Quantum Chemistry, lecture notes, 4-Jan-2011, Gerrit C. Groenenboom (version 23-Jan-2011)

I. DEFINING PROPERTIES OF A GROUP

A group G is a set for which the multiplication of any two elements is defined, satisfying the following conditions:

1. **Closure:** the product of any two elements of the group is again an element of the group:
$$g, h \in G \Rightarrow gh \in G$$
2. **Associativity:** $(ab)c = a(bc)$ for all $a, b, c \in G$
3. There is an **identity element** ($e \in G$):
$$ge = eg = g \text{ for all } g \in G$$
4. Every element has an **inverse**: for all $g \in G$ there is an $h \in G$ such that: $gh = e$.

We only consider *finite* groups. The number of elements of a finite group is called the **order** of the group. We will use the notation ${}^0G$ for the order of the group.

If all elements of the group commute, i.e.,
$$gh = hg, \quad \text{for all } g, h \in G \tag{1}$$
then the group is called **abelian**.

II. CLASSES

If, for some elements $a, b \in G$ there is some $g \in G$ such that
$$b = g^{-1}ag \tag{2}$$
then b is said to be **conjugate** to a. The transformation from a to b is called a **conjugation** transformation. With $h = g^{-1}$ we can transform b back to a,
$$a = h^{-1}bh \tag{3}$$
so if b is conjugate to a, then a is conjugate to b. Furthermore, if a and b are conjugate and b and c are conjugate, then a and c are also conjugate. For any element $g \in G$ we can find all elements that are conjugate to g. This set is called a **class** of G. Any element in a group can be assigned to a class. Two different classes cannot have any element in common.

The identity element e is not conjugate to any other element of the group, since
$$g^{-1}eg = e, \quad \text{for all } g \in G, \tag{4}$$
so the identity element forms a class by itself, $\{e\}$.

In an abelian group all elements commute, so
$$g^{-1}hg = hg^{-1}g = he = h, \quad \text{for all } g, h \in G, \tag{5}$$
so every element in the group is a class by itself.

III. MATRIX REPRESENTATIONS

A set of ${}^0G$ matrices
$$\Gamma = \{\mathbf{\Gamma}(g) | g \in G\} \tag{6}$$

is a representation of the group G, of order ${}^0G$, if

$$\mathbf{\Gamma}(gh) = \mathbf{\Gamma}(g)\mathbf{\Gamma}(h), \quad \text{for all } g, h \in G. \tag{7}$$

The matrices $\mathbf{\Gamma}(g)$ do not have to be different. A **trivial representation** can always be obtained by assigning the number 1 ("the 1×1 identity matrix") to every element of the group. If all matrices $\mathbf{\Gamma}(g)$ are different the representation is called **faithful**. A matrix-representation consisting of $n \times n$ matrices is called an n**-dimensional** representation.

By applying the same similarity transformation to each matrix of the n-dimensional representation Γ,

$$\mathbf{\Gamma}(g)' \equiv \boldsymbol{A}^{-1}\mathbf{\Gamma}(g)\boldsymbol{A}, \quad \text{for all } g \in G, \tag{8}$$

where $\boldsymbol{A}$ is a non-singular $n \times n$ matrix, we obtain a new, **equivalent** representation Γ'. Note that the matrices $\mathbf{\Gamma}(g)'$ satisfy the condition for being a representation:

$$\mathbf{\Gamma}'(gh) = \boldsymbol{A}^{-1}\mathbf{\Gamma}(gh)\boldsymbol{A} = \boldsymbol{A}^{-1}\mathbf{\Gamma}(g)\mathbf{\Gamma}(h)\boldsymbol{A}^{-1} = \boldsymbol{A}^{-1}\mathbf{\Gamma}(g)\boldsymbol{A}\boldsymbol{A}^{-1}\mathbf{\Gamma}(h)\boldsymbol{A}^{-1} = \mathbf{\Gamma}'(g)\mathbf{\Gamma}'(h). \tag{9}$$

A representation consisting of unitary matrices $\mathbf{\Gamma}(g)$ is called a **unitary representation**. Any n-dimensional representation of a finite-dimensional group is equivalent to a unitary representation. In other words, one can always find a transformation matrix $\boldsymbol{A}$ that turns every matrix $\mathbf{\Gamma}(g)$ into a unitary matrix $\mathbf{\Gamma}(g)'$ through a similarity transformation, for all elements of the group.

The representation $\mathbf{\Gamma}(e)$ of the identity element e is always the identity matrix and the representation of the inverse of an element is the inverse of the representation,

$$\mathbf{\Gamma}(g^{-1}) = [\mathbf{\Gamma}(g)]^{-1}. \tag{10}$$

For unitary representation this gives

$$\Gamma_{ij}(g^{-1}) = \Gamma^*_{ji}(g). \tag{11}$$

IV. CHARACTER OF A REPRESENTATION

The **trace** of an $n \times n$ matrix $\boldsymbol{A}$ is the sum of its diagonal elements

$$\text{tr}(\boldsymbol{A}) \equiv \sum_{i=1}^{n} A_{i,i}. \tag{12}$$

The character χ of a representation Γ is defined as

$$\chi = \{\chi(g) | g \in G\} \tag{13}$$

where

$$\chi(g) = \text{tr}[\mathbf{\Gamma}(g)]. \tag{14}$$

For the trace of the product of two matrices we have

$$\text{tr}(\boldsymbol{AB}) = \sum_i (\boldsymbol{AB})_{i,i} = \sum_i \sum_k A_{i,k}B_{k,i} = \sum_k \sum_i B_{k,i}A_{i,k} = \text{tr}(\boldsymbol{BA}). \tag{15}$$

It follows that

$$\text{tr}(\boldsymbol{A}^{-1}\boldsymbol{BA}) = \text{tr}\left((\boldsymbol{A}^{-1}\boldsymbol{B})\boldsymbol{A}\right) = \text{tr}\left(\boldsymbol{A}(\boldsymbol{A}^{-1}\boldsymbol{B})\right) = \text{tr}(\boldsymbol{B}). \tag{16}$$

If $a, b \in G$ are in the same class, i.e., $a = g^{-1}bg$ for some $g \in G$, then

$$\chi(a) = \text{tr}\left(\mathbf{\Gamma}(g^{-1}bg)\right) = \chi(b), \tag{17}$$

hence all elements in a class have the same character.

Since all representations are equivalent to some unitary representation we can use Eq. (11) to show that the character of the inverse of an element $g \in G$ is the complex conjugate of the character of g:

$$\chi(g^{-1}) = \chi(g)^*. \tag{18}$$

V. IRREDUCIBLE REPRESENTATIONS

A similarity transformation of an n-dimensional matrix representation may result in a representation where every matrix has the same **block-diagonal** form:

$$\mathbf{\Gamma}(g) = \left(\begin{array}{c|c} \mathbf{\Gamma}^{(1)}(g) & \\ \hline & \mathbf{\Gamma}^{(2)}(g) \end{array} \right), \quad \text{for all } g \in G, \tag{19}$$

i.e., all elements of the off-diagonal block are zero, all ${}^0G$ matrices $\mathbf{\Gamma}_1(g)$ are of dimension $n_1 \times n_1$ and all ${}^0G$ matrices $\mathbf{\Gamma}_2(g)$ are $n_2 \times n_2$, with $n_1 + n_2 = n$. The diagonal blocks are representations by themselves, i.e.,

$$\Gamma^{(i)} = \left\{ \mathbf{\Gamma}^{(i)}(g) | g \in G \right\}, \quad i = 1, 2 \tag{20}$$

are n_i-dimensional representations of G for $i = 1, 2$. Finding the transformation that results in the block-structure is called **reducing** the representation. This process can be repeated for the new representations, and if no transformation exists that further reduces a representation $\Gamma^{(i)}$, then $\Gamma^{(i)}$ is called an **irreducible representation** or **irrep** for short.

If two representations are equivalent, their characters are the same. The reverse is also true.

A representation Γ that is related to two other representations $\Gamma^{(1)}$ and $\Gamma^{(2)}$ as in Eq. (19) is called the **direct sum** of these representations, which is written as

$$\Gamma = \Gamma^{(1)} \oplus \Gamma^{(2)}. \tag{21}$$

The character $\chi(g)$ of representation Γ is the sum of the characters $\chi^{(i)}(g)$ of the representations $\Gamma^{(i)}$,

$$\chi(g) = \chi^{(1)}(g) + \chi^{(2)}(g), \quad \text{for all } g \in G. \tag{22}$$

Note that if this relation holds for three representations Γ, $\Gamma^{(1)}$, and $\Gamma^{(2)}$, we know that a similarity transformation must exist that gives all matrices $\mathbf{\Gamma}(g)$ the corresponding block-diagonal form.

VI. CHARACTER TABLES

For a finite-dimensional group there is a finite number of possible irreducible characters of irreducible representation. The **character table** of a group lists all possibilities: the columns of the table are labeled by the classes of the group, and each row corresponds to an irrep. The number of rows of a character table is equal to the number of columns, i.e., the number of irreps of a group is equal to the number of classes.

VII. GREAT ORTHOGONALITY THEOREM

A group G of order ${}^0G$, with n different classes, has n distinct irreps,

$$\Gamma^{(i)} = \left\{ \mathbf{\Gamma}^{(i)}(g) | g \in G \right\}, \quad \text{for } i = 1, \dots, n. \tag{23}$$

We call two irreps distinct if they are not related through a similarity transformation, or in other words, if they have different characters. According to the "Great Orthogonality Theorem" for finite groups

$$\sum_{g \in G} \Gamma^{(i)}_{mn}(g) \Gamma^{(i')}_{n'm'}(g^{-1}) = \frac{{}^0G}{{}^0\Gamma^{(i)}} \delta_{ii'} \delta_{mm'} \delta_{nn'}, \tag{24}$$

where ${}^0\Gamma^{(i)}$ is the dimension of irrep $\Gamma^{(i)}$.

If we set $n = m$ and $n' = m'$, and take the sum over m and m', the left hand side gives

$$\sum_{m=1}^{{}^0\Gamma^{(i)}} \sum_{m'=1}^{{}^0\Gamma^{(i')}} \sum_{g \in G} \Gamma^{(i)}_{mn}(g) \Gamma^{(i')}_{n'm'}(g^{-1}) = \sum_{g \in G} \chi^{(i)}(g) \chi^{(i')}(g^{-1}) = \sum_{g \in G} \chi^{(i)}(g) \chi^{(i')}(g)^*, \tag{25}$$

where we used Eq. (18) in the last step. On the right hand side we get

$$\sum_{m=1}^{{}^0\Gamma^{(i)}} \sum_{m'=1}^{{}^0\Gamma^{(i')}} \frac{{}^0G}{{}^0\Gamma^{(i)}} \delta_{ii'} \delta_{mm'} \delta_{mm'} = \frac{{}^0G}{{}^0\Gamma^{(i)}} \delta_{ii'} {}^0\Gamma^{(i)} = \delta_{ii'} {}^0G, \tag{26}$$

where we used $\delta_{mm'}^2 = \delta_{mm'}$, and for $i = i'$

$$\sum_{m'=1}^{{}^0\Gamma^{(i')}} \delta_{mm'} = 1 \tag{27}$$

and

$$\sum_{m=1}^{{}^0\Gamma^{(i)}} 1 = {}^0\Gamma^{(i)}. \tag{28}$$

Thus, we obtain an orthogonality relation for the characters of irreps

$$\sum_{g \in G} \chi^{(i)}(g) \chi^{(j)}(g)^* = {}^0G \delta_{ij}. \tag{29}$$

Elements g in the same class C have the same character, which we will denote as $\chi^{(i)}(C)$, so with ${}^0C$ elements in class C we may rewrite the relation as a sum over all classes in the group

$$\sum_{C \subset G} {}^0C \chi^{(i)}(C) \chi^{(j)}(C)^* = {}^0G \delta_{ij}. \tag{30}$$

The irreducible characters $\chi^{(i)}(C)$ are found in the row for irrep (i) and the column for class (C) of a character table.

We define the matrix U with elements

$$U_{i;C} \equiv \sqrt{\frac{{}^0C}{{}^0G}} \chi^{(i)}(C). \tag{31}$$

With this definition the orthogonality relation for the irreducible characters can be rewritten as

$$\sum_{C \subset G} U_{i;C} U_{j;C}^* = \delta_{ij}. \tag{32}$$

So the rows of U are orthonormal. Furthermore, since this matrix is square, it must be unitary, i.e., the columns are also orthonormal

$$\sum_{i=i}^{\#\text{irreps}} U_{i;C} U_{i;C'}^* = \delta_{CC'}. \tag{33}$$

Substituting the definition of the matrix elements of $\boldsymbol{U}$ [Eq. (31)] into this relation we obtain

$$\sum_{i=i}^{\#\text{irreps}} \chi^{(i)}(C) \chi^{(i)}(C')^* = \delta_{CC'} \frac{{}^0G}{{}^0C}. \tag{34}$$

For the class consisting of the identity element, $C = \{e\}$, the irreducible representation matrix $\Gamma^{(i)}(e)$ is the unit matrix of dimension ${}^0\Gamma^{(i)}$, and the irreducible character is $\chi^{(i)}(e) = {}^0\Gamma^{(i)}$. By setting $C = C'$ in the last expression, and using ${}^0C = 1$ because there is only one element in this class, we find an expression that relates the dimensions of the irreps to the order of the group:

$$\sum_{i=i}^{\#\text{irreps}} [{}^0\Gamma^{(i)}]^2 = {}^0G. \tag{35}$$

Note that the characters $\chi^{(i)}(e)$ of the identity element, which are equal to the dimensions of the irreps ${}^0\Gamma^{(i)}$ can be found in the first column of a character table.

The first row a character table corresponds to the "trivial", or "totally symmetric" representation, where every element of the group is represented by the number 1. For this row we find from Eq. (30) for $i = j = 1$,

$$\sum_{C \subset G} {}^0C = {}^0G, \tag{36}$$

i.e., adding the number of elements in each class gives the number of elements in the group.

VIII. REPRESENTATIONS OF SYMMETRY OPERATORS

In $\mathbb{R}^3$ symmetry operators are represented by 3×3 orthonormal matrices. E.g., the inversion operator is represented by the matrix

$$\boldsymbol{G} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \tag{37}$$

The definition of a symmetry operator in $\mathbb{R}^3$ by a matrix $\boldsymbol{G}$, may be extended to a corresponding symmetry operator $\hat{g}$ acting on real or complex functions defined on $\mathbb{R}^3$ through Wigner's convention:

$$(\hat{g}\phi)(\boldsymbol{r}) \equiv \phi(\boldsymbol{G}^{-1}\boldsymbol{r}). \tag{38}$$

An n-dimension linear space V spanned by n linearly independent functions $\{\phi_1, \phi_2, \ldots, \phi_n\}$, is called invariant under $\hat{g}$ if $\hat{g}$ acting on any function in V gives another function in V, i.e., if

$$\hat{g}\phi_j(\boldsymbol{r}) = \sum_{i=1}^{n} \phi_i(\boldsymbol{r})\Gamma_{i,j}(\hat{g}). \tag{39}$$

For a group G of symmetry operators $\hat{g}$ the matrices $\Gamma(\hat{g})$ with matrix elements $\Gamma_{i,j}(\hat{g})$ form a matrix representation of the group, since for all $\hat{g}, \hat{h} \in G$

$$\boldsymbol{\Gamma}(\hat{g}\hat{h}) = \boldsymbol{\Gamma}(\hat{g})\boldsymbol{\Gamma}(\hat{h}). \tag{40}$$

This follows from the relation

$$((\hat{g}\hat{h})\phi_j)(\boldsymbol{r}) \equiv (\hat{g}(\hat{h}\phi_j))(\boldsymbol{r}). \tag{41}$$

The left hand side on this equation gives

$$(\hat{g}\hat{h})\phi_j(\boldsymbol{r}) = \sum_i \phi_i(\boldsymbol{r})\Gamma_{ij}(\hat{g}\hat{h}) \tag{42}$$

and the right hand side gives

$$(\hat{g}(\hat{h}\phi_j))(\boldsymbol{r}) = \hat{g}\sum_k \phi_k(\boldsymbol{r})\Gamma_{kj}(\hat{h}) = \sum_k \sum_i \phi_i(\boldsymbol{r})\Gamma_{ik}(\hat{g})\Gamma_{kj}(\hat{h}). \tag{43}$$

Since the functions ϕ_i are assumed to be linearly independent we find

$$\Gamma_{ij}(\hat{g}\hat{h}) = \sum_k \Gamma_{ik}(\hat{g})\Gamma_{kj}(\hat{h}), \tag{44}$$

which written is matrix notation gives Eq. (40).

If an inner product is defined on the function space V, we get from Eq. (39)

$$\langle\phi_i|\hat{g}|\phi_j\rangle = \langle\phi_i|\sum_k \phi_k\Gamma_{k,j}(\hat{g})\rangle, \tag{45}$$

or,

$$\langle\phi_i|\hat{g}|\phi_j\rangle = \sum_k S_{i,k}\Gamma_{k,j}(\hat{g}), \tag{46}$$

where $S_{i,k} = \langle\phi_i|\phi_j\rangle$ are overlap matrix elements. Note that **only** if the basis is orthonormal, the matrix-representation elements can be calculated as

$$\Gamma_{i,j}(\hat{g}) = \langle\phi_i|\hat{g}|\phi_j\rangle. \tag{47}$$

Consider a new basis of $\{\phi_1', \ldots, \phi_n'\}$ for V, defined through a non-singular transformation $\boldsymbol{U}$,

$$\phi_j'(\boldsymbol{r}) = \sum_i \phi_i(\boldsymbol{r})U_{ij}. \tag{48}$$

In the new basis, $\hat{g}$ is represented by the matrix $\Gamma'(\hat{g})$,

$$\hat{g}\phi_j'(\boldsymbol{r}) = \sum_i \phi_i'(\boldsymbol{r})\Gamma'_{ij}(\hat{g}). \tag{49}$$

It can be shown that the new representation $\boldsymbol{\Gamma}'(\hat{g})$ is related to the old representation $\boldsymbol{\Gamma}(\hat{g})$ through a similarity transformation

$$\boldsymbol{\Gamma}'(\hat{g}) = \boldsymbol{U}^{-1}\boldsymbol{\Gamma}(\hat{g})\boldsymbol{U}, \tag{50}$$

so the character

$$\chi(\hat{g}) = \mathrm{tr}\,(\boldsymbol{\Gamma}(\hat{g})) = \mathrm{tr}\,(\boldsymbol{\Gamma}'(\hat{g})) \tag{51}$$

does not change. The character $\chi(\hat{g})$ can be written as a linear combination of irreducible characters, as in Eq. (22),

$$\chi(\hat{g}) = \sum_i n_i\chi^{(i)}(\hat{g}), \tag{52}$$

where n_i are integers that are given by the number of times irreducible representation $\Gamma^{(i)}$ appears when Γ' is written as a direct sum of irreducible representations. The orthogonality relation Eq. (29) allows us to compute the coefficients n_i, just from the characters, without finding the transformation $\boldsymbol{U}$ that fully reduces the representation:

$$\sum_g \chi(\hat{g})\chi^{(i)}(\hat{g})^* = \sum_g\sum_j n_j\chi^{(j)}(\hat{g})\chi^{(i)}(\hat{g})^* = \sum_j n_j\sum_g \chi^{(j)}(\hat{g})\chi^{(i)}(\hat{g})^* = \sum_j n_j{}^0G\delta_{ij} = n_i{}^0G \tag{53}$$

so

$$n_i = \frac{1}{{}^0G}\sum_g \chi(\hat{g})\chi^{(i)}(\hat{g})^*. \tag{54}$$