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Symmetry Coupling Coefficients for Point Groups and the Importance of Racah's Lemma for the Standardization of Phase

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Useful approaches to the calculation of symmetry coupling coefficients $\langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma b \rangle$ are reviewed. Since a common phase factor always remains undetermined for each trio of Γ_1, Γ_2, and Γ, a unique standardization of phase is proposed by the requirement, in Racah's lemma,

$$(j_1 \Gamma_1 a_1, j_2 \Gamma_2 a_2 | j \Gamma a b) \geqq 0 \quad \text{and real}.$$

In conjunction with the basis relations and the phase convention for Wigner coefficients, a novel method is suggested for the calculation of symmetry coupling coefficients in the group G from those in the subgroup $G \subset SU(2)$ or R_3. The results apply in full generality to any point group G, single or double group.

Key words: Coupling coefficients – Lemma of Racah – Phase standardization.

1. Introduction

The coupling of two ket vectors $|j_1 m_1\rangle$ and $|j_2 m_2\rangle$ transforming, respectively, as the irreducible representations D^{j_1} and D^{j_2} of the special unitary group $SU(2)$ or the three-dimensional rotation group R_3 may be easily accomplished by the well-known relation

$$|jm\rangle = \sum_{m_1, m_2} |j_1 m_1\rangle |j_2 m_2\rangle \langle j_1 m_1 j_2 m_2 | jm\rangle . \tag{1}$$

Here, the resulting ket vector $|jm\rangle$ transforms as a member of the sum in the direct product

$$D^{j_1} \times D^{j_2} = \sum_{j=|j_1 - j_2|}^{j_1 + j_2} D^j . \tag{2}$$

The coupling coefficients $\langle j_1 m_1 j_2 m_2 | jm\rangle$ for the group $SU(2)$ or R_3 appearing in Eq. (1) are usually called Wigner coefficients. These quantities are easily evaluated following standard procedures [1–3] and their general phase factor is fixed by the requirement [4]

$$\langle j_1 j_1 j_2 j - j_1 | jj\rangle \geqq 0 \quad \text{and real} \tag{3}$$

which is equivalent to the original phase convention due to Wigner [3][1]

$$\langle j_1 j_1 j_2 - j_2 | j, j_1 - j_2\rangle \geqq 0 \quad \text{and real} \tag{4}$$

[1] The customary phase convention of Condon and Shortley [5]

$$\langle j_1 j_1 j_2 j_2 | j_1 + j_2, j_1 + j_2\rangle = +1$$

$$\langle j_1 j_2 j m | j_{1z} | j_1 j_2, j - 1, m\rangle > 0 \quad \text{and real}$$

is implicitly included in Eq. (3).

If a finite subgroup G of $SU(2)$ or R_3 is considered, $G \subset SU(2)$, R_3, basis functions $|\Gamma_1 \gamma_1\rangle$ and $|\Gamma_2 \gamma_2\rangle$ which transform, respectively, as the irreducible representations Γ_1 and Γ_2 of G may be coupled to yield another function $|\Gamma \gamma b\rangle$ where the irreducible representation Γ occurs in the direct product

$$\Gamma_1 \times \Gamma_2 = \sum_i n_{\Gamma_i} \Gamma_i \,. \tag{5}$$

The coupling relation may then be written

$$|\Gamma \gamma b\rangle = \sum_{\gamma_1, \gamma_2} |\Gamma_1 \gamma_1\rangle |\Gamma_2 \gamma_2\rangle \langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma b\rangle \tag{6}$$

where the quantities $\langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma b\rangle$ are called symmetry coupling coefficients. The additional label b is introduced whenever the reduction according to Eq. (5) produces the irreducible representation Γ more than once. Similar to the Wigner coefficients, the numerical calculation leaves a general phase factor undetermined. In particular, the phase convention chosen for the Wigner coefficients, *viz.* Eq. (3) or Eq. (4), does not automatically fix the additional phase factors within $G \subset SU(2)$, R_3.

Symmetry coupling coefficients have been calculated on the basis of group theoretical methods by various authors [6–12]. Phases were fixed arbitrarily and, consequently, there are almost as many phase conventions as authors, although the convention actually employed has rarely been explicitly stated. Some of the phase conventions suggested or in use have been applied to special cases only [6, 8, 11] or have limited utility for other reasons. In addition, the recent proposal of so called phase-fixed 3-Γ symbols [12] implies the erroneous notion of a definition of phase based on physical principles.

It is obvious that a standardization of the general phase factor is not a necessary requirement and has, in particular, no consequence for the physical properties of the systems under consideration. Nonetheless, a definite standardization of phase is of certain convenience since actual computations are facilitated and the results of various authors may be related. The resulting advantage is demonstrated perhaps best by the general acceptance of the phase convention due to Condon and Shortley for the group R_3.

In point groups, a situation similar to that in the group R_3 has not been achieved so far. Therefore, in this paper, we investigate the available methods for the determination of the coupling coefficients $\langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma b\rangle$ in an arbitrary group G and the necessary conditions for the standardization of phase. This is accomplished by first studying the transformation behaviour of the basis functions $|jm\rangle$ within a subgroup $G \subset SU(2)$, R_3. The new basis functions $|j \Gamma \gamma a\rangle$ thus formed belong to certain irreducible representations Γ of $G \subset SU(2)$, R_3 and the label a is similar to b above except that it refers to the reduction $D^j = \sum_i a_i \Gamma_i$. If two of these functions are coupled as in Eq. (6), a new coupling coefficient $\langle j_1 \Gamma_1 \gamma_1 a_1, j_2 \Gamma_2 \gamma_2 a_2 | j \Gamma \gamma a\rangle$ is defined. On the basis of Racah's lemma, this coefficient is related to the quantity $\langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma b\rangle$ defined above. The lemma may then be employed for a unique standardization of phase of the coupling coefficients $\langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma b\rangle$. Subsequently, the coefficients $\langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma b\rangle$ may be calculat-

ed using the lemma from the related coefficients $\langle j_1 \Gamma_1 \gamma_1 a_1, j_2 \Gamma_2 \gamma_2 a_2 | j \Gamma \gamma a \rangle$ within the group $G \subset SU(2), R_3$. In this procedure, the basis relations and the phase convention for the Wigner coefficients are employed, in addition. To demonstrate the usefulness of the present method, the resulting coupling coefficients for the groups D_3 and D_3^* are presented.

2. The Calculation of Symmetry Coupling Coefficients

The symmetry coupling coefficients defined in Eq. (6) conform to the orthogonality relations

$$\sum_{\gamma_1,\gamma_2} \langle \Gamma \gamma b | \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 \rangle \langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma' \gamma' b' \rangle = \delta(\Gamma,\Gamma') \delta(\gamma,\gamma') \delta(b,b') , \tag{7}$$

$$\sum_{\Gamma,\gamma,b} \langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma b \rangle \langle \Gamma \gamma b | \Gamma_1 \gamma_1' \Gamma_2 \gamma_2' \rangle = \delta(\gamma_1,\gamma_1') \delta(\gamma_2,\gamma_2') . \tag{8}$$

Multiplication of Eq. (6) by $\langle \Gamma \gamma b | \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 \rangle$ and summation over Γ, γ, and b produces the inverse relation

$$|\Gamma_1 \gamma_1\rangle |\Gamma_2 \gamma_2\rangle = \sum_{\Gamma,\gamma,b} |\Gamma \gamma b\rangle \langle \Gamma \gamma b | \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 \rangle . \tag{9}$$

The number of linearly independent product functions $|\Gamma \gamma b\rangle$ is determined by

$$n_\Gamma = \frac{1}{g} \sum_R \chi_{\Gamma_1}(R) \chi_{\Gamma_2}(R) \chi_\Gamma(R)^* \tag{10}$$

where g is the order of the group and the summation extends over the operators R of the group.

The products of the basis functions $|\Gamma_1 \gamma_1\rangle$ and $|\Gamma_2 \gamma_2\rangle$ in Eq. (6) transform under an operation R of the group according to the direct product matrix

$$\boldsymbol{D}(R) = \boldsymbol{\Gamma}_1(R) \times \boldsymbol{\Gamma}_2(R) . \tag{11}$$

On the other hand, the coupled functions $|\Gamma \gamma b\rangle$ transform according to the matrix $\boldsymbol{\Gamma}(R)$ which is in block diagonal form, consisting of the matrices $\boldsymbol{\Gamma}_i(R)$ of Eq. (5) along its main diagonal. The representation matrices are related by

$$\boldsymbol{\Gamma}(R) = \boldsymbol{U}^+ \boldsymbol{D}(R) \boldsymbol{U} . \tag{12}$$

The symmetry coupling coefficients are now the elements of the unitary transformation matrix $\boldsymbol{U}$, *i.e.*

$$\langle \Gamma \gamma b | \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 \rangle = \langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma b \rangle^* . \tag{13}$$

In matrix component form, Eq. (12) may be written as

$$\sum_{\substack{\gamma_1,\gamma_2 \\ \gamma_1',\gamma_2'}} \langle \Gamma \gamma b | \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 \rangle D^{\Gamma_1}_{\gamma_1\gamma_1'}(R) D^{\Gamma_2}_{\gamma_2\gamma_2'}(R) \langle \Gamma_1 \gamma_1' \Gamma_2 \gamma_2' | \Gamma' \gamma' b' \rangle = D^{\Gamma}_{\gamma\gamma'}(R) \delta(\Gamma,\Gamma') \delta(b,b') . \tag{14}$$

Multiplication by $\langle \Gamma_1 \gamma_1'' \Gamma_2 \gamma_2'' | \Gamma \gamma b \rangle$ and summation over Γ, γ, and b gives a set of homogeneous linear equations

$$\sum_{\gamma_1', \gamma_2'} D^{\Gamma_1}_{\gamma_1 \gamma_1'}(R) D^{\Gamma_2}_{\gamma_2 \gamma_2'}(R) \langle \Gamma_1 \gamma_1' \Gamma_2 \gamma_2' | \Gamma \gamma' b \rangle = \sum_{\gamma} \langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma b \rangle D^{\Gamma}_{\gamma \gamma'}(R) \quad (15)$$

which may be employed to the actual calculation of the coupling coefficients $\langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma b \rangle$. This is the method used previously [9, 10, 13]. However, a simple relationship obtains only if the label b is not required, i.e. if $n_\Gamma = 1$. If, on the other hand, $n_\Gamma > 1$, the situation is more complex [13]. It should be noted that, for each arrangement of the symbols Γ_1, Γ_2, and Γ, and each b, an arbitrary phase factor remains undetermined.

Another approach is provided by the projection operator technique. A projection operator $P^{\Gamma}_{\gamma' \gamma}$ operates on the basis function $|\Gamma'' \gamma'' \rangle$ according to

$$P^{\Gamma}_{\gamma' \gamma} | \Gamma'' \gamma'' \rangle = | \Gamma \gamma' \rangle \delta(\Gamma, \Gamma'') \delta(\gamma, \gamma'') \quad (16)$$

to give the same function, a partner function or zero. Considering the case where the representation Γ is contained only once in the direct product $\Gamma_1 \times \Gamma_2$ one may write

$$P^{\Gamma}_{\gamma' \gamma} = \frac{d_\Gamma}{g} \sum_R \langle \Gamma \gamma' | R | \Gamma \gamma \rangle^* R \quad (17)$$

where d_Γ is the dimension of representation Γ and g is the order of the group. Operating with $P^{\Gamma}_{\gamma' \gamma}$ on the product function $|\Gamma_1 \gamma_1 \rangle | \Gamma_2 \gamma_2 \rangle$ of Eq. (9) generates a function belonging to the γ'-th row of irreducible representation Γ

$$P^{\Gamma}_{\gamma' \gamma} | \Gamma_1 \gamma_1 \rangle | \Gamma_2 \gamma_2 \rangle = | \Gamma \gamma' \rangle \langle \Gamma \gamma | \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 \rangle . \quad (18)$$

In the general case, the reducible product representation may contain Γ more than once, i.e. $n_\Gamma > 1$, and, therefore, a linear combination is obtained

$$P^{\Gamma}_{\gamma' \gamma} | \Gamma_1 \gamma_1 \rangle | \Gamma_2 \gamma_2 \rangle = \sum_b | \Gamma \gamma' b \rangle \langle \Gamma \gamma b | \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 \rangle . \quad (19)$$

The operators R of the group transform the basis functions $|\Gamma_1 \gamma_1 \rangle$ and $|\Gamma_2 \gamma_2 \rangle$ according to

$$R | \Gamma_1 \gamma_1 \rangle = \sum_{\gamma_1'} | \Gamma_1 \gamma_1' \rangle \langle \Gamma_1 \gamma_1' | R | \Gamma_1 \gamma_1 \rangle \quad (20)$$

where $\langle \Gamma_1 \gamma_1' | R | \Gamma_1 \gamma_1 \rangle$ are matrix elements of irreducible representation Γ_1. Introducing Eq. (17) and Eq. (20) into Eq. (19) produces

$$\sum_b | \Gamma \gamma' b \rangle \langle \Gamma \gamma b | \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 \rangle = \frac{d_\Gamma}{g} \sum_{\gamma_1' \gamma_2'} | \Gamma_1 \gamma_1' \rangle | \Gamma_2 \gamma_2' \rangle \sum_R \langle \Gamma_1 \gamma_1' | R | \Gamma_1 \gamma_1 \rangle \cdot \langle \Gamma_2 \gamma_2' | R | \Gamma_2 \gamma_2 \rangle \langle \Gamma \gamma' | R | \Gamma \gamma \rangle^* . \quad (21)$$

Application of Eq. (6) to $|\Gamma \gamma' b \rangle$ gives therefrom an expression for the symmetry coupling coefficients

$$\sum_b \langle \Gamma_1 \gamma_1' \Gamma_2 \gamma_2' | \Gamma \gamma' b \rangle \langle \Gamma \gamma b | \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 \rangle = \frac{d_\Gamma}{g} \sum_R D^{\Gamma_1}_{\gamma_1' \gamma_1}(R) D^{\Gamma_2}_{\gamma_2' \gamma_2}(R) D^{\Gamma}_{\gamma' \gamma}(R)^* . \quad (22)$$

If $n_\Gamma = 1$, the sum over b disappears and provided one lets γ_1', γ_2', and γ' assume all possible values while keeping γ_1, γ_2, and γ fixed, all the coupling coefficients are obtained with the proper phase relations. A common phase factor is still, of course, arbitrary.

In the general case, the known sum over group representations on the right hand side of Eq. (22) depends rather on a combination of n_Γ of these coefficients. Nonetheless, there is no serious problem of how to obtain the coupling coefficients. Thus one may operate with $P^{\Gamma}_{\gamma'\gamma}$ on n_Γ different product functions $|\Gamma_1\gamma_1\rangle|\Gamma_2\gamma_2\rangle$ according to Eq. (19) and Eq. (21). In this way, n_Γ different functions $|\Gamma\gamma' b\rangle$ are obtained, all of them transforming according to representation Γ. Although, in general, these functions are not orthogonal, an orthogonal set of n_Γ linearly independent functions may be obtained by any one of the usual orthogonalization procedures. If these functions are introduced into Eq. (19), the summation disappears and the required n_Γ coupling coefficients are produced in turn. In this case, considerable arbitrariness in the choice of the functions $|\Gamma\gamma' b\rangle$ remains and, therefore, the label b represents a running index only.

A more desirable procedure is to generate a set of functions $|\Gamma\gamma b\rangle$ which are eigenfunctions of some operator such that every value of b corresponds to a different eigenvalue. Often, the angular momentum operator $\boldsymbol{j}$ is employed in this way [7, 11]. Then, Eq. (22) is still applicable, although

$$D^{\Gamma}_{\gamma'\gamma}(R) = \langle\Gamma\gamma' j|R|\Gamma\gamma j\rangle\,. \tag{23}$$

Alternatively, it is often possible to differentiate functions $|\Gamma\gamma b\rangle$ equal in Γ and γ by their transformation behaviour in a higher group. This was proposed, in fact, above with respect to $SU(2)$, R_3. The same procedure as regards point groups is considered in detail by Hollebone *et al.* [14] and requires the subduction of a component of a representation of the higher group onto an irreducible component γ of the subgroup representation Γ.

The numerical values of the symmetry coupling coefficients of Eq. (6) and Eq. (9) are thus uniquely determined by the methods outlined above. However, for each possible arrangement of the three Γ symbols within the coefficient (*e.g.* Γ_1, Γ_2, and Γ, in that order) and for every value of the index b, a common phase factor remains undetermined.

3. The Determination of Symmetry Functions

Starting from the angular momentum eigenfunctions $|jm\rangle$, basis functions of the irreducible representation Γ within the subgroup $G \subset SU(2), R_3$ may be obtained according to

$$|j\Gamma\gamma a\rangle = \sum_m |jm\rangle\langle jm|j\Gamma\gamma a\rangle \tag{24}$$

where γ is the row index of Γ. It is convenient to take

$$\langle 00|0A_1 a_1\rangle = 1 \tag{25}$$

for any group G, where A_1 denotes the totally symmetric representation of G [15]. The index a is required whenever representation Γ occurs more than once in the

decomposition of D^j. In fact, the frequency n_Γ of Γ is determined by

$$n_\Gamma = \frac{1}{g} \sum_R \chi_\Gamma(R)^* \chi_j(R) . \tag{26}$$

Equation (24) determines a unitary transformation and, therefore, the orthogonality relations of the expansion coefficients $\langle jm|j\Gamma\gamma a\rangle$ as follows

$$\begin{aligned} \sum_m \langle j\Gamma\gamma a|jm\rangle\langle jm|j\Gamma\gamma a\rangle &= \delta(\Gamma,\Gamma')\delta(\gamma,\gamma')\delta(a,a') \\ \sum_{\Gamma,\gamma,a} \langle jm|j\Gamma\gamma a\rangle\langle j'\Gamma\gamma a|j'm'\rangle &= \delta(j,j')\delta(m,m') . \end{aligned} \tag{27}$$

The determination of the coefficients $\langle jm|j\Gamma\gamma a\rangle$ may be based on Eq. (16). If the projection operator Eq. (17) is applied to the basis functions of Eq. (24), the necessary and sufficient condition for the functions $|j\Gamma\gamma a\rangle$ obtains as

$$|j\Gamma\gamma a\rangle = P^\Gamma_{\gamma\gamma}|j\Gamma'\gamma' a\rangle = \frac{d_\Gamma}{g} \sum_R D^\Gamma_{\gamma\gamma}(R)^* R|j\Gamma'\gamma' a\rangle \delta(\Gamma,\Gamma')\delta(\gamma,\gamma') . \tag{28}$$

The basis functions characterized by component γ'' obtain accordingly

$$|j\Gamma\gamma'' a\rangle = P^\Gamma_{\gamma''\gamma}|j\Gamma'\gamma' a\rangle = \frac{d_\Gamma}{g} \sum_R D^\Gamma_{\gamma''\gamma}(R)^* R|j\Gamma'\gamma' a\rangle \delta(\Gamma,\Gamma')\delta(\gamma,\gamma') . \tag{29}$$

Although the relative phases between the basis functions $|j\Gamma\gamma a\rangle$ and $|j\Gamma\gamma'' a\rangle$ have thus been fixed by Eq. (29), a common phase factor for each combination of j, Γ, and a still remains undetermined.

It should be observed that the condition Eq. (28) is equally well followed by a linear combination of the functions $|j\Gamma\gamma a\rangle$ having a different index a. In the actual calculation, it is practical to use the most simple one of the functions Eq. (24). This function is formed if one operates with $P^\Gamma_{\gamma\gamma}$ on $|jm\rangle$, thus

$$P^\Gamma_{\gamma\gamma}|jm\rangle = \frac{d_\Gamma}{g} \sum_R{}' \langle\Gamma\gamma|R|\Gamma\gamma\rangle^* R|jm\rangle = |j\Gamma\gamma a\rangle . \tag{30}$$

Here, the label a is simply a running index. Functions $|j\Gamma\gamma a\rangle$ having a different value a must conform to the orthogonality condition

$$\langle j'\Gamma\gamma a'|P^\Gamma_{\gamma\gamma} \cdot P^\Gamma_{\gamma\gamma}|j\Gamma\gamma a\rangle = \delta(j,j')\delta(a,a') . \tag{31}$$

Alternatively, the characterizing index a in the functions $|j\Gamma\gamma a\rangle$ may be associated with the different eigenvalues of an operator or a set of operators. Another possibility is to apply $P^\Gamma_{\gamma\gamma}$ of Eq. (17) to the basis functions $|j\Gamma'\gamma' a'\rangle$ of the irreducible representation Γ' of a higher point group. Provided the reduction of Γ' yields a single irreducible representation Γ of the subgroup, index a may be substituted by the representation Γ' [15].

To derive an expression for the coefficients $\langle jm|j\Gamma\gamma a\rangle$ we expand the functions $|j\Gamma\gamma'' a\rangle$ in Eq. (29) according to Eq. (24) and obtain thus

$$\sum_{m'} |jm'\rangle\langle jm'|j\Gamma\gamma'' a\rangle = \frac{d_\Gamma}{g} \sum_R D^\Gamma_{\gamma''\gamma}(R)^* \sum_m R|jm\rangle\langle jm|j\Gamma'\gamma' a\rangle \delta(\Gamma,\Gamma')\delta(\gamma,\gamma') \tag{32}$$

Multiplication by $\langle jm''|$, followed by multiplication $\langle j'\Gamma'\gamma' a|j'm'\rangle$ and summation over Γ', γ', and a produces

$$\sum_{\Gamma',\gamma',a}\langle jm''|j\Gamma\gamma'' a\rangle\langle j'\Gamma'\gamma' a|j'm'\rangle=\frac{d_\Gamma}{g}\sum_R D^\Gamma_{\gamma''\gamma}(R)^*\sum_m D^j_{m''m}(R)$$
$$\cdot\sum_{\Gamma',\gamma',a}\langle jm|j\Gamma'\gamma' a\rangle\langle j'\Gamma'\gamma' a|j'm'\rangle\delta(\Gamma,\Gamma')\delta(\gamma,\gamma')\,. \tag{33}$$

Employing the orthogonality relations Eq. (27) and changing double primes into primes finally gives [15]

$$\sum_a\langle jm'|j\Gamma\gamma' a\rangle\langle j\Gamma\gamma a|jm\rangle=\frac{d_\Gamma}{g}\sum_R D^\Gamma_{\gamma'\gamma}(R)^* D^j_{m'm}(R)\,. \tag{34}$$

This equation may be used to directly evaluate the coefficients $\langle jm|j\Gamma\gamma a\rangle$, again, up to a common phase factor.

4. Symmetry Coupling Coefficients within the $\{j,\Gamma\}$ Scheme

Since the coefficients $\langle jm|j\Gamma\gamma a\rangle$ are the elements of a unitary matrix, multiplication of Eq. (24) by $\langle j\Gamma\gamma a|jm\rangle$ and summation over Γ, γ, and a yields the inverse equation

$$|jm\rangle=\sum_{\Gamma,\gamma,a}|j\Gamma\gamma a\rangle\langle j\Gamma\gamma a|jm\rangle\,. \tag{35}$$

Replacing, in Eq. (1), $|jm\rangle$, $|j_1m_1\rangle$, and $|j_2m_2\rangle$ according to Eq. (35), one obtains

$$\sum_{\Gamma,\gamma,a}|j\Gamma\gamma a\rangle\langle j\Gamma\gamma a|jm\rangle=\sum_{\substack{\Gamma_1,\gamma_1,a_1\\ \Gamma_2,\gamma_2,a_2}}\sum_{m_1,m_2}|j_1\Gamma_1\gamma_1 a_1\rangle|j_2\Gamma_2\gamma_2 a_2\rangle$$
$$\cdot\langle j_1m_1j_2m_2|jm\rangle\langle j_1\Gamma_1\gamma_1 a_1|j_1m_1\rangle\langle j_2\Gamma_2\gamma_2 a_2|j_2m_2\rangle\,. \tag{36}$$

Therefrom, multiplication by $\langle j\Gamma'\gamma' a'|jm\rangle^*$ and summation over m produces an expression for the basis functions $|j\Gamma\gamma a\rangle$ transforming according to irreducible representation Γ of the subgroup $G\subset SU(2), R_3$.

$$|j\Gamma\gamma a\rangle=\sum_{\substack{\Gamma_1,\gamma_1,a_1\\ \Gamma_2,\gamma_2,a_2}}|j_1\Gamma_1\gamma_1 a_1\rangle|j_2\Gamma_2\gamma_2 a_2\rangle\cdot\langle j_1\Gamma_1\gamma_1 a_1,j_2\Gamma_2\gamma_2 a_2|j\Gamma\gamma a\rangle\,. \tag{37}$$

In Eq. (37), the coupling coefficient within the $\{j,\Gamma\}$ scheme is defined as

$$\langle j_1\Gamma_1\gamma_1 a_1,j_2\Gamma_2\gamma_2 a_2|j\Gamma\gamma a\rangle=\sum_{m,m_1,m_2}\langle j_1m_1j_2m_2|jm\rangle$$
$$\cdot\langle j_1\Gamma_1\gamma_1 a_1|j_1m_1\rangle\langle j_2\Gamma_2\gamma_2 a_2|j_2m_2\rangle\langle j\Gamma\gamma a|jm\rangle^* \tag{38}$$

This coefficient[2] may not necessarily always be obtained in real form, even if suitable phases for the basis functions of Eq. (24) are selected.

[2] The coefficient defined in Eq. (38) relates the matrix element of a tensor operator in a subgroup G to the corresponding reduced matrix element in $SU(2)$ or R_3 as follows [16]

$$\langle j_1\Gamma_1\gamma_1 a_1|T^{j_2\Gamma_2 a_2}_{\gamma_2}|j_3\Gamma_3\gamma_3 a_3\rangle=(-1)^{2j_2}\langle j_1\Gamma_1\gamma_1 a_1|j_3\Gamma_3\gamma_3 a_3,j_2\Gamma_2\gamma_2 a_2\rangle\cdot\langle j_1\|T^{j_2}\|j_3\rangle\,.$$

The Wigner coefficients of Eq. (1) likewise define a unitary matrix and, therefore, the inverse relation readily obtains as

$$|j_1 m_1\rangle |j_2 m_2\rangle = \sum_{j,m} |jm\rangle \langle jm|j_1 m_1 j_2 m_2\rangle \tag{39}$$

Replacing all three kets in this expression according to Eq. (35) gives an equation which is the inverse of Eq. (36)

$$\begin{aligned} &\sum_{\substack{\Gamma_1,\gamma_1,a_1\\ \Gamma_2,\gamma_2,a_2}} |j_1 \Gamma_1 \gamma_1 a_1\rangle |j_2 \Gamma_2 \gamma_2 a_2\rangle \langle j_1 \Gamma_1 \gamma_1 a_1 | j_1 m_1\rangle \langle j_2 \Gamma_2 \gamma_2 a_2 | j_2 m_2\rangle \\ &\qquad = \sum_{\Gamma,\gamma,a} \sum_{j,m} |j \Gamma \gamma a\rangle \langle j \Gamma \gamma a | jm\rangle \langle jm | j_1 m_1 j_2 m_2\rangle . \end{aligned} \tag{40}$$

Multiplication by $\langle j_1 m_1 | j_1 \Gamma_1' \gamma_1' a_1'\rangle$ and by $\langle j_2 m_2 | j_2 \Gamma_2' \gamma_2' a_2'\rangle$ and summation over m_1 and m_2 produces

$$\begin{aligned} &\sum_{\substack{\Gamma_1,\gamma_1,a_1\\ \Gamma_2,\gamma_2,a_2}} |j_1 \Gamma_1 \gamma_1 a_1\rangle |j_2 \Gamma_2 \gamma_2 a_2\rangle \sum_{m_1,m_2} \langle j_1 m_1 | j_1 \Gamma_1' \gamma_1' a_1'\rangle \\ &\qquad \cdot \langle j_1 \Gamma_1 \gamma_1 a_1 | j_1 m_1\rangle \langle j_2 m_2 | j_2 \Gamma_2' \gamma_2' a_2'\rangle \langle j_2 \Gamma_2 \gamma_2 a_2 | j_2 m_2\rangle \\ &\quad = \sum_{\substack{\Gamma,\gamma,a\\ m_1,m_2}} |j \Gamma \gamma a\rangle \langle j_1 m_1 | j_1 \Gamma_1' \gamma_1' a_1'\rangle \langle j_2 m_2 | j_2 \Gamma_2' \gamma_2' a_2'\rangle \\ &\qquad \cdot \sum_{j,m} \langle j \Gamma \gamma a | jm\rangle \langle jm | j_1 m_1 j_2 m_2\rangle . \end{aligned} \tag{41}$$

Employing the orthogonality relation Eq. (27) and introducing the coefficients defined in Eq. (38) gives an equation which is the inverse of Eq. (37)

$$|j_1 \Gamma_1 \gamma_1 a_1\rangle |j_2 \Gamma_2 \gamma_2 a_2\rangle = \sum_{j,\Gamma,\gamma,a} |j \Gamma \gamma a\rangle \langle j \Gamma \gamma a | j_1 \Gamma_1 \gamma_1 a_1, j_2 \Gamma_2 \gamma_2 a_2\rangle . \tag{42}$$

On the basis of the orthogonality of their basis functions, the coefficients of Eq. (37) and Eq. (42) form a unitary matrix. The corresponding orthogonality relations are as follows

$$\begin{aligned} &\sum_{\substack{\Gamma_1,\gamma_1,a_1\\ \Gamma_2,\gamma_2,a_2}} \langle j \Gamma \gamma a | j_1 \Gamma_1 \gamma_1 a_1, j_2 \Gamma_2 \gamma_2 a_2\rangle \langle j_1 \Gamma_1 \gamma_1 a_1, j_2 \Gamma_2 \gamma_2 a_2 | j' \Gamma' \gamma' a'\rangle \\ &\qquad = \delta(j,j') \delta(\Gamma,\Gamma') \delta(\gamma,\gamma') \delta(a,a') \\ &\sum_{j,\Gamma,\gamma,a} \langle j_1 \Gamma_1 \gamma_1 a_1, j_2 \Gamma_2 \gamma_2 a_2 | j \Gamma \gamma a\rangle \langle j \Gamma \gamma a | j_1 \Gamma_1' \gamma_1' a_1', j_2 \Gamma_2' \gamma_2' a_2'\rangle \\ &\qquad = \delta(\Gamma_1 \gamma_1 a_1, \Gamma_1' \gamma_1' a_1') \delta(\Gamma_2 \gamma_2 a_2, \Gamma_2' \gamma_2' a_2') . \end{aligned} \tag{43}$$

5. Relations between Coupling Coefficients and the Standardization of Phase

It has been shown in Section 2 that the numerical values of the symmetry coupling coefficients $\langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma b\rangle$ are determined by the transformation properties of the basis functions, cf. Eq. (22). Consequently, a change of basis function will imply at least a change of phase. It has likewise been shown that a common phase factor still remains undetermined.

Similar results were derived above for symmetry coupling coefficients of the basis functions $|j\Gamma\gamma a\rangle$ within the $\{j,\Gamma\}$ scheme. Although the phase convention [viz. Eq. (3)] for the Wigner coefficients $\langle j_1 m_1 j_2 m_2 | jm\rangle$ is included in the definition of Eq. (38), an arbitrary phase factor still arises for each set of values j, Γ, and a. It is alone the phases between components γ of irreducible representation Γ which have been fixed.

The various phase factors encountered above may be related on the basis of a lemma by Racah [17]. The irreducible representations of a given group $SU(2)$ or R_3, say, are in general reducible as representations of a subgroup $G \subset SU(2)$, R_3. Racah's lemma shows that the coupling coefficients for the irreducible representations of $SU(2)$, R_3 in block diagonal form (with respect to G) are proportional to the coupling coefficients for the corresponding irreducible representations of G

$$\langle j_1 \Gamma_1 \gamma_1 a_1, j_2 \Gamma_2 \gamma_2 a_2 | j\Gamma\gamma a\rangle = \sum_b \langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma\gamma b\rangle (j_1 \Gamma_1 a_1, j_2 \Gamma_2 a_2 | j\Gamma a b) . \tag{44}$$

Here, the new coefficient in parentheses[3] is independent of the components γ and, due to the orthogonality of the two coupling coefficients, it conforms to the orthogonality relations

$$\begin{aligned}\sum_{j,a} (j_1 \Gamma_1 a_1, j_2 \Gamma_2 a_2 | j\Gamma a b)(j\Gamma a b' | j_1 \Gamma_1' a_1', j_2 \Gamma_2' a_2') \\ = \delta(\Gamma_1 \Gamma_2 \Gamma^*)\delta(\Gamma_1, \Gamma_1')\delta(\Gamma_2, \Gamma_2')\delta(a_1, a_1')\delta(a_2, a_2')\delta(b, b') \\ \sum_{\substack{\Gamma_1, a_1 \\ \Gamma_2, a_2, b}} (j\Gamma a b | j_1 \Gamma_1 a_1, j_2 \Gamma_2 a_2)(j_1 \Gamma_1 a_1, j_2 \Gamma_2 a_2 | j' \Gamma a' b) \\ = \delta(j_1 j_2 j)\delta(j, j')\delta(a, a') .\end{aligned} \tag{45}$$

In Eq. (45), $\delta(\Gamma_1 \Gamma_2 \Gamma^*)$ is one or zero, depending on whether or not the direct product $\Gamma_1 \times \Gamma_2 \times \Gamma^*$ contains the unit representation and $\delta(j_1 j_2 j)$ is the triangular delta[4]. If Eq. (44) is multiplied by

$$\begin{aligned}\langle j_1' \Gamma_1 \gamma_1 a_1', j_2' \Gamma_2 \gamma_2 a_2' | j' \Gamma' \gamma' a'\rangle^* \\ = \sum_{b'} \langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma' \gamma' b'\rangle^* (j_1' \Gamma_1 a_1', j_2' \Gamma_2 a_2' | j' \Gamma' a' b')^*\end{aligned} \tag{46}$$

summation over γ_1 and γ_2 and application of the orthogonality relation Eq. (7) gives

$$\begin{aligned}\sum_{\gamma_1, \gamma_2} \langle j_1' \Gamma_1 \gamma_1 a_1', j_2' \Gamma_2 \gamma_2 a_2' | j' \Gamma' \gamma' a'\rangle^* \langle j_1 \Gamma_1 \gamma_1 a_1, j_2 \Gamma_2 \gamma_2 a_2 | j\Gamma\gamma a\rangle \\ = \sum_{b,b'} \delta(\Gamma, \Gamma')\delta(\gamma, \gamma')\delta(b, b')(j_1' \Gamma_1 a_1', j_2' \Gamma_2 a_2' | j' \Gamma' a' b')^* \cdot (j_1 \Gamma_1 a_1, j_2 \Gamma_2 a_2 | j\Gamma a b) .\end{aligned} \tag{47}$$

[3] The argument b in the coefficient of Eq. (44) is placed following the usage of Racah [17]. This should be noticed, in particular, if sums are considered, viz. Eq. (45). The coefficient relates the reduced matrix element of a tensor operator in a subgroup G and the corresponding reduced matrix element in $SU(2)$ or R_3 according to [16]

$$\langle j_1 \Gamma_1 \| T^{j_2 \Gamma_2} \| j_3 \Gamma_3 \rangle_{b_1} = (-1)^{2j_2}(j_1 \Gamma_1 a_1 b_1 | j_3 \Gamma_3 a_3, j_2 \Gamma_2 a_2) \cdot \langle j_1 \| T^{j_2} \| j_3 \rangle .$$

[4] It is $\delta(j_1 j_2 j) = 1$ if $|j_1 - j_2| \leqq j \leqq j_1 + j_2$ and zero otherwise.

This equation enables, in principle, the calculation of the coefficients $(j_1\Gamma_1 a_1, j_2\Gamma_2 a_2|j\Gamma ab)$. If several different indices b arise, however, no simple relation obtains.

So far, the quantity b in $|\Gamma\gamma b\rangle$ has been used as a differentiating index which assumes altogether n_Γ values and which is dependent on Γ_1, Γ_2, and Γ, viz. Eq. (9). To define simple conditions, we let now the index b correspond to eigenvalues of the angular momentum operator $\boldsymbol{j}$[5]. In this case, $|j\Gamma\gamma a\rangle$ and $|\Gamma\gamma b\rangle$ are simply related, since $|j\Gamma\gamma a\rangle$ is eigenfunction of $\boldsymbol{j}$ to the same eigenvalue to which b corresponds. Only a single set of coefficients $\langle\Gamma_1\gamma_1\Gamma_2\gamma_2|\Gamma\gamma b\rangle$ is indeed required and, therefore, one defines the so-called basis relations. These basis relations are equivalent to the selection of a particularly simple set of n_Γ basis functions $|j\Gamma\gamma a\rangle$. As a consequence of the correspondence between b and j, the sums over b and b,b' in Eq. (44) and Eq. (47), respectively, disappear. It is evident that the coefficients $(j_1\Gamma_1 a_1, j_2\Gamma_2 a_2|j\Gamma ab)$ may now be calculated on the basis of Eq. (47) and again an arbitrary phase factor arises for each set of values of Γ_1, Γ_2, Γ, and j.

In addition, a standardization of the general phase factor may be easily achieved if a simple convention is introduced. To this end, we always assume, in what follows, that the correspondence between b and j discussed above is being employed. Since the coefficient $\langle j_1\Gamma_1\gamma_1 a_1, j_2\Gamma_2\gamma_2 a_2|j\Gamma\gamma a\rangle$ in Eq. (44) always occurs as product with its complex conjugate, we now require

$$(j_1\Gamma_1 a_1, j_2\Gamma_2 a_2|j\Gamma ab) \geqq 0 \quad \text{and real}. \tag{48}$$

Equation (48) implies that the coefficient $(j_1\Gamma_1 a_1, j_2\Gamma_2 a_2|j\Gamma ab)$ is calculated as the positive and real square root of Eq. (47) employing the values of j_1, j_2, j, and a_1, a_2, a as specified by the basis relations. Consequently, Eq. (47) may now be rewritten as

$$(j_1\Gamma_1 a_1, j_2\Gamma_2 a_2|j\Gamma ab) = +\left[\sum_{\gamma_1,\gamma_2} \langle j_1\Gamma_1\gamma_1 a_1, j_2\Gamma_2\gamma_2 a_2|j\Gamma\gamma a\rangle \langle j_1\Gamma_1\gamma_1 a_1, j_2\Gamma_2\gamma_2 a_2|j\Gamma\gamma a\rangle^*\right]^{\frac{1}{2}} \tag{49}$$

where the summation is over all components γ_1 and γ_2 of the irreducible representations Γ_1 and Γ_2. The convention of Eq. (48) now definitely settles the relation between the phases of the coupling coefficients $\langle\Gamma_1\gamma_1\Gamma_2\gamma_2|\Gamma\gamma b\rangle$ and $\langle j_1\Gamma_1\gamma_1 a_1, j_2\Gamma_2\gamma_2 a_2|j\Gamma\gamma a\rangle$. Consequently, the lemma of Racah [cf. Eq. (44)] now assumes the simple form

$$\langle\Gamma_1\gamma_1\Gamma_2\gamma_2|\Gamma\gamma b\rangle = \langle j_1\Gamma_1\gamma_1 a_1, j_2\Gamma_2\gamma_2 a_2|j\Gamma\gamma a\rangle / (j_1\Gamma_1 a_1, j_2\Gamma_2 a_2|j\Gamma ab). \tag{50}$$

In this form the lemma is extremely useful since it may be directly applied to the calculation of the coupling coefficients $\langle\Gamma_1\gamma_1\Gamma_2\gamma_2|\Gamma\gamma b\rangle$ from quantities already known. The derived relations are of general applicability to any point group $G \subset SU(2)$, R_3[6].

[5] If, in Eq. (44), a single j value is not sufficient for a specification of the label b, the additional index a may be introduced. The equations following Eq. (44) then remain valid except that b should be replaced everywhere by j, a. In actual practice, this requirement does not arise. Alternately, the index a alone may be employed to differentiate the functions $|\Gamma\gamma b\rangle$. However, this is of no advantage compared to the correspondence between b and j.

[6] An extension to the subgroups of the rotation-reflection groups, i.e. the direct product groups of $SU(2)$ or R_3 and the reflection group consisting of the unit E and the inversion I, is easily possible.

6. Symmetry Coupling Coefficients for the Point Group D_3^*. An Example

To illustrate in detail the method outlined in this paper, we give below a complete list of symmetry coupling coefficients for the point group D_3^* and all relevant information.

The symmetry coupling coefficients have been calculated on the basis of Eq. (50). First of all, the basis functions of Table 1 ("basis relations") are specified. The expansion coefficients involved and the corresponding Wigner coefficients are inserted into Eq. (38) and the indicated summations over m_1, m_2, and m are performed. The resulting quantity is the numerator in Eq. (50), whereas the denominator is obtained from Eq. (49) where again Eq. (38) has been used.

The point group D_3^* has been chosen, since two complex representations arise in this case, and thus a definition of symmetric V coefficients (or alike 3-Γ symbols) is not possible in the usual way [20]. The resulting coefficients possess the sym-

Table 1. Basis relations for the group D_3^*[a]

Irreducible representations	$\lvert j\Gamma\gamma\rangle$	$\sum_m \lvert jm\rangle\langle jm\lvert j\Gamma\gamma a\rangle$
A_1	$\lvert 0\ \Gamma_1\ \ 1\rangle$	$\lvert 0\ \ 0\rangle$
A_2	$\lvert 1\ \Gamma_2\ \ 1\rangle$	$\lvert 1\ \ 0\rangle$
E_1	$\lvert 1\ \Gamma_3\ \ 1\rangle$	$\lvert 1\ \ 1\rangle$
	$\lvert 1\ \Gamma_3\ -1\rangle$	$\lvert 1\ -1\rangle$
E_1	$\lvert 2\ \Gamma_3\ \ 1\rangle$	$\lvert 2\ -2\rangle$[b]
	$\lvert 2\ \Gamma_3\ -1\rangle$	$\lvert 2\ \ 2\rangle$
$E_{1/2}$	$\lvert \tfrac{1}{2}\ \Gamma_6\ \ 1\rangle$	$\lvert \tfrac{1}{2}\ \ \tfrac{1}{2}\rangle$
	$\lvert \tfrac{1}{2}\ \Gamma_6\ -1\rangle$	$\lvert \tfrac{1}{2}\ -\tfrac{1}{2}\rangle$
$E_{3/2}$	$\lvert \tfrac{3}{2}\ \Gamma_4\ \ 1\rangle$	$\frac{1}{\sqrt{2}}[\lvert \tfrac{3}{2}\ \tfrac{3}{2}\rangle - i\lvert \tfrac{3}{2}\ -\tfrac{3}{2}\rangle]$
	$\lvert \tfrac{3}{2}\ \Gamma_5\ \ 1\rangle$	$\frac{1}{\sqrt{2}}[\lvert \tfrac{3}{2}\ \tfrac{3}{2}\rangle + i\lvert \tfrac{3}{2}\ -\tfrac{3}{2}\rangle]$

[a] The symmetry transformations provide positive rotations of the physical system.

[b] This set of functions is required alone for calculation of $\langle\Gamma_3 \pm 1\,\Gamma_3 \pm 1\lvert\Gamma_3 \mp 1\rangle$.

Table 2. Symmetry coupling coefficients for D_3^*

i	j	k	l	m	n	$\langle\Gamma_i\gamma_j\Gamma_k\gamma_l\lvert\Gamma_m\gamma_n\rangle$
2	1	2	1	1	1	-1
2	1	3	1	3	1	-1
2	1	3	-1	3	-1	1
2	1	6	1	6	1	-1
2	1	6	-1	6	-1	1
2	1	4	1	5	1	-1
2	1	5	1	4	1	-1
3	1	3	1	3	-1	1
3	1	3	-1	1	1	$1/\sqrt{2}$
3	1	3	-1	2	1	$1/\sqrt{2}$
3	-1	3	-1	3	1	1
3	1	6	1	4	1	$1/\sqrt{2}$
3	1	6	1	5	1	$1/\sqrt{2}$
3	1	6	-1	6	1	1
3	-1	6	1	6	-1	-1
3	-1	6	-1	4	1	$-i/\sqrt{2}$
3	-1	6	-1	5	1	$i/\sqrt{2}$
3	1	4	1	6	-1	i
3	-1	4	1	6	1	1
3	1	5	1	6	-1	$-i$
3	-1	5	1	6	1	1
6	1	6	1	3	1	1
6	1	6	-1	1	1	$1/\sqrt{2}$
6	1	6	-1	2	1	$1/\sqrt{2}$
6	-1	6	-1	3	-1	1
6	1	4	1	3	-1	i
6	-1	4	1	3	1	-1
6	1	5	1	3	-1	$-i$
6	-1	5	1	3	1	-1
4	1	4	1	2	1	i
4	1	5	1	1	1	$-i$
5	1	5	1	2	1	$-i$

metry property

$$\langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma \rangle = (-1)^{j_1 + j_2 - j} \langle \Gamma_2 \gamma_2 \Gamma_1 \gamma_1 | \Gamma \gamma \rangle \tag{51}$$

which follows from Eq. (38) and Eq. (50) in conjunction with the properties of vector coupling coefficients. Table 2 lists all the non-zero symmetry coupling coefficients of the group D_3^* except those following from Eq. (51). To calculate the coefficient $\langle \Gamma_3 \pm 1 \Gamma_3 \pm 1 | \Gamma_3 \mp 1 \rangle = 1$ additional basis functions having $j = 2$ have to be introduced. In this special case, the phase factor in Eq. (51) disappears ($j_1 = j_2 = 1, j = 2$).

7. General Discussion and Comparison With Previous Authors

On the basis of the methods outlined above, the present authors have calculated symmetry coupling coefficients for all relevant molecular point groups, single as well as double groups. A complete listing of these coupling coefficients will be given elsewhere. The program which has been written for this purpose has now been in use for several years as part of a general program for molecular computations. This fact guarrantees, contrary to previous choices of phase, the full applicability of the present standardization and the absence of any difficulties in actual computations.

At first sight it might seem less advantageous that the present phase choice yields, in part, signs of coupling coefficients which are different from those used in the past. This consequence is unavoidable, however, and is more than compensated by the uninhibited applicability of the present method. It seems to be a propos, in this context, to briefly review the phase conventions of previous authors.

In the classic work by Tanabe and Sugano [6] and Griffith [7], the assumption

$$\langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma \rangle = \langle \Gamma_2 \gamma_2 \Gamma_1 \gamma_1 | \Gamma \gamma \rangle \tag{52}$$

has been used for $\Gamma_1 \neq \Gamma_2$. It should be noted that Eq. (52) is not consistent with the symmetry requirements for most coupling coefficients introduced thereafter and it is neither consistent with the present phase standardization. The V coefficients of Griffith [8] are related to the symmetry coupling coefficients of Eq. (6) by

$$V\begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma \\ \gamma_1 & \gamma_2 & \gamma \end{pmatrix} = (d_\Gamma)^{-1/2} \langle \Gamma_1 \gamma_1 \Gamma_2 \gamma_2 | \Gamma \gamma \rangle \tag{53}$$

where d_Γ is the dimension of irreducible representation Γ. Since the V coefficients are, at most, changed in sign by any permutation of their columns, the phases of a set of related V coefficients are well defined. However, for each different trio of Γ_1, Γ_2, and Γ, a free phase factor still arises. These remaining phases have been fixed arbitrarily. Difficulties arise if complex representations of single groups are considered, and Eq. (53) is definitely *not applicable* to double groups. The relation to the phase choice, for the octahedral group, of Tanabe and Sugano [6] and Griffith [7] has been given (viz. Appendix A of [8]). Although Golding [11] has never specified his phase choice explicitly, from the example cited it may be demonstrated that he implicitly assumes $C(j_1 j_2 j_3 \Gamma_1 \Gamma_2) \geqq 0$[7]. This coefficient corre-

[7] In Ref. [11], the coefficient $C(j_1 j_2 j_3 \Gamma_1 \Gamma_2)$ has been incorrectly assumed as independent of Γ. Note the substitution of Γ for Γ_3 in [11].

sponds, in fact, to the quantity $(j_1 \Gamma_1 a_1, j_2 \Gamma_2 a_2 | j \Gamma a b)$ which we introduced in Eq. (44) above. It follows that our phase choice is in agreement with that of Golding. However, this is of no consequence, since the latter author has considered the group O^* exclusively. In the recently suggested 3-Γ symbols [12], there is again an independent choice of phase for each ordered trio of Γ_1, Γ_2, and Γ. The indeterminacy of phase is circumvented by application of the Wigner-Eckart theorem where the reduced matrix element is arbitrarily defined as real and positive. This definition, although equivalent to Eq. (48) above, is again of no consequence. It requires, in fact, the choice of real basis functions as well as real 3-l symbols which should not be confused with the 3-j symbols of Wigner. These conventions are dictated by the requirements of the angular overlap model [18, 19] to which the application is then essentially limited. The symmetry coupling coefficients listed by Koster *et al.* [9] have been calculated on the basis of Eq. (22). As stated above, a common phase factor occurs in this case for each ordered trio of Γ_1, Γ_2, Γ, and for each b. This phase has been arbitrarily fixed, although the way in which this was done, has not been stated.

It is evident that a unique standardization of phase is required. Compared to previous conventions, the present standardization has the definite advantage of being generally applicable to any point group G, single or double group. In addition, the lemma of Racah may now be employed, in conjunction with the basis relations and the phase convention for Wigner coefficients, to calculate symmetry coupling coefficients from the known coefficients in the $\{j, \Gamma\}$ scheme. It will be shown in a separate study [20] that a definition of symmetrized 3-Γ symbols may be proposed as a consequence.

The standardization of the general phase factor is of utmost importance if completely computarized methods [16] are used for the calculation of molecular properties within a given point group G. In this case, all symmetry based quantities must be chosen in identically the same form each time they occur, rather than in an equivalent form.

The methods outlined above will be particularly useful in conjunction with the generalized Wigner-Eckart theorem [16]. This relation is being employed to rationalize the results of various physical measurements by extracting suitable sets of semi-empirical parameters from the experimental data. Well-known areas of application are, e.g., to susceptibilities and effective moments in magnetism, g values and HFS splitting constants in electron paramagnetic resonance, energies and probabilities of transition in optical and ultraviolet spectroscopy, as well as quadrupole splittings in the Mössbauer effect.

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Note Added in Proof. After submission of this manuscript, the method of phase standardization proposed here (*viz.* Eq. (48)) has been employed in the special case of the double groups O^* and I^* by two independent authors (cf. S. E. Harnung, Mol. Phys. **26**, 473 (1973) and R. M. Golding, Mol. Phys. **26**, 661 (1973)). In addition, the same correspondence for the Kronecker multiplicity index b as that discussed in Sect. 5 above has been implicitly used. In distinction to these authors, the present formulation is of general applicability to any molecular point group and provides, at the same time, a convenient scheme for computation of the required coupling coefficients.

References

1. Edmonds, A. R.: Angular momentum in quantum mechanics. Princeton University Press: 1960
2. Rose, M. E.: Elementary theory of angular momentum. John Wiley 1957
3. Wigner, E. P.: Group theory and its application to the quantum mechanics of atomic spectra. Academic Press 1959
4. Fano, U., Racah, G.: Irreducible tensorial sets. Academic Press 1959
5. Condon, E. U., Shortley, G. H.: The theory of atomic spectra. Cambridge University Press 1935
6. Tanabe, Y., Sugano, S.: J. Phys. Soc. Japan **9**, 753 (1954)
7. Griffith, J. S.: The theory of transition metal ions. Cambridge University Press 1961
8. Griffith, J. S.: The irreducible tensor method for molecular symmetry groups. Prentice-Hall 1962
9. Koster, G. F., Dimmock, J. O., Wheeler, R. G., Statz, H.: Properties of the thirty-two point groups. MIT Press 1963
10. Sugano, S., Tanabe, Y., Kamimura, H.: Multiplets of transition-metal ions in crystals. Academic Press 1970
11. Golding, R. M.: Mol. Phys. **21**, 157 (1971)
12. Harnung, S. E., Schäfer, C. E.: Struct. Bonding **12**, 201 (1972)
13. Koster, G. F.: Phys. Rev. **109**, 227 (1958)
14. Hollebone, B. R., Lever, A. B. P., Donini, J. C.: Mol. Phys. **22**, 155 (1971)
15. Kibler, M.: Int. J. Quantum Chem. **3**, 795 (1969)
16. König, E., Kremer, S.: Int. J. Quantum Chem., submitted
17. Racah, G.: Phys. Rev. **76**, 1352 (1949)
18. Schäffer, C. E., Jørgensen, C. E.: Mol. Phys. **9**, 401 (1965)
19. Schäffer, C. E.: Pure Appl. Chem. **24**, 361 (1970)
20. König, E., Kremer, S.: Theoret. Chim. Acta (Berl.), submitted

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