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Original Investigations

Concerning the Theory of Chirality Functions

VII. The Concept of Qualitative Supercompleteness*,**

Gerhard Derflinger and Hildegard Keller***

Institut für Statistik der Wirtschaftsuniversität Wien, Franz Klein-Gasse 1, A-1190 Wien, Österreich

Glossary of the most important symbols[1]

$\mathscr{E}$	ensemble operator which is an element of the group algebra of the $\mathfrak{S}_N$
$\mathfrak{G}$	group of the symmetry operations of the skeleton
$\mathfrak{G}_\mathrm{f}$	group of the covering operations of the fictively extended skeleton
g	number of enantiomeric pairs of molecules with n different ligands and a skeleton of n ligand sites
h	number of enantiomeric pairs of molecules with N different ligands and a fictively extended skeleton of N ligand sites
$\mathfrak{H}^{(r)}_{nN}$	TU-half order of the partition diagrams $\gamma^{(w)}_N$ with $t_{wr1} = 1$
$\mathfrak{h}^{(r)}_n$	half order of the partition diagrams $\delta^{(w)}_\nu$
L	vector of the symbols l_i of the N ligands attached to the proper or to the fictive ligand sites
L_e	vector of the symbols l_i of the n ligands attached to the proper ligand sites
L_f	vector of the symbols l_i of the m ligands attached to the fictive ligand sites
L_ν	vector of the symbols l_i of ν ligands attached to ν proper ligand sites, $\nu \leq n$
l_i	symbol of the ligand attached to the ith ligand site
$M^{(w)}_i$	see Eq. (B21)
m	number of fictive ligand sites or additional ligand sorts
m_w	number of times a ν-ligands function induces $\Delta^{(w)}_\nu$
N	number of ligand sites of the fictively extended skeleton or total number of ligand sorts
n	number of proper ligand sites or number of ligand sorts of a molecule with pairwise different ligands

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* Dedicated to Prof. O. E. Polansky on the occasion of his 60th birthday.

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*** Present address: Department of Organic Chemistry, University of Groningen, Zernikelaan, Groningen, Netherlands.

[1] For symbols designating functions the following holds: a function symbol without "~" or "≈" designates a function depending formally on N, explicitly on n or ν ligands; a function symbol with "~" designates a function depending formally on n, explicitly on n or ν ligands; a function symbol with "≈" designates a function depending formally and explicitly on ν ligands.

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n_r, n_w	dimension of $\Gamma_n^{(r)}$ or $\Gamma_N^{(w)}$ resp.
$\mathcal{O}(\mathscr{s})$	permutation operator induced by the permutation $\mathscr{s}$ in the function space, element of $\mathfrak{S}(\mathcal{O})$, $\mathfrak{S}_m(\mathcal{O})$, $\mathfrak{S}_n(\mathcal{O})$, $\mathfrak{S}_N(\mathcal{O})$ or $\mathfrak{S}_\nu(\mathcal{O})$ resp.
$o_1^{(r)}$, $o_1^{(w)}$	length of the first row of $\gamma_n^{(r)}$ or $\gamma_N^{(w)}$ resp.
$o_i^{(w)}$	sum of the lengths of the first i rows of $\gamma_N^{(w)}$
$o_{\max}$	$o_{\max} = \max_{\bar{r}} o_1^{(\bar{r})}$
$\mathscr{p}_{ij}^{(r)}$, $\mathscr{p}_{ij}^{(w)}$	projection and shift operators of $\Gamma_n^{(r)}$ or $\Gamma_N^{(w)}$ resp.
$\mathscr{p}_m^{(v)}$, $\mathscr{P}_m^{(v)}$	character projectors onto $\Gamma_m^{(v)}$ of $\mathfrak{S}_m$ or $\mathfrak{S}_m(\mathcal{O})$ resp.
$\mathscr{p}_n^{(r)}$, $\mathscr{P}_n^{(r)}$	character projectors onto $\Gamma_n^{(r)}$ of $\mathfrak{S}_n$ or $\mathfrak{S}_n(\mathcal{O})$ resp.
$\mathscr{p}_N^{(w)}$, $\mathscr{P}_N^{(w)}$	character projectors onto $\Gamma_N^{(w)}$ of $\mathfrak{S}_N$ or $\mathfrak{S}_N(\mathcal{O})$ resp.
$\mathscr{P}_\nu^{(w)}$	character projector onto $\Delta_\nu^{(w)}$ of $\mathfrak{S}_\nu(\mathcal{O})$
$\mathscr{p}_\sigma$, $\mathscr{P}_\sigma$	projection operators onto Γ_σ of $\mathfrak{U} = \mathfrak{S} \times \mathfrak{S}_m$ or $\mathfrak{S}(\mathcal{O}) \times \mathfrak{S}_m(\mathcal{O})$ resp.
$\mathscr{p}_\chi$, $\mathscr{P}_\chi$	projection operators onto Γ_χ of $\mathfrak{S}$ or $\mathfrak{S}(\mathcal{O})$ resp.
q_w	dimension of $\Delta_\nu^{(w)}$
r	index of an irreducible representation $\Gamma_n^{(r)}$ of the $\mathfrak{S}_n$
$\bar{r}$	index of an irreducible representation $\Gamma_n^{(r)}$ of the $\mathfrak{S}_n$ containing Γ_χ
$\mathfrak{S}$	group of the ligand permutations which correspond to symmetry operations of the skeleton
$\mathfrak{S}_0$	subgroup of $\mathfrak{S}$ the elements of which correspond to proper rotations of the skeleton
$\mathfrak{S}^*$	coset of $\mathfrak{S}_0$ in $\mathfrak{S}$ the elements of which correspond to improper rotations of the skeleton
$\mathfrak{S}_m$	symmetric group of the permutations of the m ligands attached to the fictive ligand sites
$\mathfrak{S}_n$	symmetric group of the permutations of the n ligands attached to the proper ligand sites
$\mathfrak{S}_N$	symmetric group of the permutations of all N ligands
$\mathfrak{S}_\nu$	symmetric group of the permutations of ν ligands attached to proper ligand sites, $\nu \leq n$
$\mathfrak{S}(\mathcal{O})$, $\mathfrak{S}_m(\mathcal{O})$, $\mathfrak{S}_n(\mathcal{O})$, $\mathfrak{S}_N(\mathcal{O})$, $\mathfrak{S}_\nu(\mathcal{O})$	symmetric groups the elements of which are permutation operators $\mathcal{O}(\mathscr{s})$
$\mathscr{s}_u^{(w)}$	see Eq. (B13)
s_w	see Eq. (B4)
t_{wrv}	multiplicity of $\Gamma_N^{(w)}$ in $\Gamma_n^{(r)} \otimes \Gamma_m^{(v)}$, equal to the multiplicity of $\Gamma_n^{(r)} \times \Gamma_m^{(v)}$ in $\Gamma_N^{(w)}$
$\mathfrak{U}$	group of the ligand permutations which correspond to covering operations of the fictively extended skeleton
$\mathfrak{U}_0$	subgroup of $\mathfrak{U}$ the elements of which correspond to proper rotations of the fictively extended skeleton
$\mathfrak{U}^*$	coset of $\mathfrak{U}_0$ in $\mathfrak{U}$ the elements of which correspond to improper rotations of the fictively extended skeleton
v	index of an irreducible representation $\Gamma_m^{(v)}$ of the $\mathfrak{S}_m$
w	index of an irreducible representation $\Gamma_N^{(w)}$ of the $\mathfrak{S}_N$
$\bar{w}$	index of an irreducible representation $\Gamma_N^{(w)}$ of the $\mathfrak{S}_N$ containing Γ_σ
w_r^0	index of the largest diagram $\gamma_N^{(w)} \in \mathfrak{H}_{nN}^{(r)}$ or $\delta_\nu^{(w)} \in \mathfrak{h}_n^{(r)}$ resp.
w_r^*	index of the smallest diagram $\gamma_N^{(w)} \in \mathfrak{H}_{nN}^{(r)}$ or $\delta_\nu^{(w)} \in \mathfrak{h}_n^{(r)}$ resp.
x_w	multiplicity of Γ_σ in $\Gamma_N^{(w)}$
$\mathscr{Y}_{ij}^{(w)}$	Young operator (if $i = j$) or Young unit of $\Delta_\nu^{(w)}$ of $\mathfrak{S}_\nu(\mathcal{O})$
${}_N\mathscr{Y}_{ij}^{(w)}$	Young operator (if $i = j$) or Young unit of $\Gamma_N^{(w)}$ of $\mathfrak{S}_N(\mathcal{O})$
z_r	multiplicity of Γ_χ in $\Gamma_n^{(r)}$
$\alpha_{\rho u}^{(w)}$	linear combination coefficient, see Eq. (48), (B41)
$\Gamma_m^{(v)}$, $\Gamma_n^{(r)}$, $\Gamma_N^{(w)}$	irreducible representation of $\mathfrak{S}_m$ or $\mathfrak{S}_m(\mathcal{O})$ resp., $\mathfrak{S}_n$ or $\mathfrak{S}_n(\mathcal{O})$ resp., or $\mathfrak{S}_N$ or $\mathfrak{S}_N(\mathcal{O})$, resp.
Γ_σ	σ-chirality representation
Γ_χ	chirality representation

$\gamma_m^{(v)}, \gamma_n^{(r)}, \gamma_N^{(w)}$	partition diagrams corresponding to $\Gamma_m^{(v)}, \Gamma_n^{(r)}$ or $\Gamma_N^{(w)}$ resp.
$\gamma_N^{(s)}$	partition diagram corresponding to an assortment of N ligands
$\Delta_\nu^{(w)}$	irreducible representation of $\mathfrak{S}_\nu$ or $\mathfrak{S}_\nu(\mathcal{O})$ resp.
$\delta_\nu^{(w)}$	partition diagram corresponding to $\Delta_\nu^{(w)}$, got from $\gamma_N^{(w)}$ by removing the first row
$\lambda_\rho^{(w)}(l_i)$	ρth parameter of the ligand l_i in a set up to the component $\tilde{\chi}^{(w)}(L_e)$ of $\tilde{\chi}(L_e)$
ν	number of ligands on which the set up $\tilde{\omega}^{(w)}(L_e)$ depends (=order of interaction), equal to the number of boxes of $\delta_\nu^{(w)}$, $\nu \leq n$
$\nu_i^{(w)}$	length of the ith row of $\gamma_N^{(w)}$
ρ	subscript which distinguishes between different parameter sets for a given w, $\rho = 1, \ldots, s_w$
σ_{ij}	permutation transforming a Young tableau j into a Young tableau i
$\tilde{\upsilon}_{\rho k}^{(w)}(L_e)$, $\tilde{\tilde{\upsilon}}_{\rho k}^{(w)}(L_\nu)$	product of the Vandermonde determinants of the Young tableau k multipled by the product of all parameters of L_ν
$\phi(L)$, $\tilde{\phi}(L_e)$	function describing physical properties of a molecule
$\chi(L)$, $\tilde{\chi}(L_e)$	chirality function of a molecule derived by a "Näherungsverfahren"
$\chi^{(w)}(L)$, $\tilde{\chi}^{(w)}(L_e)$	wth component of $\chi(L)$ or $\tilde{\chi}(L_e)$ resp.
$\psi_\rho(\gamma_N^{(w)}; L)$	see Eq. (B19)
$\omega(L)$, $\tilde{\omega}(L_e)$	set up to the chirality function $\chi(L)$ or $\tilde{\chi}(L_e)$ resp.
$\omega^{(w)}(L)$, $\tilde{\omega}^{(w)}(L_e)$, $\tilde{\tilde{\omega}}^{(w)}(L_\nu)$	ν-ligands function, set up to $\chi^{(w)}(L)$ or $\tilde{\chi}^{(w)}(L_e)$
$\hat{\omega}^{(w)}(L)$, $\hat{\tilde{\omega}}^{(w)}(L_e)$, $\hat{\tilde{\tilde{\omega}}}^{(w)}(L_\nu)$	$\Delta_\nu^{(w)}$-component of $\omega^{(w)}(L)$, $\tilde{\omega}^{(w)}(L_e)$ or $\tilde{\tilde{\omega}}^{(w)}(L_\nu)$ resp.
$\tilde{\omega}_u^{(w)}(L_e)$, $\tilde{\tilde{\omega}}_u^{(w)}(L_\nu)$	set up of the uth component, $u = 1, \ldots, x_w$, to a $\chi^{(w)}(L)$ or $\tilde{\chi}^{(w)}(L_e)$ resp., see Eq. (B16)

Within the scope of the theory of chirality functions, qualitatively complete chirality functions are subject to restrictions concerning both generality and applicability. In contrast thereto, the concept of qualitative supercompleteness results in less restrictive requirements for chirality functions. Consequently, the applicability of qualitatively supercomplete chirality functions is unlimited with respect to the number of ligand kinds. Given this concept, a group theoretical treatment is performed supplying the formal conditions of qualitative supercompleteness. Subsequently a construction rule for qualitiatively supercomplete chirality functions is presented, which is elaborated in detail in the appendix. On combining physical considerations with the requirement of qualitative supercompleteness the resulting chirality functions appear to include all the possible interactions within and/or between ligands and skeleton. From both a mathematical and a physical point of view these chirality functions should be adequate for describing the chiroptical properties of molecules belonging to a given skeletal class. Nevertheless, all the other critical objections to the theory of chirality functions remain.

Key words: Optical activity – Mixtures of non-isomers – Ligand–skeleton interactions.

1. Introduction and Purpose

The theory of chirality functions represents an algebraic approach to the comprehension of the chirality phenomenon [1–7]. Within this concept a molecule is assumed to consist of an achiral skeleton of given symmetry and ligands attached to the skeletal sites. Based on this model, pseudoskalar properties of the molecule are presumed to be describable by a function of ligand specific parameters, named the chirality function.

Taking into account the elementary requirements of chirality a group-theoretical treatment provides the conditions which a chirality function has to fulfill: its numerical value must be invariant under permutations of ligands corresponding to proper rotations of the molecule and must change sign under permutations corresponding to improper rotations (see also [8]). Given the algebraic framework of symmetry and transformation behaviour chirality functions are constructed by means of "Näherungsverfahren" implying "Näherungsansätze"[2]. Two examples of "Näherungsverfahren" are outlined in [3, 4].

Nevertheless, it is by no means ensured that a chirality function fulfilling all the above mentioned requirements gives a correct description of chirality observations [9, 10][3]. One discrepancy concerning the general validity and applicability of chirality functions according to [3] was removed by requiring "qualitative completeness" [4]. With respect to this point, a chirality function must not vanish for non-racemic mixtures of isomers whatever the nature of the ligands may be. Hence systematical non-racemic zero points are eliminated for mixtures of isomers.

As shown in a preceding article [10], quite a few systematical zero points for non-racemic mixtures have remained: dropping the limitation to isomers and allowing for arbitrary non-racemic mixtures the chirality functions according to [4] appear to vanish in certain cases independently of the nature of the ligands.

Consequently, to ensure generality and enable a compelling application of chirality functions at least in principle a more general requirement substituting the one of qualitative completeness (C-requirement) has to be raised. It will be called requirement of "qualitative supercompleteness" (SC-requirement)[4]. Clearly qualitative supercompleteness does not only substitute for but also include qualitative completeness.

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[2] The terms "Näherungsverfahren" and "Näherungsansatz" are always used in the sense of [3, 4].

[3] As to E. Ruch's reply (Theoret. Chim. Acta (Berl.) **49**, 106 (1979)) to our papers [9, 10], we feel that the discussion should not be continued on this basis, and we leave it to the readers to draw their own conclusions.

[4] C represents an abbreviation for "qualitatively complete" whereas SC means "qualitatively supercomplete". The term "supercomplete" should not be confounded with "overcomplete" which usually means "more than complete", i.e. "too much" because "complete" is sufficient. We have decided rather to call the requirement introduced here "qualitative supercompleteness" in order to emphasize that it is more general than the requirement of "qualitative completeness".

In the following the concept of qualitative supercompleteness is developed. First of all the concept of "quasi-isomers" or "fictive isomers" is introduced. The underlying mathematics within the framework of the symmetric group are formulated. Two construction procedures of SC-chirality functions are discussed and some examples are given. Furthermore, a comparison with the principle of many-body interactions, which is based on physical considerations, will reveal the relevance of the concept of qualitative supercompleteness.

2. Qualitative Supercompleteness and Mixtures of Non-Isomers

The requirement of qualitative supercompleteness requires that a chirality function does not vanish identically for any non-racemic mixture, whatever the nature of the ligands. Given this postulate as well as the ones derived from the elementary requirements of chirality we proceed to deduce the transformation and symmetry behaviour of chirality functions via the symmetric group. To reach this goal we have to establish a method to construct mixtures of non-isomers.

As within the C-concept let us consider molecules of a class specified by a given skeleton (skeletal class) with pairwise different ligands. In order to obtain mixtures of non-isomers the number N of ligand sorts must be chosen greater than the number n of the ligand sites. The number of additional ligand sorts is given by

$$m = N - n, \qquad m > 0. \tag{1}$$

The SC-concept to be developed equals the C-concept in the limiting case $N = n$ and $m = 0$. However, by using a trick we can establish a connection between SC-concept and C-concept in any case. The trick consists of assuming a given molecular skeleton to be extended formally by $m = N - n$ "fictive" ligand sites which do not exist in reality. Each one of these m sites has to be occupied formally by a ligand of a sort not appearing in the proper molecule. The proper molecule L_e is identified by the vector consisting of the symbols of the n proper ligands,

$$L_e = [l_1, l_2, \ldots, l_n].$$

L_f denotes the vector consisting of the symbols of ligands attached to the fictive sites,

$$L_f = [l_{n+1}, l_{n+2}, \ldots, l_N].$$

Thus the vector

$$L = [L_e | L_f] = [l_1, \ldots, l_n | l_{n+1}, \ldots, l_N] \tag{2}$$

represents the molecule extended by the ligands attached to the fictive sites (fictively extended molecule). Fig. 1 demonstrates the situation by means of the two allene derivatives **1** and **2** assuming six sorts of ligands (A, B, C, D, E, F). Note the essential fact that the two non-isomeric molecules may be assumed formally to be isomers provided that the skeleton is extended by fictive sites ("quasi-isomer" or "fictive isomer"). Consequently mixtures of non-isomers can

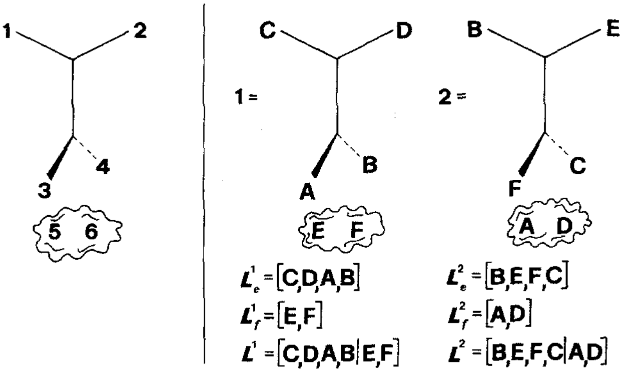

Fig. 1. Site numbering of the fictively extended allene skeleton and two allene derivatives **1** and **2** regarding six sorts of ligands A, B, C, D, E, F. The fictive skeletal sites and the ligands attached to them are situated in the cloud

be treated formally as mixtures of isomers providing the advantage that many results of the C-concept can be adapted.

Obviously we have to postulate that the fictively extended molecule equals the proper molecule in all physical properties. In other words, a function $\phi(L)$ describing physical properties must not depend on the ligands attached to the fictive sites:

$$\phi(L)=\phi(L_e|L_f)=\tilde{\phi}(L_e). \tag{3}$$

Therefore the ligand symbols $l_{n+1}, \ldots, l_N$ occur just formally in the vector of arguments L of $\phi(L)$; (e.g. $\phi(L)$ being a polynomial one can presume the corresponding ligand parameters to enter in zeroth power). These ligands do not even appear formally in the argument of $\tilde{\phi}(L_e)$.

It must be emphasized that the results of the SC-concept presented could be derived without regarding fictive ligand sites and fictive isomers (e.g. see Sect. 4 and literature cited therein). Indeed, in this case the way of concluding would be more complicated and the elegant implements and results of the theory of chirality functions developed by Ruch and Schönhofer [3, 4] could not then be adapted.

3. Group Theoretical Treatment of Mixtures of Non-Isomers

Let us now turn to the connection between the C-concept and the SC-concept:

The symmetric group $\mathfrak{S}_n$ of the $n!$ permutations of the n ligands attached to the proper skeletal sites forms the basis of the C-concept. The group $\mathfrak{S}$, being a subgroup of $\mathfrak{S}_n$, is isomorphic to the group $\mathfrak{G}$ of the symmetry operations of the skeleton. $\mathfrak{S}$ contains a subgroup $\mathfrak{S}_0$ of index 2, the permutations of which are assigned to the proper rotations of the skeleton and therefore maintain the molecule invariant. The elements of $\mathfrak{S}^*$, the coset of $\mathfrak{S}_0$ in $\mathfrak{S}$, correspond to improper rotations of the skeleton.

Concerning the SC-concept the $\mathfrak{S}_n$ is replaced by the symmetric group $\mathfrak{S}_N$, consisting of the permutations of all the N ligands. The $\mathfrak{S}_N$ includes also those permutations that interchange real and fictive ligands, thus leading to quasi-isomers. In this way mixtures of non-isomers can be managed algebraically like mixtures of isomers within the scope of the C-concept, as mentioned above.

The group $\mathfrak{G}_f$ of covering operations of the fictively extended skeleton can no longer be represented by the point group $\mathfrak{G}$ of the proper skeleton. It rather consists of all covering operations of the proper skeleton connected with any permutation of the fictive ligands. Let us now establish an isomorphic mapping of the group $\mathfrak{G}_f$ onto a subgroup $\mathfrak{U}$ of $\mathfrak{S}_N$, $\mathfrak{G}_f \rightsquigarrow \mathfrak{U}$. Given $\mathfrak{G}_f = \mathfrak{G} \times \mathfrak{S}_m$ with $\mathfrak{S}_m$ as the symmetric group of all $m!$ permutations of the m ligands attached to fictive sites an element $\mathfrak{c}_f = \mathfrak{c}\mathfrak{t}$ of $\mathfrak{G}_f$ with $\mathfrak{c} \in \mathfrak{G}$, $\mathfrak{t} \in \mathfrak{S}_m$ is mapped onto the element $\mathfrak{s}\mathfrak{t}$ of $\mathfrak{U}$ where $\mathfrak{s} \in \mathfrak{S}_n$ is the image of $\mathfrak{c}$ according to the isomorphism $\mathfrak{G} \rightsquigarrow \mathfrak{S}$. The subgroup $\mathfrak{U}$ given by

$$\mathfrak{U} = \mathfrak{S} \times \mathfrak{S}_m \tag{4}$$

takes the rôle of $\mathfrak{S}$ in the SC-concept.

Analogously to $\mathfrak{S}_0$ the direct product group

$$\mathfrak{U}_0 = \mathfrak{S}_0 \times \mathfrak{S}_m \tag{5}$$

is the group of all permutations leaving the molecule unchanged in the SC-concept. Since both the permutations of $\mathfrak{S}_0$ corresponding to proper rotations and the permutations of the fictive ligands keep the molecule invariant, one may also state that a proper rotation of the fictively extended molecule is defined by an adequate rotation of the proper molecule connected with any permutation of the fictive ligands. Because of (4) and (5) $\mathfrak{U}_0$ is a subgroup of $\mathfrak{U}$ of index 2. Within the SC-concept the coset $\mathfrak{U}^*$ of $\mathfrak{U}_0$ in $\mathfrak{U}$

$$\mathfrak{U}^* = \mathfrak{S}^* \times \mathfrak{S}_m, \tag{6}$$

takes the rôle of $\mathfrak{S}^*$. The elements of $\mathfrak{S}^*$ correspond to improper rotations of the proper molecule whereas the permutations of the m fictive ligands keep the molecule invariant. Provided that two fictively extended molecules are connected

Table 1. The important groups, subgroups and cosets within the C- and SC-concepts

Elements of the group/coset correspond to	Group/coset within C-concept	SC-concept
transitions to isomer/quasi-isomer	$\mathfrak{S}_n$	$\mathfrak{S}_N$
covering operations	$\mathfrak{S}$	$\mathfrak{U} = \mathfrak{S} \times \mathfrak{S}_m$
proper rotations	$\mathfrak{S}_0$	$\mathfrak{U}_0 = \mathfrak{S}_0 \times \mathfrak{S}_m$
improper rotations	$\mathfrak{S}^*$	$\mathfrak{U}^* = \mathfrak{S}^* \times \mathfrak{S}_m$

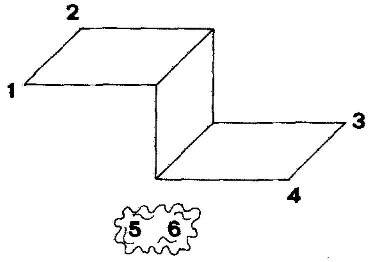

Fig. 2. A fictively extended skeleton of C_{2h}-symmetry owing the four proper skeletal sites 1–4. The two fictive skeletal sites 5 and 6 are situated in the cloud

by a permutation of $\mathfrak{U}^*$ the corresponding proper molecules can be transformed into each other by an improper rotation; thus they are antipodes.

In Table 1 the groups, subgroups and cosets just introduced within the scope of the SC-concept are opposed to their analoga in the C-concept.

The groups offered in Table 1 are explained explicitly for the skeleton of Fig. 2 in

Example 1:
Considering a skeleton of C_{2h}-symmetry with four skeletal sites and six sorts of ligands as shown in Fig. 2 we derive

$$\mathfrak{S} = \{\mathfrak{e}, (14)(23), (12)(34), (13)(24)\}$$

$$\mathfrak{S}_0 = \{\mathfrak{e}, (14)(23)\}$$

$$\mathfrak{S}^* = \{(12)(34), (13)(24)\}$$

$$\begin{aligned}\mathfrak{U} &= \mathfrak{S} \times \mathfrak{S}_m = \mathfrak{S} \times \{\mathfrak{e}, (56)\}\\ &= \{\mathfrak{e}, (14)(23), (12)(34), (13)(24), (56), (14)(23)(56),\\ &\quad (12)(34)(56), (13)(24)(56)\}\end{aligned}$$

$$\mathfrak{U}_0 = \mathfrak{S}_0 \times \mathfrak{S}_m = \{\mathfrak{e}, (14)(23), (56), (14)(23)(56)\}$$

$$\mathfrak{U}^* = \mathfrak{S}^* \times \mathfrak{S}_m = \{(12)(34), (13)(24), (12)(34)(56), (13)(24)(56)\}.$$

Within the C-concept the chirality representation Γ_χ of $\mathfrak{S}$ is of importance. Any chirality function $\tilde{\phi}(L_e)$ must transform according to this one-dimensional representation. Its characters are

$$\begin{aligned}\chi_\chi(\mathfrak{s}) &= 1 \quad \text{for } \mathfrak{s} \in \mathfrak{S}_0,\\ \chi_\chi(\mathfrak{s}) &= -1 \quad \text{for } \mathfrak{s} \in \mathfrak{S}^*.\end{aligned} \tag{7}$$

That is to say that the character is +1 for permutations leaving the molecule invariant and −1 for permutations leading to the antipode. In the SC-concept Γ_χ is substituted consequently by Γ_σ, this being a one-dimensional representation of the subgroup $\mathfrak{U}$ of $\mathfrak{S}_N$. As the permutations $\mathfrak{u} \in \mathfrak{U}_0$ leave the (fictively extended) molecule invariant and the permutations $\mathfrak{u} \in \mathfrak{U}^*$ yield the mirror image the characters of Γ_σ are

$$\begin{aligned} \chi_\sigma(\mathscr{u}) &= 1 \quad \text{for } \mathscr{u} \in \mathfrak{U}_0, \\ \chi_\sigma(\mathscr{u}) &= -1 \quad \text{for } \mathscr{u} \in \mathfrak{U}^*. \end{aligned} \tag{8}$$

We call Γ_σ the σ-chirality representation. From (4–8) it follows that Γ_σ is the direct product

$$\Gamma_\sigma = \Gamma_\chi \times \Gamma_m^{(1)} \tag{9}$$

of Γ_χ with the totally symmetric irreducible representation $\Gamma_m^{(1)}$ of the $\mathfrak{S}_m$.

We denote the projection operators onto Γ_χ and Γ_σ by $\mathscr{p}_\chi$ and $\mathscr{p}_\sigma$, respectively. For the character projectors of the irreducible representations $\Gamma_n^{(r)}$, $\Gamma_m^{(v)}$ and $\Gamma_N^{(w)}$ of the symmetric groups $\mathfrak{S}_n$, $\mathfrak{S}_m$ and $\mathfrak{S}_N$, respectively, we shall use the symbols $\mathscr{p}_n^{(r)}$, $\mathscr{p}_m^{(v)}$ and $\mathscr{p}_N^{(w)}$. Thus $\mathscr{p}_m^{(1)}$ means the projector onto the totally symmetric representation $\Gamma_m^{(1)}$ of the $\mathfrak{S}_m$. We always refer the permutations $\mathscr{s}$ to the numbered skeletal sites. By $\mathscr{O}(\mathscr{s})$ we denote the permutation operators working on functions and defined by

$$\mathscr{O}(\mathscr{s})\phi(L) = \phi(\mathscr{s}^{-1}L).$$

Here $\mathscr{s}L$ is the ligand vector obtained from L on applying the permutation $\mathscr{s}$. The $\mathscr{O}(\mathscr{s})$ form symmetric groups $\mathfrak{S}_n(\mathscr{O})$, $\mathfrak{S}_m(\mathscr{O})$ or $\mathfrak{S}_N(\mathscr{O})$ which are isomorphic to $\mathfrak{S}_n$, $\mathfrak{S}_m$ or $\mathfrak{S}_N$, respectively, under the mapping $\mathscr{s} \leftrightarrow \mathscr{O}(\mathscr{s}^{-1})$ [4]. According to [4] we denote the projection operators $\mathscr{P}_\chi$, $\mathscr{P}_\sigma$, $\mathscr{P}_n^{(r)}$, $\mathscr{P}_m^{(v)}$ and $\mathscr{P}_N^{(w)}$ associated with $\mathscr{p}_\chi$, $\mathscr{p}_\sigma$, $\mathscr{p}_n^{(r)}$, $\mathscr{p}_m^{(v)}$ and $\mathscr{p}_N^{(w)}$ by capital letters. With respect to (9) it holds

$$\mathscr{p}_\sigma = \mathscr{p}_\chi \mathscr{p}_m^{(1)}, \qquad \mathscr{P}_\sigma = \mathscr{P}_\chi \mathscr{P}_m^{(1)}. \tag{10}$$

Because of (7), the total symmetry of $\Gamma_m^{(1)}$ and (8) we find the operators $\mathscr{p}_\chi$, $\mathscr{p}_m^{(1)}$, $\mathscr{p}_\sigma$ given in (10) to be

$$\mathscr{p}_\chi = \frac{1}{|\mathfrak{S}|}\left[\sum_{\mathscr{s}\in\mathfrak{S}_0} \mathscr{s} - \sum_{\mathscr{s}'\in\mathfrak{S}^*} \mathscr{s}'\right], \qquad \mathscr{p}_m^{(1)} = \frac{1}{m!}\sum_{\mathscr{t}\in\mathfrak{S}_m} \mathscr{t}, \tag{11}$$

$$\mathscr{p}_\sigma = \frac{1}{|\mathfrak{U}|}\left[\sum_{\mathscr{u}\in\mathfrak{U}_0} \mathscr{u} - \sum_{\mathscr{u}'\in\mathfrak{U}^*} \mathscr{u}'\right]. \tag{12}$$

$\mathfrak{U}_0$ being the set of all the permutations of the form $\mathscr{s}\mathscr{t}$ and $\mathfrak{U}^*$ being the set of all the permutations of the form $\mathscr{s}'\mathscr{t}$, (10) also results directly from (11) and (12). Analogously to the C-concept (see [4], p. 235) any mixture G can be interpreted as the result of the action of an element $\mathscr{b}$,

$$\mathscr{b} = \sum_{\mathscr{s}\in\mathfrak{S}_N} b(\mathscr{s})\mathscr{s}, \tag{13}$$

of the group algebra of the $\mathfrak{S}_N$ on a vector L, which represents a given molecule:

$$G = \sum_{\mathscr{s}\in\mathfrak{S}_N} b(\mathscr{s})\mathscr{s}L. \tag{14}$$

Hereby $b(\mathscr{s})$ means the concentration of the compound $\mathscr{s}L$. Inserting (13) into (14) we can write

$$G = \mathscr{E}L. \tag{15}$$

According to ([4], p. 236) we call $\mathscr{E}$ the ensemble operator.

On treating non-isomeric mixtures as mixtures of fictive isomers the way of concluding of the C-concept can be transferred to the SC-concept:

1. A mixture $G = \mathscr{E}L$ is non-racemic if, and only if,

   $$\mathscr{p}_\sigma \mathscr{E} \neq 0 \tag{16}$$

   holds (see [4], p. 237). We designate $\mathscr{p}_\sigma \mathscr{E}$ as the σ-component of $\mathscr{E}$ (corresponding to the chiral component of [4]).
2. A function $\phi(L)$ represents a chirality function if, and only if,

   $$\phi(\mathscr{p}_\sigma L) = \phi(L) \tag{17}$$

   holds (see [4], p. 239).
3. For a chirality function $\phi(G)$

   $$\phi(G) = \phi(\mathscr{E}L) = \phi(\mathscr{p}_\sigma \mathscr{E}L) \tag{18}$$

   holds in any case.

That is to say, only the σ-component $\mathscr{p}_\sigma \mathscr{E}$ of the ensemble operator $\mathscr{E}$ regarded is decisive for the value of a chirality function of the mixture $G = \mathscr{E}L$.

In addition to point 2 we have to raise another postulate concerning chirality functions: within the scope of the SC-concept a chirality function $\phi(L) = \phi(L_e|L_f)$ must only depend on the ligands situated on the real skeletal sites (see Eq. (3)):

$$\phi(L) = \phi(L_e|L_f) = \tilde{\phi}(L_e).$$

It follows that

$$\phi(\mathscr{p}_\sigma L) = \phi(\mathscr{p}_\chi L_e | \mathscr{p}_m^{(1)} L_f) = \tilde{\phi}(\mathscr{p}_\chi L_e). \tag{19}$$

With regard to (17) it holds

$$\phi(L) = \phi(\mathscr{p}_\sigma L) = \tilde{\phi}(\mathscr{p}_\chi L_e) = \tilde{\phi}(L_e). \tag{20}$$[5]

4. The Formal Conditions for Qualitative Supercompleteness

The formal conditions for qualitative supercompleteness are obtained in the same way as those for qualitative completeness. Let us briefly repeat the conditions for

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[5] Within mathematics functions are defined as mappings: in this sense ϕ stands for a mapping of the $N!$-dimensional space $R^{N!}$ – the points of which correspond to mixtures $\sum b(\mathscr{s})\mathscr{s}L$ of molecules $\mathscr{s}L$, $\mathscr{s} \in \mathfrak{S}_N$ – onto the one-dimensional space R^1. Adequately $\tilde{\phi}$ is a mapping of $R^{n!}$ onto R^1. Equations $\phi(L) = \tilde{\phi}(L_e)$ or $\phi(L_e|L_f) = \tilde{\phi}(L_e)$, respectively, mean that the value of the function ϕ does not depend on L_f but only on L_e and that for given L_e ϕ and $\tilde{\phi}$ give the same function value. Thus the same dependence as the one of $\tilde{\phi}$ on L_e prevails.

qualitative completeness [4]:

A chirality function is qualitatively complete, if the $\sum z_r n_r$ functions

$$\tilde{\phi}(\mathscr{p}_{ij}^{(r)} L_e) \quad r \text{ with } z_r \neq 0; \quad i = 1, \ldots, z_r; \quad j = 1, \ldots, n_r \tag{21}$$

are linearly independent. n_r means the dimension of the irreducible representation $\Gamma_n^{(r)}$ of the $\mathfrak{S}_n$. z_r states how often Γ_χ appears in $\Gamma_n^{(r)}$. $\mathscr{p}_{ij}^{(r)}$ are the projection and shift operators associated with $\Gamma_n^{(r)}$.

Within the scope of the qualitative supercompleteness the numbers x_w are to be considered instead of the numbers z_r. x_w indicates how often the σ-chirality representation Γ_σ of the subgroup $\mathfrak{U}$ of $\mathfrak{S}_N$ is contained in the irreducible representation $\Gamma_N^{(w)}$ of the $\mathfrak{S}_N$. Analogously to Eq. (12a) of [4] the σ-component $\mathscr{p}_\sigma \mathscr{e}$ of an ensemble operator can be decomposed into

$$\mathscr{p}_\sigma \mathscr{e} = \sum_w \sum_{i=1}^{x_w} \sum_{j=1}^{n_w} b_{ij}^{(w)} \mathscr{p}_{ij}^{(w)}. \tag{22}$$

$\mathscr{p}_{ij}^{(w)}$, $i, j = 1, \ldots, n_w$, are the projection and shift operators of the irreducible representations $\Gamma_N^{(w)}$ of the $\mathfrak{S}_N$ forming a basis of the group algebra of this group. $b_{ij}^{(w)}$ mean the coefficients of linear combination. The n_w stand for the dimensions of $\Gamma_N^{(w)}$. Corresponding to (18) the value of the chirality function for the mixture $G = \mathscr{e} L$ is obtained as

$$\phi(G) = \phi(\mathscr{e} L) = \phi(\mathscr{p}_\sigma \mathscr{e} L) = \sum_w \sum_{i=1}^{x_w} \sum_{j=1}^{n_w} b_{ij}^{(w)} \phi(\mathscr{p}_{ij}^{(w)} L). \tag{23}$$

Similarly to the considerations of the C-concept the following results follow directly from (23):

A chirality function $\phi(L)$ is qualitatively supercomplete if, and only if, its components

$$\phi(\mathscr{p}_{ij}^{(w)} L) \quad \text{for all } w \text{ with } x_w \neq 0;\ i = 1, \ldots, x_w,\ j = 1, \ldots, n_w, \tag{24}$$

are linearly independent.

Nevertheless the conditions for qualitative supercompleteness can also be stated without using representation theory. Dugundji *et al.* [11] have demonstrated this for qualitative completeness. Their argumentation can be summarized as follows: Let $L_e^{(k)}$, $k = 1, \ldots, g$, be one enantiomer of the enantiomeric pair k. The number of enantiomeric pairs is given by

$$g = \frac{n!}{|\mathfrak{S}|}. \tag{25}$$

It holds that a chirality function $\tilde{\phi}(L_e)$ is qualitatively complete if, and only if, the functions

$$\tilde{\phi}(L_e^{(1)}),\ \tilde{\phi}(L_e^{(2)}),\ \ldots,\ \tilde{\phi}(L_e^{(g)}) \tag{26}$$

are linearly independent. This result is directly reasonable because of every isomeric mixture G being a linear combination

$$G = a_1 L_e^{(1)} + a_2 L_e^{(2)} + \cdots + a_g L_e^{(g)}. \tag{27}$$

Thereby a negative concentration a_k is to be interpreted as the positive concentration $-a_k$ of the antipode of $L_e^{(k)}$. The chirality function

$$\tilde{\phi}(G) = a_1 \tilde{\phi}(L_e^{(1)}) + \cdots + a_g \tilde{\phi}(L_e^{(g)}) \tag{28}$$

of an isomeric mixture G according to (27) cannot be identically annihilated if the $\tilde{\phi}(L_e^{(k)})$, $k = 1, \ldots, g$ are linearly independent. This deduction of the formal conditions for qualitative completeness is equivalent to the one arguing via regular induction [4, 12]. It follows that the functions $\tilde{\phi}(\wp_{ij}^{(\bar{r})} L_e)$, $i = 1, \ldots, z_{\bar{r}}$; $j = 1, \ldots, n_{\bar{r}}$, and the functions $\tilde{\phi}(L_e^{(k)})$, $k = 1, \ldots, g$, span the same function space.[6] Because of the equality of the dimensions the number of enantiomeric pairs $g = n!/|\mathfrak{S}|$ equals

$$g = \frac{n!}{|\mathfrak{S}|} = \sum_r n_r z_r = \sum_{\bar{r}} n_{\bar{r}} z_{\bar{r}}. \tag{29}$$

Hence the conditions for qualitative completeness can also be formulated without using a decomposition into irreducible representations of the $\mathfrak{S}_n$. We view this fact as an additional argument (see also [9–11]), that interpreting the decomposition into irreducible representations of $\mathfrak{S}_n$ as an appropriate decomposition of the chirality phenomenon has no physical relevance at all.

Analogous considerations are to be applied with respect to qualitative supercompleteness. With N ligand sorts and n skeletal sites the number h of enantiomeric pairs equals

$$h = \binom{N}{n} \frac{n!}{|\mathfrak{S}|}.$$

$\binom{N}{n}$ gives the number of possible selections of n different ligands and is multiplied by the number $n!/|\mathfrak{S}|$ of antipodal pairs for a given selection.

It follows $h = N!/(m!|\mathfrak{S}|)$ and because of $m!|\mathfrak{S}| = |\mathfrak{S}_m| \times |\mathfrak{S}| = |\mathfrak{S}_m \times \mathfrak{S}| = |\mathfrak{U}|$

$$h = \frac{N!}{|\mathfrak{U}|}. \tag{30}$$

Eq. (30) represents the analogue of Eq. (25). A chirality function $\phi(L) = \phi(L_e|L_f)$ depending only formally on L_f is qualitatively supercomplete if, and only if, the h functions

$$\phi(L^{(1)}), \phi(L^{(2)}), \ldots, \phi(L^{(h)}) \tag{31}$$

are linearly independent, whereby $L^{(k)}$, $k = 1, \ldots, h$, represents one enantiomer of the enantiomeric pair k. Analogously to the reasoning concerned with qualitative completeness it results from the identity of the conditions that the functions (24)

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[6] As in [4] $\bar{r}$ denotes the index of an irreducible representation $\Gamma_n^{(r)}$ containing Γ_χ.

and (31) have to span the same function space. As the number of the basis functions must be the same again it follows for the number $h = N!/|\mathfrak{U}|$ of the enantiomeric pairs

$$h = \frac{N!}{|\mathfrak{U}|} = \sum_{w} n_w x_w = \sum_{\bar{w}} n_{\bar{w}} x_{\bar{w}}. \tag{32}$$

According to the notation $\bar{r}$ of [4] the representations $\Gamma_N^{(w)}$ with $x_w \neq 0$ are denoted by $\bar{w}$, if the σ-chirality representation Γ_σ is contained in $\Gamma_N^{(w)}$.

5. The Determination of the x_w

Referring to Sect. 4 the x_w indicate how often the irreducible representations $\Gamma_N^{(w)}$ of $\mathfrak{S}_N$ contain the σ-chirality representation $\Gamma_\sigma = \Gamma_\chi \times \Gamma_m^{(1)}$ of the subgroup $\mathfrak{U} = \mathfrak{S} \times \mathfrak{S}_m$. The x_w can be easily deduced from the z_r of the C-concept (see [4], Sect. 4) by means of Froebenius' reciprocity theorem [13]: First of all let $\phi(L_e|L_f)$ be a function of two sets L_e and L_f of n and m arguments, respectively,

$$\phi(L_e|L_f) = \phi(l_1, \ldots, l_n | l_{n+1}, \ldots, l_N), \qquad N - n = m. \tag{33}$$

Considering permutations of arguments within L_e $\phi(L)$ is assumed to transform according to the irreducible representation $\Gamma_n^{(r)}$ of $\mathfrak{S}_n$. Likewise, $\phi(L)$ might transform according to $\Gamma_m^{(v)}$ of $\mathfrak{S}_m$ with respect to permutations of arguments within L_f. Thus on permuting arguments within each of the two argument vectors simultaneously the resulting functions form a basis of the direct product $\Gamma_n^{(r)} \times \Gamma_m^{(v)}$ which is an irreducible representation of the subgroup $\mathfrak{S}_n \times \mathfrak{S}_m$ of $\mathfrak{S}_N$. However, by allowing for all $N!$ permutations of the N arguments, i.e. including those between L_e and L_f the functions obtained form a basis of the so-called outer product $\Gamma_n^{(r)} \otimes \Gamma_m^{(v)}$. Generally the outer product is a reducible representation of the $\mathfrak{S}_N$, see [14]. Table 2 offers a view of the transformation properties cited above.

From the reciprocity theorem one can deduce the following corollary: The coefficients t_{wrv} in the decomposition

$$\Gamma_n^{(r)} \otimes \Gamma_m^{(v)} = \sum_{w} t_{wrv} \Gamma_N^{(w)} \tag{34}$$

Table 2. Representations spanned on permuting the arguments of $\phi(L_e|L_f)$

Kind of permutations	Representations spanned	Properties of the representation
only within L_e	$\Gamma_n^{(r)}$	irred. repr. of $\mathfrak{S}_n$
only within L_f	$\Gamma_m^{(v)}$	irred. repr. of $\mathfrak{S}_m$
simultaneously within L_e and within L_f	$\Gamma_n^{(r)} \times \Gamma_m^{(v)}$	irred. repr. of $\mathfrak{S}_n \times \mathfrak{S}_m \subset \mathfrak{S}_N$
all permutations (including those between L_e and L_f)	$\Gamma_n^{(r)} \otimes \Gamma_m^{(v)}$	red. repr. of $\mathfrak{S}_N$

of the outer product $\Gamma_n^{(r)}\otimes\Gamma_m^{(v)}$ according to the irreducible representations $\Gamma_N^{(w)}$ of $\mathfrak{S}_N$ equal the coefficients t_{wrv} in the decomposition

$$\Gamma_N^{(w)} = \sum_r \sum_v t_{wrv}(\Gamma_n^{(r)}\times\Gamma_m^{(v)}) \tag{35}$$

of Γ_N with respect to the irreducible representations $\Gamma_n^{(r)}\times\Gamma_m^{(v)}$ of the subgroup $\mathfrak{S}_n\times\mathfrak{S}_m$ of $\mathfrak{S}_N$. As the reciprocity theorem is related to the theorem of Ruch and Schönhofer on regular induction [12], this result can also be got directly by the latter[7]. With respect to this point one has to bear in mind that $\Gamma_n^{(r)}\otimes\Gamma_m^{(v)}$ arises from $\Gamma_n^{(r)}\times\Gamma_m^{(v)}$ by regular induction.

Considering the right hand side of (35) the representations $\Gamma_n^{(r)}$ contain the chirality representation Γ_χ z_r times, and the $\Gamma_m^{(v)}$ contain the totally symmetric representation $\Gamma_m^{(1)}$ δ_{v1} times, δ_{v1} standing for the Kronecker delta. $\Gamma_m^{(1)}$ is included in $\Gamma_m^{(v)}$ if, and only if, $v=1$. It follows, that the σ-chirality representation $\Gamma_\sigma=\Gamma_\chi\times\Gamma_m^{(1)}$ is contained in $\Gamma_n^{(r)}\times\Gamma_m^{(v)}$ exactly $z_r\delta_{v1}$ times. With respect to the decomposition (35) we obtain

$$x_w = \sum_r \sum_v t_{wrv} z_r \delta_{v1}$$

implying

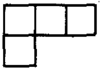
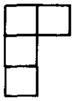
$$x_w = \sum_{\bar{r}} t_{w\bar{r}1} z_{\bar{r}}. \tag{36}$$

With this we could confine the summation to the indices $\bar{r}$, with $z_{\bar{r}}\neq 0$. t_{wr1} and $t_{w\bar{r}1}$, respectively, can be determined by the decomposition of the outer product (34) in quite a simple way. The decomposition can be performed by a graphic rule, that is especially simple if one of the factors is the totally symmetric representation:

The outer product $\Gamma_n^{(r)}\otimes\Gamma_m^{(1)}$ contains an irreducible representation $\Gamma_N^{(w)}$ of $\mathfrak{S}_N$ exactly once if the diagram $\gamma_N^{(w)}$ of $\Gamma_N^{(w)}$ can be formed by adding the m boxes of the single line diagram $\gamma_m^{(1)}$ of $\Gamma_m^{(1)}$ to the diagram $\gamma_n^{(r)}$ of $\Gamma_n^{(r)}$ without putting any two boxes added into the same column. All the other $\Gamma_N^{(w)}$ are not contained in the outer product. Therefore t_{wr1} only takes the value zero or one.

Example 2:

Consider the skeleton of Fig. 2 with C_{2h}-symmetry, and four ligand sites. Let us assume seven sorts of ligands, thus $n=4$, $m=3$, $N=7$. Only two of the five irreducible representations $\Gamma_4^{(r)}$ of $\mathfrak{S}_4$ contain the chirality representation Γ_χ namely $\Gamma_4^{(2)}$ and $\Gamma_4^{(4)}$ with $z_2=z_4=1$.

$\gamma_4^{(2)} =$  , $\gamma_4^{(4)} =$  .

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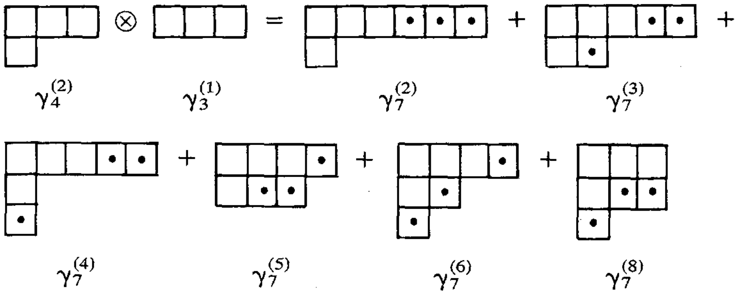
[7] We thank an anonymous referee for calling our attention to this point.

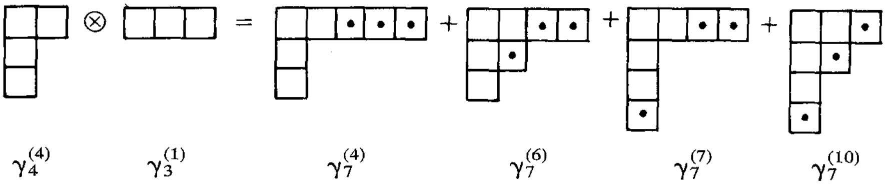
According to (36) we have to sum over $\bar{r} = 2, 4$ obtaining

$$x_w = t_{w21} + t_{w41}. \tag{37}$$

To derive t_{w21} and t_{w41} let us turn to the decomposition (34). We identify the $\Gamma_7^{(w)}$ with the partition diagrams $\gamma_7^{(w)}$ and apply the graphic reduction rule:



(38)[8]



(39)[8]

Consequently, t_{w21} equals one if the diagram $\gamma_7^{(w)}$ is found in the right hand side of Eq. (38). The corresponding statement applies to t_{w41} referring to (39). Because of (37) it follows $x_w = 2$, if $\gamma_7^{(w)}$ appears both in (38) and (39), $x_w = 1$, if $\gamma_7^{(w)}$ is present in exactly one equation and $x_w = 0$, if $\gamma_7^{(w)}$ is met with neither equation.

Thus the following x_w are derived to differ from zero:

$$x_4 = x_6 = 2,$$

$$x_2 = x_3 = x_5 = x_7 = x_8 = x_{10} = 1.$$

For the following considerations let us arrange the partition diagrams $\gamma_N^{(w)}$ (obtained by adding $m = N - n$ boxes to a diagram $\gamma_n^{(\bar{r})}$ without repetition in the same column) in a half order $\mathfrak{H}_{nN}^{(\bar{r})}$. (For the concept of half orders see [16]). $\mathfrak{H}_{nN}^{(\bar{r})}$ is formed by the set

$$\mathfrak{H}_{nN}^{(\bar{r})} = \{\gamma_N^{(w)} \mid t_{w\bar{r}1} = 1\}. \tag{40}$$

Given Example 2, the half order $\mathfrak{H}_{47}^{(2)}$ or $\mathfrak{H}_{47}^{(4)}$, resp., is built by the diagrams of the right hand side of Eq. (38) or (39). The half order to be defined which we call TU-half order[9], is not identical with the half order of Ruch and Schönhofer [4],

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[8] For the sake of clarity the three boxes added to the $\gamma_4^{(\bar{r})}$ are marked by a point. The numbering of the irreducible representations of the $\mathfrak{S}_7$ obeys Young's order.

[9] For this notation we have chosen T, U as being the two letters following R, S in the alphabet.

named RS-half order here. In the sense of the RS-half order a diagram γ' is defined smaller than another diagram γ, $\gamma' \subset \gamma$, if it can be obtained from γ by transferring boxes from upper lines to lower ones. Within the scope of the TU-half order, however, we define a diagram $\gamma_N^{(w')}$ to be smaller than another diagram $\gamma_N^{(w)}$, $\gamma_N^{(w')} \subset \gamma_N^{(w)}$, if we can construct it by moving boxes from the first line downwards. Analogously to the RS-half order $\gamma_N^{(w)} \subset \gamma_N^{(w)}$ is valid. If a diagram is smaller than another one in the TU-half order, the same holds with respect to the RS-half order. Nevertheless, the converse is not true.

It should be emphasized that the TU-half order does not represent the analogue to the RS-half order. From the TU-half orders the x_w can be derived. But a TU-half order cannot be used to discuss the problem of active partitions. For this purpose we still make use of the RS-half order (see below).

$\mathfrak{H}_{nN}^{(\bar{r})}$ contains a largest diagram $\gamma_N^{(w_{\bar{r}}^0)}$ derived from $\gamma_n^{(\bar{r})}$ on extending the first line by m boxes. Proceeding step by step from $\gamma_N^{(w_{\bar{r}}^0)}$ to smaller diagrams $\gamma_N^{(w)} \in \mathfrak{H}_{nN}^{(\bar{r})}$ just one, if any, of the boxes removed from the first row may be put under each column. Reversing this procedure, a larger diagram can be obtained from a smaller one solely by pulling one box at most from each column to the first line. Fig. 3 gives the TU-half orders $\mathfrak{H}_{4N}^{(2)}$ and $\mathfrak{H}_{4N}^{(4)}$ for the skeleton of Fig. 2 with $N = 4, 5, 6, 7, 8$.

$t_{w\bar{r}1}$ equals one just for the representations $\Gamma_N^{(w)}$ with diagrams $\gamma_N^{(w)} \in \mathfrak{H}_{nN}^{(\bar{r})}$. Since it is zero in any other case, we may rewrite (36)

$$x_w = \sum_{\substack{\bar{r} \\ \gamma_N^{(w)} \in \mathfrak{H}_{nN}^{(\bar{r})}}} z_{\bar{r}} \tag{41}$$

Eq. (41) expresses x_w to be composed additively by those $z_{\bar{r}}$, for which $t_{w\bar{r}1} = 1$, $\gamma_N^{(w)} \in \mathfrak{H}_{nN}^{(\bar{r})}$ holds. Both Eq. (36) and (41) are easily verified by substituting them into Eq. (32) deduced for the number h of enantiomeric pairs:

$$h = \sum_{\bar{r}} z_{\bar{r}} \sum_{\substack{w \\ \gamma_N^{(w)} \in \mathfrak{H}_{nN}^{(\bar{r})}.}} n_w \tag{42}$$

In the case of a skeleton of C_{2h}-symmetry (see Fig. 2) with $z_2 = z_4 = 1$, it follows therefore that the number h of enantiometric pairs equals the sum of the dimensions n_w of the representations met with $\mathfrak{H}_{4N}^{(2)}$ and $\mathfrak{H}_{4N}^{(4)}$. Fig. 3 gives the dimension n_w beside each diagram. (For the calculation of n_w see [17]). The last row contains the sums h. We leave it to the reader to control h in quite an elementary way by counting the number of enantiomeric pairs according to (30).

Let us briefly turn to the question which ligand assortments are "active" thus treating compounds with partially equal ligands. An assortment of N ligands is characterized by a partition diagram $\gamma_N^{(s)}$. The length $\nu_i^{(s)}$ of the ith row of $\gamma_N^{(s)}$ is equal to the number of ligands of the ith kind. As the ligands are to be distributed over the fictively extended skeleton $\nu_i^{(s)}$ is the greatest possible number of ligands of the sort i in the real molecule. A ligand assortment is termed active for a chiral ensemble operator $\mathscr{e}$ (with $\wp_\sigma \mathscr{e} \neq 0$) if the ligands can be attached to the sites of the fictively extended skeleton in such a way that the mixture $\mathscr{e}L$ is non-racemic.

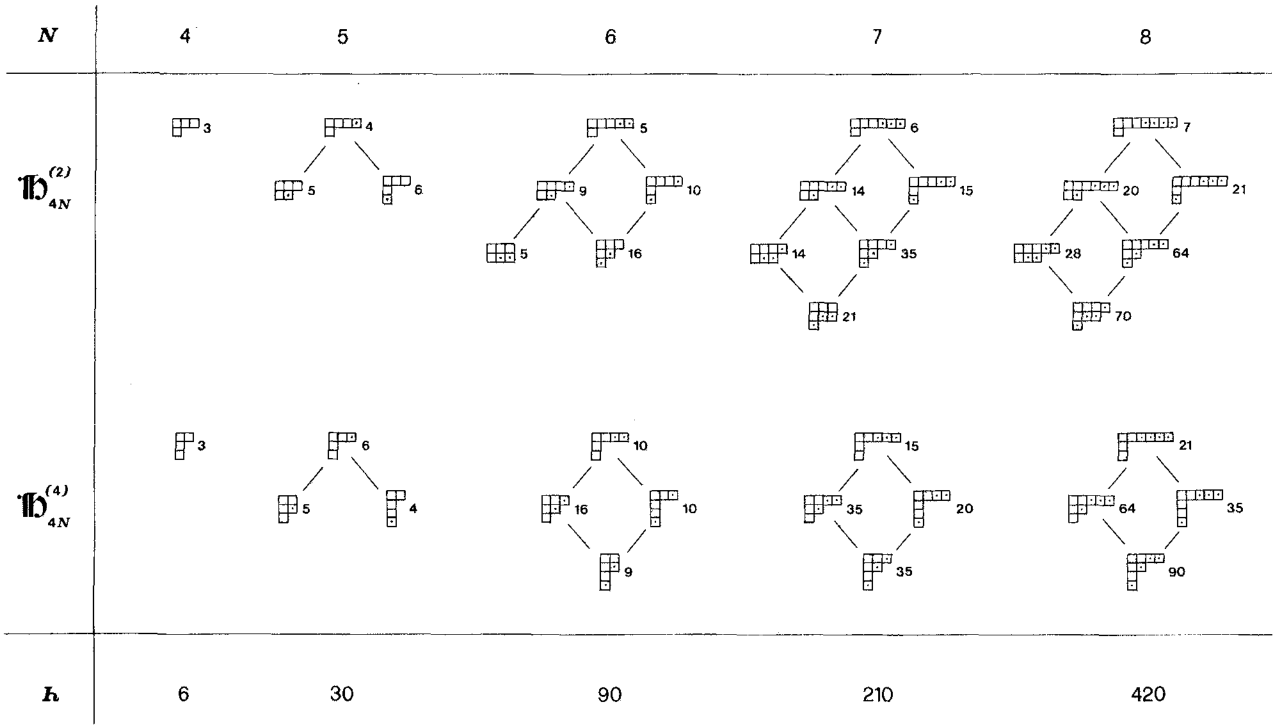

Fig. 3. The TU-half order $\mathfrak{H}_{4N}^{(2)}$ and $\mathfrak{H}_{4N}^{(4)}$, $N=4, \ldots, 8$, for the skeleton of C_{2h}-symmetry given in Fig. 2 with N-n fictive sites. For the sake of clarity the boxes added are marked by a point. The dimensions $n_{\bar{r}}$ and n_w are given on the right hand side of the $\gamma_n^{(\bar{r})}$ and $\gamma_N^{(w)}$. The last row contains the number h of enantiomeric pairs

In analogy to [4] one obtains the following results:

1. The ligand assortment corresponding to an assortment diagram $\gamma_N^{(s)}$ can be filled into a representation diagram $\gamma_N^{(w)}$ without repetition of identical ligands in the same column, exactly if $\gamma_N^{(s)}$ is smaller than $\gamma_N^{(w)}$, $\gamma_N^{(s)} \subset \gamma_N^{(w)}$ in the sense of the RS-half order defined in [4].

2. A ligand assortment corresponding to an assortment diagram $\gamma_N^{(s)}$ is active with respect to a chiral ensemble operator $\mathscr{b}$, if, and only if, $\gamma_N^{(s)} \subset \gamma_N^{(\bar w)}$ holds in the sense of the RS-half order at least for one $\bar w$ with $\wp_\sigma \mathscr{b} \wp_N^{(\bar w)} \neq 0$.

3. A ligand assortment is active with respect to all chiral ensemble operators $\mathscr{b}$, if, and only if, $\gamma_N^{(s)} \subset \gamma_N^{(\bar w)}$ for all $\bar w$. If there exists a smallest diagram $\gamma_N^{(w^*_{\bar r})}$ in every $\mathfrak{H}_{nN}^{(\bar r)}$ this condition is equivalent to the condition that $\gamma_N^{(s)} \subset \gamma_N^{(w^*_{\bar r})}$ holds for all $\bar r$.

4. By setting $\mathscr{b} = \mathscr{e}$ we conclude from 1 that those ligand assortments are active for the molecule for which $\gamma_N^{(s)} \subset \gamma_N^{(\bar w)}$ holds at least for one $\bar w$. This is equivalent to $\gamma_N^{(s)} \subset \gamma_N^{(w^0_{\bar r})}$ for at least one $\bar r$.

6. The Homomorphism of the TU-Half Orders $\mathfrak{H}_{nN}^{(\bar r)}$

Now we start to discuss some of the properties of the TU-half order which we shall need later. Inspecting Fig. 3 one concludes that the number $\xi_N^{(\bar r)}$ of diagrams of $\mathfrak{H}_{nN}^{(\bar r)}$ grows with increasing N up to a maximum value $\xi_{\max}^{(\bar r)}$ remaining constant for all greater N. This constancy holds if the number $m = N - n$ of boxes added equals at least the length $o_1^{(\bar r)}$ of the first row of $\gamma_n^{(\bar r)}$ (notation according to [4]). To realize this consider the fact, that all possibilities of putting boxes, if any, below columns of $\gamma_n^{(\bar r)}$ are exhausted by $m = o_1^{(\bar r)}$. Supplied with as many boxes as there exist columns an overstocking of $m > o_1^{(\bar r)}$ does not increase the number of possibilities, since only the first lines of the $\gamma_N^{(w)}$ are extended.

In Sect. 5 the rule of forming the elements of $\mathfrak{H}_{nN}^{(\bar r)}$ as well as the relation $\subset$ have been defined. According to these statements we find the mapping $f_{N_1N_2}$,

$$f_{N_1N_2}: \mathfrak{H}_{nN_1}^{(\bar r)} \rightsquigarrow \mathfrak{H}_{nN_2}^{(\bar r)}, \qquad N_2 \geq N_1, \tag{43}$$

to be a homomorphism, $f_{N_1N_2}$ maps each element $\gamma_{N_1}^{(w)} \in \mathfrak{H}_{nN_1}^{(\bar r)}$ onto the element $\gamma_{N_2}^{(w)} = f_{N_1N_2}(\gamma_{N_1}^{(w)}) \in \mathfrak{H}_{nN_2}^{(\bar r)}$, the first row of which differs from $\gamma_{N_1}^{(w)}$ by $N_2 - N_1$ boxes[10]. If $\gamma_{N_1}^{(w')}$ is obtained from $\gamma_{N_1}^{(w)}$ by pulling boxes from the first line downwards, $\gamma_{N_1}^{(w')} \subset \gamma_{N_1}^{(w)}$, the same must hold with respect to diagrams the first line of which is extended by $N_2 - N_1$ boxes.

$$\gamma_{N_1}^{(w')} \subset \gamma_{N_1}^{(w)} \Rightarrow \gamma_{N_2}^{(w')} \subset \gamma_{N_2}^{(w)}.$$

If $N_1 \geq n + o_1^{(\bar r)}$ (implying $N_2 \geq n + o_1^{(\bar r)}$ the homomorphism reduces to an isomorphism.

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[10] The numbering index w of $\gamma_N^{(w)}$ and $\Gamma_N^{(w)}$ is no longer derived from the $\mathfrak{S}_N$, since we wish to prevent corresponding diagrams from being denoted in a different way. Rather the indices are to be taken from $\mathfrak{S}_{N'}$, with $N' = n + o_{\max}$. Subsequently they are transferred from $\gamma_{N'}^{(w)} \in \mathfrak{H}_{nN'}^{(\bar r)}$ to the diagrams of all the other half orders $\mathfrak{H}_{nN}^{(\bar r)}$. $o_{\max}$ gives the chirality order $o_{\max} = \max\{o_1^{(\bar r)}\}$ in accordance with [4]. $N' + n + o_{\max}$ marks the smallest number of ligand sorts exhibiting $\xi_N^{(\bar r)} = \xi_{\max}^{(\bar r)}$ with respect to all $\bar r$.

Concerning the number $\xi^{(\bar r)}_{\max}$ of the diagrams of a half order $\mathfrak{H}^{(\bar r)}_{nN}$ with $N \geq n + o^{(\bar r)}_1$ there exists a simple formula,

$$\xi^{(\bar r)}_{\max} = \Pi(\varepsilon^{(\bar r)}_i + 1). \tag{44}$$

$\varepsilon^{(\bar r)}_i$ stands for the number of columns of the length i of the diagram $\gamma^{(\bar r)}_n$. ($\varepsilon^{(\bar r)}_i = 0$ leading just to a factor one we need not assign a limiting value to the subscript i of (44)). Eq. (44) can be proved as follows: Given $N \geq n + o^{(\bar r)}_1$, which equals $m \geq o^{(\bar r)}_1$, there exist enough boxes to put one below each column of $\gamma^{(\bar r)}_n$. Provided $\gamma^{(\bar r)}_n$ contains $\varepsilon^{(\bar r)}_i$ columns of length i we may transfer none or one or ... or $\varepsilon^{(\bar r)}_i$ boxes below these columns. Thus we end with $\varepsilon^{(\bar r)}_i + 1$ possibilities, from which (44) follows.

For the case of $m < o^{(\bar r)}_1$ no simple formula to obtain $\xi^{(\bar r)}_N$ by means of the diagram $\gamma^{(\bar r)}_n$ can be derived. From the definition of t_{wr1} it follows

$$\xi^{(\bar r)}_N = \sum_w t_{w\bar r 1}. \tag{45}$$

7. A Construction Rule for Qualitatively Supercomplete Chirality Functions

In the following we give a simplified description of the rule how to construct qualitatively supercomplete chirality functions. The exact derivation is a bit troublesome and not of primary importance for discussing the properties of these functions. For the complete method of derivation, including all the definitions and proofs the reader is referred to the appendix.

7.1 Requirements and Conditions

Let us recall the two essential postulates chirality functions have to fulfill. Firstly, a chirality function has to meet the requirement of qualitative supercompleteness. For that purpose the properties of a set up to a chirality function $\phi(L)$ are determined by the smallest diagrams $\gamma^{(w^*_{\bar r})}_N$ of every $\mathfrak{H}^{(\bar r)}_{nN}$ with $N \geq n + o^{(\bar r)}_1$ as shown in Appendix A. Secondly, a chirality function may depend explicitly only on parameters of ligands attached to proper skeletal sites according to Eq. (3), $\phi(L) = \phi(L_e|L_f) = \tilde\phi(L_e)$. As a consequence the construction procedure acts within the frame of the $\mathfrak{S}_n$, if the formal properties of chirality functions derived via a formal extension to N arguments are known (see Appendices A and B).

We now introduce diagrams $\delta^{(w)}_\nu$ obtained from $\gamma^{(w)}_N$ by removing the first rows. For the number ν of their boxes $\nu \leq n$ holds; w is transferred from $\gamma^{(w)}_N$. $\Delta^{(w)}_\nu$ means the representation of $\mathfrak{S}_\nu$ to which $\delta^{(w)}_\nu$ is assigned. Let $\chi(L) = \tilde\chi(L_e)$ be a "Näherungsansatz" to $\phi(L) = \tilde\phi(L_e)$ obtained by a "Näherungsverfahren". Combining the two postulates it follows with respect to the set ups $\omega(L_e)$ to a chirality function $\tilde\chi(L_e)$, that the number of arguments and the transformation behaviour are determined by the diagrams $\delta^{(w^*_{\bar r})}_\nu$ obtained from the smallest diagrams $\gamma^{(w^*_{\bar r})}_N$ of $\mathfrak{H}^{(\bar r)}_{nN}$ with $N \geq n + o^{(\bar r)}_1$ on removing the first line. As the resulting diagrams $\delta^{(w^*_{\bar r})}_\nu$ equal $\gamma^{(\bar r)}_n$ the necessary condition results that a SC-chirality function has to consist at least of $z_{\bar r} = x_{w^*_{\bar r}}$ components for every $\bar r$ with set-ups $\tilde\omega^{(w^*_{\bar r})}_u(L_e)$ with $u = 1, \ldots, x_{w^*_{\bar r}}$ depending on exactly n ligand parameters and transforming according to the $\Delta^{(w^*_{\bar r})}_\nu$ which equal the $\Gamma^{(\bar r)}_n$ concerned (see Appendix A).

There emerge some important results:

a) On removing the first lines diagrams belonging to different half orders $\mathfrak{H}_{nN}^{(\bar{r})}$ of the same $\bar{r}$ become identical if they are associated to each other by the homomorphism (43). For $N \geq n + o_{\max}$ the homomorphisms reduce to isomorphisms for all $\bar{r}$. Thus independence of the number N of ligand kinds can be reached for $N \geq n + o_{\max}$: the diagrams $\delta_{\nu}^{(w\overset{*}{\bar{r}})}$ arising from the smallest diagrams $\gamma_{N}^{(w\overset{*}{\bar{r}})}$ equal $\gamma_{n}^{(\bar{r})}$ for all $\bar{r}$. From a practical viewpoint this seems a matter of course, since the number of ligand kinds should normally be unlimited. The concept developed leaves us with a cancellation of the upper limit thus rendering an arbitrary choice of N possible, if N equals at least $n + o_{\max}$[11]. We shall treat the case $N \geq n + o_{\max}$ in the following and accept it *by definition* as the general one supplying us with an appropriate molecular chirality function of a skeletal class, independently of the number N of ligand kinds.

b) The principle of pairwise (or better: many-body) interactions [18] assumes a chirality observation of a molecule to consist of all possible interactions of two (or more) atoms or groups that do not vanish for symmetry reasons [18]. In analogy to this principle the components $\bar{\omega}_{u}^{(w)}(L_{\mathrm{e}})$ derived from the $\tilde{\omega}_{u}^{(w)}(L_{\mathrm{e}})$ may be interpreted as interaction terms of a certain number of ligands [4]. Applying this interpretation to SC-chirality functions it follows, that qualitative supercompleteness requires the highest interactions available; i.e. its components $\bar{\omega}_{u}^{(w)}(L_{\mathrm{e}})$ depend on the maximum number of ligand parameters.

   Since the molecular skeleton is inherent to the basic model of the theory of chirality functions a separation into all-ligand and all-ligand-skeleton interactions cannot be performed.

However, this comparison calls our attention to a crucial point: The components of C-chirality functions depend on the minimum number of ligand parameters, while those of the SC-chirality functions depend on the maximum number of ligand parameters. While C-chirality functions imply the lowest interactions necessary for every $\bar{r}$, the SC-concept gives the highest possible ones. From a physical point of view both the results seem unsound. If one takes into account the physical considerations of [18] all the possible interactions should be included. One could also apply mathematical considerations: Let us require a chirality function to be of the most general form under the given restrictions. This requirement is called the *requirement of greatest possible generality*. It represents the mathematical analogue of the physical concept of the principle of many-body interactions. This mathematical principle leads independently to chirality functions of the same properties, namely that all possible interactions are included.

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[11] The limitation downwards, i.e. to all the cases $N < n + o_{\max}$, arises from the treatise of the problem within the $\mathfrak{S}_N$ (or $\mathfrak{S}_n$, resp., for the C-concept). This limitation–thought to be devoid of physical meaning–cannot be prevented as within this formalism molecular properties are to be derived via properties of mixtures.

Setting up functions $\tilde{\omega}_u^{(w{}^{*}_{\bar{r}})}(L_e)$ according to the $\gamma_n^{(\bar{r})}$ or $\delta_\nu^{(w{}^{*}_{\bar{r}})}$, respectively, concerned, all the possibilities of highest interaction terms to be considered are exhausted. There do not exist other $\tilde{\omega}_u^{(w)}(L_e)$ depending on exactly n ligands but differing in the transformation properties (compare also Appendix A). Thus the next step is to take into account all the components the set-up $\tilde{\omega}_u^{(w)}(L_e)$ of which represents a function depending explicitly on $(n-1)$ ligands. This procedure is continued until one ends with the lowest interaction term for every $\mathfrak{H}_{nN}^{(\bar{r})}$. Fortunately the SC-concept renders favorable conditions for the construction of chirality functions complying not only with the postulate of qualitative supercompleteness but also with compelling physical arguments and/or the mathematical requirement of greatest possible generality.

7.2. The "Näherungsverfahren"

Concerning the second "Näherungsverfahren" the above considerations result in the following: The orders of the lowest interactions, i.e. the number of arguments in the set-ups, can be obtained from the C-concept. Furthermore they can be given by removing the first lines of the largest diagrams of the appropriate $\mathfrak{H}_{nN}^{(\bar{r})}$. Then the order equals the number of boxes of the remaining diagram. Thus the highest and the lowest interactions are known. All the other kinds of interaction can be obtained by removing boxes one by one from the diagram representing the highest interaction till the one standing for the lowest interaction is formed. Each intermediate diagram gives a new interaction term. This procedure can be reformulated in terms of the $\mathfrak{H}_{nN}^{(\bar{r})}$. By eliminating the first lines of all $\gamma_N^{(w)} \in \mathfrak{H}_{nN}^{(\bar{r})}$ a half order $\mathfrak{h}_n^{(\bar{r})}$ arises the diagrams $\delta_\nu^{(w)}$ of which designate all the kinds of interactions possible. According to the skeletal class we thus get all ν-ligands(-skeleton)-interactions up to n-ligands(-skeleton)-interactions. Some of the elements of the $\mathfrak{H}_{nN}^{(\bar{r})}$ with constant n,N and different $\bar{r}$ appear to be alike. As there does not exist any convincing argument for differentiating between the components of a chirality function with respect to $\bar{r}$, like diagrams are collected and their x_w obtained by summation according to (36): $x_w = \sum t_{wr1} z_r$. The components $\tilde{\chi}^{(w)}(L_e)$ of the chirality function are set up according to

$$\tilde{\chi}^{(w)}(L_e) = \mathcal{P}_\chi \sum_{u=1}^{x_w} \mathcal{O}\,(\sigma_u^{(w)})\, \mathcal{Y}_{kk}^{(w)}\, \tilde{\omega}_u^{(w)}(L_e), \tag{46}$$

(see the appendix) with $\tilde{\omega}_u^{(w)}(L_e)$ representing the set-up for each $\delta_\nu^{(w)}$ depending explicitly on ν ligand parameters, $\nu \leq n$. $\mathcal{Y}_{kk}^{(w)} = \tilde{\mathcal{Q}}_k^{(w)} \mathcal{Q}_k^{(w)}$ denotes the Young operator of the $\tilde{\mathcal{Q}}\mathcal{Q}$-type of an arbitrarily chosen Young tableau k to the partition diagram $\delta_\nu^{(w)}$. $\tilde{\mathcal{Q}}_k^{(w)}$ is the sum over all vertical permutations φ_v of the given tableau multiplied by the parity δ_{φ_v} of the permutation, $\tilde{\mathcal{Q}}_k^{(w)} = \sum \delta_{\varphi_v} \varphi_v$, and $\mathcal{Q}_k^{(w)}$ represents the sum over all horizontal permutations φ_h, $\mathcal{Q}_k^{(w)} = \sum \varphi_h$ (see [14]). For a simple notation $\tilde{\omega}_u^{(w)}(L_e) = \tilde{\omega}_u^{(w)}(l_1, \ldots, l_\nu | l_{\nu+1}, \ldots, l_n)$ will be written as $\tilde{\omega}_u^{(w)}(l_1, \ldots, l_\nu)$ exhibiting $l_{\nu+1}, \ldots, l_n$ to appear only formally in the argument of $\tilde{\omega}_u^{(w)}(L_e)$. Furthermore, we shall abbreviate $\mathcal{Y}_{kk}^{(w)} \tilde{\omega}_u^{(w)}(l_1, \ldots, l_\nu | l_{\nu+1}, \ldots, l_n) = \mathcal{Y}_{kk}^{(w)} \tilde{\omega}_u^{(w)}(l_1, \ldots, l_\nu)$ by $\bar{\omega}_u^{(w)}(l_1, \ldots, l_\nu)$. The operators $\mathcal{O}(\sigma_u^{(w)})$–working on functions (see Sect. 3)–correspond to x_w suitably chosen permutations $s_u^{(w)} \in \mathscr{S}_n$. Besides on w the choice of the $s_u^{(w)}$ depends also on the selected k (see Appendix B). Consequently, the chirality function is given by

$$\tilde{\chi}(L_e) = \sum_{\substack{w \\ x_w \neq 0}} \tilde{\chi}^{(w)}(L_e). \tag{47}$$

Now the procedure is shown by means of an example.

Example 3:
Consider a skeleton of symmetry C_{2h} with four skeletal sites (e.g. the skeleton of Fig. 2). Obviously $o_{\max} = 3$, thus we choose $N = 7$. The half orders $\mathfrak{H}_{47}^{(2)}$ and $\mathfrak{H}_{47}^{(4)}$ are given in Fig. 3. On removing the first lines of the diagrams $\gamma_7^{(w)}$ we obtain the half orders $\mathfrak{h}_4^{(2)}$ and $\mathfrak{h}_4^{(4)}$ of all diagrams $\delta_\nu^{(w)}$, see Fig. 4 and Appendix B.

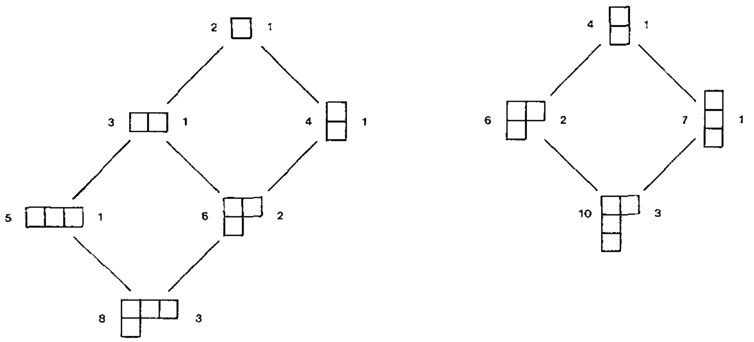
After having collected those diagrams containing equal numbers of boxes we get one first order term

$$\nu = 1 \qquad \delta_1^{(2)} = \square\,, \qquad x_2 = 1, \qquad q_2 = 1$$

three second order terms

$$\nu = 2 \qquad \delta_2^{(3)} = \square\!\square\,, \qquad x_3 = 1, \qquad q_3 = 1 \qquad \text{and}$$

$$\delta_2^{(4)} = \begin{smallmatrix}\square \\ \square\end{smallmatrix}\,, \qquad x_4 = 2, \qquad q_4 = 1$$



$\mathfrak{h}_4^{(2)}$ $\mathfrak{h}_4^{(4)}$

Fig. 4. The half orders $\mathfrak{h}_4^{(2)}$ and $\mathfrak{h}_4^{(4)}$ obtained on removing the first lines of $\mathfrak{H}_{4N}^{(2)}$ and $\mathfrak{H}_{4N}^{(4)}$ of Fig. 3 with $N \leq n + o_{\max}$. The numbers on the left side of the diagrams $\delta_\nu^{(w)} \in \mathfrak{h}_4^{(r)}$ indicate the superscripts w, the numbers on the right side the dimensions q_w of the $\Delta_\nu^{(w)}$. ν equals the number of boxes of each diagram

four third order terms

$\nu = 3 \qquad \delta_3^{(5)} = \begin{array}{|c|c|c|}\hline \ & \ & \ \\ \hline\end{array}, \qquad x_5 = 1, \qquad q_5 = 1,$

$\delta_3^{(6)} = \begin{array}{|c|c|}\hline \ & \ \\ \hline \ & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}, \qquad x_6 = 2, \qquad q_6 = 2$ and

$\delta_3^{(7)} = \begin{array}{|c|}\hline \ \\ \hline \ \\ \hline \ \\ \hline\end{array}, \qquad x_7 = 1, \qquad q_7 = 1$

and two fourth order terms

$\nu = 4 \qquad \delta_4^{(8)} = \begin{array}{|c|c|c|}\hline \ & \ & \ \\ \hline \ & \multicolumn{2}{c}{} \\ \cline{1-1}\end{array}, \qquad x_8 = 1, \qquad q_8 = 3$ and

$\delta_4^{(10)} = \begin{array}{|c|c|}\hline \ & \ \\ \hline \ & \multicolumn{1}{c}{} \\ \cline{1-1} \ & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}, \qquad x_{10} = 1, \qquad q_{10} = 3$

with corresponding diagrams $\delta_\nu^{(w)}$, x_w and dimensions q_w, thus rendering ten components of $\tilde{\chi}(L_e)$. We choose $\mathcal{Y}_{kk}^{(w)}$ with $k = 1$ according to the Young tableau given beside $\delta_\nu^{(w)}$ in the following and omit the index k of $\mathcal{Y}_{kk}^{(w)}$. Given $\mathcal{P}_\chi = \mathcal{O}(e + (14)(23) - (12)(34) - (13)(24))$ the components $\tilde{\chi}^{(w)}(L_e)$ are derived according to (46):

With $\delta_1^{(2)} = \begin{array}{|c|}\hline \ \\ \hline\end{array}$, $x_2 = 1$, $q_2 = 1$; the standard tableau $\boxed{1}$, the set up $\tilde{\omega}^{(2)}(l_1)$ and the Young operator $\mathcal{Y}^{(2)} = \mathcal{O}(e)$, the basis is given by $[\mathcal{Y}^{(2)}\tilde{\omega}^{(2)}(l_1)] = [\tilde{\omega}^{(2)}(l_1)]$ showing trivial transformation behaviour. Putting $\mathcal{O}(\sigma_1^{(2)}) = \mathcal{O}(e)$, $\tilde{\chi}^{(2)}(L_e)$ is established to be

$$\tilde{\chi}^{(2)}(L_e) = \tilde{\omega}^{(2)}(l_1) - \tilde{\omega}^{(2)}(l_2) - \tilde{\omega}^{(2)}(l_3) + \tilde{\omega}^{(2)}(l_4)$$

$\delta_2^{(3)} = \begin{array}{|c|c|}\hline \ & \ \\ \hline\end{array}, \qquad x_3 = 1, \qquad q_3 = 1; \qquad \begin{array}{|c|c|}\hline 1 & 2 \\ \hline\end{array}$

$\tilde{\omega}^{(3)}(l_1, l_2)$

$\mathcal{Y}^{(3)} = \mathcal{O}(e + (12))$

basis $[\mathcal{Y}^{(3)}\tilde{\omega}^{(3)}(l_1, l_2)] = [\tilde{\omega}^{(3)}(l_1, l_2)]$

transformation behaviour:

$\tilde{\omega}^{(3)}(l_2, l_1) = \tilde{\omega}^{(3)}(l_1, l_2)$

$\mathcal{O}(\sigma_1^{(3)}) = \mathcal{O}((14))$

$\tilde{\chi}^{(3)}(L_e) = \tilde{\omega}^{(3)}(l_1, l_4) - \tilde{\omega}^{(3)}(l_2, l_3)$

$\delta_2^{(4)} = \begin{array}{|c|}\hline \ \\ \hline \ \\ \hline\end{array}, \qquad x_4 = 2, \qquad q_4 = 1; \qquad \begin{array}{|c|}\hline 1 \\ \hline 2 \\ \hline\end{array}$

$\tilde{\omega}_1^{(4)}(l_1, l_2) \qquad \tilde{\omega}_2^{(4)}(l_1, l_2)$

$\mathcal{Y}^{(4)} = \mathcal{O}(e - (12))$

basis $[\mathcal{Y}^{(4)}\tilde{\omega}_u^{(4)}(l_1, l_2)] = [\tilde{\omega}_u^{(4)}(l_1, l_2)]$

transformation behaviour:

$\bar{\omega}_u^{(4)}(l_2, l_1) = -\bar{\omega}_u^{(4)}(l_1, l_2)$

$\mathcal{O}(\mathscr{s}_1^{(4)}) = \mathcal{O}(\mathscr{e}) \qquad \mathcal{O}(\mathscr{s}_2^{(4)}) = \mathcal{O}((13))$

$\tilde{\chi}^{(4)}(L_e) = \bar{\omega}_1^{(4)}(l_1, l_2) - \bar{\omega}_1^{(4)}(l_3, l_4) + \bar{\omega}_2^{(4)}(l_1, l_3) - \bar{\omega}_2^{(4)}(l_2, l_4)$

$\delta_3^{(5)} = \square\square\square\,, \qquad x_5 = 1, \qquad q_5 = 1; \qquad \boxed{1}\boxed{2}\boxed{3}$

$\tilde{\omega}^{(5)}(l_1, l_2, l_3)$

$\mathcal{Y}^{(5)} = \mathcal{O}(\mathscr{e} + (12) + (13) + (23) + (123) + (132))$

basis $[\mathcal{Y}^{(5)}\tilde{\omega}^{(5)}(l_1, l_2, l_3)] = [\bar{\omega}^{(5)}(l_1, l_2, l_3)]$

transformation behaviour:

$$\bar{\omega}^{(5)}(l_2, l_1, l_3) = \bar{\omega}^{(5)}(l_3, l_2, l_1) = \bar{\omega}^{(5)}(l_1, l_3, l_2) = \bar{\omega}^{(5)}(l_2, l_3, l_1)$$
$$= \bar{\omega}^{(5)}(l_3, l_1, l_2) = \bar{\omega}^{(5)}(l_1, l_2, l_3)$$

$\mathcal{O}(\mathscr{s}_1^{(5)}) = \mathcal{O}(\mathscr{e})$

$\tilde{\chi}^{(5)}(L_e) = \bar{\omega}^{(5)}(l_1, l_2, l_3) - \bar{\omega}^{(5)}(l_1, l_2, l_4) - \bar{\omega}^{(5)}(l_1, l_3, l_4) + \bar{\omega}^{(5)}(l_2, l_3, l_4)$

$\delta_3^{(6)} = \begin{array}{l}\square\square\\ \square\end{array}\,, \qquad x_6 = 2, \qquad q_6 = 2; \qquad \begin{array}{l}\boxed{1}\boxed{3}\\ \boxed{2}\end{array}$

$\tilde{\omega}_1^{(6)}(l_1, l_2, l_3) \qquad \tilde{\omega}_2^{(6)}(l_1, l_2, l_3)$

$\mathcal{Y}^{(6)} = \mathcal{O}((\mathscr{e} - (12))(\mathscr{e} + (13))) \qquad \mathcal{Y}_{21}^{(6)} = \mathcal{O}((23))\mathcal{Y}^{(6)}$

basis $[\mathcal{Y}^{(6)}\tilde{\omega}_u^{(6)}(l_1, l_2, l_3)\ \mathcal{Y}_{21}^{(6)}\tilde{\omega}_u^{(6)}(l_1, l_2, l_3)] = [\bar{\omega}_u^{(6)}(l_1, l_2, l_3)\ \bar{\omega}_u^{(6)}(l_1, l_3, l_2)]$

transformation behaviour:

$\bar{\omega}_u^{(6)}(l_2, l_1, l_3) = -\bar{\omega}_u^{(6)}(l_1, l_2, l_3)$

$\bar{\omega}_u^{(6)}(l_1, l_3, l_2) = \bar{\omega}_u^{(6)}(l_1, l_3, l_2)$

$\bar{\omega}_u^{(6)}(l_3, l_2, l_1) = \bar{\omega}_u^{(6)}(l_2, l_3, l_1) = \bar{\omega}_u^{(6)}(l_1, l_2, l_3) - \bar{\omega}_u^{(6)}(l_1, l_3, l_2)$

$\bar{\omega}_u^{(6)}(l_3, l_1, l_2) = -\bar{\omega}_u^{(6)}(l_1, l_3, l_2)$

$\mathcal{O}(\mathscr{s}_1^{(6)}) = \mathcal{O}(\mathscr{e}), \qquad \mathcal{O}(\mathscr{s}_2^{(6)}) = \mathcal{O}((14))$

$$\tilde{\chi}^{(6)}(L_e) = \bar{\omega}_1^{(6)}(l_1, l_2, l_3) + \bar{\omega}_1^{(6)}(l_4, l_3, l_2) - \bar{\omega}_1^{(6)}(l_2, l_1, l_4) - \bar{\omega}_1^{(6)}(l_3, l_4, l_1)$$
$$+ \bar{\omega}_2^{(6)}(l_1, l_3, l_2) + \bar{\omega}_2^{(6)}(l_4, l_2, l_3) - \bar{\omega}_2^{(6)}(l_2, l_4, l_1) - \bar{\omega}_2^{(6)}(l_3, l_1, l_4)$$

$\delta_3^{(7)} = \begin{array}{l}\square\\ \square\\ \square\end{array}\,, \qquad x_7 = 1, \qquad q_7 = 1; \qquad \begin{array}{l}\boxed{1}\\ \boxed{2}\\ \boxed{3}\end{array}$

$\tilde{\omega}^{(7)}(l_1, l_2, l_3)$

$\mathcal{Y}^{(7)} = \mathcal{O}(\mathscr{e} - (12) - (13) - (23) + (123) + (132))$

basis $[\mathcal{Y}^{(7)}\tilde{\omega}^{(7)}(l_1, l_2, l_3)] = [\bar{\omega}^{(7)}(l_1, l_2, l_3)]$

transformation behaviour:

$$\bar{\omega}^{(7)}(l_2, l_1, l_3) = \bar{\omega}^{(7)}(l_3, l_2, l_1) = \bar{\omega}^{(7)}(l_1, l_3, l_2) = -\bar{\omega}^{(7)}(l_2, l_3, l_1)$$
$$= -\bar{\omega}^{(7)}(l_3, l_1, l_2) = -\bar{\omega}^{(7)}(l_1, l_2, l_3)$$

$$\mathcal{O}(\sigma_1^{(7)}) = \mathcal{O}(e)$$

$$\tilde{\chi}^{(7)}(L_e) = \bar{\omega}^{(7)}(l_1, l_2, l_3) - \bar{\omega}^{(7)}(l_2, l_3, l_4) - \bar{\omega}^{(7)}(l_1, l_3, l_4) + \bar{\omega}^{(7)}(l_1, l_2, l_4)$$

$$\delta_4^{(8)} = \begin{array}{|c|c|c|}\hline & & \\ \hline \\ \cline{1-1}\end{array}, \qquad x_8 = 1, \qquad q_8 = 3; \qquad \begin{array}{|c|c|c|}\hline 1 & 2 & 3 \\ \hline 4 \\ \cline{1-1}\end{array}$$

$$\bar{\omega}^{(8)}(l_1, l_2, l_3, l_4)$$

$$\mathcal{Y}^{(8)} = \mathcal{O}((e - (14))(e + (12) + (13) + (23) + (123) + (132)))$$

$$\mathcal{Y}_{21}^{(8)} = \mathcal{O}((34))\mathcal{Y}^{(8)} \qquad \mathcal{Y}_{31}^{(8)} = \mathcal{O}((234))\mathcal{Y}^{(8)}$$

basis $[\mathcal{Y}^{(8)}\bar{\omega}^{(8)}(l_1, l_2, l_3, l_4)\ \mathcal{Y}_{21}^{(8)}\bar{\omega}^{(8)}(l_1, l_2, l_3, l_4)\ \mathcal{Y}_{31}^{(8)}\bar{\omega}^{(8)}(l_1, l_2, l_3, l_4)] =$
$[\bar{\omega}^{(8)}(l_1, l_2, l_3, l_4)\ \bar{\omega}^{(8)}(l_1, l_2, l_4, l_3)\ \bar{\omega}^{(8)}(l_1, l_3, l_4, l_2)]$

transformation behaviour:

$$\bar{\omega}^{(8)}(l_1, l_3, l_2, l_4) = -\bar{\omega}^{(8)}(l_4, l_2, l_3, l_1) = -\bar{\omega}^{(8)}(l_4, l_3, l_2, l_1) = \bar{\omega}^{(8)}(l_1, l_2, l_3, l_4)$$

$$\bar{\omega}^{(8)}(l_1, l_2, l_4, l_3) = \bar{\omega}^{(8)}(l_1, l_4, l_2, l_3) = -\bar{\omega}^{(8)}(l_3, l_2, l_4, l_1) = -\bar{\omega}^{(8)}(l_3, l_4, l_2, l_1)$$
$$= \bar{\omega}^{(8)}(l_1, l_2, l_4, l_3)$$

$$\bar{\omega}^{(8)}(l_1, l_3, l_4, l_2) = \bar{\omega}^{(8)}(l_1, l_4, l_3, l_2) = -\bar{\omega}^{(8)}(l_2, l_4, l_3, l_1) = -\bar{\omega}^{(8)}(l_2, l_3, l_4, l_1)$$
$$= \bar{\omega}^{(8)}(l_1, l_3, l_4, l_2)$$

$$\bar{\omega}^{(8)}(l_2, l_1, l_3, l_4) = \bar{\omega}^{(8)}(l_2, l_3, l_1, l_4) = -\bar{\omega}^{(8)}(l_4, l_1, l_3, l_2) = -\bar{\omega}^{(8)}(l_4, l_3, l_1, l_2)$$
$$= \bar{\omega}^{(8)}(l_1, l_2, l_3, l_4) - \bar{\omega}^{(8)}(l_1, l_3, l_4, l_2)$$

$$\bar{\omega}^{(8)}(l_3, l_2, l_1, l_4) = \bar{\omega}^{(8)}(l_3, l_1, l_2, l_4) = -\bar{\omega}^{(8)}(l_4, l_2, l_1, l_3) = -\bar{\omega}^{(8)}(l_4, l_1, l_2, l_3)$$
$$= \bar{\omega}^{(8)}(l_1, l_2, l_3, l_4) - \bar{\omega}^{(8)}(l_1, l_2, l_4, l_3)$$

$$\bar{\omega}^{(8)}(l_2, l_1, l_4, l_3) = -\bar{\omega}^{(8)}(l_3, l_4, l_1, l_2) = -\bar{\omega}^{(8)}(l_3, l_1, l_4, l_2) = \bar{\omega}^{(8)}(l_2, l_4, l_1, l_3)$$
$$= \bar{\omega}^{(8)}(l_1, l_2, l_4, l_3) - \bar{\omega}^{(8)}(l_1, l_3, l_4, l_2)$$

$$\mathcal{O}(\sigma_1^{(8)}) = \mathcal{O}((12))$$

$$\tilde{\chi}^{(8)}(L_e) = \bar{\omega}^{(8)}(l_1, l_2, l_3, l_4) - \bar{\omega}^{(8)}(l_1, l_3, l_4, l_2) - \bar{\omega}^{(8)}(l_1, l_2, l_4, l_3)$$

$$\delta_4^{(10)} = \begin{array}{|c|c|}\hline & \\ \hline \\ \cline{1-1} \\ \cline{1-1}\end{array}, \qquad x_{10} = 1, \qquad q_{10} = 3; \qquad \begin{array}{|c|c|}\hline 1 & 4 \\ \hline 2 \\ \cline{1-1} 3 \\ \cline{1-1}\end{array}$$

$$\bar{\omega}^{(10)}(l_1, l_2, l_3, l_4)$$

$$\mathcal{Y}^{(10)} = \mathcal{O}((e - (12) - (13) - (23) + (123) + (132))(e + (14)))$$

$$\mathcal{Y}_{21}^{(10)} = \mathcal{O}((34))\mathcal{Y}^{(10)} \qquad \mathcal{Y}_{31}^{(10)} = \mathcal{O}((234))\mathcal{Y}^{(10)}$$

basis $[\mathscr{Y}^{(10)}\tilde{\omega}^{(10)}(l_1, l_2, l_3, l_4)\ \mathscr{Y}_{21}^{(10)}\tilde{\omega}^{(10)}(l_1, l_2, l_3, l_4)\ \mathscr{Y}_{31}^{(10)}\tilde{\omega}^{(10)}(l_1, l_2, l_3, l_4)]$

$= [\bar{\omega}^{(10)}(l_1, l_2, l_3, l_4)\ \bar{\omega}^{(10)}(l_1, l_2, l_4, l_3)\ \bar{\omega}^{(10)}(l_1, l_3, l_4, l_2)]$

transformation behaviour:

$$\begin{aligned}
\bar{\omega}^{(10)}(l_2, l_1, l_3, l_4) &= \bar{\omega}^{(10)}(l_3, l_2, l_1, l_4) = \bar{\omega}^{(10)}(l_1, l_3, l_2, l_4) = -\bar{\omega}^{(10)}(l_2, l_3, l_1, l_4)\\
&= -\bar{\omega}^{(10)}(l_3, l_1, l_2, l_4) = -\bar{\omega}^{(10)}(l_1, l_2, l_3, l_4)\\
\bar{\omega}^{(10)}(l_1, l_2, l_4, l_3) &= -\bar{\omega}^{(10)}(l_2, l_1, l_4, l_3) = -\bar{\omega}^{(10)}(l_4, l_2, l_1, l_3)\\
&= -\bar{\omega}^{(10)}(l_1, l_4, l_2, l_3) = \bar{\omega}^{(10)}(l_2, l_4, l_1, l_3)\\
&= \bar{\omega}^{(10)}(l_4, l_1, l_2, l_3) = -\bar{\omega}^{(10)}(l_1, l_2, l_4, l_3)\\
\bar{\omega}^{(10)}(l_1, l_3, l_4, l_2) &= -\bar{\omega}^{(10)}(l_1, l_4, l_3, l_2) = \bar{\omega}^{(10)}(l_3, l_4, l_1, l_2) = \bar{\omega}^{(10)}(l_4, l_1, l_3, l_2)\\
&= -\bar{\omega}^{(10)}(l_3, l_1, l_4, l_2) = -\bar{\omega}^{(10)}(l_4, l_3, l_1, l_2) = \bar{\omega}^{(10)}(l_1, l_3, l_4, l_2)\\
\bar{\omega}^{(10)}(l_4, l_2, l_3, l_1) &= -\bar{\omega}^{(10)}(l_2, l_4, l_3, l_1) = \bar{\omega}^{(10)}(l_3, l_2, l_4, l_1) = -\bar{\omega}^{(10)}(l_4, l_3, l_2, l_1)\\
&= \bar{\omega}^{(10)}(l_2, l_3, l_4, l_1) = \bar{\omega}^{(10)}(l_3, l_4, l_2, l_1)\\
&= \bar{\omega}^{(10)}(l_1, l_2, l_3, l_4) - \bar{\omega}^{(10)}(l_1, l_2, l_4, l_3) + \bar{\omega}^{(10)}(l_1, l_3, l_4, l_2)
\end{aligned}$$

$\mathcal{O}(\mathscr{s}_1^{(10)}) = \mathcal{O}(\mathscr{e})$

$\tilde{\chi}^{(10)}(L_e) = \bar{\omega}^{(10)}(l_1, l_2, l_4, l_3) - \bar{\omega}^{(10)}(l_1, l_3, l_4, l_2)$

The first "Näherungsverfahren" can be considered as a special case of the second one. For a component $\tilde{\chi}^{(w)}(L_e)$ of the chirality function we set up polynomials of lowest degree which induce $\Gamma_N^{(w)}$ and depend only on $\nu = N - o_1^{(w)}$ ligand parameters[12]. Such a set-up is represented by $\tilde{v}_{\rho k}^{(w)}(L_e)$, the product of the Vandermonde determinants of the variables situated in each column, multiplied by the totally symmetric product of all variables for an arbitrarily chosen Young tableau k of $\delta_\nu^{(w)}$. By the subscript ρ we distinguish between the different parameter sets used. As within the second "Näherungsverfahren" a suitable choice of x_w permutations $\mathscr{s}_u^{(w)} \in \mathfrak{S}_n$ is to be made. This choice depends on the k selected but is independent of ρ. On performing first $\mathcal{O}(\mathscr{s}_u^{(w)})$, followed by the projection $\mathscr{P}_\chi$ a component $\tilde{\chi}^{(w)}(L_e)$ is derived equal to

$$\tilde{\chi}^{(w)}(L_e) = \mathscr{P}_\chi \sum_{\rho=1}^{x_w} \sum_{u=1}^{x_w} \alpha_{\rho u}^{(w)} \mathcal{O}(\mathscr{s}_u^{(w)}) \tilde{v}_{\rho k}^{(w)}(L_e) \tag{48}$$

(compare Appendix B).

$\alpha_{\rho u}^{(w)}$ represent the coefficients of linear combination. The summation over all components gives the chirality function according to Eq. (47). We have to use x_w different parameter sets for each w. Parameters sets of different w, however, may be identical. So one needs max $\{x_w\}$ sets at the least whilst the most general set-up requires $\sum x_w$ parameters for every ligand. Within Example 4 we shall deal with the minimum set-up of max $\{x_w\}$ parameter sets. Though this might represent a

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[12] $o_1^{(w)}$ is the length of the first row of $\gamma_N^{(w)}$.

loss of generality, a choice of independent parameter sets would render an application difficult because of the complexity.

Example 4:
Let us consider the skeleton of Fig. 2 in analogy to Example 3. Again $\tilde{\upsilon}_{\rho k}^{(w)}(L_e) = \tilde{\upsilon}_{\rho k}^{(w)}(l_1, \ldots, l_\nu | l_{\nu+1}, \ldots, l_n)$ will be written as $\tilde{\upsilon}_{\rho k}^{(w)}(l_1, \ldots, l_\nu)$. Furthermore, the parameter $\lambda_\rho(l_i)$ of the ligand i will be abbreviated by λ_i, if $\rho = 1$, and by λ'_i, if $\rho = 2$. The chosen Young tableau is given beside $\delta_\nu^{(w)}$ and its index k omitted. Regarding all $\delta_\nu^{(w)}$ we thus obtain the components of the chirality function:

$$\delta_1^{(2)} = \begin{array}{|c|}\hline \\ \hline\end{array}\,, \qquad x_2 = 1; \qquad \begin{array}{|c|}\hline 1 \\ \hline\end{array}$$

$$\tilde{\upsilon}_1^{(2)} = \lambda_1$$

$$\mathcal{O}(s_1^{(2)}) = \mathcal{O}(e)$$

$$\tilde{\chi}^{(2)}(L_e) = \alpha^{(2)}(\lambda_1 - \lambda_2 - \lambda_3 + \lambda_4)$$

$$\delta_2^{(3)} = \begin{array}{|c|c|}\hline & \\ \hline\end{array}\,, \qquad x_3 = 1; \qquad \begin{array}{|c|c|}\hline 1 & 2 \\ \hline\end{array}$$

$$\tilde{\upsilon}_1^{(3)} = \lambda_1\lambda_2$$

$$\mathcal{O}(s_1^{(3)}) = \mathcal{O}((24))$$

$$\tilde{\chi}^{(3)}(L_e) = \alpha^{(3)}[\lambda_1\lambda_4 - \lambda_2\lambda_3]$$

$$\delta_2^{(4)} = \begin{array}{|c|}\hline \\ \hline \\ \hline\end{array}\,, \qquad x_4 = 2; \qquad \begin{array}{|c|}\hline 1 \\ \hline 2 \\ \hline\end{array}$$

$$\tilde{\upsilon}_1^{(4)} = \lambda_1\lambda_2(\lambda_1 - \lambda_2) \quad \tilde{\upsilon}_2^{(4)} = \lambda'_1\lambda'_2(\lambda'_1 - \lambda'_2)$$

$$\mathcal{O}(s_1^{(4)}) = \mathcal{O}(e) \qquad \mathcal{O}(s_2^{(4)}) = \mathcal{O}((23))$$

$$\begin{aligned}\tilde{\chi}^{(4)}(L_e) = \alpha_{11}^{(4)}&[\lambda_1\lambda_2(\lambda_1 - \lambda_2) - \lambda_3\lambda_4(\lambda_3 - \lambda_4)]\\ &+ \alpha_{21}^{(4)}[\lambda'_1\lambda'_2(\lambda'_1 - \lambda'_2) - \lambda'_3\lambda'_4(\lambda'_3 - \lambda'_4)]\\ &+ \alpha_{12}^{(4)}[\lambda_1\lambda_3(\lambda_1 - \lambda_3) - \lambda_2\lambda_4(\lambda_2 - \lambda_4)]\\ &+ \alpha_{22}^{(4)}[\lambda'_1\lambda'_3(\lambda'_1 - \lambda'_3) - \lambda'_2\lambda'_4(\lambda'_2 - \lambda'_4)]\end{aligned}$$

$$\delta_3^{(5)} = \begin{array}{|c|c|c|}\hline & & \\ \hline\end{array}\,, \qquad x_5 = 1; \qquad \begin{array}{|c|c|c|}\hline 1 & 2 & 3 \\ \hline\end{array}$$

$$\tilde{\upsilon}_1^{(5)} = \lambda_1\lambda_2\lambda_3$$

$$\mathcal{O}(s_1^{(5)}) = \mathcal{O}(e)$$

$$\tilde{\chi}^{(5)}(L_e) = \alpha^{(5)}[\lambda_1\lambda_2(\lambda_3 - \lambda_4) - \lambda_3\lambda_4(\lambda_1 - \lambda_2)]$$

$$\delta_3^{(6)} = \begin{array}{|c|c|}\hline & \\ \hline & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}\,, \qquad x_6 = 2; \qquad \begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 & \multicolumn{1}{c}{} \\ \cline{1-1}\end{array}$$

$$\tilde{\upsilon}_1^{(6)} = \lambda_1\lambda_2\lambda_3(\lambda_1 - \lambda_2) \qquad \tilde{\upsilon}_2^{(6)} = \lambda'_1\lambda'_2\lambda'_3(\lambda'_1 - \lambda'_2)$$

$$\mathcal{O}(s_1^{(6)}) = \mathcal{O}(e) \qquad \mathcal{O}(s_2^{(6)}) = \mathcal{O}((23))$$

$$\begin{aligned}\tilde{\chi}^{(6)}(L_e) = {} & \alpha_{11}^{(6)}[\lambda_1\lambda_2(\lambda_1-\lambda_2)(\lambda_3+\lambda_4)-\lambda_3\lambda_4(\lambda_3-\lambda_4)(\lambda_1+\lambda_2)] \\ & +\alpha_{21}^{(6)}[\lambda_1'\lambda_2'(\lambda_1'-\lambda_2')(\lambda_3'+\lambda_4')-\lambda_3'\lambda_4'(\lambda_3'-\lambda_4')(\lambda_1'+\lambda_2')] \\ & +\alpha_{12}^{(6)}[\lambda_1\lambda_3(\lambda_1-\lambda_3)(\lambda_2+\lambda_4)-\lambda_2\lambda_4(\lambda_2-\lambda_4)(\lambda_1+\lambda_3)] \\ & +\alpha_{22}^{(6)}[\lambda_1'\lambda_3'(\lambda_1'-\lambda_3')(\lambda_2'+\lambda_4')-\lambda_2'\lambda_4'(\lambda_2'-\lambda_4')(\lambda_1'+\lambda_3')]\end{aligned}$$

$$\delta_3^{(7)} = \begin{array}{|c|}\hline \ \\ \hline \ \\ \hline \ \\ \hline\end{array}, \qquad x_7 = 1; \qquad \begin{array}{|c|}\hline 1 \\ \hline 2 \\ \hline 3 \\ \hline\end{array}$$

$$\tilde{v}_1^{(7)} = \lambda_1\lambda_2\lambda_3(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)(\lambda_2-\lambda_3)$$

$$\mathcal{O}(\mathscr{s}^{(7)}) = \mathcal{O}(\mathscr{e})$$

$$\begin{aligned}\tilde{\chi}^{(7)}(L_e) = {} & \alpha^{(7)}[\lambda_1^2\lambda_2^2(\lambda_1-\lambda_2)(\lambda_3+\lambda_4)-\lambda_1^2\lambda_3^2(\lambda_1-\lambda_3)(\lambda_2+\lambda_4) \\ & +\lambda_2^2\lambda_4^2(\lambda_2-\lambda_4)(\lambda_1+\lambda_3)-\lambda_3^2\lambda_4^2(\lambda_3-\lambda_4)(\lambda_1+\lambda_2) \\ & -(\lambda_1^2\lambda_4^2-\lambda_2^2\lambda_3^2)(\lambda_1-\lambda_4)(\lambda_2-\lambda_3)]\end{aligned}$$

$$\delta_4^{(8)} = \begin{array}{|c|c|c|}\hline \ & \ & \ \\ \hline \ \\ \cline{1-1}\end{array}, \qquad x_8 = 1; \qquad \begin{array}{|c|c|c|}\hline 1 & 2 & 3 \\ \hline 4 \\ \cline{1-1}\end{array}$$

$$\tilde{v}_1^{(8)} = \lambda_1\lambda_2\lambda_3\lambda_4(\lambda_1-\lambda_4)$$

$$\mathcal{O}(\mathscr{s}_1^{(8)}) = \mathcal{O}((234))$$

$$\tilde{\chi}^{(8)}(L_e) = \alpha^{(8)}[\lambda_1\lambda_2\lambda_3\lambda_4(\lambda_1-\lambda_2-\lambda_3+\lambda_4)]$$

$$\delta_4^{(10)} = \begin{array}{|c|c|}\hline \ & \ \\ \hline \ \\ \cline{1-1} \ \\ \cline{1-1}\end{array}, \qquad x_{10} = 1; \qquad \begin{array}{|c|c|}\hline 1 & 4 \\ \hline 2 \\ \cline{1-1} 3 \\ \cline{1-1}\end{array}$$

$$\tilde{v}_1^{(10)} = \lambda_1\lambda_2\lambda_3\lambda_4(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)(\lambda_2-\lambda_3)$$

$$\mathcal{O}(\mathscr{s}^{(10)}) = \mathcal{O}(\mathscr{e})$$

$$\tilde{\chi}^{(10)}(L_e) = \alpha^{(10)}[\lambda_1\lambda_2\lambda_3\lambda_4(\lambda_1-\lambda_4)(\lambda_2-\lambda_3)(\lambda_1-\lambda_2-\lambda_3+\lambda_4)]$$

Example 5:
Consider a skeleton of D_{2d}-symmetry with four ligand sites, e.g. of the allene type as shown in Fig. 1. Since $o_{\max} = 2$ we choose $N = 6$. The diagrams $\delta_\nu^{(w)}$ of the half orders $\mathfrak{h}_4^{(r)}$ arising from $\mathfrak{H}_{46}^{(r)}$ are arranged in Fig. 5 according to the relation defined.

The components of a chirality function derived via the first "Näherungsverfahren" according to (48) with $\mathscr{P}_\chi = \mathcal{O}(\mathscr{e}+(12)(34)+(13)(24)+(14)(23)-(12)-(34)-(1324)-(1423))$

are given by:

$$\delta_2^{(3)} = \begin{array}{|c|c|}\hline \ & \ \\ \hline\end{array}, \qquad x_3 = 1; \qquad \begin{array}{|c|c|}\hline 1 & 2 \\ \hline\end{array}$$

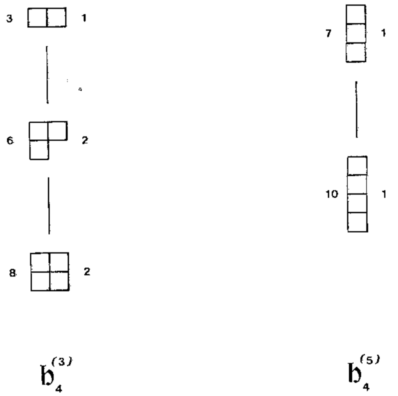

Fig. 5. The half orders $\mathfrak{h}_4^{(3)}$ and $\mathfrak{h}_4^{(5)}$ for a skeleton of D_{2d}-symmetry as shown in Fig. 1. The numbers on the left side of the diagrams $\delta_\nu^{(w)}$ indicate the superscript w, the numbers on the right side the dimensions q_w of the $\delta_\nu^{(w)}$. ν equals the number of boxes of each diagram

$$\tilde{v}_1^{(3)} = \lambda_1\lambda_2$$

$$\mathcal{O}(\sigma_1^{(3)}) = \mathcal{O}(e)$$

$$\tilde{\chi}^{(3)}(L_e) = \alpha^{(3)}[(\lambda_1-\lambda_2)(\lambda_3-\lambda_4)]$$

$$\delta_3^{(6)} = \begin{array}{|c|c|}\hline \ & \ \\ \hline \ \\ \cline{1-1}\end{array}\,, \qquad x_6 = 1; \qquad \begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 \\ \cline{1-1}\end{array}$$

$$\tilde{v}_1^{(6)} = \lambda_1\lambda_2\lambda_3(\lambda_1-\lambda_3)$$

$$\mathcal{O}(\sigma_1^{(6)}) = \mathcal{O}((23))$$

$$\tilde{\chi}^{(6)}(L_e) = \alpha^{(6)}[(\lambda_1-\lambda_2)(\lambda_3-\lambda_4)(\lambda_1\lambda_2-\lambda_3\lambda_4)]$$

$$\delta_3^{(7)} = \begin{array}{|c|}\hline \ \\ \hline \ \\ \hline \ \\ \hline\end{array}\,, \qquad x_7 = 1; \qquad \begin{array}{|c|}\hline 1 \\ \hline 2 \\ \hline 3 \\ \hline\end{array}$$

$$\tilde{v}_1^{(7)} = \lambda_1\lambda_2\lambda_3(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)(\lambda_2-\lambda_3)$$

$$\mathcal{O}(\sigma_1^{(7)}) = \mathcal{O}(e)$$

$$\begin{aligned}\tilde{\chi}^{(7)}(L_e) = \alpha^{(7)}[&\lambda_1^2\lambda_2^2(\lambda_1-\lambda_2)(\lambda_3-\lambda_4)-\lambda_1^2\lambda_3^2(\lambda_1-\lambda_3)(\lambda_2-\lambda_4)\\ &+\lambda_1^2\lambda_4^2(\lambda_1-\lambda_4)(\lambda_2-\lambda_3)+\lambda_2^2\lambda_3^2(\lambda_1-\lambda_4)(\lambda_2-\lambda_3)\\ &-\lambda_2^2\lambda_4^2(\lambda_1-\lambda_3)(\lambda_2-\lambda_4)+\lambda_3^2\lambda_4^2(\lambda_1-\lambda_2)(\lambda_3-\lambda_4)]\end{aligned}$$

$$\delta_4^{(8)} = \begin{array}{|c|c|}\hline \ & \ \\ \hline \ & \ \\ \hline\end{array}\,, \qquad x_8 = 1; \qquad \begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & 4 \\ \hline\end{array}$$

$$\tilde{v}_1^{(8)} = \lambda_1\lambda_2\lambda_3\lambda_4(\lambda_1-\lambda_3)(\lambda_2-\lambda_4)$$

$$\mathcal{O}(\sigma_1^{(8)}) = \mathcal{O}((23))$$

$$\tilde{\chi}^{(8)}(L_e) = \alpha^{(8)}[\lambda_1\lambda_2\lambda_3\lambda_4(\lambda_1-\lambda_2)(\lambda_3-\lambda_4)]$$

$$\delta_4^{(10)} = \begin{array}{|c|}\hline \\ \hline \\ \hline \\ \hline \\ \hline \end{array}\,, \qquad x_{10} = 1; \qquad \begin{array}{|c|}\hline 1 \\ \hline 2 \\ \hline 3 \\ \hline 4 \\ \hline \end{array}$$

$$\tilde{\upsilon}_1^{(10)} = \lambda_1\lambda_2\lambda_3\lambda_4(\lambda_1-\lambda_2)(\lambda_1-\lambda_3)(\lambda_1-\lambda_4)(\lambda_2-\lambda_3)(\lambda_2-\lambda_4)(\lambda_3-\lambda_4)$$

$$\mathcal{O}(\sigma_1^{(10)}) = \mathcal{O}(e)$$

$$\tilde{\chi}^{(10)}(L_e) = \alpha^{(10)}[\lambda_1\lambda_2\lambda_3\lambda_4(\lambda_1-\lambda_2)(\lambda_2-\lambda_3)(\lambda_3-\lambda_1)(\lambda_4-\lambda_1)(\lambda_4-\lambda_2)(\lambda_4-\lambda_3)]$$

8. Conclusion and Final Remarks

Taking into account the principle of qualitative supercompleteness as well as physically compelling requirements the chirality functions derived appear to differ from C-chirality functions in some important points:

a) By means of chirality functions derived via (46), the components of which can be interpreted as interaction terms (see also [4, 5, 7]), all the interactions within and/or between ligands and skeleton for a given molecular class are included. Resulting from the basic model, i.e. assuming a molecule to consist of a skeleton and ligands attached to its skeletal sites, a decomposition into interactions within ligands and between ligands and skeleton cannot be performed. It follows that – provided the basic model of decomposing a molecule into skeleton and ligands is "true" – the correct description of a chirality observation is ensured on principle.

b) Any SC-chirality function – hence already a function with $\sum z_{\bar{r}}$ components derived from the smallest diagrams $\gamma_N^{(w_{\bar{r}}^*)} \in \mathfrak{H}_{nN}^{(\bar{r})}$ – suffices to yield m linearly independent chirality functions for any choice of m molecules out of m enantiomeric pairs. Therefore systematical dependencies regarding non-racemic mixtures of non-isomers are excluded according to the requirement of qualitative supercompleteness[13].

c) With the intention of describing chiroptical properties of molecules which belong to a given molecular class, any relevant situation exhibits the number of ligand kinds N as large as possible – confined only by chemical facts and certainly much larger than n. SC-chiralty functions are appropriate to describe this situation, since they are not subject to an upper limit of N. Furthermore it must be emphasized that in connection with the cancellation of the upper limit

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[13] We are quite pleased to find C. A. Mead having become a comrade-in-arms in matters of qualitative supercompleteness. In his paper submitted to "Theoretica Chimica Acta" he shares our opinion – although this may be a bit hidden – namely that C-chirality functions according to [4] are incapable of describing completely the experimental data. He also makes an effort to derive functions, which we view as being in fact SC-functions. We want to thank him for leaving a preprint to us.

SC-chirality functions become independent of the number of ligand kinds. This independence is warranted by the structure of the functions.

In order to describe experimental data one would now have to fit the ligand specific parameters $\lambda_{\rho}^{(w)}(l_i)$ and linear combination coefficients $\alpha_{\rho u}^{(w)}$ of the component $\tilde{\chi}^{(w)}(L_e)$ on using a chirality function according to the first "Näherungsverfahren". Applying a chirality function according to the second "Näherungsverfahren" it is first of all essential that one finds appropriate functions $\tilde{\omega}_u^{(w)}$. Thereafter the corresponding fit of ligand parameters has to be performed.

Normally such a fit should have some of the components $\tilde{\chi}^{(w)}(L_e)$ being large, some small and some zero thus weighting the "interaction components" with respect to their importance. From this it could be deduced which kind of interaction dominates the chirality observations regarded.

However, though the chirality functions derived are free from systematical linear dependencies all the other critical objections expressed in [9] remain. Those objections are connected with the basic model. The nature of this model – i.e. to assume a molecule as consisting of a skeleton and of ligands – brings about that only a few and strongly restricted cases of molecular classes can be treated.

Finally, it is necessary to search by independent methods for the physical content to be reconciled with the propositions deduced from consistencies or inconsistencies of chirality functions.

As the most important results we consider the fact that qualitative supercompleteness combined with physical reasoning provides chirality functions including all the interactions within ligands and/or between ligands and skeleton for a molecular class. These chirality functions are also the most general ones available. Thus from both a mathematical and a physical point of view qualitatively supercomplete chirality functions prove more adequate for describing the chiroptical properties of molecules belonging to a given skeletal class.

Appendix

A. *Qualitatively Supercomplete Minimum Set-Ups*

Pursuing the point to derive a qualitatively supercomplete chirality function $\phi(L)$ it is to be seen that there results a principal difference with respect to the C-concept. Within the scope of the C-concept a qualitatively complete chirality function consists of components each of which transforms according to an irreducible representation $\Gamma_n^{(\bar{r})}$ of the $\mathfrak{S}_n$. The analogous procedure cannot be applied within the SC-concept, because a component of a chirality function which transforms according to a $\Gamma_N^{(w)}$ of $\mathfrak{S}_N$ usually depends on all N ligands. Thus a chirality function consisting of such components represents a chirality function for a mixture. A chirality function

$$\tilde{\phi}(L_e) = \phi(L_e|L_f) \tag{A1}$$

for the molecule, however, may depend explicitly only on the n ligands of the proper skeletal sites (the symbols of which form the vector L_e). This fact leads us to the solution of the problem. We have to set up functions depending only on L_e and to extend their argument formally by L_f according to Eq. (A1). This formal extension followed by a permutation σ of ligands between L_e and L_f leads to the chirality function of a non-isomer $\sigma L = \sigma[L_e|L_f]$ of L_e:

$$\tilde{\phi}(L_e) = \phi(L_e|L_f) = \phi(L) \xrightarrow{\sigma} \phi(\sigma L).$$

If we replace σ by an element ℓ of the group algebra of the $\mathfrak{S}_N$, i.e. an ensemble operator, we get the chirality function $\phi(\ell L)$ for the mixture ℓL being generally a mixture of non-isomers.

As a qualitatively complete chirality function induces every irreducible representation $\Gamma_n^{(r)}$ of $\mathfrak{S}_n$ z_r times [4] a qualitatively supercomplete chirality function must induce every irreducible representation $\Gamma_N^{(w)}$ of $\mathfrak{S}_N$ x_w times. In order to derive a qualitatively supercomplete $\phi(L)$ we make use of some kind of "Näherungsverfahren". Thus a "Näherungsansatz" to $\phi(L)$ is denoted by $\chi(L)$. However, for the moment we do not need to specify the kind of "Näherungsverfahren" and "Näherungsansatz". It suffices to state that within a "Näherungsverfahren" functions $\omega(L)$ have to be set up to derive $\chi(L)$.

Disregarding as well the principle of greatest possible generality within the given restrictions of the "Näherungsverfahren" as the physical considerations according to Sect. 7 qualitatively supercomplete chirality functions appear to be of a much simpler form than the ones of Eq. (46) or (48). The following considerations are confined to $N \geq n + o_{\max}$, because chirality functions $\chi(L)$ do not exhibit dependence on N in this case, as stated in Sect. 7. Now let us discuss a chirality function required to induce a certain $\Gamma_N^{(w)}$ and denote it by $\chi^{(w)}(L)$. This requirement causes both $\chi^{(w)}(L)$ and the corresponding set up $\omega^{(w)}(L)$ to adopt definite properties, which will be examined in the following. Note that these properties are derived from the formal conditions of qualitative supercompleteness and let us term them formal properties. They are not at all connected with the properties that arise from a "Näherungsverfahren". It rather is essential to know the formal properties in order to specify some "Näherungsansatz".

Let us assume $\omega^{(w)}(L)$ to depend explicitly on ν' arguments, $\omega^{(w)}(l_1, \ldots, l_{\nu'}|l_{\nu'+1}, \ldots, l_N)$. This $\omega^{(w)}(L)$ can be got from a $\tilde{\tilde{\omega}}^{(w)}(L_{\nu'}) = \tilde{\tilde{\omega}}^{(w)}(l_1, \ldots, l_{\nu'})$ by formal extension. From (A1) it follows that both the set up $\omega^{(w)}(L)$ to a chirality function and $\tilde{\tilde{\omega}}^{(w)}(L_{\nu'})$ may depend just on ligands attached to the proper skeletal sites, thus $\nu' \leq n$. Given the condition that $\tilde{\tilde{\omega}}^{(w)}(L_{\nu'})$ is intended to induce the irreducible representation $\Gamma_N^{(w)}$ of the $\mathfrak{S}_{N}$, if extended formally, a lower limit of ν' emerges. $\omega^{(w)}(l_1, \ldots, l_{\nu'}|l_{\nu'+1}, \ldots, l_N)$ obtained by formal extension of $\tilde{\tilde{\omega}}^{(w)}(L_{\nu'})$ is totally symmetric with respect to arguments it depends on just formally – i.e., the arguments $\nu'+1, \ldots, N$. Consequently, $\omega^{(w)}(l_1, \ldots, l_{\nu'}|l_{\nu'+1}, \ldots, l_N)$ can only induce such representations $\Gamma_N^{(w)}$ of $\mathfrak{S}_N$, the diagrams $\gamma_N^{(w)}$ of which can be filled with indices $1, \ldots, N$ without repetition of two of the indices $\nu'+1, \ldots, N$ in the same column. That is possible, if, and only if, the number $N-\nu'$ does not exceed the number of columns of $\gamma_N^{(w)}$. Since the number of columns equals the length of the first row $o_1^{(w)}$, it follows $N-\nu' \leq o_1^{(w)}$ or $N-o_1^{(w)} \leq \nu'$. We have denoted the number $N-o_1^{(w)}$ of boxes of $\gamma_N^{(w)}$ not situated in the first row by ν for every w. It holds

$$\nu \leq \nu' \leq n. \tag{A2}$$

Therefore in order to induce $\Gamma_N^{(w)}$, a function has to contain components depending on ν ligands at least. Furthermore these components must not be sums of terms depending on fewer than ν ligands exclusively. (To verify this one only needs to perform the induction separately for each term.) A special kind of functions fulfilling these conditions are functions consisting exclusively of terms depending on exactly ν ligands. We call such functions $\tilde{\tilde{\omega}}^{(w)}(L_\nu)$ as well as the extended functions $\omega^{(w)}(L)=\omega^{(w)}(l_1, \ldots, l_\nu | l_{\nu+1}, \ldots, l_N)$ ν-ligands functions. A ν-ligands function $\tilde{\tilde{\omega}}^{(w)}(L_\nu)$ can induce $\Gamma_N^{(w)}$ only if it contains a non-vanishing $\Delta_\nu^{(w)}$-component $\hat{\tilde{\tilde{\omega}}}^{(w)}(L_\nu)=\mathscr{P}_\nu^{(w)}\tilde{\tilde{\omega}}^{(w)}(L_\nu)$; this follows from the fact that an outer product of the form $\Delta_\nu^{(w')} \otimes \Gamma_{N-\nu}^{(1)}$, contains $\Gamma_N^{(w)}$ if, and only if, $w'=w$. $\Delta_\nu^{(w)}$ is characterized by a diagram $\delta_\nu^{(w)}$, which is specified by the property that each of its columns is shorter by one box than the corresponding column of $\gamma_N^{(w)}$. $\mathscr{P}_\nu^{(w)}$ is the character projector onto $\Delta_\nu^{(w)}$.

Let us now present a theorem answering the question, which representations $\Gamma_N^{(w')}$ such a ν-ligands function induces besides $\Gamma_N^{(w)}$, and how often it induces a representation.

Theorem A1: Let $\Gamma_N^{(w')}$ be a representation characterized by the property that each column of its diagram $\gamma_N^{(w')}$ is of equal length or longer by one box than the corresponding column of $\delta_\nu^{(w)}$. Then the $\Delta_\nu^{(w)}$-component $\hat{\tilde{\tilde{\omega}}}^{(w)}(L_\nu)$ of a ν-ligands function $\tilde{\tilde{\omega}}^{(w)}(L_\nu)$ induces, if extended formally to $\hat{\omega}^{(w)}(l_1, \ldots, l_\nu | l_{\nu+1}, \ldots, l_N)$, each irreducible representation $\Gamma_N^{(w')}$ as many times as it induces $\Delta_\nu^{(w)}$.

The diagrams $\gamma_N^{(w')}$ with the properties cited above form a TU-half order denoted by $\mathfrak{L}_{\nu N}^{[w]}$. $\gamma_N^{(w)}$ represents the smallest element of $\mathfrak{L}_{\nu N}^{[w]}$. There may exist elements $\gamma_N^{(w)} \in \mathfrak{L}_{\nu N}^{[w]}$ which do not appear in any $\mathfrak{H}_{nN}^{(\bar{r})}$, i.e. $x_w=0$. On the other hand $\mathfrak{L}_{\nu N}^{[w]}$ contains every $\gamma_N^{(w')}$, $x_{w'} \neq 0$, with $\gamma_N^{(w')} \supset \gamma_N^{(w)}$. If $w=w_{\bar{r}}^*$, the half order $\mathfrak{L}_{\nu N}^{[w]}$ becomes identical with $\mathfrak{H}_{nN}^{(\bar{r})}$:

$$\mathfrak{L}_{\nu N}^{[w_{\bar{r}}^*]}=\mathfrak{H}_{nN}^{(\bar{r})}. \tag{A3}$$

Since only the $\Delta_\nu^{(w)}$-component of a ν-ligands function induces $\Gamma_N^{(w)}$ it follows from theorem A1: A ν-ligands function inducing $\Gamma_N^{(w)}$ m_w times induces each $\Gamma_N^{(w')}$, given $\gamma_N^{(w')} \supset \gamma_N^{(w)}$, m_w times at least. Other components of the ν-ligands function may induce $\Gamma_N^{(w')}$, but not $\Gamma_N^{(w)}$.

Proof of theorem A1: A diagram $\gamma_N^{(w')}$ can be obtained from $\delta_\nu^{(w)}$ by adding $N-\nu$ boxes in such a way, that one box at most is put below each column (the remaining boxes just extend the first row). Let us assign a standard tableau $\gamma_{Ni}^{(w')}$ – corresponding to $\Gamma_N^{(w')}$ – to each standard tableau $\delta_{\nu i}^{(w)}$ of $\Delta_\nu^{(w)}$, $i=1, \ldots, q_w$. Thereby the indices $\nu+1, \ldots, N$ have to be filled into the boxes added in an appropriate way. Since there exist many fillings, we choose an arbitrary one retaining it for all $i=1,\dots,q_w$. Thus the indices $\nu+1,\dots,N$ are filled into the q_w standard tableaux in the same manner. The Young operators ${}_N\mathcal{Y}_{ii}^{(w')}$ of $\Gamma_N^{(w')}$, which are assigned to $\mathcal{Y}_{ii}^{(w)}$ of $\Delta_\nu^{(w)}$, can be decomposed according to

$${}_N\mathcal{Y}_{ii}^{(w')}=\mathcal{Y}_{ii}^{(w)}\mathcal{Z}+\mathcal{R}. \tag{A4}$$[14]

$\mathcal{Z}$ is the sum of all permutations exchanging the $l_{\nu+1},\dots,l_N$ arguments just within themselves and only within each row of $\gamma_N^{(w')}$. Since none of the columns of $\gamma_N^{(w')}$ contains two of the arguments $l_{\nu+1},\dots,l_N$, the item $\mathcal{Y}_{ii}^{(w)}\mathcal{Z}=\mathcal{Z}\mathcal{Y}_{ii}^{(w)}$ of (A4) is an algebraic sum of permutations exchanging arguments only within $l_1,\dots,l_\nu$ and within $l_{\nu+1},\dots,l_N$. On the contrary $\mathcal{R}$ consists of exclusively of permutations interchanging arguments between $l_1,\dots,l_\nu$ and $l_{\nu+1},\dots,l_N$. The permutation σ_{ij}, which transforms $\delta_{\nu j}^{(w)}$ into $\delta_{\nu i}^{(w)}$, changes $\gamma_{Nj}^{(w')}$ into $\gamma_{Ni}^{(w')}$ as well. Furthermore $\mathcal{O}(\sigma_{ij}^{-1})$ commutes with $\mathcal{Z}$. By applying $\mathcal{O}(\sigma_{ij}^{-1})$ from the right it results

$${}_N\mathcal{Y}_{ij}^{(w')}=\mathcal{Y}_{ij}^{(w)}\mathcal{Z}+\mathcal{R}_1 \tag{A5}$$

with $\mathcal{R}_1=\mathcal{R}\mathcal{O}(\sigma_{ij}^{-1})$ consisting likewise of permutations interchanging arguments between $l_1,\dots,l_\nu$ and $1_{\nu+1},\dots,l_N$. The function $\hat{\tilde{\omega}}^{(w)}(L_\nu)=\mathcal{P}_\nu^{(w)}\tilde{\tilde{\omega}}^{(w)}(L_\nu)$ may be extended formally to $\hat{\omega}^{(w)}(L)=\mathcal{P}_\nu^{(w)}\,\omega\,(l_1,\dots,l_\nu|l_{\nu+1},\dots,l_N)$. It holds that $\mathcal{Z}\hat{\omega}^{(w)}(L)=c\hat{\omega}^{(w)}(L)$ with a constant $c\neq 0$.[15] Applying (A5) to $\hat{\omega}^{(w)}(\mathrm{L})$ we get

$${}_N\mathcal{Y}_{ij}^{(w')}\hat{\omega}^{(w)}(L)=c\mathcal{Y}_{ij}^{(w)}\hat{\omega}^{(w)}(L)+\mathcal{R}_1\hat{\omega}^{(w)}(L). \tag{A6}$$

If $\hat{\omega}^{(w)}(L)=\hat{\tilde{\omega}}^{(w)}(L_\nu)$ induces $\Delta_\nu^{(w)}$ m_w times, there exist m_w linearly independent bases of the form

$$[\mathcal{Y}_{1j_t}^{(w)}\hat{\omega}^{(w)}(L)\quad \mathcal{Y}_{2j_t}^{(w)}\hat{\omega}^{(w)}(L)\quad \dots\quad \mathcal{Y}_{q_wj_t}^{(w)}\hat{\omega}^{(w)}(L)],\qquad t=1,\dots,m_w. \tag{A7}$$

$j_t, t=1,\dots,m_w$ denotes suitably chosen indices. The linear independence of the m_w corresponding elements

$$\mathcal{Y}_{ij_1}^{(w)}\hat{\omega}^{(w)}(L),\qquad \mathcal{Y}_{ij_2}^{(w)}\hat{\omega}^{(w)}(L),\dots,\mathcal{Y}_{ij_{m_w}}^{(w)}\hat{\omega}^{(w)}(L) \tag{A8}$$

is equivalent to the linear independence of the m_w bases (A7). Now we substitute j of (A6) by the indices $j=j_1,\dots,j_{m_w}$ according to (A8), multiply by linear combination coefficients β_t and sum

$$\sum_{t=1}^{m_w}\beta_t\,{}_N\mathcal{Y}_{ij_t}^{(w')}\hat{\omega}^{(w)}(L)=c\sum_{t=1}^{m_w}\beta_t\mathcal{Y}_{ij_t}^{(w)}\hat{\omega}^{(w)}(L)+\sum_{t=1}^{m_w}\beta_t\mathcal{R}_1\hat{\omega}^{(w)}(L). \tag{A9}$$

Let us abbreviate the first sum of the right-hand side by $\theta(L)$, the second one by $\rho(L)$

$$\theta(L)=\sum_{t=1}^{m_w}\beta_t\mathcal{Y}_{ij_t}^{(w)}\hat{\omega}^{(w)}(L),\qquad \rho(L)=\sum_{t=1}^{m_w}\beta_t\mathcal{R}_1\hat{\omega}^{(w)}(L).$$

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[14] The decomposition can be performed by applying the procedure described in Ref. [19], p 28, $(N-\nu)$ times.

[15] Since $\mathcal{Z}$ contains exactly $(N-\nu)!$ permutations exchanging only the formal arguments within rows of $\Gamma_N^{(w')}$ c takes the value $(N-\nu)!$. However, this value is of no importance.

As $\hat{\omega}^{(w)}(L)$ depends explicitly on $l_1, \ldots, l_\nu$ ligands, being a ν-ligands function, application of $\mathcal{R}_1$ causes each item of $\rho(L)$ to depend on one of the $l_{\nu+1}, \ldots, l_N$ ligands at least. On the other hand, $\theta(L)$ only includes items depending on $l_1, \ldots, l_\nu$ ligands. Thus no item out of either sum is able to compensate one out of the other sum. Because of the linear independence of $\mathcal{Y}_{ij_t}^{(w)}\hat{\omega}^{(w)}(L)$, $t = 1, \ldots, m_w$ it holds $\theta(L) \neq 0$ unless all $\beta_t = 0$. It follows for the left-hand side of (A9)

$$\sum_{t=1}^{m_w} \beta_t\, {}_N\mathcal{Y}_{ij_t}^{(w')}\hat{\omega}^{(w)}(L) \neq 0.$$

Consequently, the ${}_N\mathcal{Y}_{ij_t}^{(w')}\hat{\omega}^{(w)}(L)$, $t = 1, \ldots, m_w$ are linearly independent. From this the linear independence of the m_w bases

$$[{}_N\mathcal{Y}_{1j_t}^{(w')}\hat{\omega}^{(w)}(L) \quad {}_N\mathcal{Y}_{2j_t}^{(w')}\hat{\omega}^{(w)}(L) \quad \cdots \quad {}_N\mathcal{Y}_{n_wj_t}^{(w')}\hat{\omega}^{(w)}(L)], \qquad t = 1, \ldots, m_w$$

of m_w representation spaces of $\Gamma_N^{(w')}$ follows. Therewith it is established that $\hat{\omega}^{(w)}(L)$ induces $\Gamma_N^{(w')}$ m_w times, thus proving Theorem A1.

In the limiting case $N = n$ Theorem A1 turns to a statement concerning the induction of representations $\Gamma_n^{(r)}$ of the $\mathfrak{S}_n$: The $\Delta_\nu^{(w)}$-component $\hat{\hat{\omega}}^{(w)}(L_e) = \mathcal{P}_\nu^{(w)}\tilde{\omega}^{(w)}(l_1, \ldots, l_\nu | l_{\nu+1}, \ldots, l_n)$ derived from a ν-ligands function $\hat{\tilde{\omega}}^{(w)}(L_\nu)$ induces each irreducible component $\Gamma_n^{(r)}$ of the outer product $\Delta_\nu^{(w)} \otimes \Gamma_{n-\nu}^{(1)}$ as many times as it induces $\Delta_\nu^{(w)}$.

According to Theorem A1 we imply a minimum set-up for an irreducible representation $\Gamma_N^{(w)}$ – containing Γ_σ x_w times – to be given by a chirality function that induces $\Gamma_N^{(w)}$ x_w times and consists of components depending on a minimum number of ligands. Obviously such a minimum set-up can be obtained via a ν-ligands function $\hat{\tilde{\omega}}^{(w)}(L_\nu)$, which induces the corresponding $\Delta_\nu^{(w)}$ x_w times. Thereby it follows from Theorem A1 that a minimum set up $\hat{\omega}^{(w)}(L)$ according to $\Gamma_N^{(w)}$ and derived from $\hat{\tilde{\omega}}^{(w)}(L_\nu)$ induces not only $\Gamma_N^{(w)}$ but also all $\Gamma_N^{(w')}$ with $\gamma_N^{(w')} \supset \gamma_N^{(w)}$ x_w times.

Consequently the minimum set-up of a molecular chirality function $\tilde{\chi}_{\min}(L_e)$ has to consist of terms $\tilde{\chi}^{(w^*_{\bar r})}(L_e)$ each of which induces $\Gamma_N^{(w^*_{\bar r})}$ $x_{w^*_{\bar r}} = z_{\bar r}$ times:

$$\tilde{\chi}_{\min}(L_e) = \sum_{\bar r} \tilde{\chi}^{(w^*_{\bar r})}(L_e). \tag{A10}$$

Because of Theorem A1 and Eq. (A3) a $\Gamma_N^{(w)}$ is induced by $\tilde{\chi}^{(w^*_{\bar r})}(L_e)$ if, and only if, $\gamma_N^{(w)} \in \mathfrak{H}_{nN}^{(\bar r)}$. As in this case $\tilde{\chi}^{(w^*_{\bar r})}(L_e)$ induces $\Gamma_N^{(w)}$ $z_{\bar r}$ times $\tilde{\chi}_{\min}(L_e)$ induces $\Gamma_N^{(w)}$

$$\sum_{\bar r} z_{\bar r} = x_w,$$

$$\gamma_N^{(w)} \in \mathfrak{H}_{nN}^{(\bar r)}$$

times, cf. Eq. (41). The components $\tilde{\chi}^{(w^*_{\bar r})}(L_e)$ of the minimum set up $\tilde{\chi}_{\min}(L_e)$ are obtained from $\hat{\tilde{\omega}}^{(w^*_{\bar r})}(L_\nu)$ or $\hat{\omega}^{(w^*_{\bar r})}(L)$, respectively. The $\delta_\nu^{(w^*_{\bar r})} \in \mathfrak{h}_n^{(\bar r)}$ equal the $\gamma_n^{(\bar r)}$ in any case from which it follows $\nu = n$, $L_\nu = L_e$. Thus it can be seen that the set-ups $\hat{\tilde{\omega}}^{(w^*_{\bar r})}(L_\nu) = \hat{\hat{\omega}}^{(w^*_{\bar r})}(L_e)$ from which the minimum set-up of a molecular chirality function can be obtained, represent n-ligands functions, $\nu = n$. Additionally, all n-ligands functions giving an appropriate set-up to $\tilde{\chi}_{\min}(L_e)$ are exhausted by the $\tilde{\tilde{\omega}}^{(w\overset{*}{\bar{r}})}(L_e)$ of the $\Delta_\nu^{(w\overset{*}{\bar{r}})}$. Any other n-ligands function $\tilde{\tilde{\omega}}^{(w')}(L_e)$ not containing a $\Delta_\nu^{(w\overset{*}{\bar{r}})}$-component would be annihilated via the projection onto the σ-chirality representation Γ_σ; to verify this remember that outer products of the form $\Gamma_n^{(r)} \otimes \Gamma_m^{(1)}$ contain Γ_σ only, if $r = \bar{r}$. If $\nu < n$ an analogous statement can be deduced. Taking into account all the $\hat{\tilde{\tilde{\omega}}}^{(w)}(L_\nu)$ with a fixed value ν according to the $\Delta_\nu^{(w)}$ or $\Gamma_N^{(w)}$, with $x_w \neq 0$, there do not exist other $\tilde{\tilde{\omega}}^{(w')}(L_\nu)$ that can contribute to the chirality function.

B. Qualitatively Supercomplete Chirality Functions

Within the preceding appendix we have dealt with qualitatively supercomplete minimum set-ups of a chirality function and with minimum set-ups for a definite irreducible representation $\Gamma_N^{(w)}$. Nevertheless, for the construction of qualitatively supercomplete chirality functions we shall not confine ourselves to the minimum set-up. It rather seems suggestive to regard both the principle of greatest possible generality and physical considerations (see Sect. 7). On doing so we find it appropriate to take into account components $\chi^{(w)}(L)$ differing for the $\Gamma_N^{(w)}$. The corresponding set-ups $\hat{\omega}^{(w)}(L)$ are those functions that form the minimum set-ups for the $\Gamma_N^{(w)}$ and can be obtained via the ν-ligands functions $\tilde{\tilde{\omega}}^{(w)}(L_\nu)$ inducing the appropriate $\Delta_\nu^{(w)}$ x_w times. We make use of these minimum set-ups $\tilde{\tilde{\omega}}^{(w)}(L_\nu)$ for $\chi^{(w)}(L)$, since all the $\tilde{\tilde{\omega}}^{(w)}(L_{\nu'})$, $\nu' > \nu$, have already been taken into account via the $\chi^{(w')}(L)$, with $\gamma_N^{(w')} \neq \gamma_N^{(w)}$.

Therefore we set up a qualitatively supercomplete Näherungsansatz $\chi(L)$ as the sum

$$\chi(L) = \sum_{\substack{w \\ x_w \neq 0}} \chi^{(w)}(L) \tag{B1}$$

where the component $\chi^{(w)}(L)$ induces the representation $\Gamma_N^{(w)}$ in $\mathfrak{S}_N$ x_w times.

Having deduced the formal properties of the $\hat{\omega}^{(w)}(L) = \hat{\tilde{\omega}}^{(w)}(L_e) = \hat{\tilde{\tilde{\omega}}}^{(w)}(L_\nu)$ we may omit the extension to L and make use of Eq. (A1) $\tilde{\phi}(L_e) = \phi(L_e|L_f)$. Eq. (B1) now turns to

$$\chi(L) = \tilde{\chi}(L_e) = \sum_{\substack{w \\ x_w \neq 0}} \tilde{\chi}^{(w)}(L_e). \tag{B2}$$

According to the second Näherungsverfahren we set up for $\tilde{\chi}^{(w)}(L_e)$ a ν-ligands function $\tilde{\tilde{\tau}}_\rho^{(w)}(l_1, \ldots, l_\nu)$.[16] The number ν of ligands equals the number of boxes of $\gamma_N^{(w)}$ not situated in the first row (compare Appendix A and [4], p. 260); it holds $\nu \leq n$. Furthermore $\tilde{\tilde{\tau}}_\rho^{(w)}(L_\nu)$, where $L_\nu = [l_1, \ldots, l_\nu]$, must induce the irreducible representation $\Delta_\nu^{(w)}$ of the $\mathfrak{S}_\nu$, the diagram $\delta_\nu^{(w)}$ of which arises from $\gamma_N^{(w)}$ by removing the first line. The number m_w indicates how many times $\tilde{\tilde{\tau}}_\rho^{(w)}(L_\nu)$ induces

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[16] The following considerations also refer to the first Näherungsverfahren, since it can be considered as a special case of the second one.

$\Delta_\nu^{(w)}$. It cannot be greater than the dimension q_w of $\Delta_\nu^{(w)}$, so that we have

$$1 \leq m_w \leq q_w. \tag{B3}$$

Because a qualitatively supercomplete chirality function has to induce $\Gamma_N^{(w)}$ x_w times we take s_w different functions $\overset{\approx}{\tau}{}_\rho^{(w)}(L_\nu)$, $\rho = 1, \ldots, s_w$, of the same structure (see [4], p. 253) obeying the condition that the s_w induced representation spaces are linearly independent. Evidently it must hold

$$s_w m_w \geq x_w. \tag{B4}$$

As the diagrams $\delta_\nu^{(w)}$ play an important rôle we define for each r a half order $\mathfrak{h}_n^{(r)}$ consisting of those $\delta_\nu^{(w)}$ which can be obtained from diagrams of $\mathfrak{H}_{nN}^{(r)}$, $N \geq n + o_1^{(r)}$, by removing the first row. The relation is transferred from $\mathfrak{H}_{nN}^{(r)}$. Figs. 4 and 5 show the $\mathfrak{h}_4^{(2)}$, $\mathfrak{h}_4^{(3)}$, $\mathfrak{h}_4^{(4)}$, $\mathfrak{h}_4^{(5)}$ derived from $\mathfrak{H}_{4N}^{(r)}$. Note that in the case of the skeleton of Fig. 2 $\mathfrak{h}_4^{(2)}$ and $\mathfrak{h}_4^{(4)}$ are $\mathfrak{h}_4^{(\bar r)}$, while $\mathfrak{h}_4^{(3)}$ and $\mathfrak{h}_4^{(5)}$ are $\mathfrak{h}_4^{(\bar r)}$ for the allene skeleton shown in Fig. 1. A diagram $\delta_\nu^{(w)} \in \mathfrak{h}_n^{(r)}$ is greater than a diagram $\delta_{\nu'}^{(w')}$, $\delta_{\nu'}^{(w')} \subset \delta_\nu^{(w)}$, if it can be formed from $\delta_{\nu'}^{(w')}$ by removing boxes. There exist a smallest and a largest diagram in $\mathfrak{h}_n^{(\bar r)}$, the smallest diagram $\delta_\nu^{(w \overset{*}{\bar r})}$ with $\nu = n$ being identical with $\gamma_n^{(\bar r)}$. The largest diagram $\delta_\nu^{(w \overset{0}{\bar r})}$ with $\nu = n - o_1^{(\bar r)}$ is also got from $\gamma_n^{(\bar r)}$ by removing the first row.

Theorem B1: The half order $\mathfrak{h}_n^{(r)}$ contains exactly those diagrams $\delta_\nu^{(w)}$ from which $\gamma_n^{(r)}$ can be built by adding $n - \nu$ boxes without repetition in the same column.

Proof: $\gamma_N^{(w)}$ arises from $\gamma_n^{(r)}$ by adding one box to each column at most. Therefore a column of $\gamma_N^{(w)}$ is either of the same length as the corresponding column of $\gamma_n^{(r)}$ or longer by one box. It follows that a column of the diagram $\delta_\nu^{(w)}$ which one gets from $\gamma_N^{(w)}$ by removing the first row is either shorter by one box than the corresponding column of $\gamma_n^{(r)}$ or is of the same length. Therefore $\gamma_n^{(r)}$ can be obtained from $\delta_\nu^{(w)}$ by adding one box to each column at most.

As defined in Sect. 5, $t_{wr1} = 1$ if $\gamma_N^{(w)} \in \mathfrak{H}_{nN}^{(r)}$ and $t_{wr1} = 0$, otherwise. Since the condition $\gamma_N^{(w)} \in \mathfrak{H}_{nN}^{(r)}$ is equivalent to $\delta_\nu^{(w)} \in \mathfrak{h}_n^{(r)}$ it holds

$$t_{wr1} = \begin{cases} 1 & \text{if } \delta_\nu^{(w)} \in \mathfrak{h}_n^{(r)} \\ 0 & \text{if } \delta_\nu^{(w)} \notin \mathfrak{h}_n^{(r)} \end{cases} \tag{B5}$$

The outer product $\Delta_\nu^{(w)} \otimes \Gamma_{n-\nu}^{(1)}$ induced in $\mathfrak{S}_n$ by $\tilde{\tau}_\rho^{(w)}(L_e)$ contains an irreducible representation $\Gamma_n^{(r)}$ once if its diagram $\gamma_n^{(r)}$ can be got from $\delta_\nu^{(w)}$ by adding $n - \nu$ boxes without repetition in the same column. All the other $\Gamma_n^{(r')}$ are not contained. From Theorem B1 it follows that this is the case if, and only if, $\delta_\nu^{(w)} \in \mathfrak{h}_n^{(r)}$. Using Eq. (B5) we get

$$\Delta_\nu^{(w)} \otimes \Gamma_{n-\nu}^{(1)} = \sum_r t_{wr1} \Gamma_n^{(r)}. \tag{B6}$$

As $\Gamma_n^{(r)}$ contains Γ_χ z_r times $\Delta_\nu^{(w)} \otimes \Gamma_{n-\nu}^{(1)}$ contains Γ_χ

$$\sum_r t_{wr1} z_r = x_w \tag{B7}$$

times. Comparison with Eq. (36) shows that $\Delta_\nu^{(w)} \otimes \Gamma_{n-\nu}^{(1)}$ contains Γ_χ as many times as $\Gamma_N^{(w)}$ contains Γ_σ.

a) *Second Näherungsverfahren*

We choose for each $\Gamma_N^{(w)}$ with $x_w \neq 0$ s_w functions

$$\tilde{\tilde{\tau}}_\rho^{(w)}(L_\nu) = \tilde{\tau}_\rho^{(w)}(L_e) = \tau_\rho^{(w)}(L), \qquad \rho = 1, \ldots, s_w \tag{B8}$$

of the same structure being sufficiently general to induce $\Delta_\nu^{(w)}$ q_w times, i.e. $m_w = q_w$. The outer products $\Delta_\nu^{(w)} \otimes \Gamma_{n-\nu}^{(1)}$ and $\Delta_\nu^{(w)} \otimes \Gamma_{N-\nu}^{(1)}$ are also induced q_w times by the $\tau_\rho^{(w)}$ of (B8). $\Gamma_N^{(w)}$, contained once in $\Delta_\nu^{(w)} \otimes \Gamma_{N-\nu}^{(1)}$, is induced q_w times, too. Let $\mathcal{Y}_{ij}^{(w)}$, $i, j = 1, \ldots, q_w$, be the Young operators of the $\tilde{\mathcal{Q}}\mathcal{Q}$-type [14] or the Young units, respectively, related to the q_w standard tableaux of the $\Delta_\nu^{(w)}$ of $\mathfrak{S}_\nu$ [14][17]. Then the functions

$$\mathcal{Y}_{1j}^{(w)} \tilde{\tilde{\tau}}_\rho^{(w)}(L_\nu), \;\; \mathcal{Y}_{2j}^{(w)} \tilde{\tilde{\tau}}_\rho^{(w)}(L_\nu), \ldots, \mathcal{Y}_{q_w j}^{(w)} \tilde{\tilde{\tau}}_\rho^{(w)}(L_\nu) \tag{B9}$$

form for each pair of ϱ, j ($\varrho = 1, \ldots, s_w$; $j = 1, \ldots, q_w$) a base for $\Delta_\nu^{(w)}$. The $s_w q_w$ bases are linearly independent. The functions

$$O(\mathfrak{s}) Y_{ij}^{(w)} \tilde{\tau}_\varrho^{(w)}(L_e), \qquad i = 1, \ldots, q_w; \qquad \mathfrak{s} \in \mathfrak{S}_n, \quad \text{given } \rho, j, \tag*{(B10)[18]}$$

obtained by extension of the argument and by admitting all permutations $\mathfrak{s}$ of $l_1, \ldots, l_n$ form a representation space of $\Delta_\nu^{(w)} \otimes \Gamma_{n-\nu}^{(1)}$. The $\mathcal{Y}_{ij}^{(w)}$ can be expressed by $\mathcal{Y}_{ij}^{(w)} = \mathcal{O}(\sigma_{ik}^{-1}) \mathcal{Y}_{kk}^{(w)} \mathcal{O}(\sigma_{kj}^{-1})$ where $\mathcal{Y}_{kk}^{(w)}$ is an arbitrary Young operator of the $\Delta_\nu^{(w)}$ which needs not to correspond to a standard tableau. $\sigma_{ik}^{-1} = \sigma_{ki}$ is the permutation of the $\mathfrak{S}_\nu$ which transforms the standard tableau i into the tableau k. So the functions of (B10) can be written as

$$\mathcal{O}(\mathfrak{s}) \mathcal{Y}_{kk}^{(w)} \mathcal{O}(\sigma_{jk}) \tilde{\tau}_\rho^{(w)}(L_e), \qquad \mathfrak{s} \in \mathfrak{S}_n. \tag{B11}$$

As $\Delta_\nu^{(w)} \otimes \Gamma_{n-\nu}^{(1)}$ contains Γ_χ x_w times there are x_w linearly independent chirality functions among

$$\mathcal{P}_\chi \mathcal{O}(\mathfrak{s}) \mathcal{Y}_{kk}^{(w)} \mathcal{O}(\sigma_{jk}) \tilde{\tau}_\rho^{(w)}(L_e), \qquad \mathfrak{s} \in \mathfrak{S}_n. \tag{B12}$$

We pick out x_w such functions from (B12) by a suitable choice of x_w permutations $\mathfrak{s}_u^{(w)}$, $u = 1, \ldots, x_w$, of $\mathfrak{S}_n$. This choice is independent of ρ and j. It follows that the most general set-up for a chirality function within the present considerations is

$$\tilde{\chi}(L_e) = \mathcal{P}_\chi \sum_w \sum_{\rho=1}^{s_w} \sum_{j=1}^{q_w} \sum_{u=1}^{x_w} \alpha_{\rho u j}^{(w)} \mathcal{O}(\mathfrak{s}_u^{(w)}) \mathcal{Y}_{kk}^{(w)} \mathcal{O}(\sigma_{jk}) \tilde{\tau}_\rho^{(w)}(L_e) \tag{B13}$$

where $\alpha_{\rho u j}^{(w)}$ are coefficients of linear combination. As in [4], p. 261, we let s_w approach infinity and suppose the $\tilde{\tau}_\rho^{(w)}(L_e)$ to form a complete system of functions.

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[17] A Young unit $\mathcal{Y}_{ij}$ is defined by $\mathcal{Y}_{ij} = \mathcal{O}(\sigma_{ij}^{-1}) \mathcal{Y}_{jj} = \mathcal{O}(\sigma_{ij}^{-1}) \tilde{\mathcal{Q}}_j \mathcal{Q}_j = \tilde{\mathcal{Q}}_i \mathcal{O}(\sigma_{ij}^{-1}) \mathcal{Q}_j = \hat{\mathcal{Q}}_i \mathcal{Q}_i \mathcal{O}(\sigma_{ij}^{-1}) = \mathcal{Y}_{ii} \mathcal{O}(\sigma_{ij}^{-1})$, where σ_{ij} is that permutation which transforms the Young tableau j into the Young tableau i. For the definition of $\mathcal{Q}_i$, $\tilde{\mathcal{Q}}_i$ see Sect. 7.

[18] $\mathcal{O}(\mathfrak{s})$ means the operator induced in the function space by the permutation $\mathfrak{s} \in \mathfrak{S}_n$, (see Sect. 3).

Thus the sum

$$\tilde{\eta}_{uj}^{(w)}(L_e) = \sum_{\rho=1}^{\infty} \alpha_{\rho uj}^{(w)} \tilde{\tau}_{\rho}^{(w)}(L_e) \tag{B14}$$

is a general function of the same structure as the $\tilde{\tau}_{\rho}^{(w)}(L_e)$. Making use of (B14) we get

$$\tilde{\chi}(L_e) = \mathscr{P}_{\chi} \sum_{w} \sum_{j=1}^{q_w} \sum_{u=1}^{x_w} \mathscr{O}(\mathscr{s}_u^{(w)}) \mathscr{Y}_{kk}^{(w)} \mathscr{O}(\sigma_{jk}) \tilde{\eta}_{uj}^{(w)}(L_e). \tag{B15}$$

Since all $\mathscr{O}(\sigma_{jk})\tilde{\eta}_{uj}^{(w)}(L_e) = \tilde{\eta}_{uj}^{(w)}(\sigma_{kj}L_e)$ depend on the same ν ligands $l_1, \ldots, l_\nu$ we can perform the summation over j obtaining again a function

$$\tilde{\omega}_u^{(w)}(L_e) = \sum_{j=1}^{q_w} \tilde{\eta}_{uj}^{(w)}(\sigma_{kj}L_e) \tag{B16}$$

of the chosen structure. Inserting (B16) into (B15) we get the definite form of the set-up according to the second Näherungsverfahren:

$$\tilde{\chi}(L_e) = \mathscr{P}_{\chi} \sum_{w} \sum_{u=1}^{x_w} \mathscr{O}(\mathscr{s}_u^{(w)}) \mathscr{Y}_{kk}^{(w)} \tilde{\omega}_u^{(w)}(L_e). \tag{B17}$$

Recalling (B2), a component $\tilde{\chi}^{(w)}(L_e)$ is given by

$$\tilde{\chi}^{(w)}(L_e) = \mathscr{P}_{\chi} \sum_{u=1}^{x_w} \mathscr{O}(\mathscr{s}_u^{(w)}) \mathscr{Y}_{kk}^{(w)} \tilde{\omega}_u^{(w)}(L_e). \tag{B18}$$

b) First Näherungsverfahren

The set-up of a qualitatively supercomplete chirality function according to the first Näherungsverfahren consists of the most general polynomial of lowest degree which exhibits the necessary transformation behavior. The polynomials of lowest degree induce an irreducible representation $\Gamma_N^{(w)}$ of $\mathfrak{S}_N$ once ([4], p. 284). The corresponding representation space can be spanned by the monomials

$$\psi_\rho(\gamma_N^{(w)}; \mathscr{s}L) = \mathscr{O}(\mathscr{s}^{-1})\psi_\rho(\gamma_N^{(w)}; L) \tag{B19}$$

which arise from putting variables of zeroth power into the first row of $\gamma_N^{(w)}$, variables of first power into the second row, etc. By the subscript ρ we distinguish between the different parameter sets that we have to deal with concerning the first Näherungsverfahren. So $f_\rho^{(w)}(L)$ may be understood as a shorthand for

$$f_\rho^{(w)}(L) = f[\lambda_\rho^{(w)}(l_1),\ \lambda_\varrho^{(w)}(l_2), \ldots, \lambda_\varrho^{(w)}(l_N)]$$

where $\lambda_\rho^{(w)}(l_j)$ is the ρth of those parameters of the ligand l_j which are used in connexion with the representation $\Gamma_N^{(w)}$. The functions (B19) can be defined by

$$\psi_\rho(\gamma_N^{(w)}; L) = \sum_{i=1}^{\mu_1^{(w)}} \sum_{j=o_{i-1}^{(w)}+1}^{o_i^{(w)}} [\lambda_\rho^{(w)}(l_j)]^{i-1}. \tag{B20}$$

This definition corresponds to a standard tableau with the ligands filled in row by row in ascending order[19] of their index j. The monomials corresponding to the other tableaux can be obtained by means of (B19). $o_i^{(w)}$ are the partial sums $o_i^{(w)} = \nu_1^{(w)} + \ldots + \nu_i^{(w)}$ of the lengths $\nu_i^{(w)}$ of the rows of $\gamma_N^{(w)}$, $o_0^{(w)} = 0$ by definition. $\mu_1^{(w)}$ is the length of the first column of $\gamma_N^{(w)}$ which equals the number of rows. We denote by $M_i^{(w)}$ the factors

$$M_i^{(w)} = \sum_{j=o_{i-1}^{(w)}+1}^{o_i^{(w)}} [\lambda_\rho^{(w)}(l_j)]^{i-1} \tag{B21}$$

of $\psi_\rho(\gamma_N^{(w)}; L)$ in which every parameter appears with the same exponent $i-1$. Therefore $M_i^{(w)}$ is a basis of the totally symmetric irreducible representation $\Gamma_{\nu_i}^{(1)}$ of the symmetric group $\mathfrak{S}_{\nu_i}$ where $\nu_i^{(w)} = o_i^{(w)} - o_{i-1}^{(w)}$ is the length of the ith row of $\gamma_N^{(w)}$. As all $N!/(\nu_1^{(w)}!\nu_2^{(w)}! \ldots \nu_{\mu_1^{(w)}}^{(w)}!)$ monomials, which one gets from $\psi_\rho(\gamma_N^{(w)}; L)$ by permuting all arguments are different, it follows that

$$\psi_\rho(\gamma_N^{(w)}; L) = M_1^{(w)} M_2^{(w)} \cdots M_{\mu_1^{(w)}}^{(w)} \tag{B22}$$

induces the whole outer product

$$D(\gamma_N^{(w)}) = \Gamma_{\nu_1^{(w)}}^{(1)} \otimes \Gamma_{\nu_2^{(w)}}^{(1)} \otimes \cdots \otimes \Gamma_{\nu_{\mu_1^{(w)}}^{(w)}}^{(1)} \tag{B23}$$

once.

The number ν of boxes of the diagram $\delta_\nu^{(w)}$ obtained from $\gamma_N^{(w)}$ by removing the first row is equal to $\nu = \nu_2^{(w)} + \cdots + \nu_{\mu_1^{(w)}}^{(w)}$, therefore $\nu_1^{(w)} = o_1^{(w)} = N - \nu$. As the outer product

$$\Delta_\nu^{(w)} \otimes \Gamma_{N-\nu}^{(1)} \tag{B24}$$

plays the basic rôle in our consideration we modify (B22) as well as (B23). For this purpose we define

$$\Psi_\rho(\delta_\nu^{(w)}; L_\nu) = M_2^{(w)} M_3^{(w)} \cdots M_{\mu_1^{(w)}}^{(w)}. \tag{B25}$$

It holds

$$\Psi_\rho(\delta_\nu^{(w)}; L_\nu) = T_\rho^{(w)}(L_\nu) \psi_\rho(\delta_\nu^{(w)}; L_\nu) \tag{B26}$$

where the monomial $\psi_\rho(\delta_\nu^{(w)}; L_\nu)$ is obtained analogously to (B20) by putting variables of zeroth power into the first row of $\delta_\nu^{(w)}$, etc. As the exponent of a variable in $\delta_\nu^{(w)}$ is one less than the exponent of the same variable in $\gamma_N^{(w)}$ there arises the totally symmetric factor

$$T_\rho^{(w)}(L_\nu) = \lambda_\rho^{(w)}(l_{N-\nu+1}) \lambda_\rho^{(w)}(l_{N-\nu+2}) \cdots \lambda_\rho^{(w)}(l_N). \tag{B27}$$

It follows that $\Psi_\rho(\delta_\nu^{(w)}; L_\nu)$ in the same way as $\psi_\rho(\delta_\nu^{(w)}; L_\nu)$, once induces in $\mathfrak{S}_\nu$ the outer product

$$D(\delta_\nu^{(w)}) = \Gamma_{\nu_2^{(w)}}^{(1)} \otimes \Gamma_{\nu_3^{(w)}}^{(1)} \otimes \cdots \otimes \Gamma_{\nu_{\mu_1^{(w)}}^{(w)}}^{(1)}. \tag{B28}$$

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[19] We now label the ligands on which $\psi_\rho(\gamma_N^{(w)}; L)$ does not depend by the indices $1, \ldots, o_1^{(w)}$ whereby $o_1^{(w)} = N - \nu$. The remaining ligands which form the vector L_ν are then numbered according

$$L_\nu = [l_{N-\nu+1}, \ldots, l_N].$$

Since it follows from the reduction rule of the outer product that $D(\delta_\nu^{(w)})$ contains $\Delta_\nu^{(w)}$ once, both $\psi_\rho(\delta_\nu^{(w)}; L_\nu)$ and $\Psi_\varrho(\delta_\nu^{(w)}; L_\nu)$ induce $\Delta_\nu^{(w)}$ once. This agrees with the fact that $\psi_\rho(\delta_\nu^{(w)}; L_\nu)$ is a polynomial of lowest degree with respect to $\Delta_\nu^{(w)}$. Inserting (B25), (B28) into (B22) and (B23), respectively, gives

$$\psi_\rho(\gamma_N^{(w)}; L) = \Psi_\rho(\delta_\nu^{(w)}; L_\nu) \,.\, M_1^{(w)}, \tag{B29}$$

$$D(\gamma_N^{(w)}) = D(\delta_\nu^{(w)}) \otimes \Gamma_{N-\nu}^{(1)}. \tag{B30}$$

The factor $\Gamma_{N-\nu}^{(1)}$ of (B30) is spanned by the monomial $M_1^{(w)}$ which does not depend on ligand parameters, i.e. is a constant. As a qualitatively supercomplete chirality function must induce $\Gamma_N^{(w)}$ we have to find those irreducible components $\Delta_\nu^{(x)}$ of $D(\delta_\nu^{(w)})$ the outer product of which $\Delta_\nu^{(x)} \otimes \Gamma_{N-\nu}^{(1)}$ with $\Gamma_{N-\nu}^{(1)}$ contains $\Gamma_N^{(w)}$. It follows that a column of the diagram $\delta_\nu^{(x)}$ of such a representation must be of the same length as the corresponding column of $\gamma_N^{(w)}$ or by one box shorter. Since the difference $N - \nu = \nu_1^{(w)}$ between the number N of boxes of $\gamma_N^{(w)}$ and the number ν of boxes of $\delta_\nu^{(w)}$ is equal to the number of columns of $\gamma_N^{(w)}$ this condition can be fulfilled only if every column of $\delta_\nu^{(x)}$ is by one box shorter than the corresponding column of $\gamma_N^{(w)}$. There exists only one $\delta_\nu^{(x)}$ of this property, namely $\delta_\nu^{(x)} = \delta_\nu^{(w)}$. Therefore the only $\Delta_\nu^{(x)}$ which furnishes $\Gamma_N^{(w)}$ on outer multiplication by $\Gamma_{N-\nu}^{(1)}$ is $\Delta_\nu^{(x)} = \Delta_\nu^{(w)}$. So we arrive at the outer product $\Delta_\nu^{(w)} \otimes \Gamma_{N-\nu}^{(1)}$ of (B24) the factor $\Delta_\nu^{(w)}$ of which is contained once in $D(\delta_\nu^{(w)})$, as follows from the reduction rule of the outer product. (This follows also from the fact that $\psi_\rho(\delta_\nu^{(w)}; L_\nu)$, $\Psi_\rho(\delta_\nu^{(w)}; L_\nu)$ induce $\Delta_\nu^{(w)}$ once.)

Comparing this with (B29), (B30) it is desirable to separate the component transforming according to $\Delta_\nu^{(w)}$ from $\Psi_\rho(\delta_\nu^{(w)}; L_\nu)$. This means that $\Psi_\rho(\delta_\nu^{(w)}; L_\nu)$ plays the role of the function $\tilde{\tilde{\tau}}_\rho^{(w)}(L_\nu)$ of (B8) with the exception that now $m_w = 1$.

$$\tilde{\tilde{\tau}}_\rho^{(w)}(L_\nu) = \Psi_\rho(\delta_\nu^{(w)}; L_\nu) = T_\rho^{(w)}(L_\nu)\psi_\rho(\delta_\nu^{(w)}; L_\nu). \tag{B31}$$

By means of the Young operators $\mathcal{Y}_{ii}^{(w)}$ of the $\tilde{\mathcal{Q}}\mathcal{Q}$-type and Young units $\mathcal{Y}_{ik}^{(w)}$ of the standard tableaux of $\Delta_\nu^{(w)}$ we get a basis analogous to (B9)

$$[\mathcal{Y}_{1k}^{(w)}\tilde{\tilde{\tau}}_\rho^{(w)}(L_\nu) \quad \mathcal{Y}_{2k}^{(w)}\tilde{\tilde{\tau}}_\rho^{(w)}(L_\nu) \quad \cdots \quad \mathcal{Y}_{q_w k}^{(w)}\tilde{\tilde{\tau}}_\rho^{(w)}(L_\nu)] \tag{B32}$$

of $\Delta_\nu^{(w)}$. A basis element $\mathcal{Y}_{ik}^{(w)}\tilde{\tilde{\tau}}_\rho^{(w)}(L_\nu)$ may be expressed by

$$\mathcal{Y}_{ik}^{(w)}\tilde{\tilde{\tau}}_\rho^{(w)}(L_\nu) = \mathcal{O}(\sigma_{ki})\mathcal{Y}_{kk}^{(w)}\tilde{\tilde{\tau}}_\rho^{(w)}(L_\nu) \tag{B33}$$

where σ_{ki} is that permutation which transforms the standard tableau i into the standard tableau k. It holds

$$\mathcal{Y}_{kk}^{(w)}\psi_\rho(\delta_\nu^{(w)}; L_\nu) = \tilde{\tilde{\theta}}_{\rho k}^{(w)}(L_\nu) \tag{B34}$$

with $\tilde{\tilde{\theta}}_{\rho k}^{(w)}(L_\nu)$ as the product of the Vandermonde determinants corresponding to the columns of the kth standard tableau of $\Delta_\nu^{(w)}$ ([4], *p.* 283). Taking into account the total symmetry of $T_\rho^{(w)}(L_\nu)$ we get from (B31), (B34)

$$\mathcal{Y}_{kk}^{(w)}\tilde{\tilde{\tau}}_\rho(L_\nu) = T_\rho^{(w)}(L_\nu)\tilde{\tilde{\theta}}_{\rho k}^{(w)}(L_\nu). \tag{B35}$$

On the right-hand side of (B35) there appears the product of the Vandermonde determinants for the standard tableau k multiplied by the product of all parameters of L_ν. We abbreviate this expression by

$$\tilde{\tilde{\upsilon}}^{(w)}_{\rho k}(L_\nu) = T^{(w)}_\rho(L_\nu)\tilde{\tilde{\theta}}^{(w)}_{\rho k}(L_\nu) \tag{B36}$$

and can write

$$\mathcal{Y}^{(w)}_{kk}\tilde{\tilde{\tau}}_\rho(L_\nu) = \tilde{\tilde{\upsilon}}^{(w)}_{\rho k}(L_\nu). \tag{B37}$$

Inserted into (B33) this gives for the basis elements

$$\mathcal{Y}^{(w)}_{ik}\tilde{\tilde{\tau}}^{(w)}_\varrho(L_\nu) = \mathcal{O}(\sigma_{ki})\tilde{\tilde{\upsilon}}^{(w)}_{\rho k}(L_\nu). \tag{B38}$$

As $\tilde{\tilde{\upsilon}}^{(w)}_{\rho k}(L_\nu) \neq 0$ we get for every $k = 1, \ldots, q_w$ a basis. Because $\tilde{\tilde{\tau}}^{(w)}_\rho(L_\nu) = \Psi_\rho(\delta^{(w)}_\nu; L_\nu)$ induces $\Delta^{(w)}_\nu$ only once every k gives the same basis. Therefore we can choose an arbitrary k. As $m_w = 1$, we set $s_w = x_w$ which fulfills (B4). This means that we use x_w different parameter sets. The functions

$$\mathcal{O}(\mathscr{s})\tilde{\upsilon}^{(w)}_{\rho k}(L_\mathrm{e}), \qquad \mathscr{s} \in \mathfrak{S}_n, \quad \text{given } \rho, k \tag{B39}$$

obtained from (B38) by extending the argument and by admitting all permutations of the $\mathfrak{S}_n$ form a representation space of $\Delta^{(w)}_\nu \otimes \Gamma^{(1)}_{n-\nu}$. This representation space remains the same even in the case of the Young tableau k being non-standard. Therefore we drop the condition that k must be an index assigned to a standard tableau. The outer product $\Delta^{(w)}_\nu \otimes \Gamma^{(1)}_{n-\nu}$ contains Γ_χ x_w times (see Eq. (B7)). Hence there are x_w linearly independent chirality functions among

$$\mathcal{P}_\chi \mathcal{O}(\mathscr{s})\tilde{\upsilon}^{(w)}_{\rho k}(L_\mathrm{e}), \qquad \mathscr{s} \in \mathfrak{S}_n. \tag{B40}$$

These can be selected by a suitable choice of x_w permutations $\mathscr{s}^{(w)}_u \in \mathfrak{S}_n$, $u = 1, \ldots, x_w$. As we take the same k for all ρ this choice is independent of ρ. Therefore the general set-up for a qualitatively supercomplete chirality function according to the first Näherungsverfahren takes the form

$$\tilde{\chi}(L_\mathrm{e}) = \mathcal{P}_\chi \sum_w \sum_{\rho=1}^{x_w} \sum_{u=1}^{x_w} \alpha^{(w)}_{\rho u} \mathcal{O}(\mathscr{s}^{(w)}_u)\tilde{\upsilon}^{(w)}_{\rho k}(L_\mathrm{e}) \tag{B41}$$

where $\alpha^{(w)}_{\rho u}$ are coefficients of linear combination. The components of $\tilde{\chi}(L_\mathrm{e})$ are now given by

$$\tilde{\chi}^{(w)}(L_\mathrm{e}) = \mathcal{P}_\chi \sum_{\rho=1}^{x_w} \sum_{u=1}^{x_w} \alpha^{(w)}_{\rho u} \mathcal{O}(\mathscr{s}^{(w)}_u)\tilde{\upsilon}^{(w)}_{\rho k}(L_\mathrm{e}). \tag{B42}$$

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