lambda_n)) = 0 \tag{37}$$

Proof: Consider the transformation $\lambda \to \zeta$ with

$$\zeta_1 = \lambda_1, \qquad \zeta_2 = \lambda_2 - \lambda_1, \ldots, \qquad \zeta_n = \lambda_n - \lambda_1 \tag{38}$$

then for $i, j \neq 1$:

$$\lambda_i - \lambda_j = \zeta_i - \zeta_j \tag{39}$$

The inverse transformation obtains as:

$$\lambda_1 = \zeta_1, \qquad \lambda_2 = \zeta_2 + \zeta_1, \ldots, \qquad \lambda_n = \zeta_n + \zeta_1 \tag{40}$$

1) If a rational integral function $g(\lambda_1, \ldots, \lambda_n)$ depends solely on differences of the variables, then one gets:

$$g(\lambda_1, \ldots, \lambda_n) = \bar{g}(\zeta_2, \ldots, \zeta_n) \tag{41}$$

thus

$$0 = \frac{\partial}{\partial \zeta_1} \bar{g}(\zeta_2, \ldots, \zeta_n) = \sum_i^{1,n} \frac{\partial}{\partial \lambda_i} g(\lambda_1, \ldots, \lambda_n) \frac{\partial \lambda_i}{\partial \zeta_1} \tag{42}$$

$$\sum_i^{1,n} \frac{\partial}{\partial \lambda_i} g(\lambda_1, \ldots, \lambda_n) = 0$$

2) If a rational integral function $g(\lambda_1, \ldots, \lambda_n)$ has the property

$$\sum_i^{1,n} \frac{\partial}{\partial \lambda_i} g(\lambda_1, \ldots, \lambda_n) = 0$$

then

$$0 = \sum_i^{1,n} \frac{\partial}{\partial \lambda_i} g(\lambda_1, \ldots, \lambda_n) = \sum_i^{1,n} \frac{\partial}{\partial \lambda_i} g(\lambda_1, \ldots, \lambda_n) \frac{\partial \lambda_i}{\partial \zeta_1}$$

$$g(\lambda_1, \ldots, \lambda_n) = \bar{g}(\zeta_2, \ldots, \zeta_n) \tag{43}$$

The operator

$$\sum_i^{1,n} \frac{\partial}{\partial \lambda_i} \tag{44}$$

is totally symmetric under any permutation of the $\lambda_1, \ldots, \lambda_n$. Thus, if $f(\lambda_1, \ldots, \lambda_n)$ is a chirality function with respect to some permutation group S of the variables, then

$$\sum_i^{1,n} \frac{\partial}{\partial \lambda_i} f(\lambda_1, \ldots, \lambda_n) \tag{45}$$

is a chirality function with respect to that group, too. If f is a chirality polynomial of lowest degree, then obviously:

$$\sum_i^{1,n} \frac{\partial}{\partial \lambda_i} f(\lambda_1, \ldots, \lambda_n) = 0 \tag{46}$$

For molecular classes of category (b) only the basis element of lowest degree, therefore, depends of necessity solely on differences of the variables $\lambda_1, \ldots, \lambda_n$. As a consequence, an "ansatz" which comprises only the chirality polynomial of lowest degree is distinguished in that one is able to choose an arbitrary origin on the λ-scale on account of the translational invariance of that polynomial.

3. Chirality Functions in Several Ligand Parameters

Let λ, μ be two independent ligand parameters. Then, a chirality function

$$F(\lambda, \mu) = F(\lambda_1, \ldots, \lambda_n, \mu_1, \ldots, \mu_n) \tag{47}$$

constitutes a relative simultaneous invariant of grade 2 with the factor system $\{+1, -1\}$[8]. In the set of the rational integral simultaneous invariants of any factor system there again exists a finite module basis $\{\varphi_1, \ldots, \varphi_m\}$ such that any analytic chirality function $F(\lambda, \mu)$ obtains as a linear combination in the basis elements:

$$F = T_1 \varphi_1 + \cdots + T_m \varphi_m \tag{48}$$

The functions $T_1, \ldots, T_m$ represent analytic absolute simultaneous invariants of grade 2 in the two ligand parameters λ, μ.

For simultaneous invariants of any grade higher than 1 the module basis contains at least two elements φ_1, φ_2. Thus, any analytic function in two or more independent ligand parameters necessarily possesses chiral zeros in the $2n$-dimensional (or higher dimensional) parameter space.

Let $\{\chi_1, \ldots, \chi_r\}$ be a module basis of the chirality functions of grade 1 in a single ligand parameter λ (or any subset of such a basis). To construct some basis elements of the chirality functions of grade 2 in the ligand parameters λ, μ the following totally symmetric operators (of grade 2) can be applied to the basis functions $\chi_1, \ldots, \chi_r$:

$$B_1 = \sum_{i}^{1, n} \mu_i \frac{\partial}{\partial \lambda_i} \tag{49}$$

$$B_2 = \sum_{i}^{1, n} \mu_i \frac{\partial^2}{\partial \lambda_i^2} \tag{50}$$

$$B_{11} = \sum_{i, j}^{1, n} \mu_i \mu_j \frac{\partial^2}{\partial \lambda_i \partial \lambda_j} \tag{51}$$

etc.

As the operators B_1, B_2, B_{11} are totally symmetric with respect to any simultaneous permutation of the two rows of parameters $(\lambda_1, \ldots, \lambda_n)$ and $(\mu_1, \ldots, \lambda_n)$, the application of these operators to any rational integral chirality function χ in λ results in simultaneous chirality functions in λ and μ (if a nontrivial result is obtained). The new chirality functions are polynomials in λ and μ of a degree not higher than that of the polynomial χ in λ.

In the individual case it has to be shown (e.g. by complete induction) whether the set of functions obtained by this procedure constitutes a module basis of the chirality functions in the two parameters λ, μ.

Let $\chi_1 = \chi_1(\lambda_1, \ldots, \lambda_n)$ be the element of the module basis of the chirality functions of grade 1 which is of lowest degree in λ. Then any element φ_i of the module basis of the chirality functions of grade 2 which is derived from χ_1 by the application of one of the B-operators (49), (50) is linear in $\mu_1, \ldots, \mu_n$. Thus, φ_i has the property (37):

$$\sum_{j}^{1, n} \frac{\partial}{\partial \mu_j} \varphi_i = 0 \tag{52}$$

This is because χ_1 is the chirality polynomial of lowest degree in one variable. φ_i, then, is dependent on differences in the parameters $\mu_1, \ldots, \mu_n$, only.

Example: Symmetry group C_{3v}.

The frame defines a molecular class of category a, the module basis of the chirality functions of grade 1 contains one element χ only:
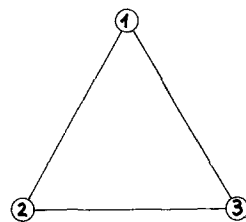

Fig. 3.

$$\chi(\lambda) = (\lambda_1 - \lambda_2)(\lambda_2 - \lambda_3)(\lambda_3 - \lambda_1)$$
$$= \lambda_1 \lambda_2^2 - \lambda_1^2 \lambda_2 - \lambda_2^2 \lambda_3 + \lambda_2 \lambda_3^2 - \lambda_1 \lambda_3^2 + \lambda_1^2 \lambda_3 \tag{53}$$

The module basis of the chirality functions of grade 2 (ligand parameters λ, μ) contains, obviously, the elements $\chi(\lambda)$ and $\chi(\mu)$. From the application of the operators B_1, B_2, B_{11} obtains:

$$B_1 \chi(\lambda) = \mu_1(\lambda_2^2 - \lambda_3^2) + \mu_2(\lambda_3^2 - \lambda_1^2) + \mu_3(\lambda_1^2 - \lambda_2^2)$$
$$+ 2\mu_1 \lambda_1(\lambda_3 - \lambda_2) + 2\mu_2 \lambda_2(\lambda_1 - \lambda_3) + 2\mu_3 \lambda_3(\lambda_2 - \lambda_1) \tag{54}$$

$$B_2 \chi(\lambda) = 2(\lambda_1 \mu_2 - \lambda_2 \mu_1 + \lambda_2 \mu_3 - \lambda_3 \mu_2 + \lambda_3 \mu_1 - \lambda_1 \mu_3) \tag{55}$$

$$B_{11} \chi(\lambda) = 4(\mu_1 \mu_3 \lambda_1 - \mu_1 \mu_2 \lambda_1 + \mu_1 \mu_2 \lambda_2 - \mu_2 \mu_3 \lambda_2 + \mu_2 \mu_3 \lambda_3 - \mu_1 \mu_3 \lambda_3)$$
$$+ 2(\mu_1^2(\lambda_3 - \lambda_2) + \mu_2^2(\lambda_1 - \lambda_3) + \mu_3^2(\lambda_2 - \lambda_1)) \tag{56}$$

From this obtains the module basis $\{\varphi_0, \varphi_1, \ldots, \varphi_4\}$ for analytic chirality functions of grade 2 in the ligand parameters λ, μ, which can be shown to be complete by complete induction:

$$\varphi_0(\lambda, \mu) = \lambda_1 \mu_2 - \lambda_2 \mu_1 + \lambda_2 \mu_3 - \lambda_3 \mu_2 + \lambda_3 \mu_1 - \lambda_1 \mu_3 \tag{57}$$

$$\varphi_1(\lambda, \mu) = \lambda_2^2 \mu_1 - \lambda_1^2 \mu_2 + \lambda_1^2 \mu_3 - \lambda_3^2 \mu_1 + \lambda_3^2 \mu_2 - \lambda_2^2 \mu_3 \tag{58}$$

$$\varphi_2(\lambda, \mu) = \lambda_1 \mu_2^2 - \lambda_2 \mu_1^2 + \lambda_3 \mu_1^2 - \lambda_1 \mu_3^2 + \lambda_2 \mu_3^2 - \lambda_3 \mu_2^2 \tag{59}$$

$$\varphi_3(\lambda, \mu) = \mu_1 \mu_2^2 - \mu_1^2 \mu_2 + \mu_2 \mu_3^2 - \mu_2^2 \mu_3 + \mu_1^2 \mu_3 - \mu_1 \mu_3^2 \tag{60}$$

$$\varphi_4(\lambda, \mu) = \lambda_1 \lambda_2^2 - \lambda_1^2 \lambda_2 + \lambda_2 \lambda_3^2 - \lambda_2^2 \lambda_3 + \lambda_1^2 \lambda_3 - \lambda_1 \lambda_3^2 \tag{61}$$

In the 6-dimensional (λ, μ)-parameter space one again classifies the zeros of a chirality function of grade 2 as to whether they represent chiral or achiral molecules.

In the following, the algebraic set of the basis elements $\{\varphi_0, \varphi_1, \ldots, \varphi_4\}$ in the 6-dimensional parameter space is investigated using Kronecker's method of elimination (comp. [13]). Let $u_1, \ldots, u_4$ be some parameters, then one can construct the resultant

$$R_{\lambda_1}(\varphi_0, H) \tag{62}$$

of the polynomials φ_0 and $H = u_1 \varphi_1 + \cdots + u_4 \varphi_4$ with respect to the parameter λ_1. The condition

$$R_{\lambda_1}(\varphi_0, H) = 0 \tag{63}$$

furnishes a polynomial in $u_1, \ldots, u_4$ which vanishes identically in $u_1, \ldots, u_4$ on the algebraic set of the basis elements $\varphi_0, \varphi_1, \ldots, \varphi_4$. The sole precondition to be met is that φ_0 and H are regular polynomials in λ_1. This implies:

$$\mu_2 \neq \mu_3 \tag{64}$$

The vanishing of the resultant (63) furnishes the following system of 4 equations:

$$u_1 : (\mu_3 - \mu_2)(\lambda_2(\mu_3 - \mu_1) + \lambda_3(\mu_1 - \mu_2))^2$$
$$+ (\mu_2 - \mu_3)^2(\mu_1(\lambda_2^2 - \lambda_3^2) + \lambda_3^2 \mu_2 - \lambda_2^2 \mu_3) = 0 \tag{65}$$

$$u_2 : (\mu_3^2 - \mu_2^2)(\mu_2 - \mu_3)(\lambda_2(\mu_3 - \mu_1) + \lambda_3(\mu_1 - \mu_2))$$
$$+ (\mu_2 - \mu_3)^2(\mu_1^2(\lambda_3 - \lambda_2) + \lambda_2 \mu_3^2 - \lambda_3 \mu_2^2) = 0 \tag{66}$$

$$u_3 : (\mu_2 - \mu_3)^3(\mu_1 - \mu_2)(\mu_3 - \mu_1) = 0 \tag{67}$$

$$u_4 : (\lambda_3 - \lambda_2)(\lambda_2(\mu_3 - \mu_1) + \lambda_3(\mu_1 - \mu_2))^2 + (\lambda_3^2 - \lambda_2^2)(\mu_2 - \mu_3)$$
$$\times (\lambda_2(\mu_3 - \mu_1) + \lambda_3(\mu_1 - \mu_2)) + (\mu_2 - \mu_3)^2 \lambda_2 \lambda_3(\lambda_3 - \lambda_2) = 0 \tag{68}$$

From (67) one gets on account of (64):

$$\mu_1 = \mu_2 \quad \text{or} \quad \mu_1 = \mu_3 \tag{69}$$

For

$$\mu_1 = \mu_2 \neq \mu_3 \tag{70}$$

(65), (66) and (68) hold. To determine λ_1, one gets from

$$\varphi_0 = 0 \tag{71}$$

on account of (70):

$$(\lambda_1 - \lambda_2)(\mu_1 - \mu_3) = 0 \tag{72}$$

Because of $\mu_1 \neq \mu_3$ the common zeros

$$(\mu_1 = \mu_2 \neq \mu_3, \quad \lambda_1 = \lambda_2) \tag{73}$$

of the module basis obtain. Alternatively, for

$$\mu_1 = \mu_3 \neq \mu_2 \tag{74}$$

(65), (66), (68) hold and from (71) one gets because of $\mu_1 \neq \mu_2$:

$$(\mu_1 = \mu_3 \neq \mu_2, \quad \lambda_1 = \lambda_3) \tag{75}$$

If Kronecker's method of elimination is applied to λ_2 or λ_3 the points defined by

$$(\mu_2 = \mu_3 \neq \mu_1, \quad \lambda_2 = \lambda_3) \tag{76}$$

of the algebraic set of $\{\varphi_0, \varphi_1, \ldots, \varphi_4\}$ obtain. Finally, under the condition

$$\mu_1 = \mu_2 = \mu_3 \tag{77}$$

one obtains: $\varphi_0 = 0$, $\varphi_1 = 0$, $\varphi_2 = 0$, $\varphi_3 = 0$. Using (61), one then arrives at:

$$(\mu_1 = \mu_2 = \mu_3, \lambda_1 = \lambda_2 \quad \text{or} \quad \lambda_1 = \lambda_3 \quad \text{or} \quad \lambda_2 = \lambda_3) \tag{78}$$

Thus, in consequence of (73), (75), (76) and (78) the algebraic set of $\{\varphi_0, \varphi_1, \ldots, \varphi_4\}$ contains exactly the set of achiral points of the (λ, μ)-parameter space.

By the same kind of analysis one can show that already the algebraic set of the subset

$$\{\varphi_0, \varphi_3, \varphi_4\} \tag{79}$$

of the module basis $\{\varphi_0, \varphi_1, \ldots, \varphi_4\}$ spans exactly the set of achiral points in the parameter space. In consequence, there are relations of the kind (18) between φ_1 resp. φ_2 and the subset (79). Therefore, the elements of the module basis are linearly dependent and syzygies between them (comp. (22)) exist, if nontrivial relations of the kind (22) exist.

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