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Towards "Inverse" Character Tables?

A One-Step Method for Decomposing Reducible Representations

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Group theory has been extensively used to study various chemical problems, such as the determination of Raman- and infrared-active vibrations or the construction of symmetry adapted linear combinations (SALC) in the linear combination of atomic orbitals (LCAO) theory. For a given molecular point group, the first step is to construct a reducible representation that will be subsequently reduced to a direct sum of the irreducible representations belonging to the relevant group. In a number of favorable cases, a reducible representation can be reduced quickly just by searching for each irreducible representation in a row of the character table of the molecular point group for the correct combination matching the character of the reducible representation. However, for more complicated cases, the following equation is used *(1, 2)*

$$a_i = \frac{1}{h}\sum_{\mathbf{R}} \chi(\mathbf{R})\, \chi_i^*(\mathbf{R}) \qquad (1)$$

where a_i is the number of times the ith irreducible representation appears in the reducible representation where h is the order of the group, $\chi(\mathbf{R})$ is the character of the matrix corresponding to operation $\mathbf{R}$ in the reducible representation, and $\chi_i^*(\mathbf{R})$ is the character of the matrix corresponding to operation $\mathbf{R}$ in the ith irreducible rpresentation.

For groups having many similar operations in distinct classes, the use of this equation is often tedious. Hence, computer programs have been developed to make this laborious task easier *(3, 4)*. In this article, we propose a simple and straightforward procedure for decomposing a given reducible representation directly using a spreadsheet template. It is based on the inversion of the central part of the character table, which is considered as a matrix. To illustrate this topic, two basic examples are developed: (i) the SALC of the Γ_σ representation for the O_h symmetry and (ii) molecular orbitals (MOs) obtained from symmetry orbitals (SOs) for the benzene molecule.

Table 1. General Form of a Character Table

Group	C_1	C_2	…	C_n
Γ_1	χ_{11}	χ_{12}	…	χ_{1n}
Γ_2	χ_{21}	χ_{22}	…	χ_{2n}
…	…	…	…	…
Γ_i	χ_{i1}	χ_{i1}	…	χ_{in}
Γ_{red}	χ_1	χ_2	…	χ_n

NOTE: C_n are the classes; Γ_i are the irreducible representations for a given molecular point group; Γ_{red} are the reducible representations; and χ_{in} are the character of the matrix corresponding to an operation of the ith irreducible representation for the nth class C_n.

For a given point group, the character table has the general form presented in Table 1 and a reducible representation can be written as:

$$\Gamma_{red} = a\Gamma_1 \oplus b\Gamma_2 \oplus c\Gamma_3 \ \ldots \oplus \ \ldots z\Gamma_z \qquad (2)$$

where $a, b, c, \ldots, z$ indicate the number of times the ith irreducible representation occurs in the reducible representation Γ_{red}. For a given class C_n, each character χ_n of the reducible representation Γ_{red} can be expressed as a linear combination of the characters of the appropriate irreducible representations belonging to the point group under study:

$$\chi_1 = a\chi_{11} + b\chi_{21} + c\chi_{31} + \ldots + z\chi_{i1} \qquad (3)$$

$$\chi_2 = a\chi_{12} + b\chi_{22} + c\chi_{32} + \ldots + z\chi_{i2} \qquad (4)$$

$$\vdots$$

$$\chi_n = a\chi_{1n} + b\chi_{2n} + c\chi_{3n} + \ldots + z\chi_{in} \qquad (5)$$

This set of linear combinations can be summarized using the following matrix notation:

$$\begin{bmatrix}\chi_1 & \chi_2 & \cdots & \chi_n\end{bmatrix} = \begin{bmatrix}a & b & \cdots & z\end{bmatrix}\begin{bmatrix}\chi_{11} & \chi_{12} & \chi_{13} & \cdots & \chi_{1n}\\ \chi_{21} & \chi_{22} & \chi_{23} & \cdots & \chi_{2n}\\ \chi_{31} & \chi_{32} & \chi_{33} & \cdots & \chi_{3n}\\ \vdots & \cdots & \cdots & \cdots & \cdots\\ \chi_{i1} & \chi_{i2} & \chi_{i3} & \cdots & \chi_{in}\end{bmatrix} \qquad (6)$$

Note that the matrix corresponds to the central part of Table 1 and will be denoted $\mathbf{T}$. Hence, the $a, b, c, \ldots, z$ coefficients are easily obtained using the inverse matrix $\mathbf{T}^{-1}$:

$$\begin{bmatrix}a & b & \cdots & z\end{bmatrix} = \begin{bmatrix}\chi_1 & \chi_2 & \cdots & \chi_n\end{bmatrix}\mathbf{T}^{-1} \qquad (7)$$

If one is able to determine $\mathbf{T}^{-1}$, the reduction of Γ_{red} is obtained directly without needing to use eq 1. At first sight, the inversion of $\mathbf{T}$ appears to be complicated but it can be performed easily by means of the matrix inversion function (called Miniverse in Excel) and also matrix product function of a spreadsheet software (e.g., Excel or OpenOffice). Note that spreadsheets have already been used in group theory calculations, for example, to compute the number of IR- and Raman-active bands *(5)*.

The first example deals with a $[ML_6]$ transition metal in octahedral symmetry. It is of general importance in inorganic chemistry to determine the SALC of atomic orbitals that can be mixed to give rise to the σ molecular orbitals. The first task is to obtain the reducible representation Γ_σ. This is easily performed by considering that each combination is represented by a vector

Table 2. O_h Character Table

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 (= C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	Linear, Rotations	Quadratic
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	−1	−1	1	1	-1	1	1	−1		
E_g	2	−1	0	0	2	2	0	-1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		
Γ_σ	6	0	0	2	2	0	0	0	4	2		

Table 3. Inverse O_h Character Table

1/48	1/48	1/24	1/16	1/16	1/48	1/48	1/24	1/16	1/16
1/6	1/6	−1/6	0	0	1/6	1/6	−1/6	-0	0
1/8	−1/8	0	−1/8	1/8	1/8	−1/8	0	−1/8	1/8
1/8	−1/8	0	1/8	−1/8	1/8	−1/8	0	1/8	−1/8
1/16	1/16	1/8	−1/16	−1/16	1/16	1/16	1/8	−1/16	−1/16
1/48	1/48	1/24	1/16	1/16	−1/48	−1/48	−1/24	−1/16	−1/16
1/8	−1/8	0	1/8	−1/8	−1/8	1/8	0	−1/8	1/8
1/6	1/6	−1/6	0	0	−1/6	−1/6	1/6	0	−0
1/16	1/16	1/8	−1/16	−1/16	−1/16	−1/16	−1/8	1/16	1/16
1/8	−1/8	0	−1/8	1/8	−1/8	1/8	0	1/8	−1/8

pointing in the appropriate direction for the point group chosen *(1, 2)*. The resulting characters for Γ_σ in an O_h complex are given in the last row of Table 2.

Afterwards, either the reduction rule is laboriously applied with the corresponding O_h character table (10 classes and $h = 48$) or the reduction is performed automatically using a spreadsheet template with the inverse O_h character table (Table 3). Details of the calculations are presented as follows for the chosen reducible representation Γ_σ, according to eq 7:

$$\begin{aligned}\left[a_{A_{1g}}\ b_{A_{2g}}\ c_{E_g}\ d_{T_{1g}}\ e_{T_{2g}}\ f_{A_{1u}}\ g_{A_{2u}}\ h_{E_u}\ i_{T_{1u}}\ j_{T_{2u}}\right] &= \left[6\ 0\ 0\ 2\ 2\ 0\ 0\ 0\ 4\ 2\right]\left[O_h\right]^{-1} \quad (8)\\ &= \left[1\ 0\ 1\ 0\ 0\ 0\ 0\ 0\ 1\ 0\right]\end{aligned}$$

The resulting row matrix corresponds to the number of times each irreducible representation occurs in the reducible representation studied. Note that all these calculations are made in a single step using the spreadsheet template. Finally, the Γ_σ representation is reduced in one step to $A_{1g} \oplus E_g \oplus T_{1u}$.

For additional practice the students can also be asked to reduce the Γ_π representation corresponding to the SALCs of π ligands in an O_h environment. The answer is $\Gamma_\pi = T_{1g} \oplus T_{2g} \oplus T_{1u} \oplus T_{2u}$.

The use of the so-called inverse character tables is not restricted to those containing only real numbers. Indeed, every teacher has observed that students, when first exposed to group theory in chemistry, are generally puzzled by the complex characters that appear in the cyclic groups C_n. Within the Mulliken–Schoenflies notation, these correspond to the characters of the doubly degenerate irreducible representation, denoted E, that are separated here for the sake of convenience into two irreducible representations, denoted E' and E''. It is worth noting that these characters are none other than the nth-order squares of the number 1 and are given by the De Moivre formula:

$$\varepsilon = \exp\left(\mathrm{i}\frac{2\pi}{n}m\right) = \cos\left(\frac{2\pi}{n}m\right) + \mathrm{i}\sin\left(\frac{2\pi}{n}m\right) \quad (9)$$

with $m = 0$ to $n - 1$ and i the imaginary symbol ($\mathrm{i} = \sqrt{-1}$). Accordingly, a further potentiality of the method proposed is illustrated by the search for the six π LCAO–MOs of benzene, C_6H_6, in the framework of the Hückel approximation. Although the molecule belongs to the group D_{6h}, it is well known that the useful symmetry properties of the MOs are determined by the uniaxial rotational subgroup C_6, as pointed out in all textbooks *(1, 2)*. By using the six $2p_z$ carbon orbitals, the reducible representation Γ_p is easily obtained and is given in the last line in Table 4.

Given that (i) the spreadsheet software cannot inverse a complex matrix, (ii) the chemist always works on real objects, and (iii) real MOs are obtained by combining complex ones,

Table 4. C_6 Character Table

	E	C_6	C_3	C_2	C_3^2	C_6^5
A	1	1	1	1	1	1
B	1	−1	1	−1	1	−1
E_1'	1	ε	−ε*	−1	−ε	ε*
E_1''	1	ε*	−ε	−1	−ε*	ε
E_2'	1	−ε*	−ε	1	−ε*	−ε
E_2''	1	−ε	−ε*	1	−ε	−ε*
Γ_p	6	0	0	0	0	0

Note: ε = exp (i2π/6) and ε* = exp (–i2π/6), the conjugate of ε.

Table 5. Modified "Real" $C_{6,mr}$ Character Table

	E	C_6	C_3	C_2	C_3^2	C_6^5
A	1	1	1	1	1	1
B	1	−1	1	−1	1	−1
E_1'	1	1/2	−1/2	−1	−1/2	1/2
E_1''	0	√3/2	√3/2	0	-√3/2	−√3/2
E_2'	1	−1/2	−1/2	1	−1/2	−1/2
E_2''	0	√3/2	−√3/2	0	√3/2	−√3/2
Γ_p	6	0	0	0	0	0

Table 6. Inverse $C_{6,mr}$ Character Table

	1/6	1/6	1/3	0	1/3	0
	1/6	−1/6	1/6	1/(2√3)	−1/6	1/(2√3)
	1/6	1/6	−1/6	1/(2√3)	−1/6	−1/(2√3)
	1/6	−1/6	−1/3	0	1/3	0
	1/6	1/6	−1/6	−1/(2√3)	−1/6	1/(2√3)
	1/6	−1/6	1/6	−1/(2√3)	−1/6	−1/(2√3)
SO	Ψ_1	Ψ_4	Ψ_2'	Ψ_2''	Ψ_3'	Ψ_3''

we built up a so-called modified real character table (Table 5) named $C_{6,mr}$. This is obtained by first summing the two lines E_1' and $E_1''$of the original C_6 table (Table 4) and then subtracting them, and finally dividing by 2 and 2i, respectively, to get cos[(2π/6)m] and sin[(2π/6)m] with m = 0, 1, 2, 3, 4, and 5, respectively. Although such a manipulation may appear to be a "horror", as stated by Kettle (*2*), since the new real irreducible representation E do not fully obey the underlying theorems of group theory (mainly the theorems indicating that the sum of the squares of the dimensions of the irreducible representations in a group and, of the characters in any irreducible representation are, respectively, equal to h; refs *1* and *2*), it is convenient for computer calculations and, last but not least, leads directly to the real MOs suitable for the chemist.

The use of eq 7 with the inverse C_6 matrix leads to

$$\left[a_A \; b_B \; c_{E_1'} \; d_{E_1''} \; e_{E_2'} \; f_{E_2''}\right] = \left[6 \; 0 \; 0 \; 0 \; 0 \; 0\right]\left[C_{6,\mathrm{mr}}\right]^{-1} = \left[1 \; 1 \; 2 \; 0 \; 2 \; 0\right] \quad (10)$$

The matrix on the second line of eq 10 corresponds to the linear combination of irreducible representations related to Γ_p. In this matrix, the numbers 2 and 0 associated either with E_1' and E_1'' or with E_2' and E_2'' should be read 1 and 1 because the representation must contain both complex-conjugate irreducible representations if it contains either, as quoted by Carter *(6)*. Thus

$$\Gamma_p = A \oplus B \oplus 2E_1 \oplus 2E_2 = A \oplus B \oplus E_1' \oplus E_1'' \oplus E_2' \oplus E_2''$$

Moreover, since the irreducible representation are all of dimension 1, the student can read at a glance from Table 6 the six SOs that are here six (non-normalized) real MOs:

- Ψ_1: the lowest-energy bonding A-type orbital, without any nodal plane (same positive sign for each component of the first column)
- Ψ_2' and Ψ_2'': the two doubly degenerate bonding orbitals E_1-type, each with only one nodal plane
- Ψ_3' and Ψ_3'': the next two doubly degenerate E_2-type anti-bonding orbitals with their two nodal planes
- Ψ_4: the highest anti-bonding B-type orbital with three nodal planes (alternating signs for each component in the second column)

Note that group theory is unable to give quantitative information on the energies of these six MOs but, as every student knows, the energy increases with the number of nodal planes *(1, 2)*.

Conclusion

A very easy one-step method for reducing reducible representations is presented. It is based on the elaboration of a template by means of the inverse and product matrix functions available in spreadsheet software. The procedure proposed is an alternative to the tedious application of the well known reduction formula, and should find interesting developments in the teaching of problems usually associated with group theory (such as spectroscopy or molecular orbital combinations).

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Supplement
Automated reductions of reducible representations in the O_h, T_d, and D_{4h} point groups using a spreadsheet template (Excel)