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Theory of Chirality Functions, Generalized for Molecules with Chiral Ligands

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The theory of chirality functions described in a previous publication is generalized to allow for chiral ligands. In the earlier theory, all symmetry operations of the molecular frame could be thought of as permutations of the ligands among the sites; in the present work, improper rotations not only permute the ligands, but convert them into mirror images. The group that generates all isomers from a given ordered molecule belonging to a frame with n sites is now the "hyperoctahedral" group of order $2^n n!$ consisting of all possible combinations of permutations and site reflections. The representation theory of these groups is described, and applied to the problem of constructing qualitatively complete chirality functions, and of deciding which ligand partitions, and which isomer mixtures, are chiral. It is found useful to classify chiral representations of the covering group as "ligand specific" and "class specific". The ligand specific representations describe chiral properties which are common to all frames and arise purely from the chirality of the ligands, while the class specific representations describe the chiral properties of the frame. A number of examples are explicitly worked out.

1. Introduction and Statement of Problem

A chirality function is defined as a function which describes a pseudoscalar property of molecules belonging to a class in its dependence on the nature of the particular molecules. If the molecular class is characterized by a frame, or skeleton, with n sites for ligands, and if molecules belonging to the class are distinguished by the nature of the ligands and their distribution among the sites, then a chirality function for this class is partially determined by the frame, and depends on variables ℓ_r with indices r for the ligands.

A general theory of chirality functions [10], formulated without reference to the particular physical phenomenon being studied, enables one, under any set of special assumptions about the nature of the molecular class, to make various meaningful statements.

The frame is assumed to be achiral. If two isomers differ from one another by a rearrangement of the ligands corresponding to a symmetry operation of the frame, they must bei either identical or mirror images. This leads to a requirement on the symmetry, placement, and orientation of the ligands. Achiral ligands must be so fixed in space that all symmetry operations of the frame which leave a given site invariant are symmetry operations for the ligand found on that site. Up to now, our theory has been restricted to molecules with exclusively achiral ligands.

In this article, we drop the restriction to achiral ligands. Only symmetry operations of the first kind (pure rotations) which leave a site invariant are required to be symmetry operations for the ligand located on the site. Symmetry operations of the second kind transform chiral ligands into their mirror images[1]. The concept of isomer is to be understood as also including molecules in which chiral ligands may be replaced by their mirror images. Isomers which differ from one another only by a permutation of ligands among the sites (without inversion of any ligand) will be referred to as permutational isomers.

The basic formulation and definitions will be the same as, or analogous to, those used in [10]. $\mathfrak{G}$ is the symmetry group of the frame, $\mathfrak{D}$ the invariant subgroup of the pure rotations. The column matrix

$$L=\begin{pmatrix}\ell_1\\ \ell_2\\ \vdots\\ \ell_n\end{pmatrix} \tag{1}$$

represents a given "ordered molecule" („geordnetes Molekül", cf. [10]). To each rotation of $\mathfrak{D}$ there corresponds a ligand permutation σ on the fixed frame. The application of σ to L leads to the ordered molecule

$$\sigma L=\begin{pmatrix}\ell_{i_1}\\ \ell_{i_2}\\ \vdots\\ \ell_{i_n}\end{pmatrix}.$$

This determines a homomorphic mapping of $\mathfrak{D}$ onto a permutation group $\mathfrak{N}$. In the case of achiral ligands, in which one need not consider their conversion to mirror images, one can also associate permutations with the rotary reflections of $\mathfrak{G}$ (elements of the coset of $\mathfrak{D}$ in $\mathfrak{G}$). In this way, all elements of $\mathfrak{G}$ may be described by pure permutations. In the case of chiral ligands, however, representation of an improper rotation must include the simultaneous transformation of all ligands into mirror images.

The operation which transforms the ligand on site k into its mirror image will be denoted by τ_k, and the mirror image of ℓ_i by ℓ_i^*. Thus, we have

$$\tau_k\begin{pmatrix}\ell_{i_1}\\ \vdots\\ \ell_{i_k}\\ \vdots\\ \ell_{i_n}\end{pmatrix}=\begin{pmatrix}\ell_{i_1}\\ \vdots\\ \ell_{i_k}^*\\ \vdots\\ \ell_{i_n}\end{pmatrix}.$$

τ_k is therefore a reflection, restricted to the ligand located on the site k, in a mirror plane of the frame which contains site k; or, if there is no such mirror plane, in a plane containing a symmetry axis of the first kind passing through site k; or, if there also is no such axis, in a plane chosen in such a way that the

[1] Note that the symmetry requirement for the ligands is automatically satisfied if the ligands are assumed to be freely rotating, or if an ensemble average over conformations is to be taken.

reflection leads to the natural orientation of the mirror image ligand. We shall refer to such an operation as a "site reflection".

If $\tau_0 = \tau_1\,\tau_2 \ldots \tau_n$ denotes the simultaneous site reflection of all ligands, then each improper rotation of $\mathfrak{G}$ can be represented by an operation of the form $\vartheta'\tau_0 = \tau_0\vartheta'$, in which ϑ' denotes the corresponding rearrangement of the ligands among the sites. Thus, we find

$$\tau_0\vartheta' L = \begin{pmatrix} \ell_{i_1}^* \\ \ell_{i_2}^* \\ \vdots \\ \ell_{i_n}^* \end{pmatrix}.$$

The totality of the improper rotations, i.e., the coset of $\mathfrak{D}$ in $\mathfrak{G}$ is mapped in this way onto the set of elements $\tau_0\vartheta'$, in which ϑ' is a permutation describing only the reordering of the ligands under an improper rotation of $\mathfrak{G}$. We have the homomorphism

$$\mathfrak{G} \rightsquigarrow \bar{\mathfrak{S}}'$$

of the group $\mathfrak{G}$ on $\bar{\mathfrak{S}} = \{\mathfrak{N}, \tau_0\vartheta'\mathfrak{N}\}$.

We also have the isomorphism

$$\bar{\mathfrak{S}} \cong \mathfrak{S} = \{\mathfrak{N}, \vartheta'\mathfrak{N}\}$$

in which $\mathfrak{S}$ denotes the permutation group whose elements describe the symmetry operations of $\mathfrak{G}$ neglecting the reflection of ligands. In the case of exclusively achiral ligands, the τ_k are symmetry operations for the corresponding ligands, and it is therefore permissible, as in [10], to make use of the group $\mathfrak{S}$ instead of $\bar{\mathfrak{S}}$.

The group of all operations transforming a given ordered molecule into all its isomers, in our extended definition of the term, shall be denoted by $\bar{\mathfrak{S}}_n$. Its elements σ are pure permutations, pure site reflections and products of the two. The subgroup $\mathfrak{T}$ of site reflections on fixed sites, without simultaneous reordering, consists of all possible products $\tau_i\,\tau_j \ldots \tau_r$ of site reflections on sites i, $j, \ldots r$. Since the ordering does not affect the result of a sequence of site reflections on fixed sites, it follows that $\mathfrak{T}$ is a direct product of groups $\mathfrak{T}_i = \{e, \tau_i\}$, each of which consists of the unit element and the reflection on one site:

$$\mathfrak{T} = \mathfrak{T}_1 \times \mathfrak{T}_2 \times \cdots \times \mathfrak{T}_n .$$

It is clear that the result of a site reflection operation of $\mathfrak{T}$ followed by a permutation, can also be reached by the same permutation followed by site reflections on other sites. It follows that

$$\sigma = \vartheta\tau = \tau'\vartheta , \qquad \vartheta\tau\vartheta^{-1} = \tau' .$$

This, together with the commutativity of all site reflections, leads to the conclusion that $\mathfrak{T}$ is an abelian invariant subgroup of $\bar{\mathfrak{S}}_n$. The subgroup $\mathfrak{S}_n$ of the pure permutations, on the other hand, is not invariant. Since $\mathfrak{S}_n$ and $\mathfrak{T}$ have only the unit element in common, $\bar{\mathfrak{S}}_n$ is a semidirect product of $\mathfrak{T}$ and the symmetric group $\mathfrak{S}_n$:

$$\bar{\mathfrak{S}}_n = \mathfrak{T} \vee \mathfrak{S}_n , \qquad |\bar{\mathfrak{S}}_n| = n!\,2^n .$$

As in [10], with completely analogous definitions and the same reasoning, we may consider the elements of the group algebra of $\bar{\mathfrak{S}}_n$ as denoting ensemble operators. Application of an element a of the group algebra to a column matrix L of type (1), i.e., the application of an ensemble operator a to an ordered molecule, leads to a linear combination of ordered molecules with complex coefficients,

$$aL = \Sigma a(\sigma)\,\sigma L\,.$$

Special ensemble operators are the projection operators

$$\not{p}_{\mathfrak{N}} = \frac{1}{|\mathfrak{N}|}\sum_{\sigma\in\mathfrak{N}}\sigma \quad \text{and} \quad \not{p}_{\chi} = \frac{1}{2}\{\not{p}_{\mathfrak{N}} - \not{p}_{\mathfrak{N}}\tau_0\sigma'\}$$

which can be applied to an arbitrary a to give

$$\bar{a} = \not{p}_{\mathfrak{N}}a \quad \text{and} \quad \not{p}_{\chi}a = \not{p}_{\chi}\bar{a}\,.$$

The operator $\bar{a}$ is expressible in the form

$$\bar{a} = \not{p}_{\mathfrak{N}}\sum_j \bar{a}(\sigma_j)\sigma_j \text{ with coefficients } \bar{a}(\sigma_j) = \sum_{\sigma\in\mathfrak{N}} a(\sigma\sigma_j)$$

and elements σ_j running through a representative system for right cosets of $\mathfrak{N}$ in $\bar{\mathfrak{S}}_n$.

The coefficients $\bar{a}(\sigma_j)$ in $\not{p}_{\mathfrak{N}}aL = \Sigma\bar{a}(\sigma_j)\not{p}_{\mathfrak{N}}\sigma_j L$ refer to a collection of ordered molecules $\not{p}_{\mathfrak{N}}\sigma_j L$ differing only by their orientation in space if the numbering of sites is ignored. Therefore different $\not{p}_{\mathfrak{N}}\sigma_j L$ with $j = 1, 2\ldots$ are representative for different isomers provided the ligand assortment does not contain like ligands. Because of the equation $\not{p}_{\chi}\tau_0\sigma' = -\not{p}_{\chi}$, for any element $\tau_0\sigma'$ of the coset of $\mathfrak{N}$ in $\bar{\mathfrak{S}}$, each coefficient in $\not{p}_{\chi}aL$ can be replaced by the negative coefficient of a corresponding enantiomer; if all coefficients of a are real, $\not{p}_{\chi}aL$ can therefore be written with positive coefficients which may be interpreted as concentrations of the components of an isomeric mixture. Because the application of $\tau_0\sigma'$ on $\not{p}_{\chi}aL$ changes the sign of all coefficients, the condition $\not{p}_{\chi}a \neq 0$ is necessary and sufficient for the existence of non-racemic mixtures aL or $\bar{a}L$. $\not{p}_{\chi}a$ will be referred to as the chiral component of the ensemble operator a. An ensemble operator will be called chiral if $\not{p}_{\chi}a \neq 0$. Extension of the ensemble operator concept to elements of the group algebra with complex coefficients is formally permissible, making possible the formulation and solution of our problem in terms of the language and methods of representation theory.

A chirality function $\phi(|L)$ is, by definition, invariant under a reorientation of the molecule which effects a symmetry operation of the skeleton. This behaviour expressed in terms of the site numbers, corresponds to invariance under the operator $\not{p}_{\mathfrak{N}}$. Since $\phi(|L)$ changes sign under reflections of the molecule, we can define a chirality function by means of the equation

$$\mathscr{P}_{\chi}\phi(|L) = \phi(|L)\,,$$

where $\mathscr{P}_{\chi}$ is an operator corresponding to $\not{p}_{\chi}$, but operating on functions. This definition assures that $\phi(|L)$ transforms according to the chirality representation Γ_{χ} of the group $\bar{\mathfrak{S}}$. For an isomer σL, the chirality function $\phi(|\sigma L)$ has the same value as another function $\phi(\sigma|L)$ of the original molecule:

$$\phi(|\sigma L) \triangleq \phi(\sigma|L)\,.$$

There are a number of qualitative requirements on a chirality function for a molecular class which must be fulfilled if the function is to give a satisfactory description of pseudoscalar observations on chiral molecules. By means of the present formalism, as derived in [10], these requirements can be collected and expressed by a *single* physically realistic property of the function for isomeric mixtures.

A linear combination of functions $\phi(\sigma|L)$, with $\sigma \in \bar{\mathfrak{S}}_n$, is related to the chirality function for a corresponding isomer mixture $\bar{a}L$ as follows:

$$\sum_{\alpha \in \bar{\mathfrak{S}}_n} a(\sigma)\phi(\sigma|L) = \sum_j \bar{a}(\sigma_j)\phi(\sigma_j|L) \triangleq \sum_j \bar{a}(\sigma_j)\phi(|\sigma_j L) = \sum_{\sigma \in \bar{\mathfrak{S}}_n} a(\sigma)\phi(|\sigma L)\,.$$

Thus, seemingly completely different states of affairs for molecules and isomer mixtures lead to results which are reciprocally related. It is desirable that a chirality function not vanish for all chiral molecules in which certain numbers of identical ligands are prescribed, i.e., for molecules possessing a certain "active ligand partition". It is also desirable that a particular type of chirality function for a molecular class remain useable when the frame is continuously distorted into a frame of higher symmetry without altering the number of sites or at any intermediate point decreasing the symmetry. These and similar, seemingly trivial properties are not automatically present in the great majority of cases if functions of the usual type are used. Such properties are all encompassed in a property which we have named "qualitative completeness" („qualitative Vollständigkeit", cf. [10]), a concept which may be defined as follows in terms of isomer mixtures:

> A chirality function for molecules of a certain class is called qualitatively complete if there is no nonracemic isomer mixture for which the function is identically zero, independently of the nature of the ligands.

This definition remains meaningful for the extended concept of isomers, hence for molecules with chiral ligands; the reasons for utilizing qualitatively complete chirality functions are the same as before. The following mathematical formulation is equivalent:

> A chirality function $\phi(|L)$ is qualitatively complete if it gives rise to "regular" [9] induction from $\mathfrak{S}$ to $\bar{\mathfrak{S}}_n$.

Or in other words:

> The functions $\phi(\sigma|L)$ for $\sigma \in \bar{\mathfrak{S}}_n$ form a basis for a representation $\bar{\Gamma}$ of $\bar{\mathfrak{S}}_n$ which, on decomposition into irreducible components $\bar{\Gamma}_r$, contains each $\bar{\Gamma}_r$ exactly as many times as the chirality representation Γ_χ is contained in $\bar{\Gamma}_r$.

If we denote this number for $\bar{\Gamma}_r$ by z_r, then we must have

$$\bar{\Gamma} = \sum_r z_r \bar{\Gamma}_r\,. \tag{2}$$

As the treatment of the achiral ligand case has shown, this property expresses a structural aspect of the chirality phenomenon for a molecular class which furnishes much relevant information. A great deal of this information (such as chirality numbers, statements about active ligand partitions, and so forth) is in

practice – and sometimes in principle as well – expressible only in terms of special properties of the irreducible representations of $\mathfrak{S}_n$. Among these special properties are the one-to-one correspondence between irreducible representations and so-called Young diagrams, Young operators, and a newly discovered lattice structure for Young diagrams. In the generalization to the group $\bar{\mathfrak{S}}_n$ it is thus worthwhile to seek corresponding relations between representations and diagrams, and a corresponding lattice structure. It is equally desirable to formulate corresponding approximation procedures which lead to qualitatively complete chirality functions.

2. Properties of the Group $\bar{\mathfrak{S}}_n$ and Its Representations

In this Section we state without proof some properties of the $\bar{\mathfrak{S}}_n$ which we shall need. Proofs of statements in subsection 2A are to be found in the mathematical literature. Since this literature is somewhat inaccessible to the non-mathematician, we give these proofs in Appendix 1.

A. *The Group $\bar{\mathfrak{S}}_n$, Some Subgroups, Its Young Operators and Partition Diagrams*

A class of conjugate elements in the group $\mathfrak{S}_n$ is known to be characterized by the cyclic structure of the permutations, i.e., by the type of cyclic permutation factors into which the permutations can be decomposed such that each of the numbers 1, 2,... occur in one and only one of the cycles. Like the decomposition of a certain permutation into cycles, a certain decomposition of n into a sum of integers denoting the cycle-lengths is representative for a class of conjugate elements. Such a partition of n, on the other hand, may be visualized by the lengths of rows in a partition diagram. A partition diagram of order n consists of n boxes arranged in rows and columns such that the number of boxes in a column or row does not increase if going from left to right or from top to bottom, respectively. In the case of $n = 10$, for example, one of the classes is denoted in three equivalent ways in Fig. 1.

An element of $\bar{\mathfrak{S}}_n$ is a product of a reflection operation τ and a permutation σ, which may be assumed written in cyclic form. Moreover, since each site reflection τ_j commutes with permutations not involving site (j), we may reorder the factors so that each cyclic permutation is followed immediately by reflections on sites involved in the cycle. Thus, each element of $\bar{\mathfrak{S}}_n$ can be expressed as a product of commuting operations, each of which consists of a cyclic permutation among q sites followed by reflections on some of these sites. If the number of these reflections is even, we call the cycle even and denote it by $q^{(+)}$; if the number of reflections is odd, we call the cycle odd and denote it by $q^{(-)}$. It has been shown [11], and is also proved in Appendix 1.A, that this indexed cyclic structure determines the

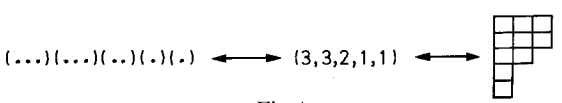

Fig. 1

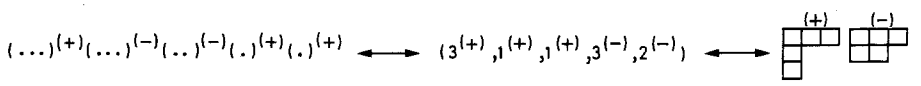

Fig. 2

classes of $\bar{\mathfrak{S}}_n$: two elements are mutually conjugate if and only if they possess the same indexed cyclic structure. Thus, a class of $\bar{\mathfrak{S}}_n$ may be represented by a partition of n into a sum of integers indexed by $(+)$ or $(-)$ respectively, or equivalently by a two-part diagram of order n, consisting of two ordinary diagrams, a "plus" part of order $n^{(+)}$, and a "minus" part of order $n^{(-)}$. Figure 2 shows three equivalent ways of representing one of the classes of $\bar{\mathfrak{S}}_{10}$. We will also sometimes omit the signs, separating even and odd cycles by a semicolon. In this notation, the class of Fig. 2 would be denoted by (3, 1, 1; 3, 2).

In Ref. [10], we drew much advantage from the fact that, in the case of $\mathfrak{S}_n$, there is also a one-to-one correspondence between the set of all possible diagrams of order n, $\gamma^{(r)}$, and the irreducible representations Γ_r of $\mathfrak{S}_n$:

$$\Gamma_r \leftrightarrow \gamma^{(r)} .$$

As we shall see presently, a precisely analogous correspondence holds between two-part diagrams $\bar{\gamma}^{(r)}$ of order n and irreducible representations $\bar{\Gamma}_r$ of $\bar{\mathfrak{S}}_n$:

$$\bar{\Gamma}_r \leftrightarrow \bar{\gamma}^{(r)} .$$

A two-part diagram whose n boxes are filled in any order with the symbols $1, 2, \ldots, n$ (which may be thought of as representing the numbered sites) will be called a (two-part) tableau of order n[2]. A tableau in which the numbers appear in their natural order when one reads first the plus part and then the minus part as in a book, each row from left to right and the rows from top to bottom, will be called the book tableau. For each tableau $\bar{t}^{(r)}$ belonging to the two-part diagram $\bar{\gamma}^{(r)}$, we can define some particular subgroups of $\bar{\mathfrak{S}}_n$, as follows:

Let $\mathfrak{A}^{(r)} = \mathfrak{A}^{(r+)} \times \mathfrak{A}^{(r-)}$ be the subgroup of $\mathfrak{S}_n$ containing all those permutations which effect only rearrangements within the rows of both component tableaux $t^{(r+)}$ and $t^{(r-)}$ in a tableau $\bar{t}^{(r)}$ of $\bar{\gamma}^{(r)}$ and $\mathfrak{B}^{(r)} = \mathfrak{B}^{(r+)} \times \mathfrak{B}^{(r-)}$ be the corresponding subgroup of permutations within columns.

We will sometimes denote an arbitrary member of $\mathfrak{A}^{(r+)}$ by α_+, one of $\mathfrak{A}^{(r-)}$ by α_-, with α (without a subscript) denoting an arbitrary member of $\mathfrak{A}^{(r)}$. β will play the analogous role for $\mathfrak{B}^{(r)}$.

Let $\mathfrak{T}^{(r+)}$ and $\mathfrak{T}^{(r-)}$ be subgroups of $\mathfrak{T}$ containing all site reflections in $t^{(r+)}$ and $t^{(r-)}$ respectively, and consisting of elements τ_+, τ_-.

With the semidirect products $\mathfrak{T}^{(r+)} \vee \mathfrak{A}^{(r+)}$ and $\mathfrak{T}^{(r-)} \vee \mathfrak{B}^{(r-)}$ being direct products of groups $\bar{\mathfrak{S}}_\vee$ for each row in the plus- and each column in the minus-diagram respectively we get the needed subgroups $\mathfrak{Q}^{(r)}$ and $\hat{\mathfrak{Q}}^{(r)}$ of $\bar{\mathfrak{S}}_n$ according

[2] The definition of tableau given in Ref. [10] is different from the one used here. The present definition corresponds to normal usage, and to the requirements of the present article.

to the following definition:

$$\mathfrak{Q}^{(r)} = \mathfrak{T}^{(r+)} \vee \mathfrak{A}^{(r+)} \times \mathfrak{A}^{(r-)} \quad \text{and} \quad \hat{\mathfrak{Q}}^{(r)} = \mathfrak{B}^{(r+)} \times \mathfrak{B}^{(r-)} \vee \mathfrak{T}^{(r-)}.$$

We note that $\mathfrak{Q}^{(r)}$ and $\hat{\mathfrak{Q}}^{(r)}$ have only the unit element of $\bar{\mathfrak{S}}_n$ in common,

$$\mathfrak{Q}^{(r)} \cap \hat{\mathfrak{Q}}^{(r)} = e.$$

We define the "alternating representation" of $\hat{\mathfrak{Q}}^{(r)}$ as the one having the character -1 for odd permutations and for single site reflections. Therefore an element σ of $\hat{\mathfrak{Q}}^{(r)}$ has the character $(+1)$ if both the permutation and the number of site reflections are even, or both odd, otherwise it has (-1).

The projection operators for the identity representation of $\mathfrak{Q}^{(r)}$ and for the alternating representation of $\hat{\mathfrak{Q}}^{(r)}$ which we need are

$$\mathcal{Q}^{(r)} = \mathcal{E}^{(r+)} \mathcal{A}^{(r+)} \mathcal{A}^{(r-)} \quad \text{and} \quad \hat{\mathcal{Q}}^{(r)} = \mathcal{E}^{(r-)} \mathcal{E}^{(r-)} \mathcal{E}^{(r+)}.$$

The factors, which are commutable, are defined as follows:

$$\mathcal{A}^{(r+)} = \frac{1}{|\mathfrak{A}^{(r+)}|} \sum_{\sigma \in \mathfrak{A}^{(r+)}} \sigma, \quad \mathcal{A}^{(r-)} = \frac{1}{|\mathfrak{A}^{(r-)}|} \sum_{\sigma \in \mathfrak{A}^{(r-)}} \sigma, \quad \mathcal{E}^{(r+)} = \frac{1}{|\mathfrak{T}^{(r+)}|} \prod_{\tau_i \in \mathfrak{T}^{(r+)}} (e + \tau_i),$$

$$\mathcal{E}^{(r+)} = \frac{1}{|\mathfrak{B}^{(r+)}|} \sum_{\sigma \in \mathfrak{B}^{(r+)}} \varepsilon_\sigma \sigma, \quad \mathcal{E}^{(r-)} = \frac{1}{|\mathfrak{B}^{(r-)}|} \sum_{\sigma \in \mathfrak{B}^{(r-)}} \varepsilon_\sigma \sigma, \quad \mathcal{E}^{(r-)} = \frac{1}{|\mathfrak{T}^{(r-)}|} \prod_{\tau_i \in \mathfrak{T}^{(r-)}} (e - \tau_i),$$

where $\varepsilon_\sigma = +1$ if σ is even and $\varepsilon_\sigma = -1$ if σ is odd.

These operators may be combined to define the Young operator

$$\bar{\mathcal{Y}}^{(r)} = \mathcal{Q}^{(r)} \hat{\mathcal{Q}}^{(r)}$$

associated with the tableau in question. If the Young operator belonging to the book tableau is denoted by $\bar{\mathcal{Y}}_b^{(r)}$, then any other Young operator belonging to $\bar{\gamma}^{(r)}$ may be expressed as

$$\bar{\mathcal{Y}}_\sigma^{(r)} = \sigma \bar{\mathcal{Y}}_b^{(r)} \sigma^{-1}$$

with a properly chosen σ.

The Young operators possess the following properties, proved in Appendix 1.B:

Each Young operator is, apart from a constant coefficient, a primitive idempotent projecting onto a single component of an irreducible representation of $\bar{\mathfrak{S}}_n$. Young operators generated by tableaux belonging to the same two-part diagram project onto equivalent irreducible representations, those from different diagrams onto inequivalent ones. Thus, the correspondence

$$\bar{\Gamma}_r \leftrightarrow \bar{\gamma}^{(r)}$$

is made precise by the statement that Young operators belonging to $\bar{\gamma}^{(r)}$ project onto the irreducible representation $\bar{\Gamma}_r$. All projection operators onto $\bar{\Gamma}_r$ may be expressed linearly in terms of the $\bar{\mathcal{Y}}^{(r)}$ and products $\bar{\mathcal{Y}}^{(r)\prime} \sigma \bar{\mathcal{Y}}^{(r)}$. Moreover, since the number of different two-part diagrams is obviously equal to the number of classes, and hence to the number of irreducible representations, of $\bar{\mathfrak{S}}_n$, we know that we obtain all irreducible representations in this way.

We will also need another subgroup of $\bar{\mathfrak{S}}_n$, called $\mathfrak{S}'_n$, which contains both $\bar{\mathfrak{S}}$ and $\mathfrak{S}_n$ as subgroups. It consists of all pure permutations, as well as $\tau_0 = \tau_1 \tau_2 \cdots \tau_n$, and products of the two, and may be defined as the direct product

$$\mathfrak{S}'_n = \mathfrak{S}_n \times \mathfrak{T}_0 \quad \text{where} \quad \mathfrak{T}_0 = \{e, \tau_0\} .$$

Because the element τ_0 commutes with all permutations, classes of conjugate elements are the classes in $\mathfrak{S}_n$ and those arising by multiplication with τ_0. A characterization of classes may be given therefore by single diagrams as for $\mathfrak{S}_n$, but marked with an additional index distinguishing a class with the factor τ_0 from a class without this factor.

Because the subduction from an irreducible representation of $\mathfrak{S}'_n$ to the subgroup $\mathfrak{S}_n$ gives rise to an irreducible representation Γ_r of $\mathfrak{S}_n$ and because the subduction to the subgroup $\mathfrak{T}_0$ leads to a multiple of either the identity or alternating representation we can denote the irreducible representations of $\mathfrak{S}'_n$ by Γ_{rg} and Γ_{ru}. The corresponding notation for diagrams with an index g or u yields the one-to-one correspondence between irreducible representations of $\mathfrak{S}'_n$ and diagrams with n boxes

$$\Gamma_{rg} \leftrightarrow \gamma^{(rg)} , \qquad \Gamma_{ru} \leftrightarrow \gamma^{(ru)} .$$

Corresponding Young operators follow from those defined for the irreducible representations of $\mathfrak{S}_n$ according to

$$\mathscr{Y}^{(rg)} = \tfrac{1}{2}(e + \tau_0)\, \mathscr{Y}^{(r)} \quad \text{and} \quad \mathscr{Y}^{(ru)} = \tfrac{1}{2}(e - \tau_0)\, \mathscr{Y}^{(r)}$$

and the definition $\mathscr{Y}^{(r)} = \mathscr{A}^{(r)} \mathscr{E}^{(r)}$ where $\mathscr{A}^{(r)}$ and $\mathscr{E}^{(r)}$ refer to a single diagram $\gamma^{(r)}$ with n boxes.

B. The Regular Induction from $\mathfrak{S}_n$ and $\mathfrak{S}'_n$ to $\bar{\mathfrak{S}}_n$

As we saw in Section 1, the construction of a qualitatively complete chirality function requires the determination of the integer coefficients z_r of formula (2). z_r is the minimum number of different chirality functions transforming like linearly independent vectors of an irreducible representation space for $\bar{\Gamma}_r$ which we need, properly chosen as additional components in a qualitatively complete chirality function for each r. z_r is simultaneously the number which tells us how often the chirality representation is contained in $\bar{\Gamma}_r$. If character tables for $\bar{\mathfrak{S}}_n$ are available, z_r can be determined in a straightforward manner. If not, the characters may be calculated by means of the formula derived in appendix (1.B, Theorem 4). Even for relatively low n, however, this procedure becomes extremely tedious. The induction is much more easily carried out by means of another procedure, which we now proceed to explain. It is based on the knowledge of the readily available characters for $\mathfrak{S}'_n$ and consists of a decomposition of the induction process into the induction from $\bar{\mathfrak{S}}$ to $\mathfrak{S}'_n$ and from $\mathfrak{S}'_n$ to $\bar{\mathfrak{S}}_n$.

If the chirality representation is contained X_l times in the irreducible representation Γ'_l of $\mathfrak{S}'_n$ and if Γ'_l is contained Y_{lr} times in $\bar{\Gamma}_r$ of $\bar{\mathfrak{S}}_n$, then z_r can be determined by the formula

$$z_r = \sum_l X_l\, Y_{lr} .$$

As the character tables of $\mathfrak{S}'_n$ allow us to determine the X_l, our problem reduces to finding the Y_{lr}. For this purpose, we first note that a two-part diagram $\bar{\gamma}^{(r)}$ is characteristic not only for the irreducible representation $\bar{\Gamma}_r$ of $\bar{\mathfrak{S}}_n$, but also for the irreducible representation $\Gamma_{r+} \times \Gamma_{r-}$ of the direct product group $\mathfrak{S}_{n^{(r+)}} \times \mathfrak{S}_{n^{(r-)}}$ because $\gamma^{(r+)}$ and $\gamma^{(r-)}$ are the diagrams for the irreducible representations Γ_{r+} and Γ_{r-} of the factors $\mathfrak{S}_{n^{(r+)}}$ and $\mathfrak{S}_{n^{(r-)}}$.

In Appendix 1.C we prove the following theorem:

The representation of $\mathfrak{S}_n$ which we get by means of the regular induction with an irreducible representation of $\mathfrak{S}_{n^{(r+)}} \times \mathfrak{S}_{n^{(r-)}}$ associated with the diagram pair $\bar{\gamma}^{(r)}$ is the same as that obtained by subduction of $\bar{\Gamma}_r$ to $\mathfrak{S}_n$.

Because the induction from $\mathfrak{S}_{n^{(r+)}} \times \mathfrak{S}_{n^{(r-)}}$ to $\mathfrak{S}_n$ is known [5a, 7], we need only reverse this process to induce from $\mathfrak{S}_n$ to $\bar{\mathfrak{S}}_n$. By a slight modification we get the step we want, the induction from $\mathfrak{S}'_n$ to $\bar{\mathfrak{S}}_n$.

The representation $[\Gamma_r]^{\bar{\mathfrak{S}}_n}$ of $\bar{\mathfrak{S}}_n$ regularly induced by Γ_r of $\mathfrak{S}_n$ is constructed as follows:

We fill a single diagram $\gamma^{(r)}$ containing n boxes with κ_1 symbols 1, κ_2 symbols $2, \cdots \kappa_t$ symbols t subject to the conditions $\kappa_1 \geqq \kappa_2 \geqq \cdots \kappa_t$ and $\kappa_1 + \kappa_2 + \cdots + \kappa_t \leqq \frac{n}{2}$ in such a way that

1) No two symbols of the same kind may be in the same column.

2) When all the boxes containing the symbol t are removed the remaining boxes constitute a diagram; it must remain so when all boxes with t and $t-1$ are removed etc.

3) Reading from right to left along the rows, beginning with the top row and working down, one must get a "lattice permutation" of 111...22.... That is, at each point one must have read at least as many 1's as 2's, as many 2's as 3's, etc. For each way of doing this, the induced representation contains an irreducible representation whose $(+)$ diagram is the diagram of empty boxes and whose $(-)$ diagram has rows of lengths $\kappa_1, \kappa_2, \ldots, \kappa_t$. If the plus and minus diagram are of different order, the induced representation also contains a second irreducible representation corresponding to a two-part diagram in which the plus and minus diagrams are interchanged, otherwise not[3].

The induction from $\mathfrak{S}'_n$ to $\bar{\mathfrak{S}}_n$ is the same, except that the induced diagram pairs reduce to those with an even or odd number of boxes in the negative part according as the inducing representation is Γ_{rg} or Γ_{ru}.

In Fig. 3, we give an example of the induction from $\mathfrak{S}_7$ to $\bar{\mathfrak{S}}_7$.

With reference to the inducing process from $\mathfrak{S}'_7$ we must distinguish between the indices of the inducing representation g or u and consequently ignore induced diagram pairs with an odd or even number of boxes in the minus component. Thus, referring to Fig. 3, if the inducing representation of $\mathfrak{S}'_7$ is $(3, 2, 2)_u$, we obtain only the representations under column (u) in the figure; if it is $(3, 2, 2)_g$ we get only those in column (g).

[3] If the two parts are of the same order, but are not identical, there is always another allowed way of filling in the symbols which leads to the diagram pair with interchanged signs. The prescription as stated prevents this from being counted twice.

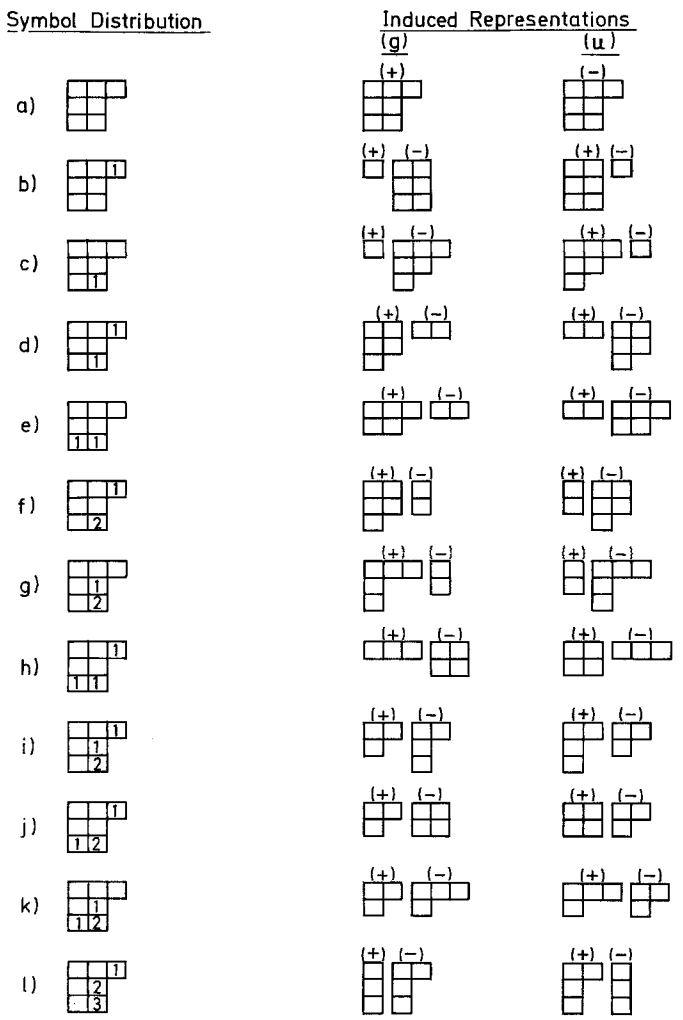

Fig. 3

C. Remainder Diagrams and the Transfer Condition

In Ref. [10], the investigation of active ligand partitions, and of other questions of physical importance, was greatly facilitated by studying the properties of the "partition lattice". In the present subsection, we lay the groundwork for an analogous treatment for the case of chiral ligands.

For single diagrams of order n, the partition lattice provides a very simple answer to the following question:

Consider two single diagrams of order n, $\gamma^{(r)}$ and $\gamma^{(l)}$, the boxes of the latter being filled with symbols 1 in the first row, 2 in the second, etc. Is it possible to transfer all the symbols into the boxes of $\gamma^{(r)}$ in such a way that no two like symbols appear in the same column? ("column condition", or "C-condition").

When this transfer is possible, we will say that the transfer condition (*T*-condition) is satisfied.

The answer to the question turned out to be: The *T*-condition is satisfied if and only if

$$\gamma^{(r)} \supset \gamma^{(l)}$$

($\gamma^{(r)}$ is greater than $\gamma^{(l)}$). The "greater" relation may be defined in three equivalent ways, viz:

i) $\gamma^{(r)} \supset \gamma^{(l)}$ if and only if $\gamma^{(l)}$ is obtained from $\gamma^{(r)}$ by moving boxes downward.

ii) Let v_j denote the length of the j'th row of a diagram and

$$o_i = \sum_{j=1}^{i} v_j .$$

Then $\gamma^{(r)} \supset \gamma^{(l)}$ if and only if

$$o_i^{(r)} \geqq o_i^{(l)} \quad \text{for all } i.$$

iii) Let μ_j denote the length of the j'th column of a diagram and

$$u_i = \sum_{j=1}^{i} \mu_j .$$

Then $\gamma^{(r)} \supset \gamma^{(l)}$ if and only if

$$u_i^{(r)} \leqq u_i^{(l)} \quad \text{for all } i.$$

It is proved in Ref. [10] that these three definitions are equivalent, that the partial ordering of diagrams so defined is a lattice, and that this ordering has the stated relation to the *T*-condition.

As will become clear in the next Section, the appropriate generalization of the *T*-condition for our problem is the following:

Consider two two-part diagrams of order n, $\bar{\gamma}^{(r)}$ and $\bar{\gamma}^{(l)}$, the boxes of the latter being filled with symbols 1 in the first row, 2 in the second, etc., with the symbols in the minus part distinguished by primes. The "generalized *T*-condition" is said to be satisfied if all the symbols can be transferred into the boxes of $\bar{\gamma}^{(r)}$ in such a way that

1) No two like symbols appear in the same column of the same part of $\bar{\gamma}^{(r)}$ (primed and unprimed symbols being counted as different for this purpose); and

2) All the unprimed symbols are in the plus part of $\bar{\gamma}^{(r)}$ (though primed symbols may be in either part).

We now consider what properties the diagrams must have in order to satisfy this condition.

First, the plus part of $\bar{\gamma}^{(r)}$ must be able to accommodate all the unprimed symbols with no two like ones in the same column, though some boxes may be left unfilled. This means that the first row of $\gamma^{(r+)}$ must be long enough to accommodate all the 1's, the leftover boxes in the first row plus those in the second row enough for the 2's, etc. Continuing in this way, by reasoning exactly analogous to that used in Ref. [10] for single diagrams, one concludes that, to fulfill this part of the *T*-condition, it is necessary and sufficient that

$$o_i^{(r+)} \geqq o_i^{(l+)}, \text{ all } i.$$

Second, there must be enough different kinds of primed symbols to fill the first column of $\gamma^{(r-)}$, the unused ones plus those of which there are at least two must be enough to fill the second column, etc. Again, by reasoning analogous to that in [10], one concludes that this part of the T-condition is satisfied if and only if

$$u_i^{(r-)} \leqq u_i^{(l-)}, \text{ all } i.$$

The above two conditions are necessary, though not sufficient, for the T-condition. By means of them, we can define a "greater" relation for two-part diagrams which is analogous to the known one for ordinary diagrams, as follows:

We say that $\bar{\gamma}^{(r)} \supset \bar{\gamma}^{(l)}$ ($\bar{\gamma}^{(r)}$ greater than $\bar{\gamma}^{(l)}$) if

$$o_i^{(r+)} \geqq o_i^{(l+)}, \text{ all } i,$$

and

$$u_i^{(r-)} \leqq u_i^{(l-)}, \text{ all } i.$$

A second, equivalent, definition is: $\bar{\gamma}^{(r)}$ is greater than $\bar{\gamma}^{(l)}$ if and only if $\bar{\gamma}^{(l)}$ can be obtained from $\bar{\gamma}^{(r)}$ by moving boxes from the plus to the minus part, and/or downward within each part.

It is shown in Appendix 2.A that this partial ordering defines a lattice.

If $\bar{\gamma}^{(r)} \supset \bar{\gamma}^{(l)}$, then the above considerations show that we can transfer all the unprimed symbols into $\gamma^{(r+)}$, with no two like ones in the same column and $n_{rl} = n^{(r+)} - n^{(l+)} = n^{(l-)} - n^{(r-)}$ boxes remaining empty. Also, we can fill $\gamma^{(r-)}$ with primed symbols, no two like ones in the same column, with n_{rl} symbols not being used. In general, this partial transfer can be done in several different ways. The T-condition now will be satisfied if we can transfer the n_{rl} remaining unprimed symbols into the n_{rl} empty boxes with no two like symbols going into the same column. We can express this condition as a T-condition for ordinary diagrams as follows: First, form a diagram $\gamma^{(rl+)}$ of order n_{rl} whose column lengths are the numbers of empty boxes in the columns of $\gamma^{(r+)}$. Form another diagram $\gamma^{(rl-)}$ of order n_{rl} whose row lengths are equal to the numbers of unused primed symbols of each kind. These diagrams will be called remainder diagrams. In terms of them, the question of transferability of the unused symbols becomes: "Can all the symbols be transferred from $\gamma^{(rl-)}$ to $\gamma^{(rl+)}$ in such a way that no two symbols from the same row of $\gamma^{(rl-)}$ go into the same column of $\gamma^{(rl+)}$?" This, however, is just the ordinary T-condition for $\gamma^{(rl-)}$ into $\gamma^{(rl+)}$, and we know that it is satisfied if and only if $\gamma^{(rl+)} \supset \gamma^{(rl-)}$.

The remainder diagrams, however, are not uniquely determined, as the partial transfer of the symbols can in general be carried out in many ways. To satisfy the T-condition, we need only *one* way of doing the partial transfer which will make $\gamma^{(rl+)} \supset \gamma^{(rl-)}$. Since the two parts of the partial transfer are independent of each other, we can transfer the unprimed symbols into $\gamma^{(r+)}$ in such a way as to make $\gamma^{(rl+)}$ as large as possible, and similarly transfer the primed symbols so as to make $\gamma^{(rl-)}$ as small as possible. The possibility of doing this depends on the existence of a unique "largest remainder" for the transfer of the unprimed symbols, and a "smallest remainder" for the transfer of the primed symbols. In Appendix 2.B, it is shown that such unique largest and smallest remainders exist, and that they are constructed in the following way:

1) Largest Remainder: Given two diagrams $\gamma^{(a)}$ and $\gamma^{(b)}$, with $o_i^{(a)} \geqq o_i^{(b)}$ for all i, the boxes in the first row of $\gamma^{(b)}$ being filled with 1's, the second row with 2's, etc. Transfer the symbols into the boxes of $\gamma^{(a)}$ one at a time, in any order, placing each symbol as far down as possible subject to the condition that it does not go into a column already occupied by a symbol of its own kind. If there are two or more boxes satisfying this condition and equally low down, choose the one farthest to the right. When all the symbols have been transferred, the unfilled boxes will be in diagram form without further rearrangement, and this diagram will be the largest remainder $\gamma_{\max}(\gamma^{(a)}, \gamma^{(b)})$.

The question of the smallest remainder $\gamma^{(rl-)}$ takes a completely analogous form if we reformulate it somewhat. Instead of transferring the symbols from $\gamma^{(l-)}$ into $\gamma^{(r-)}$, we imagine that the boxes of $\gamma^{(r-)}$ are transferred into $\gamma^{(l-)}$, with no two from the same column going into the same row of $\gamma^{(l-)}$. The symbols remaining uncovered by transferred boxes form the remainder. It is obvious that this is equivalent (as far as forming the remainder is concerned) to the formulation in terms of symbol transfer, and that it differs from the situation of (1) above only in the interchange of the roles of rows and columns. The construction of the smallest remainder is therefore carried out as follows:

2) Smallest Remainder: Given two diagrams, $\gamma^{(a)}$ and $\gamma^{(b)}$, with $u_i^{(a)} \geqq u_i^{(b)}$ for all i, and with the first column of $\gamma^{(b)}$ filled with symbols 1, the second with 2's, etc. Transfer the symbols into the boxes of $\gamma^{(a)}$ one at a time, in any order, placing each symbol as far to the right as possible consistent with the condition that it not go into a row already occupied by a symbol of its own kind. If there are two or more allowed boxes equally far to the right, choose the one farthest down. When all the symbols have been transferred, the unfilled boxes will be in diagram form without further rearrangement, and this diagram will be the smallest remainder $\gamma_{\min}(\gamma^{(a)}, \gamma^{(b)})$.

Examples of largest and smallest remainder construction are shown in Fig. 4.

From the above discussion, we see immediately the criterion for satisfying the T-condition for $\bar{\gamma}^{(l)}$ into $\bar{\gamma}^{(r)}$. It is satisfied if and only if

$$1)\ \bar{\gamma}^{(r)} \supset \bar{\gamma}^{(l)} \text{ and}$$

$$2)\ \gamma_{\max}(\gamma^{(r+)}, \gamma^{(l+)}) \supset \gamma_{\min}(\gamma^{(l-)}, \gamma^{(r-)}).$$

We note that the T-condition is not transitive. For example, referring to Fig. 5, we see that the T-condition is satisfied for $\bar{\gamma}^{(3)}$ into $\bar{\gamma}^{(2)}$, and for $\bar{\gamma}^{(2)}$ into $\bar{\gamma}^{(1)}$, but not for $\bar{\gamma}^{(3)}$ into $\bar{\gamma}^{(1)}$.

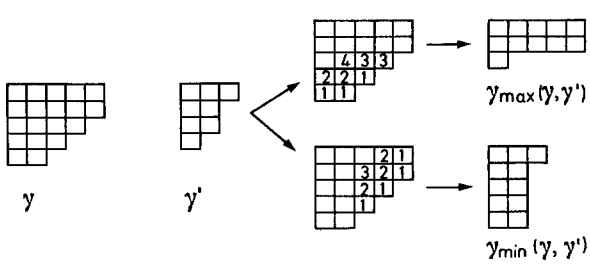

Fig. 4

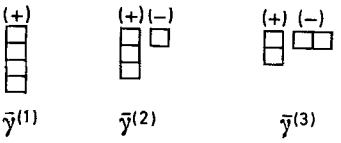

Fig. 5

In the case of $\mathfrak{S}'_n$, we have the partition lattice for $\mathfrak{S}_n$ twice, one containing all the diagrams with the index g, the other those with index u. If we allow transfer between diagrams no matter what the index, the T-condition reduces to

$$\gamma^{(r)} \supset \gamma^{(l)} \text{ neglecting the indices } g, u.$$

3. Active Ligand Partitions

According to the statements in the end of Section 1 and the technique developed in Section 2 we can construct qualitatively complete chirality functions for classes of molecules with chiral ligands. Approximate ansaetze for such chirality functions according to the first and second methods, of Ref. [10], shortened ansaetze for subclasses, specifications of classes according to the minimum-interaction between ligands needed for physical pseudoscalar phenomena, and other related matters, discussed in [10] for achiral ligands may be best understood on the basis of a discussion of "active ligand partitions" and their representation in the partition lattice. Analogous results in our case will be found discussing these questions with reference to chiral ligands. A ligand partition specifies the number of each type of equivalent ligands. For achiral ligands, equivalent means identical in its configuration, for chiral ligands equivalence is defined as including ligands which are identical or enantiomers. The reason for this definition will become obvious later. A ligand partition according to this definition may be characterized by a two-part diagram $\bar{\gamma}^{(l)}$ where the numbers of boxes in rows correspond to the numbers of equivalent ligands, achiral ligands being represented by $\gamma^{(l+)}$ and chiral ones by $\gamma^{(l-)}$. We denote with $L^{(l)}$ an ordered molecule with a ligand assortment belonging to the partition $\bar{\gamma}^{(l)}$.

We call a partition $\bar{\gamma}^{(l)}$ *active* if there is at least one chiral ordered molecule $L^{(l)}$. It is said to be active with respect to an ensemble operator $\mathscr{a}$ if there is an $L^{(l)}$ such that $\mathscr{a} L^{(l)}$ is not racemic. Recalling that negative coefficients in $\mathscr{a}$ are to be interpreted in terms of positive concentrations of enantiomers, we see that the statement that the mixture is not racemic means formally

$$\not{p}_\chi \mathscr{a} L^{(l)} \neq 0 ,$$

i.e., the total coefficient of each particular ordered molecule in $\not{p}_\chi \mathscr{a} L^{(l)}$ is formally not equal to zero. Conversely, the mixture is racemic if

$$\not{p}_\chi \mathscr{a} L^{(l)} = 0 .$$

Each ensemble operator $\mathscr{a}$ can be expressed as an achiral component plus a sum of terms of the form $\not{p}_\chi \bar{\not{p}}^{(r)} \mathscr{a}$, where $\bar{\not{p}}^{(r)}$ is the projection operator onto

an irreducible representation $\bar{\Gamma}_r$ with $z_r \neq 0$. We call $\bar{\gamma}^{(l)}$ "$\bar{\Gamma}_r$-active" if there is an $L^{(l)}$ with $\not{p}_\chi \bar{\not{p}}^{(r)} L^{(l)} \neq 0$. Obviously, $\bar{\gamma}^{(l)}$ is active with respect to $\mathscr{a}$ if and only if it is $\bar{\Gamma}_r$-active for some $\bar{\Gamma}_r$ with $\not{p}_\chi \bar{\not{p}}^{(r)} \mathscr{a} \neq 0$. Equally obviously, it is active if it is $\bar{\Gamma}_r$-active for some $\bar{\Gamma}_r$. Hence, essentially all questions about active ligand partitions are answered if we can decide when a partition $\bar{\gamma}^{(l)}$ is $\bar{\Gamma}_r$-active.

We note that an ordered molecule $L^{(l)}$ is left invariant by the following operations:

(1) Permutation of any two identical ligands.

(2) Permutation of any two enantiomeric ligands followed by site reflections applied to both.

(3) Site reflections applied to achiral ligands.

Since the projection $\bar{\not{p}}^{(r)}$ can be built up out of the Young operators $\bar{\mathscr{Y}}^{(r)}$, we can study the question of $\bar{\Gamma}_r$-activity by studying the effect of the $\bar{\mathscr{Y}}^{(r)}$ (considered formally as ensemble operators) on $L^{(l)}$. Consider an arbitrary one of the $\bar{\mathscr{Y}}^{(r)}$, belonging to the tableau $\bar{t}^{(r)}$. The operator $\bar{\mathscr{Y}}^{(r)}$ antisymmetrizes with respect to the following operations:

(1) Permutation of any two ligands located on sites in the same column of $\bar{t}^{(r)}$.

(2) Site reflection on any site located in $t^{(r-)}$.

(3) Permutation of any two ligands located in the same column of $\bar{t}^{(r)}$ followed by site reflection applied to both.

Thus, if $L^{(l)}$ has any two identical or equivalent ligands on sites in the same column of $\bar{t}^{(r)}$, or any achiral ligand in a site located in $t^{(r-)}$, then $\bar{\mathscr{Y}}^{(r)}$ will antisymmetrize with respect to at least one operation which leaves $L^{(l)}$ invariant, and we have $\bar{\mathscr{Y}}^{(r)} L^{(l)} = 0$. If this is not the case, $\bar{\mathscr{Y}}^{(r)} L^{(l)} \neq 0$.

Thus, there will be an $L^{(l)}$ with $\bar{\mathscr{Y}}^{(r)} L^{(l)} \neq 0$ if and only if it is possible to distribute the symbols from $\bar{\gamma}^{(l)}$ among the sites in such a way that no symbol from $\gamma^{(l+)}$ goes into a site in $t^{(r-)}$ and no two symbols from the same row of $\bar{\gamma}^{(l)}$ go into sites in the same column of $\bar{t}^{(r)}$. This, however, is just the T-condition for $\bar{\gamma}^{(l)}$ into $\bar{\gamma}^{(r)}$. If the condition is not fulfilled, we have $\bar{\mathscr{Y}}^{(r)} L^{(l)} = 0$ for all $\bar{\mathscr{Y}}^{(r)}$ and $L^{(l)}$. If the condition is fulfilled, then for each $\bar{\mathscr{Y}}^{(r)}$ there is an $L^{(l)}$ such that $\bar{\mathscr{Y}}^{(r)} L^{(l)} \neq 0$. Since $\not{p}_\chi$ cannot be orthogonal to all the $\bar{\mathscr{Y}}^{(r)}$, it follows that, if the T-condition is satisfied, there is also an $L^{(l)}$ with $\not{p}_\chi \bar{\not{p}}^{(r)} L^{(l)} \neq 0$, and we conclude that $\bar{\gamma}^{(l)}$ is $\bar{\Gamma}_r$-active.

Summarizing, we have found that a necessary and sufficient condition for $\bar{\gamma}^{(l)}$ to be $\bar{\Gamma}_r$-active is that the T-condition be satisfied for $\bar{\gamma}^{(l)}$ into $\bar{\gamma}^{(r)}$, i.e. that

$$\bar{\gamma}^{(r)} \supset \bar{\gamma}^{(l)}$$

and

$$\gamma_{\max}(\gamma^{(r+)}, \gamma^{(l+)}) \supset \gamma_{\min}(\gamma^{(l-)}, \gamma^{(r-)}) .$$

4. $\mathscr{L}$- and $\mathscr{C}$-Partitions and the Corresponding Decomposition of Chirality Functions

In contrast to the case in which all ligands are required to be achiral, in the present case we have chirality functions which are the same for all permutational isomers, and which are present for all molecular skeletons. To study their

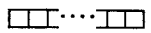

Fig. 6

properties, we note that the representation Γ_{1u} of $\mathfrak{S}'_n$, whose diagram is shown in Fig. 6, always has $z_{1u}=1$, regardless of the skeleton. For the representation is one-dimensional, so z_{1u} cannot be greater than one. On the other hand, the representation is symmetric under all $\sigma \in \mathfrak{S}_n$, in particular under those in $\mathfrak{N}$, and antisymmetric under all $\tau_0\sigma$, in particular those in $\tau_0\sigma'\mathfrak{N}$, so it follows that it contains Γ_χ. Moreover, Γ_{1g} is symmetric under the elements of $\tau_0\sigma'\mathfrak{N}$, so that always $z_{1g}=0$. We conclude, then, that there are always chirality functions belonging to the totally symmetric representation of $\mathfrak{S}_n$, all of these belonging to Γ_{1u} of $\mathfrak{S}'_n$. We call these functions $\mathscr{L}$-chirality functions (ligand specific), since they arise purely from the chirality of the ligands, and are independent of the nature of the skeleton and of the distribution of the ligands among the sites.

If we define the projection operators

$$\mathcal{P}_{\mathscr{L}} = \frac{1}{n!} \sum_{\sigma \in \mathfrak{S}_n} \sigma$$

and

$$\mathcal{P}_{\mathscr{C}} = e - \mathcal{P}_{\mathscr{L}},$$

then we can decompose any chirality function into independent components as follows:

$$\phi(|L) = \phi(\mathcal{P}_{\mathscr{L}}|L) + \phi(\mathcal{P}_{\mathscr{C}}|L).$$

The functions $\phi(\mathcal{P}_{\mathscr{C}}|L)$ will be referred to as class-specific, or $\mathscr{C}$-chirality functions. Unlike the $\mathscr{L}$-chirality functions $\phi(\mathcal{P}_{\mathscr{L}}|L)$, they depend on the nature of the skeleton. Because the operator $\not{p}_\chi \overline{\not{p}}^{(r)}$ commutes with $\mathcal{P}_{\mathscr{L}}$, this decomposition is compatible with the decomposition according to representations of $\overline{\mathfrak{S}}_n$.

The designation of a chirality function as $\mathscr{L}$ or $\mathscr{C}$, it is to be noted, refers to the representation of $\mathfrak{S}'_n$ to which it belongs, not to that of $\overline{\mathfrak{S}}_n$. The two, however, are not independent. According to the induction procedure of Section 2.B, the representations of $\overline{\mathfrak{S}}_n$ induced by Γ_{1u} are:

$$(n-1;1), (n-3;3), \ldots.$$

There is always one $\mathscr{L}$-chirality function belonging to each of these representations, and there may be $\mathscr{C}$-chirality functions as well, depending on the skeleton. Chirality functions belonging to other representations are always $\mathscr{C}$-chirality functions.

Thus, for any $\overline{\Gamma}_r$ with $z_r \neq 0$, we may express z_r as a sum

$$z_r = z_r^{\mathscr{L}} + z_r^{\mathscr{C}}.$$

For the representations listed above, we always have $z_r^{\mathscr{L}}=1$, $z_r^{\mathscr{C}}=z_r-1$. For all other representations, we have $z_r^{\mathscr{L}}=0$, $z_r^{\mathscr{C}}=z_r$.

It is easy to see that $\mathscr{L}$-chirality functions vanish identically if the ligand assortment is racemic, i.e., if the ligands are all either achiral or pairwise enantiomeric.

5. Chirality Numbers

By means of the *T*-condition, we may easily determine maximum numbers for identical or equivalent ligands and minimum numbers for types of nonequivalent ligands in molecules with $\bar{\Gamma}_r$-active ligand partitions $\bar{\gamma}^{(l)}$. This means, if any one of these numbers is exceeded or not reached respectively, then $\phi(\bar{\mathscr{F}}^{(r)}|L^{(l)})$ vanishes even if the molecule is chiral and the isomer mixture $\bar{\mathscr{F}}^{(r)}\,a\,L$ becomes racemic.

We need only the relation $\bar{\gamma}^{(r)} \supset \bar{\gamma}^{(l)}$ to derive the following relations for the lengths of first columns and rows.

$$o_1^{(r+)} \geqq o_1^{(l+)},\ u_1^{(r-)} \leqq u_1^{(l-)},\ o_1^{(r+)} + o_1^{(r-)} \geqq o_1^{(l-)},\ \max(u_1^{(r+)}, u_1^{(r-)}) \leqq u_1^{(l+)} + u_1^{(l-)}.$$

All these limiting numbers are attained in at least one $\bar{\Gamma}_r$-active partition; the first and the second inequalities become equalities for $\bar{\gamma}^{(r)} = \bar{\gamma}^{(l)}$ representing a $\bar{\Gamma}_r$-active partition. The third and fourth inequalities become equalities for the diagram $\bar{\gamma}^{(l)}$ whose plus part vanishes and whose minus part consists of the columns of $\gamma^{(r+)}$ and $\gamma^{(r-)}$ properly ordered. It is active as it is smaller than $\bar{\gamma}^{(r)}$ and $\max(\gamma^{(r+)}, \gamma^{(l+)}) = \bar{\gamma}^{(r)} \supset \min(\gamma^{(r-)}, \gamma^{(l-)})$. Therefore we may conclude that for $\bar{\Gamma}_r$-active molecules

$o_1^{(r+)}$	is the maximum number of identical achiral ligands
$o_1^{(r+)} + o_1^{(r-)}$	is the maximum number of equivalent chiral ligands
$u_1^{(r-)}$	is the minimum number of inequivalent chiral ligands
$\max(u_1^{(r+)}, u_1^{(r-)})$	is the minimum number of inequivalent ligands.

Each of these numbers occur in at least one $\bar{\Gamma}_r$-active ligand partition.

By forming the maxima or minima respectively of these quantities, the extrema being taken over all r with $z_r^{\mathscr{C}} \neq 0$, we get chirality numbers which are characteristic properties of the frame. It should be emphasized that the condition is $z_r^{\mathscr{C}} \neq 0$ and not $z_r \neq 0$ because the latter would only lead to trivial numbers which express the fact that a ligand partition is active for any achiral frame if it contains at least one chiral ligand. The non-trivial numbers we want should present information about the pseudoscalar properties of the particular molecular class in question. We find these "chirality numbers" from the following maxima and minima:

$$\left.\begin{array}{lll} \text{chirality order} & o^+ = \max\{o_1^{(r+)}\} & \\ & o = \max\{o_1^{(r+)} + o_1^{(r-)}\} & \\ \text{chirality index} & u^- = \min\{u_1^{(r-)}\} & \\ & \bar{u} = \min\{\max(u_1^{(r+)}, u_1^{(r-)})\} & \end{array}\right\} \text{maxima and minima are to be taken over all } r \text{ with } z_r^{\mathscr{C}} \neq 0.$$

We call a molecule $\mathscr{C}$-chiral if its pseudoscalar property depends on the particular frame with its sites and not only on the composition of the ligand assortment, i.e., if it possesses a nonvanishing $\mathscr{C}$-chirality function. Correspondingly we call a ligand partition $\mathscr{C}$-active if there are $\mathscr{C}$-chiral molecules belonging to this ligand partition. Now we may formulate the meaning of the

chirality numbers as follows:

- o^+ is the maximum number of identical achiral ligands which may be present in a $\mathscr{C}$-chiral molecule.
- o is the maximum number of equivalent ligands which may be present in a $\mathscr{C}$-chiral molecule.
- u^- is the minimum number of inequivalent chiral ligands which must be present in a $\mathscr{C}$-chiral molecule.
- $\bar{u}$ is the minimum number of inequivalent ligands which must be present in a $\mathscr{C}$-chiral molecule.

In a "chiral class" which by definition contains chiral molecules with exclusively achiral ligands, all these chiral molecules are $\mathscr{C}$-chiral. In an "achiral class" the chirality is only due to $\mathscr{L}$-chirality. Therefore, we have for any class

$$u^- = 0 .$$

For chiral classes we have proved in Ref. [10], under the restriction to achiral ligands, that the chirality order has the lower limit $n-3$ and the upper limit n which characterizes chiral skeletons. If chiral ligands are admitted we have the relation $o > o^+$ and therefore the same limits for o.

$$n-3 \leqq o \leqq n$$

6. Explicit Forms of Qualitatively Complete Chirality Functions

A. General Remarks

The general form of a qualitatively complete chirality function is

$$\phi(\,|L) = \sum_{r}^{z_r \neq 0} \phi(\overline{\mathscr{P}}^{(r)}|L)$$

where the irreducible representation $\bar{\Gamma}_r$ is induced z_r-times by the component $\phi(\overline{\mathscr{P}}^{(r)}|L)$.

According to Ref. [10], Section 2, we may achieve the required property of $\phi(\overline{\mathscr{P}}^{(r)}|L)$ starting with a set of functions $\omega_\varrho^{(r)}(\,|L)$, $\varrho = 1, 2, \ldots t_r$ for which $\overline{\mathscr{P}}^{(r)}\omega_\varrho^{(r)}(\,|L)$ does not vanish. Let the choice be such that the operator $\overline{\mathscr{Y}}^{(r)}$ does not annihilate $\omega_\varrho^{(r)}(\,|L)$ and denote the resulting projection with $\psi_\varrho^{(r)}(\,|L)$. In this section, Young operators without subscripts refer to the book tableau.

$$\overline{\mathscr{Y}}^{(r)}\omega_\varrho^{(r)}(\,|L) = \psi_\varrho^{(r)}(\,|L) \quad \text{and} \quad \omega_\varrho^{(r)}(\sigma|L) = \overline{\mathscr{Y}}_\sigma^{(r)}\omega_\varrho^{(r)}(\sigma|L) \triangleq \psi_\varrho^{(r)}(|\sigma L) .$$

Then, a component $\phi(\overline{\mathscr{P}}^{(r)}|L)$ with the desired properties is constructed by a sum of expressions

$$\mathscr{P}_\chi \psi_\varrho^{(r)}(\sigma|L) \text{ with properly chosen } \varrho \text{ and } \sigma \in \mathfrak{S}_n{}^4.$$

These expressions, being chirality functions as well, are obviously again linear combinations of $\omega_\varrho^{(r)}(\sigma|L)$ with a given ϱ and some elements $\sigma \in \mathfrak{S}'_n$. $\psi_\varrho^{(r)}(\,|L)$ refers

[4] Note that even here the group elements may be chosen to be pure permutations. This follows from the form of the projection operator $\mathscr{P}^{(r)}$ where the sum index is also confined to elements of $\mathfrak{S}_n$.

to the book tableau of $\bar{\gamma}^{(r)}$ and the ordered molecule (1) of Sect. 1. It transforms under site reflections as follows:

$$\mathcal{O}(\tau_i)\,\psi_\varrho^{(r)}(\,|L) \begin{array}{l} = +\psi_\varrho^{(r)}(\,|L) \text{ if } 1 \leqq i \leqq n^{(r+)} \\ = -\psi_\varrho^{(r)}(\,|L) \text{ if } n^{(r+)}+1 \leqq i \leqq n\,. \end{array}$$

Without loss of generality we may define a pseudoscalar function $\kappa(\ell_i)$ for single ligands, i.e.,

$$\mathcal{O}(\tau_i)\,\kappa(\ell_i) = \kappa(\ell_i^*) = -\kappa(\ell_i)$$

and write $\psi_\varrho^{(r)}(|L)$ in the form

$$\psi_\varrho^{(r)}(\,|L) = \kappa(\ell_{n^{(r+)}+1}) \cdots \kappa(\ell_n)\,\overline{\psi}_\varrho^{(r)}(\,|L)$$

where $\overline{\psi}_\varrho^{(r)}(\,|L)$ satisfies the relation $\mathscr{E}^{(r+)}\mathscr{A}^{(r+)}\mathscr{E}^{(r-)}\mathscr{A}^{(r-)}\overline{\psi}_\varrho^{(r)}(\,|L) = \overline{\psi}_\varrho^{(r)}(\,|L)$ and is symmetric under all site reflections. From $\overline{\mathscr{Y}}^{(r)}\omega_\varrho^{(r)}(\,|L) = \psi_\varrho^{(r)}(\,|L)$ it follows that the same decomposition may be chosen for $\omega_\varrho^{(r)}(\,|L)$

$$\omega_\varrho^{(r)}(|L) = \prod_{i=n^{(r+)}+1}^{n} \kappa(\ell_i) \cdot \overline{\omega}_\varrho^{(r)}(|L)\,,$$

$\overline{\omega}_\varrho^{(r)}(|L)$ being invariant under site reflections and $\mathscr{E}^{(r+)}\mathscr{A}^{(r+)}\mathscr{E}^{(r-)}\mathscr{A}^{(r-)}\overline{\omega}_\varrho^{(r)} = \overline{\omega}_\varrho^{(r)}$. Since the above decomposition is always permissible we shall use it for the two approximate procedures of [10] which will be generalized in Section B and C. Two further remarks are worth making beforehand:

1) $\kappa(\ell_i)$ may, in principle, be chosen quite arbitrarily, though a particular choice may recommend itself in certain cases or for specific purposes. There is no need to use the same κ for different equivalent or inequivalent representations $\overline{\Gamma}_r$.

2) Without loss of generality we have expressed the pseudoscalar ligand properties by *one* pseudoscalar ligand parameter κ. On the other hand, $\psi_\varrho^{(r)}(\ell_1 \cdots \ell_n)$, which is a function of the scalar properties of the ligands, does not necessarily depend on values of single ligand parameters only. Rather, this is an additional postulate, which we use for an approximate type of qualitatively complete chirality function as outlined in subsection B.

B. First Procedure: Polynomials of Lowest Degree

We use the form (1) for $\omega_\varrho^{(r)}(|L)$ and choose $\overline{\omega}_\varrho^{(r)}(|L)$ to depend only upon values of a one-parameter achiral property of the single ligands $\lambda(\ell_i)$ and being a polynomial of lowest degree in $\lambda(\ell_i)$ such that the operator $\mathscr{E}^{(r+)}\mathscr{A}^{(r+)}\mathscr{E}^{(r-)}\mathscr{A}^{(r-)}$ does not annihilate $\overline{\omega}_\varrho^{(r)}(|L)$. Because this operator is the product of two commuting operators $\mathscr{E}^{(r+)}\mathscr{A}^{(r+)}$ and $\mathscr{E}^{(r-)}\mathscr{A}^{(r-)}$, for single tableaux of $\gamma^{(r+)}$ and $\gamma^{(r-)}$, we may choose $\overline{\omega}_\varrho^{(r)}(\,|L)$ as in Ref. [10] and we choose $\overline{\psi}_\varrho^{(r)}(\,|L)$ to be a polynomial of lowest possible degree in the $\lambda(\ell_i)$. For this purpose we start with a polynomial

$$\omega(|L) = \prod_{i=n^{(r+)}+1}^{n} \kappa(\ell_i)\,\overline{\omega}(\lambda(\ell_i) \cdots \lambda(\ell_n))$$

which is of lowest degree $g^{(r)}$ in $\lambda(\ell_i)$ such that $\overline{\mathscr{Y}}^{(r)}\omega_\varrho^{(r)}(|L)$ does not vanish. The operator $\mathscr{E}^{(r+)}\mathscr{A}^{(r+)}\mathscr{E}^{(r-)}\mathscr{A}^{(r-)}$ in the equation $\mathscr{E}^{(r+)}\mathscr{A}^{(r+)}\mathscr{E}^{(r-)}\mathscr{A}^{(r-)}\overline{\omega}_\varrho^{(r)}(|L) = \psi_\varrho^{(r)}(|L)$ is the product of two commuting Young operators $\mathscr{E}^{(r+)}\mathscr{A}^{(r+)}$ and $\mathscr{E}^{(r-)}\mathscr{A}^{(r-)}$ for the single tableaux of $\gamma^{(r+)}$ and $\gamma^{(r-)}$. Therefore we may choose $\overline{\omega}_\varrho^{(r)}(|L)$ as in

Ref. [10] as a monomial in $\lambda(\ell_i)$ where each $\lambda(\ell_i)$ occurs in the $(i-1)$th power if i is the row number in $\gamma^{(r+)}$ or $\gamma^{(r-)}$. As we concluded from [10], this is a monomial of lowest degree which does not vanish when $\ell^{(r+)}a^{(r+)}\ell^{(r-)}a^{(r-)}$ is applied. Its degree is

$$g^{(r)} = \sum_{i=1}^{n} (i-1)\,(v_i^{(r+)} + v_i^{(r-)})\,.$$

The application of $\bar{\mathscr{Y}}^{(r)}$ on $\omega_\varrho^{(r)}$ leads therefore to the homogeneous polynomials

$$\bar{\mathscr{Y}}^{(r)}\omega_\varrho^{(r)}(|L) = \psi_\varrho^{(r)}(|L) = \prod_{i=n^{(r+)}+1}^{n} \kappa(\ell_i)\,\bar{\psi}_\varrho^{(r)}(|L)\,.$$

They are of degree $n^{(r-)}$ in κ and $g^{(r)}$ in $\lambda(\ell_i)$, and this is also true for the chirality functions $\mathscr{P}_\chi\psi_\varrho^{(r)}(\sigma|L)$ which can be used according to Ref. [10] to construct $\phi(\bar{\mathscr{R}}^{(r)}|L)$ with the required properties.

Exactly as in [10], it can be proved that a polynomial of lowest degree induces $\bar{\Gamma}_r$ only once. Therefore, we need z_r polynomials depending upon different types of parameters $\lambda^{(1)}, \lambda^{(2)}, \ldots, \lambda^{(r)}$, but the $\kappa(\ell_i)$ may be chosen to be the same. The polynomial of lowest degree depends only upon differences of the scalar parameters. This is proved by introducing new variables $\xi_1 = \Sigma\,\lambda(\ell_i)$, $\xi_2 = \lambda(\ell_1) - \lambda(\ell_2), \ldots, \xi_n = \lambda(\ell_{n-1}) - \lambda(\ell_n)$ and from the fact (which follows from the symmetry) that ξ_1 must occur as a factor of the polynominal if present at all. One infers as in [10] that ξ_1 does not occur if the degree is the lowest. We denote the qualitatively complete chirality function according to the first method with $\chi(|L)$.

C. *Second Procedure: Linear Combinations of Functions Depending on as Few Ligands as Possible*

In this subsection, we do not restrict the number of scalar parameters for single ligands, but we postulate that $\omega_\varrho^{(r)}(|L)$ depends on as few ligands as possible, again using the form:

$$\omega_\varrho^{(r)}(|L) = \prod_{i=n^{(r+)}+1}^{n} \kappa(l_i)\,\bar{\omega}_\varrho^{(r)}(|L)\,.$$

This postulate implies a minimum number of ℓ_i occurring in $\bar{\omega}_\varrho^{(r)}(|L)$. Assume $\bar{\omega}_\varrho^{(r)}(|L)$ depending on h ligands; then it is certainly totally symmetric under permutations among the remaining $n-h$ ligands. Because $\ell^{(r+)}a^{(r+)}\ell^{(r-)}a^{(r-)}\bar{\omega}_\varrho^{(r)}(|L)$ is antisymmetrical with respect to permutations within columns, ligands which do not occur in $\bar{\omega}_\varrho^{(r)}(|L)$ must all be in different columns. From this it follows that

$$v_1^{(r+)} + v_1^{(r-)} \geqq h\,,$$

where, if h denotes the minimum number, the equal sign is to be taken. Consequently, $\bar{\omega}_\varrho^{(r)}(|L)$ depends upon at least $n - v_1^{(r+)} - v_1^{(r-)}$, $\omega_\varrho^{(r)}(|L)$ depends therefore upon $h(r) = n - v_1^{(r+)}$ ligands and the chirality functions $\mathscr{P}_\chi\phi_\varrho^{(r)}(\sigma|L)$ are linear combinations of functions depending upon $h(r) = n - v_1^{(r+)}$ ligands each. They can be used to construct the components $\phi(\bar{\mathscr{R}}^{(r)}|L)$ of a qualitatively complete chirality function $\tilde{\chi}(|L)$ according to the second procedure outlined in Ref. [10].

Because all components of $\tilde{\chi}(|L)$ depend on a minimum number $k^{(r)}$ of ℓ_i, which cannot be decomposed into sums of functions depending on fewer variables, $k^{(r)}$ is the minimum number of ligands between which interaction has to be taken into account in order to describe the phenomenon due to $\bar{\Gamma}_r$. Recalling the chirality numbers we conclude:

$k = n - o^+$ is the minimum interaction between ligands to be taken into account in order to describe pseudoscalar phenomena on the class in question. Of course, a qualitatively complete description also necessitates, in general, components with higher interactions.

Because of the bounds on o^+, the number k has one of the values 1, 2 or 3. This is a very useful aspect for general statements about properties of classes as pointed out in [10], or for the quantum mechanical treatment of special pseudoscalar phenomena such as the optical rotatory power shown in [3] and [4].

7. Examples

Some examples may help to make the derived results clearer. In connection with special classes (examples B, C, and D) we give the partition lattices for two, three and four sites. The chosen numbering of diagrams is arbitrary but allows one to design the representations of $\bar{\mathfrak{S}}_n$ correspondingly. With reference to given classes, all diagram pairs with $z_r^{\mathscr{C}} \neq 0$ are shaded, those for which $z_r^{\mathscr{L}} \neq 0$ have a heavy border. The induction from $\mathfrak{S}'_n$ to $\bar{\mathfrak{S}}_n$ is presented for all those diagrams of $\mathfrak{S}'_n$ which correspond to irreducible representations of $\mathfrak{S}'_n$ containing Γ_χ. In the discussed examples Γ_χ is contained only once and the induction from a given Γ' to $\bar{\mathfrak{S}}_n$ delivers each induced representation of $\bar{\mathfrak{S}}_n$ only once as well. Therefore these numbers are not mentioned. In example D a representation of $\bar{\mathfrak{S}}_n$ is induced from two different representations of $\mathfrak{S}'_n$. The corresponding two components for chirality functions are adapted to the originating representations of $\mathfrak{S}'_n$. The advantage of this choice becomes clear from the comparison of the T_d and D_{2d}-frame, where one of both components of D_{2d} vanishes in the T_d case.

A) $\mathscr{L}$-chirality Functions

$\mathscr{L}$-chirality functions are functions transforming according to Γ_{1u} of $\mathfrak{S}'_n$ represented by the diagram $(n)^{(u)}$. The induced representations of $\bar{\mathfrak{S}}_n$ correspond to the diagram pairs $[(n-1)^{(+)}, 1^{(-)}]$; $[(n-3)^{(+)}, 3^{(-)}]$ and so on. Because the component diagrams have not more than one row, we find with help of the derived formulas for the order $g^{(r)}$ of the polynomials and for the minimum number $h^{(r)}$ that $\bar{\omega}(|L)$ according to both methods becomes a constant. Both methods lead therefore to identical chirality functions

$$(n)^u \rightarrow \begin{cases} \{(n-1)^{(+)}, (1)^{(-)}\} \leftrightarrow \sum_{i=1}^{n} \kappa(\ell_i) \\ \{(n-3)^{(+)}, (3)^{(-)}\} \leftrightarrow \sum_{i<j<k}^{i,n} \kappa(\ell_i)\,\kappa(\ell_j)\,\kappa(\ell_k) \\ \cdots\cdots\cdots \\ \cdots\cdots\cdots \end{cases}$$

B) Frame with Two Sites, Skeleton Symmetry C_s Fig. 7, Induction Fig. 8, Partition Lattice for $\bar{\mathfrak{S}}_2$ Fig. 9

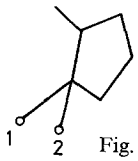

Fig. 7

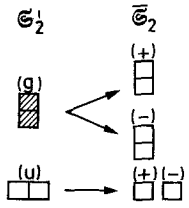

Fig. 8

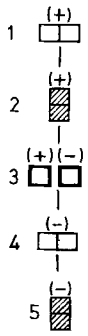

Fig. 9

$$\tilde{\chi}(\bar{\mathcal{H}}^{(2)}|L) = \chi(\bar{\mathcal{H}}^{(2)}|L) = \lambda(1) - \lambda(2)$$

$$\tilde{\chi}(\bar{\mathcal{H}}^{(5)}|L) = \chi(\bar{\mathcal{H}}^{(5)}|L) = \kappa(1)\,\kappa(2)\,[\lambda(1) - \lambda(2)]$$

$$\tilde{\chi}(\bar{\mathcal{H}}^{(3)}|L) = \chi(\bar{\mathcal{H}}^{(3)}|L) = \kappa(1) + \kappa(2)$$

C) Frame with Three Sites, Skeleton Symmetry C_{3v} Fig. 10, Induction Fig. 11, Partition Lattice for $\bar{\mathfrak{S}}_3$ Fig. 12

$$\chi(\bar{\mathcal{H}}^{(3)}|L) = [\lambda(1) - \lambda(2)]\,[\lambda(1) - \lambda(3)]\,[\lambda(2) - \lambda(3)]$$

$$\tilde{\chi}(\bar{\mathcal{H}}^{(3)}|L) = \omega(1,2) + \omega(2,3) + \omega(3,1) \quad \text{with} \quad \omega(i,k) = -\omega(k,i)$$

$$\begin{aligned}\tilde{\chi}(\bar{\mathcal{H}}^{(7)}|L) &= \chi(\bar{\mathcal{H}}^{(7)}|L) \\ &= \kappa(1)\,\kappa(2)\,[\lambda(1) - \lambda(2)] + \kappa(2)\,\kappa(3)\,[\lambda(2) - \lambda(3)] \\ &\quad + \kappa(3)\,\kappa(1)\,[\lambda(3) - \lambda(1)]\end{aligned}$$

$$\tilde{\chi}(\bar{\mathcal{H}}^{(4)}|L) = \chi(\bar{\mathcal{H}}^{(4)}|L) = \kappa(1) + \kappa(2) + \kappa(3)$$

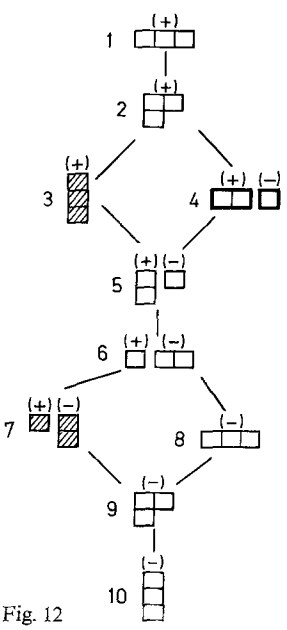

Fig. 12

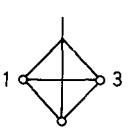

Fig. 10

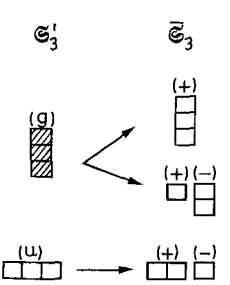

Fig. 11

D) Frame with Four Sites, Partition Lattice for $\mathfrak{S}_4$ *Fig. 16*

a) Skeleton symmetry D_{2d} Fig. 13, induction / / / / / shaded Fig. 15.
b) Skeleton symmetry T_d Fig. 14, induction \ \ \ \ \ shaded Fig. 15.

$$\chi(\not{\pi}^{(3)}|L) = [\lambda(1)-\lambda(2)]\,[\lambda(3)-\lambda(4)]$$

$$\tilde{\chi}(\not{\pi}^{(3)}|L) = \omega(1,3)-\omega(1,4)-\omega(2,3)+\omega(2,4)$$
with $\omega(i,k)=\omega(k,i)$

$$\begin{aligned}\chi_1(\not{\pi}^{(13)}|L) = {} & 2[\kappa(1)\kappa(2)+\kappa(3)\kappa(4)]\,[\lambda(1)-\lambda(2)]\,[\lambda(3)-\lambda(4)]\\ & -[\kappa(1)\kappa(3)+\kappa(2)\kappa(4)]\,[\lambda(3)-\lambda(1)]\,[\lambda(2)-\lambda(4)]\\ & -[\kappa(1)\kappa(4)+\kappa(2)\kappa(3)]\,[\lambda(1)-\lambda(2)]\,[\lambda(2)-\lambda(3)]\end{aligned}$$

$$\begin{aligned}\tilde{\chi}_1(\not{\pi}^{(13)}|L) = {} & 2[\kappa(1)\kappa(2)+\kappa(3)\kappa(4)]\,[\omega(1,3)-\omega(1,4)-\omega(2,3)+\omega(2,4)]\\ & -[\kappa(1)\kappa(3)+\kappa(2)\kappa(4)]\,[\omega(3,2)-\omega(3,4)-\omega(1,2)+\omega(1,4)]\\ & -[\kappa(1)\kappa(4)+\kappa(2)\kappa(3)]\,[\omega(1,2)-\omega(1,3)-\omega(4,2)+\omega(4,3)]\\ & \text{with } \omega(i,k)=\omega(k,i)\end{aligned}$$

$$\tilde{\chi}(\not{\pi}^{(9)}|L) = \chi(\not{\pi}^{(9)}|L) = [\kappa(1)-\kappa(2)]\,[\kappa(3)-\kappa(4)]$$

$$\chi(\not{\pi}^{(18)}|L) = \kappa(1)\kappa(2)\kappa(3)\kappa(4)\,[\lambda(1)-\lambda(2)]\,[\lambda(3)-\lambda(4)]$$

$$\begin{aligned}\tilde{\chi}(\not{\pi}^{(18)}|L) = {} & \kappa(1)\kappa(2)\kappa(3)\kappa(4)\,[\omega(1,3)-\omega(1,4)-\omega(2,3)+\omega(2,4)]\\ & \text{with } \omega(i,k)=\omega(k,i)\end{aligned}$$

$$\begin{aligned}\tilde{\chi}(\not{\pi}^{(7)}|L) = {} & \chi(\not{\pi}^{(7)}|L) = \kappa(1)\,[2\lambda(2)-\lambda(3)-\lambda(4)]+\kappa(2)\,[2\lambda(1)-\lambda(3)-\lambda(4)]\\ & +\kappa(3)\,[2\lambda(4)-\lambda(1)-\lambda(2)]+\kappa(4)\,[2\lambda(3)-\lambda(1)-\lambda(2)]\end{aligned}$$

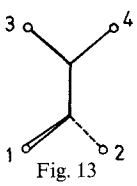

Fig. 13

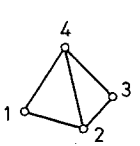

Fig. 14

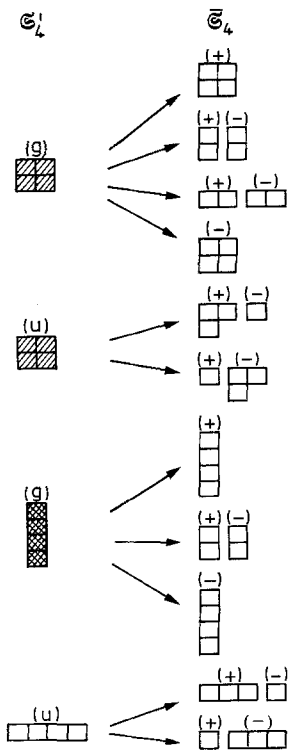

Fig. 15

$$\tilde{\chi}(\mathcal{F}^{(15)}|L) = \chi(\mathcal{F}^{(15)}|L) = \kappa(1)\,\kappa(2)\,\kappa(3)\,[2\lambda(3) - \lambda(1) - \lambda(2)] + \kappa(1)\,\kappa(2)\,\kappa(4)\,[2\lambda(4) - \lambda(1) - \lambda(2)] + \kappa(1)\,\kappa(3)\,\kappa(4)\,[2\lambda(1) - \lambda(3) - \lambda(4)] + \kappa(2)\,\kappa(3)\,\kappa(4)[2\lambda(2) - \lambda(3) - \lambda(4)]$$

$$\chi(\mathcal{F}^{(6)}|L) = [\lambda(1) - \lambda(2)]\,[\lambda(1) - \lambda(3)]\,[\lambda(1) - \lambda(4)]\,[\lambda(2) - \lambda(3)]\,[\lambda(2) - \lambda(4)]\,[\lambda(3) - \lambda(4)]$$

$$\tilde{\chi}(\mathcal{F}^{(6)}|L) = \omega(1, 2, 3) - \omega(1, 2, 4) + \omega(1, 3, 4) - \omega(2, 3, 4) \text{ with } \omega(i, k, l) \text{ totally antisymmetric}$$

$$\chi_2(\mathcal{F}^{(13)}|L) = [\kappa(1)\,\kappa(2) + \kappa(3)\,\kappa(4)]\,[\lambda(1) - \lambda(2)]\,[\lambda(3) - \lambda(4)] + [\kappa(1)\,\kappa(3) + \kappa(2)\,\kappa(4)]\,[\lambda(3) - \lambda(1)]\,[\lambda(2) - \lambda(4)] + [\kappa(1)\,\kappa(4) + \kappa(2)\,\kappa(3)]\,[\lambda(1) - \lambda(4)]\,[\lambda(2) - \lambda(3)]$$

$$\tilde{\chi}_2(\mathcal{F}^{(13)}|L) = [\kappa(1)\,\kappa(2) + \kappa(3)\,\kappa(4)]\,[\omega(1, 3) - \omega(1, 4) - \omega(2, 3) + \omega(2, 4)] + [\kappa(1)\,\kappa(3) + \kappa(2)\,\kappa(4)]\,[\omega(2, 3) - \omega(3, 4) - \omega(1, 2) + \omega(1, 4)] + [\kappa(1)\,\kappa(4) + \kappa(2)\,\kappa(3)]\,[\omega(1, 2) - \omega(1, 3) - \omega(4, 2) + \omega(4, 3)]$$
with $\omega(i, k) = \omega(k, i)$

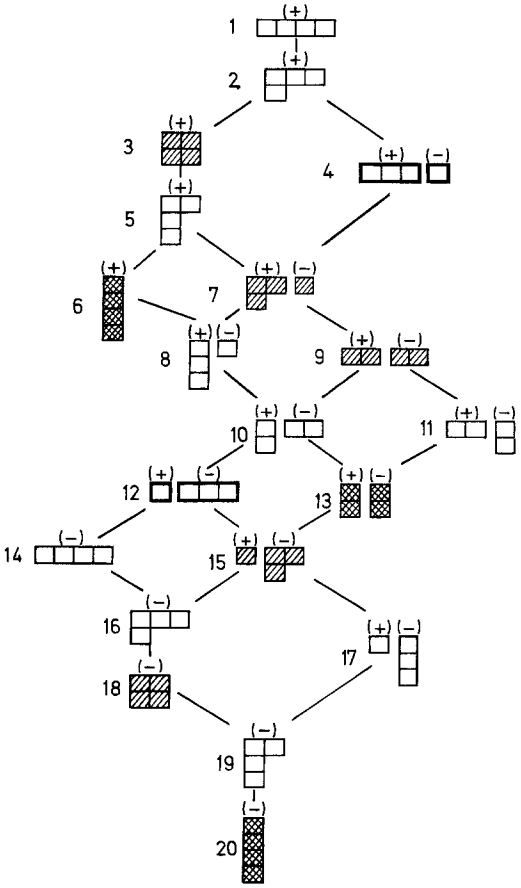

Fig. 16

$$\chi(\overline{\mathscr{P}}^{(20)}|L) = \kappa(1)\,\kappa(2)\,\kappa(3)\,\kappa(4)\,[\lambda(1)-\lambda(2)]\,[\lambda(1)-\lambda(3)]\,[\lambda(1)-\lambda(4)] \cdot [\lambda(2)-\lambda(3)]\,[\lambda(2)-\lambda(4)]\,[\lambda(3)-\lambda(4)]$$

$$\tilde{\chi}(\overline{\mathscr{P}}^{(20)}|L) = \kappa(1)\,\kappa(2)\,\kappa(3)\,\kappa(4)\,[\omega(1,2,3)-\omega(1,2,4)+\omega(1,3,4)-\omega(2,3,4)]$$
with $\omega(i,k,l)$ totally antisymmetric

$$\tilde{\chi}(\overline{\mathscr{P}}^{(4)}|L) = \chi(\overline{\mathscr{P}}^{(4)}|L) = \kappa(1)+\kappa(2)+\kappa(3)+\kappa(4)$$

$$\tilde{\chi}(\overline{\mathscr{P}}^{(12)}|L) = \chi(\overline{\mathscr{P}}^{(12)}|L) = \kappa(1)\,\kappa(2)\,\kappa(3)+\kappa(1)\,\kappa(2)\,\kappa(4)+\kappa(1)\,\kappa(3)\,\kappa(4)+\kappa(2)\,\kappa(3)\,\kappa(4)$$

a) In case of D_{2d}, $\overline{\Gamma}_{13}$ occurs twice; therefore we have to use each of the two components for $\overline{\Gamma}_{13}$ twice with different parameters in order to have the general ansatz according to the first method. But if we use these components only once, the ansatz is qualitatively complete and reads as follows:

$$\chi(|L) = \chi(\overline{\mathscr{P}}^{(3)}|L)+\chi(\overline{\mathscr{P}}^{(4)}|L)+\chi(\overline{\mathscr{P}}^{(6)}|L)+\chi(\overline{\mathscr{P}}^{(7)}|L)+\chi(\overline{\mathscr{P}}^{(9)}|L)+(\overline{\mathscr{P}}^{(12)}|L) + \chi_1(\overline{\mathscr{P}}^{(13)}|L)+\chi_2(\overline{\mathscr{P}}^{(13)}|L)+\chi(\overline{\mathscr{P}}^{(15)}|L)+\chi(\overline{\mathscr{P}}^{(18)}|L)+\chi(\overline{\mathscr{P}}^{(20)}|L)$$

(analogously for $\tilde{\chi}$).

b) In case of T_d, $\overline{\Gamma}_{13}$ occurs only once, and the ansatz is as follows:

$$\chi(|L) = \chi(\overline{\mathscr{P}}^{(4)}|L)+\chi(\overline{\mathscr{P}}^{(6)}|L)+\chi(\overline{\mathscr{P}}^{(12)}|L)+\chi_2(\overline{\mathscr{P}}^{(13)}|L)+\chi(\overline{\mathscr{P}}^{(20)}|L)$$

(analogously for $\tilde{\chi}$).

8. Discussion

We have seen that, by means of the theory of the groups $\mathfrak{S}'_n$ and $\overline{\mathfrak{S}}_n$, the theory of chirality functions can be conveniently generalized to allow for chiral ligands. Although the groups are of large order even for relatively small n, the existence of a general representation theory nevertheless makes a systematic investigation feasible.

There are two obvious directions in which the theory could be further generalized, viz:

(a) One could consider the theory, not just of pseudoscalar, but also of vector and tensor properties of molecules. This could be done with the groups already at hand, simply by considering induction, not just of the chiral representation, but of an arbitrary representation, from the molecular symmetry group to the covering group.

(b) One could allow the ligands to have arbitrary transformation properties under the symmetry operations of the frame. In this case, the covering group would no longer be $\overline{\mathfrak{S}}_n$, but an arbitrary wreath product group [6].

Appendix 1. Representation Theory of the Groups $\overline{\mathfrak{S}}_n$

A. General Properties; Classes

The group $\overline{\mathfrak{S}}_n$ consists of all products $\tau\sigma$, where σ is a member of $\mathfrak{S}_n$ (permutation of n ligands among n sites), and $\tau = \prod_j \tau(j)$, with the product running over an arbitrary subset of the n sites. The order of the group is obviously $2^n n!$ This is not a direct product group, since the τ and σ do not necessarily commute. For example, reflection at site 1 followed by permuting 1

and 2 leaves a reflected ligand on site 2, while permutation followed by reflection on 1 leaves the reflected ligand on site 1. It is, however, a semidirect product: The subgroup $\mathfrak{T}$, consisting of all the reflection operations τ, is, as we shall see presently, an invariant subgroup, while the subgroup $\mathfrak{S}_n$ is not.

These groups were first studied by Young [11] who called them "hyper-octahedral groups". Further properties of these groups have been discussed by Frame [2]. In modern notation [6], they may be thought of as special cases of "wreath product" groups.

To elucidate the class structure, we first note that, since the operators τ do not move the ligands, we always have

$$\tau\sigma\,\tau'\sigma' = \tau''\sigma\sigma', \tag{1}$$

i.e., the permutation part (σ) follows the multiplication table of $\mathfrak{S}_n$. The τ operators do not commute with the σ, but they do with each other, and each τ is its own inverse.

Because of (1), we can write

$$\sigma\tau = \tau'\sigma, \tag{2}$$

$$\tau' = \sigma\tau\sigma^{-1}. \tag{3}$$

Now, if $\tau = \prod_j \tau(j)$, and σ takes the ligand on j to the site s_j, then $\sigma\tau\sigma^{-1}$ first takes the ligand on s_j to j, where it is reflected, then taken back to s_j. The net effect, therefore, is to reflect on all the sites s_j, and we have

$$\tau' = \prod_j \tau(s_j) \equiv \tau^{(s)}. \tag{4}$$

Now consider a group element $\tau\sigma$, and conjugate it with a pure permutation $\pi(j \to r_j)$. Because of (3), (4), we can write

$$\pi\tau\sigma\pi^{-1} = \tau^{(r)}\pi\sigma\pi^{-1}.$$

It is known from the usual theory [1a, 5b] of $\mathfrak{S}_n$ that $\pi\sigma\pi^{-1}$ has the same cyclic structure as σ. If σ has the cyclic form

$$\sigma = (j_1 j_2 \dots j_m)\,(j_{m+1} j_{m+2} \dots j_{m+m'}) \dots,$$

then

$$\pi\sigma\pi^{-1} = (r_{j_1} r_{j_2} \dots r_{j_m})\,(r_{j_{m+1}} r_{j_{m+2}} \dots r_{j_{m+m'}}) \dots.$$

Also, from (4), if $\tau = \prod_j \tau(j)$, then

$$\tau^{(r)} = \prod_j \tau(r_j). \tag{5}$$

Thus, conjugation of $\tau\sigma$ with a pure permutation gives an element whose permutation part has the same cyclic structure, and whose reflections are distributed in the same way among the sites in the permutation cycles. For example, if σ has l reflections on the m sites which are permuted in an m-cycle, then $\pi\sigma\pi^{-1}$ will also have l reflections on the sites belonging to an m-cycle.

Next, we consider conjugation with a reflection, at first restricting ourselves to the case of a single reflection $\tau(j)$. We find

$$\tau(j)\,\tau\sigma\tau\,(j)^{-1} = \tau(j)\,\tau\sigma\tau(j) = \tau(j)\,\tau\,\tau(s_j)\sigma = \tau(j)\tau(s_j)\tau\,\sigma,$$

where we have used (4), plus the fact that the τ commute with each other and are their own inverses. Conjugation with $\tau(j)$, therefore, has the same effect as multiplication with $\tau(j)\tau(s_j)$. Conjugation with a general reflection operation can be thought of as a series of successive conjugations with single reflections. By conjugating first with $\tau(j)$ and then with $\tau(s_j)$, we achieve the net result of multiplying by $\tau(j)\tau(s_j^2)$, where s_j^2 is the site to which the ligand on j is taken by two successive applications of the permutation σ. Continuing in this way, we can multiply by any two reflections on sites belonging to the same cycle of σ. Thus, conjugation with an arbitrary τ is equivalent to a series of operations in which one carries out two reflections on sites belonging to the same cycle of σ. The net effect, therefore, is always to change the number of reflections in each cycle (if at all) by an even number, and all combinations are possible subject to this restriction. Conjugation with an arbitrary group element can be thought of as conjugation first with a permutation and then with a reflection. Combining the above results, we arrive at the prescription for classes given in Sec. 2.A of the text.

B. Young Operators and Irreducible Representations

Our method of proof in this subsection will closely parallel that of Boerner [1] for $\mathfrak{S}_n$. For definitions, the reader is referred to Section 2.A of the text.

Theorem 1. The number of different two-part diagrams of order n is equal to the number of classes of $\bar{\mathfrak{S}}_n$, hence also to the number of its irreducible representations.

No further proof of this theorem is needed, beyond the argument already given in Section 2.B of the text.

We now state and prove

Theorem 2. The operator $\bar{\mathscr{Y}}^{(r)}$ (defined in Section 2.B) is, up to a multiplicative constant, a primitive idempotent for the group $\bar{\mathfrak{S}}_n$ (that is, it projects onto a particular coordinate belonging to an irreducible representation). $\bar{\mathscr{Y}}$-operators from tableaux belonging to the same diagram project onto equivalent irreducible representations, while those from different diagram pairs project onto inequivalent representations. All irreducible representations are found in this way.

In the following, we omit the superscript on $\bar{\mathscr{Y}}^{(r)}$. The proof of the first part of the theorem is based on the known theorem: [1b]. If an operator $u=\Sigma u(\sigma)\sigma$, with $u(e)\neq 0$, has the property that, for all x in the group algebra,

$$uxu = gu\,, \tag{6}$$

(g a number, in general a function of x), then u is, up to a multiplicative constant, a primitive idempotent, and conversely.

We will show that $\bar{\mathscr{Y}}$ has the property (6). We first note that, for any $\alpha_+, \beta_+, \alpha_-, \beta_-$,

$$\alpha_+ a^{(r+)} = a^{(r+)};\ \alpha_- a^{(r-)} = a^{(r-)};\ \ell^{(r+)}\beta_+ = \varepsilon(\beta_+)\,\ell^{(r+)};\ \ell^{(r-)}\beta_- = \varepsilon(\beta_-)\,\ell^{(r-)}. \tag{7}$$

One also has, trivially, for arbitrary τ_+, τ_-:

$$\tau_+ \ell^{(r+)} = \ell^{(r+)}\tau_+ = \ell^{(r+)};\ \tau_- \ell^{(r-)} = \ell^{(r-)}\tau_- = \varepsilon(\tau_-)\,\ell^{(r-)}. \tag{8}$$

Because of (7) and (8), it follows that, if $c=\bar{\mathscr{Y}}x\bar{\mathscr{Y}}$ (x arbitrary), then

$$\tau_+ \alpha c \beta \tau_- = \varepsilon(\beta)\varepsilon(\tau_-)\,c\,, \tag{9}$$

for arbitrary α, β, τ_+, τ_-. We now show that any operator with the property (9) satisfies $c = g\bar{\mathscr{Y}}$. This will complete the proof that $\bar{\mathscr{Y}}$ has the property of u in (6), as we know that $\bar{\mathscr{Y}} x \bar{\mathscr{Y}}$ has the property (9).

We write the operator c as

$$c = \sum_{\sigma} c(\sigma)\sigma$$

where the sum goes over all group elements σ. Equation (9) means

$$\sum_{\sigma} c(\sigma)\,\tau_+ \alpha\sigma\beta\tau_- = \varepsilon(\beta)\varepsilon(\tau_-)\sum_{\sigma} c(\sigma)\sigma\,, \tag{10}$$

for arbitrary α, β, τ_+, τ_-. First, consider terms whose permutation part is of the form $\alpha\beta$. We multiply[5] by $\tau_+\alpha\ldots\beta\tau_-$. On the left-hand side of (10), the term $\tau_+\alpha\beta\tau_-$ appears for $\sigma = e$, on the right-hand side for $\sigma = \tau_+\alpha\beta\tau_-$. We thus have, for arbitrary α, β, τ_+, τ_-

$$c(e) = \varepsilon(\beta)\,\varepsilon(\tau_-)\,c\,(\tau_+\alpha\beta\tau_-)\,.$$

This means that the coefficients $c(\sigma)$ for those terms σ which appear in $\bar{\mathscr{Y}}$ (permutation part $= \alpha\beta$) are equal to the coefficients of the same terms in $\bar{\mathscr{Y}}$, multiplied by $c(e)$. We must now show that, when the permutation part of σ is not $\alpha\beta$, $c(\sigma) = 0$. If $\sigma = \tau\vartheta$, $\vartheta \neq \alpha\beta$, there are two possibilities to consider:

i) ϑ does not mix the $(+)$ and $(-)$ tableaux. In this case, σ can be written as $\tau_+\vartheta\tau_-$, and it can be shown [1d] that there exist a transposition α and a transposition β such that

$$\alpha\vartheta\beta = \vartheta\,.$$

Choosing this $\alpha\beta$ pair, we multiply by $\tau_+\tau_+^{(\alpha)}\alpha\ldots\beta\tau_-^{(\beta^{-1})}\tau_-$. For this operation, $\varepsilon(\beta)\,\varepsilon(\tau_-) = -1 : \beta$, being a transposition, is odd, and $\tau_-\tau_-^{(\beta^{-1})}$ is even. Applying this to our term σ, we have

$$\tau_+\tau_+^{(\alpha)}\alpha\,\tau_+\vartheta\,\tau_-\beta\,\tau_-^{(\beta^{-1})}\tau_- = \tau_+\alpha\vartheta\,\beta\,\tau_- = \tau_+\vartheta\,\tau_-\,.$$

Thus, the term $\tau_+\vartheta\,\tau_-$ appears on both sides of Eq. (10) for $\sigma = \tau_+\vartheta\,\tau_-$, and we have

$$c(\sigma) = -\,c(\sigma)\,, \qquad c(\sigma) = 0\,.$$

ii) If ϑ mixes the two parts, then there is at least one site j in the $(-)$ tableau such that s_j is in the $(+)$ tableau. We choose $\tau_+ = \tau(s_j)$, $\tau_- = \tau(j)$, and multiply by $\tau_+\ldots\tau_-$. Again $\varepsilon(\beta)\,\varepsilon(\tau_-) = -1$. We find

$$\tau_+\tau\vartheta\tau_- = \tau(s_j)\tau\tau(s_j)\vartheta = \tau\vartheta\,.$$

The term $\tau\vartheta$, therefore, appears on both sides of (10) for $\sigma = \tau\vartheta$ and we have again $c(\tau\vartheta) = -\,c(\tau\vartheta)$, $c(\tau\vartheta) = 0$.

This completes the proof that $\bar{\mathscr{Y}}$ is a number times a primitive idempotent. To prove the statement about equivalence of representations, we must consider the behavior of the $\bar{\mathscr{Y}}$ operators under conjugation. We first consider conjugation with a pure reflection operator $\tau = \tau_+\tau_-$. We obtain

$$\tau\bar{\mathscr{Y}}\tau^{-1} = \tau\bar{\mathscr{Y}}\tau = \tau_+\tau_-\mathscr{t}_+\mathscr{Y}_+\mathscr{Y}_-\mathscr{t}_-\tau_-\tau_+ = \tau_+\mathscr{t}_+\mathscr{Y}_+\tau_+\tau_-\mathscr{Y}_-\mathscr{t}_-\tau_-\,, \tag{11}$$

[5] This notation means: multiply on the left by $\tau_+\alpha$, on the right by $\beta\,\tau_-$.

where $\mathscr{Y}_+ = a^{(r+)}\ell^{(r+)}$, $\mathscr{Y}_- = a^{(r-)}\ell^{(r-)}$, and we abbreviate $t^{(r+)}$, $t^{(r-)}$ with t_+, t_-.

Consider the portion $t_+\mathscr{Y}_+\tau_+$. It may be written, apart from the normalization factors, as

$$t_+\mathscr{Y}_+\tau_+ = t_+\Sigma\varepsilon(\beta_+)\,\alpha_+\beta_+\tau_+ = t_+\Sigma\,\varepsilon(\beta_+)\,\tau_+^{(\alpha_+\,\beta_+)}\alpha_+\beta_+ = t_+\mathscr{Y}_+$$

where we have used (4) and (8). With another application of (8), we have $\tau_+ t_+\mathscr{Y}_+\tau_+ = t_+\mathscr{Y}_+$. Similarly, one proves

$$\tau_-\mathscr{Y}_- t_-\tau_- = \mathscr{Y}_- t_- .$$

Thus, we see that

$$\tau\bar{\mathscr{Y}}\tau^{-1} = \bar{\mathscr{Y}} . \tag{12}$$

We now take up the conjugation of the Young operator $\bar{\mathscr{Y}} = \bar{\mathscr{Y}}(\bar{t})$ with an arbitrary element $\sigma = \tau\vartheta$. Let $\bar{t}'$ be the tableau obtained from $\bar{t}$ by applying the permutation ϑ, and denote the corresponding operators also by primes. We find

$$\begin{aligned}\sigma\bar{\mathscr{Y}}\sigma^{-1} &= \tau\vartheta t_+\mathscr{Y}_+\mathscr{Y}_- t_-\vartheta^{-1}\tau = \tau\,\tau'_+\vartheta\mathscr{Y}_+\mathscr{Y}_-\vartheta^{-1}t'_-\tau \\ &= \tau t'_+\mathscr{Y}'_+\mathscr{Y}'_- t'_-\tau = \tau\bar{\mathscr{Y}}'\tau = \bar{\mathscr{Y}}' ,\end{aligned} \tag{13}$$

where we have used (4), (12), and a trivial generalization of a theorem [1e] on the conjugation of ordinary Young operators: $\vartheta\mathscr{Y}\vartheta^{-1} = \mathscr{Y}'$.

Now, a necessary and sufficient condition [1f] for the equivalence of the representations generated by two idempotents $\bar{\mathscr{Y}}$ and $\bar{\mathscr{Y}}'$ is that there exist some x in the group algebra such that

$$\bar{\mathscr{Y}}' x\bar{\mathscr{Y}} \neq 0 . \tag{14}$$

First, let $\bar{\mathscr{Y}}$, $\bar{\mathscr{Y}}'$ belong to the same diagram. Then, because of (13), there is a group element σ with the property $\sigma\bar{\mathscr{Y}}\sigma^{-1} = \bar{\mathscr{Y}}'$. It follows that

$$\bar{\mathscr{Y}}'\sigma\bar{\mathscr{Y}} = \bar{\mathscr{Y}}'\sigma\bar{\mathscr{Y}}\sigma^{-1}\sigma = \bar{\mathscr{Y}}'^2\sigma = k\bar{\mathscr{Y}}'\sigma \neq 0$$

where we have used the fact that $\bar{\mathscr{Y}}'$ is a multiple of an idempotent, $\bar{\mathscr{Y}}'^2 = k\bar{\mathscr{Y}}'\cdot\bar{\mathscr{Y}}'\sigma = \sigma\bar{\mathscr{Y}}$ is not zero, since if it were, $\bar{\mathscr{Y}}' = \sigma\bar{\mathscr{Y}}\sigma^{-1}$ would also be zero. Thus, the condition (14) is satisfied with $x = \sigma$, and we conclude that the representations are equivalent.

If $\bar{\mathscr{Y}}$, $\bar{\mathscr{Y}}'$ refer to different diagrams, then there are two possibilities:

i) $n_+ \neq n'_+$. In this case, there is at least one site j which belongs to the $(-)$ part of $\bar{t}$ and to the $(+)$ part of $\bar{t}'$ (or vice versa). Thus, $t'_+(t_+)$ contains $(e+\tau_j)$ as a factor, and $t_-(t'_-)$ contains $(e-\tau_j)$. Hence, either $t'_+ t_- = 0$ or $t'_- t_+ = 0$, and we have

$$\bar{\mathscr{Y}}'\bar{\mathscr{Y}} = t'_+\mathscr{Y}'_+\mathscr{Y}'_- t'_- t_+\mathscr{Y}_+\mathscr{Y}_- t_- = t'_-\mathscr{Y}'_+\mathscr{Y}'_- t'_+ t_-\mathscr{Y}_+\mathscr{Y}_- t_+ = 0 .$$

ii) $n_+ = n_-$. If the sites are divided differently between the $(+)$ and $(-)$ parts of the two tableau pairs, then again there is a site which belongs to the $(+)$ part of one pair and to the $(-)$ part of the other, and we see, just as in case (i), that $\bar{\mathscr{Y}}'\bar{\mathscr{Y}} = 0$. If they are distributed in the same way, then it follows immediately from a known theorem [1g] that either

$$\mathscr{Y}'_+\mathscr{Y}_+ = 0, \quad \text{or} \quad \mathscr{Y}'_-\mathscr{Y}_- = 0 .$$

Hence,

$$\mathscr{Y}'\mathscr{Y} = t'_+ t'_- \mathscr{Y}'_+ \mathscr{Y}'_- \mathscr{Y}_- \mathscr{Y}_+ t_+ t_- = t'_+ t'_- \mathscr{Y}'_- \mathscr{Y}'_+ \mathscr{Y}_+ \mathscr{Y}_- t_+ t_- = 0 .$$

Thus, for tableau pairs belonging to different diagram pairs,

$$\bar{\mathscr{Y}}'\bar{\mathscr{Y}} = 0 . \tag{15}$$

But also, for any group element σ,

$$\bar{\mathscr{Y}}'\sigma\bar{\mathscr{Y}} = \bar{\mathscr{Y}}'\sigma\bar{\mathscr{Y}}\sigma^{-1}\sigma = \bar{\mathscr{Y}}'\bar{\mathscr{Y}}''\sigma = 0 ,$$

where $\bar{\mathscr{Y}}''$ is the Young operator generated according to (13) from $\bar{\mathscr{Y}}$ by σ. Since $\bar{\mathscr{Y}}''$ refers to the same diagram as $\bar{\mathscr{Y}}$, the last equality follows from (15). For an arbitrary element x of the group algebra, we have

$$\bar{\mathscr{Y}}' x \bar{\mathscr{Y}} = \sum_\sigma x(\sigma)\, \bar{\mathscr{Y}}'\sigma\bar{\mathscr{Y}} = 0 .$$

Thus, the condition (14) cannot be satisfied, and the two representations are inequivalent.

The Young operators, therefore, generate a set of inequivalent irreducible representations equal in number to the number of different two-part diagrams. But, according to Theorem 1, this is also equal to the number of classes in the group, hence to the total number of inequivalent irreducible representations. Hence, we have found all the irreducible representations.

This completes the proof of Theorem 2, which encompasses the statements made in Section 2.A of the text.

We now proceed to define a "standard two-part tableau", analogously to the definition of the "standard tableau" in the usual theory of $\mathfrak{S}_n$.

A standard two-part tableau is a tableau in which, in each part, reading from left to right along the rows, or from top to bottom along the columns, the numbers always increase.

Theorem 3. The $\bar{\mathscr{Y}}$ operators corresponding to different standard tableaux (same diagram) are linearly independent. The number of different standard tableaux is equal to the dimension of the corresponding irreducible representation.

Proof. For each distribution (d) of the sites between the (+) and (−) parts, arrange the standard tableau pairs in "dictionary" order [1h], $\bar{t}_{d1}$, $\bar{t}_{d2}$, ... If $\bar{\mathscr{Y}}$, $\bar{\mathscr{Y}}'$ belong to different d's, then $\bar{\mathscr{Y}}\bar{\mathscr{Y}}' = 0$ because of the orthogonality of the t parts, as used in the proof of Theorem 2. Within the same d, a trivial generalization of a known theorem [1i] gives

$$\bar{\mathscr{Y}}_{dk}\bar{\mathscr{Y}}_{di} = 0 \quad \text{for} \quad i < k. \tag{16}$$

Now consider a linear combination

$$\sum_{d,j} a_{dj}\bar{\mathscr{Y}}_{dj} = 0 .$$

Multiplication from the right by $\bar{\mathscr{Y}}_{d1}$ gives zero for all terms except $d1$; from which we conclude $a_{d1} = 0$. Then we multiply from the right by $\bar{\mathscr{Y}}_{d2}$, and conclude $a_{d2} = 0$. Continuing in this way, we find that all the $a_{dj} = 0$, which proves the linear independence.

Because of the linear independence, it follows [1j] that the number of standard tableaux, $F_{\bar{\Gamma}}$, belonging to a given representation $\bar{\Gamma}$ cannot be greater than the dimension of the representation. We show the equality by showing that

$$\sum_{\bar{\Gamma}} F_{\bar{\Gamma}}^2 = n!\, 2^n, \text{ the order of the group.}$$

For a diagram pair with $n_+ = l$, $n_- = n - l$, there are $\dfrac{n!}{l!\,(n-l)}$ distributions d. For each d, the two parts must separately be standard tableaux, and the number of ways of achieving this is just the product $F_l^{(\gamma_+)} F_{n-l}^{(\gamma_-)}$ of the number of standard tableaux belonging to the $(+)$ and $(-)$ diagrams, γ_+ and γ_-. Hence

$$F_{\bar{\Gamma}} = \frac{n!}{l!\,(n-l)!} F_l^{(\gamma_+)} F_{n-l}^{(\gamma_-)}.$$

The sum of the squares is

$$\sum_{\bar{\Gamma}} F_{\bar{\Gamma}}^2 = \sum_{l=0}^{n} \frac{(n!)^2}{(l!)^2[(n-l)!]^2} \sum_{\gamma_+,\,\gamma_-} F_l^{(\gamma_+)^2} F_{n-l}^{(\gamma_-)^2}.$$

From the theory of $\mathfrak{S}_n$, we know that

$$\sum_{\gamma} F_l^{(\gamma)^2} = l!.$$

Hence,

$$\sum_{\bar{\Gamma}} F_{\bar{\Gamma}}^2 = \sum_{l=1}^{n} \frac{(n!)^2}{l!(n-l)!} = n!\, 2^n,$$

which completes the proof.

We now turn our attention to the calculation of the characters of the irreducible representations. For a two-part diagram $\bar{\gamma} = (\gamma_+, \gamma_-)$ we can use the $\mathscr{Y}$ operators for the standard tableaux, applied to some suitable function or set of functions (of suitable variables, such as properties of ligands on sites), to generate a complete set of linearly independent basis functions which will transform among themselves under $\bar{\mathfrak{S}}_n$ according to the representation $\bar{\Gamma}$. Functions corresponding to different d's will already be orthogonal because of their different reflection symmetries. Within a given d, we can assume that the functions ψ_{dj} have been orthogonalized and normalized.

Now consider the effect of a group element σ with cycle structure

$$\xi = (\nu_1^{(+)}, \nu_2^{(+)}, \ldots ; \nu_1^{(-)}, \nu_2^{(-)}, \ldots).$$

The character $\chi_\xi^{(\bar{\Gamma})}$ is the sum of the diagonal elements $\sigma_{dj;dj}$ in the F expressions

$$\sigma \psi_{dj} = \sum_{d',j'} \sigma_{dj;d'j'} \psi_{d'j'}.$$

If d is such that σ mixes the two parts, then the diagonal element is zero, since $\sigma\psi$ gives a function belonging to another d. Hence, only those d contribute to the character for which each cycle of σ has all its members (sites) in the same part of the tableau pair. In other words, the cycle structure ξ breaks up into parts ξ_+, ξ_-, of cycles belonging completely to the $(+)$ and $(-)$ parts, respectively. Within such a d, however, the permutation part of σ acts simply as a direct product of two operators: one a member of $\mathfrak{S}_{n+}$, with cycle structure ξ_+ in a

space belonging to the representation Γ_+; the other a member of $\mathfrak{S}_{n-}$, cyclic structure ξ_-, in a space belonging to the representation Γ_-. As for the reflections, those in ξ_+ simply multiply by unity, while each reflection in ξ_- multiplies by (-1). The overall effect, then, is simply to multiply by ε_d, where $\varepsilon_d = \pm 1$ according as the number of odd cycles in ξ_- is even or odd. So we find the character

Theorem 4.

$$\chi_\xi^{(\bar{\Gamma})} = \sum_d{}' \varepsilon_d \chi_{\xi_+}^{(\Gamma_+)} \chi_{\xi_-}^{(\Gamma_-)}$$

where the sum goes over the above-described "compatible" distributions d. In this way, the character for $\bar{\mathfrak{S}}_n$ can be calculated from the known ones for the $\mathfrak{S}_n$.

As an example, we calculate the character of $\bar{\mathfrak{S}}_6$ belonging to the representation

$$\bar{\Gamma} \leftrightarrow \overset{(+)}{\square\!\square} \quad \overset{(-)}{\square\!\square\!\square\!\square}$$

for the class with cycle structure

$$\xi = (1, 2; 1, 2).$$

The different contributions are:

d	ξ_+	ξ_-	ε_d	$\chi_{\xi_+}^{(\Gamma_+)}$	$\chi_{\xi_-}^{(\Gamma_-)}$	contribution to χ
1.	(2;)	(1; 1, 2)	1	−1	0	0
2.	(; 2)	(1, 2; 1)	−1	−1	0	0
3.	(1; 1)	(2; 2)	−1	1	2	−2

Total character $= -2$.

It should be noted that d's which differ in the exchange of two cycles of the same kind count as different. Thus, in the above example, the first two d's would still be different for the class (1, 2, 2; 1)

C. Induction and Subduction Between $\bar{\mathfrak{S}}_n$, $\mathfrak{S}'_n$, $\mathfrak{S}_n$

A representation $\bar{\Gamma}$ of $\bar{\mathfrak{S}}_n$, applied only to the members of the subgroup $\mathfrak{S}_n$ "subduces" a representation of $\mathfrak{S}_n$, in general reducible, which may be broken up into its irreducible parts. Symbolically

$$\bar{\Gamma} \to \sum_\Gamma C_{\bar{\Gamma}\Gamma} \Gamma . \tag{17}$$

Because of the Frobenius induction theorem [1b, 9], $C_{\bar{\Gamma}\Gamma}$ is also the number of times $\bar{\Gamma}$ is contained in the representation of $\bar{\mathfrak{S}}_n$ "regularly induced" by the representation Γ of $\mathfrak{S}_n$. From the general formula for coefficients in terms of characters, we have

$$C_{\bar{\Gamma}\Gamma} = \frac{1}{n!} \sum_\sigma \chi^{(\Gamma)}(\sigma)\, \chi^{(\bar{\Gamma})}(\sigma)$$

where the sum goes over all σ, i.e., over all members of the subgroup $\mathfrak{S}_n$. Because of Theorem 4, the expression can be rewritten as

$$C_{\bar{\Gamma}\Gamma} = \frac{1}{n!} \sum_{\sigma} \chi^{(\Gamma)}(\sigma) \sum_{d}{}' \chi^{(\Gamma_+)}_{\xi_+} \chi^{(\Gamma_-)}_{\xi_-}.$$

In this case, σ contains no odd cycles, so we have $\varepsilon_d = 1$ for all d. The sum goes over all σ, and for each σ over all "compatible" d. However, it may equally well be thought of as a sum over d, and for each d over compatible σ, i.e., $\sigma \in (\mathfrak{S}_{n_+} \times \mathfrak{S}_{n_-})$. Thus, it may also be written as

$$C_{\bar{\Gamma}\Gamma} = \frac{1}{n!} \sum_{d} \sum_{\sigma}{}' \chi^{(\Gamma)}(\sigma)\, \chi^{(\Gamma_+)}_{\xi_+} \chi^{(\Gamma_-)}_{\xi_-}.$$

The sum over σ is obviously independent of d, with the consequence that the sum over d just gives the number of different d's, $\dfrac{n!}{n_-!\, n_+!}$. So we find

$$C_{\bar{\Gamma}\Gamma} = \frac{1}{n_+!\, n_-!} \sum_{\sigma \in (\mathfrak{S}_{n_+} \times \mathfrak{S}_{n_-})} \chi^{(\Gamma)}(\sigma)\, \chi^{(\Gamma_+)}_{\xi_+} \chi^{(\Gamma_-)}_{\xi_-}.$$

This is obviously just the number of times the representation $(\Gamma_+ \times \Gamma_-)$ is contained in the representation of $(\mathfrak{S}_{n_+} \times \mathfrak{S}_{n_-})$ subduced by Γ. The answer to this subduction problem is known, however, and corresponds to the procedure used in the text [5a, 7].

As for subduction from $\bar{\mathfrak{S}}_n$ to $\mathfrak{S}'_n$, we note that the representation $\bar{\Gamma}$ is g or u with respect to the operator τ_0 according as n_- is even or odd, and that further subduction to $\mathfrak{S}_n$ must give (17). Clearly, therefore, in the subduced representation of $\mathfrak{S}'_n$ by a $\bar{\Gamma}$ with even n_-, each representation Γ_g appears $C_{\bar{\Gamma}\Gamma}$ times, the Γ_u not at all; if n_- is odd, the roles of g and u are reversed.

In induction from $\mathfrak{S}'_n$ to $\bar{\mathfrak{S}}_n$, the procedure is reversed: In the representation induced by Γ_g, each $\bar{\Gamma}$ with even n_- appears $C_{\bar{\Gamma}\Gamma}$ times, the others not all; in that induced by Γ_u, those with odd n_- appear $C_{\bar{\Gamma}\Gamma}$ times, the others not at all. This completes the justification for the induction (subduction) procedures described in Section 2.C and used in the text.

Appendix 2. Proofs of Assertions Made in Section 3

A. Lattice Structure of $\supset$ *Relation*

The set of diagram pairs is a partial ordering defined by

$$\bar{\gamma}^{(r)} \supset \gamma^{(l)} \leftrightarrow o_i^{(r+)} \geqq o_i^{(l+)}, \qquad u_i^{(r-)} \leqq u_i^{(l-)}.$$

Contention: It is also a lattice.

Proof. The union of $\bar{\gamma}^{(1)}$ and $\bar{\gamma}^{(2)}$ must be larger, therefore provided it is existent it must satisfy the condition

$$o_i \geqq \max\,(o_i^{(1)}, o_i^{(2)}),$$
$$u_i \leqq \min\,(u_i^{(1)}, u_i^{(2)}).$$

Let us construct "pseudo diagram" γ with the partial sums

$$o_i^{(+)} = \max(o_i^{(1)}, o_i^{(2)}),$$
$$u_i^{(-)} = \min\,(u_i^{(1)}, u_i^{(2)});$$

because of

$$u_i^{(-)} - u_{i+1}^{(-)} = 2u_i^{(-)} - u_{i-1}^{(-)} - u_{i+1}^{(-)} = 2\min(u_i^{(1)}, u_i^{(2)}) - \min(u_{i-1}^{(1)}, u_{i-1}^{(2)}) - \min(u_{i+1}^{(1)}, u_{i+1}^{(2)}) \geqq 2\min(u_i^{(1)}, u_i^{(2)}) - \min(u_{i-1}^{(1)} + u_{i+1}^{(1)}, u_{i-1}^{(2)} + u_{i+1}^{(2)}) = \min(2u_{i-1}^{(1)} + 2\mu_i^{(1)}, 2u_{i-1}^{(2)} + 2\mu_i^{(2)}) - \min(2u_{i-1}^{(1)} + \mu_i^{(1)} + \mu_{i+1}^{(1)}, 2u_{i-1}^{(2)} + \mu_i^{(2)} + \mu_{i+1}^{(2)}) \geqq 0$$

the lengths of columns do not increase with increasing indices. Therefore $\gamma^{(-)}$ is a diagram; the pseudodiagram $\gamma^{(+)}$ has rows for which increasing cannot be excluded. Let us take therefore the columns of $\gamma^{(+)}$, they do not increase with increasing indices as follows from the construction of $\gamma^{(+)}$. Now we construct the diagram $\gamma'^{(+)}$ with the same columns. For this we have $o_i'^{(+)} \geqq o_i^{(+)}$. Any single diagram which is larger has other columns, therefore it is the smallest single diagram. It follows that the diagram pair with $o_i'^{(+)}$ and $u_i'^{(-)} = u_i^{(-)}$ is the smallest of all larger ones and we may call it union of $\bar{\gamma}^{(1)}$ and $\bar{\gamma}^{(2)}$ ($\bar{\gamma}^{(1)}, \bar{\gamma}^{(2)}$).

B. "Largest Remainder"

In the beginning of this section, we consider the largest remainder prescription with the transfer being carried out in a particular order: First the 1's, then the 2's, etc. At the end, we will see that the order is irrelevant.

To prove the validity of the prescription, we start with some definitions and preliminary remarks.

We call two allowed arrangements of the symbols among the boxes "equivalent" if they have the same remainder. Since the remainder, as well as the *C*-condition, depends only on the number of symbols in each column, we can assume without loss of generality that all symbols in a given column are piled up at the bottom of the column. Now, for fixed number of symbols in each column, we define a "standard" arrangement as one in which the 1's are placed as low down as is compatible with (*C*) and the fixed column distribution (number of symbols in each column), the 2's as low as is compatible with (*C*), the column distribution, and the placement of the 1's, etc.

Now, starting with an arbitrary arrangement $\mathscr{A}$, we can rearrange it into standard form as follows:

We rearrange the symbols among the occupied boxes so that the 1's are at the bottoms of the $\nu_1^{(b)}$ longest occupied columns (i.e., in the $\nu_1^{(b)}$ lowest-lying occupied boxes with no two in the same column), the 2's are at the bottoms of the $\nu_2^{(b)}$ longest columns of the remainder which still have space available, etc. This standard arrangement $\mathscr{A}_s$ is equivalent to $\mathscr{A}$, as the same boxes are occupied as before, though not necessarily by the same symbols. Now, if we can move an entire pile of symbols from one column into a longer, previously unoccupied one, we obtain an arrangement with a larger remainder than $\mathscr{A}_s$, since we have increased the length of a shorter column of the remainder at the expense of a longer one. Let us do this with all the "1-piles" (piles with 1's at the bottoms), i.e., move the 1-piles into the ν_1 longest columns of $\gamma^{(a)}$, choosing the columns farthest to the right in case of ties. (This will not displace any other piles, as the 1-piles already are in the longest occupied columns.) The resulting arrangement has the 1's placed according to the prescription, and has a larger remainder than does $\mathscr{A}_s$. It is standard as far as the placement of the 1's is concerned; if it

is not also standard for the other symbols, we rearrange them as before to form a standard arrangement, $\mathscr{A}'_s$ whose remainder is larger than that of $\mathscr{A}_s$. Similarly, we now move the 2-piles (the 2's, plus whatever else may be on top of them) into longer columns (of $\gamma^{(a)}$ minus the squares already occupied by 1's) where possible and rearrange into a standard arrangement, $\mathscr{A}''_s$, in which the 1's and 2's are arranged according to the prescription and whose remainder is larger than that of $\mathscr{A}'_s$, hence also larger than that of $\mathscr{A}_s$. Continuing this procedure for the 3's, 4's, etc., we end up with the prescribed arrangement. Its remainder is greater than that of $\mathscr{A}_s$, hence also greater than that of the equivalent arrangement $\mathscr{A}$. But $\mathscr{A}$ was arbitrary, so the prescribed arrangement has a larger remainder than any other, and the validity of the prescription is proved.

It is evident from the nature of the proof that the prescription is, as claimed in Section 3, independent of the order of placement of the symbols. To prove the prescription for another order of placement, one need only redefine "standard arrangement" in such a way that first preference (i.e., the lowest available places) is given to the symbols which are to go in first, then those which go in next, etc.

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