Correcting Two Long-Standing Errors in Point Group Symmetry Character Tables

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Most undergraduate students learn to use point group symmetry character tables in a physical or inorganic chemistry class, and most current physical chemistry and inorganic chemistry textbooks include character tables. Advanced undergraduate and graduate classes often study group theory and the content of character tables in greater depth and detail. Published character tables are routinely accepted as being authoritative, so most chemists would be surprised to find out that some character tables have included minor errors that have been copied and propagated for up to 50 years.

The symmetry operations of any molecule form a mathematical group. Matrix representations of symmetry operations can be defined by determining how basis functions such as atomic orbitals, rotational motions, translational motions, and so forth transform under group operations. These matrix representations can typically be reduced by taking linear combinations of the basis functions such that the matrices block diagonalize into smaller matrices. Theorems of group theory show that the number of distinct irreducible representations is limited to the number of different classes of group operations. For each one of these irreducible matrix representations, the character of an operation is the sum of the diagonal elements. Because many problems such as the construction of molecular orbitals, normal modes of vibration, and ligand field splitting can be simplified using the properties of the characters of irreducible group representations, characters have been tabulated and published for all of the chemically important point symmetry groups. The errors discussed below are not in the characters themselves, but in their labeling and assignment of bases to the irreducible representations.

Early History of Character Table Publication

The analysis of crystal field splitting using group theory by Hans Bethe in 1929 *(1)* is perhaps the earliest known use of the characters of point group operations. In 1930, Eugene Wigner presented a groundbreaking group theoretical treatment of molecular vibration *(2).* Laszlo Tisza *(3)* compiled complete character tables of a limited collection of point groups in his 1933 study of vibrational spectra. He separately included statements about under which irreducible representations the components of angular momentum and the polarizability tensor transformed. Robert Mulliken *(4)* published the first set of character tables in English for a large number of point groups in his 1933 treatment of the symmetry properties of molecular orbitals, and E. Bright Wilson, Jr. *(5)* used character tables in 1934 to predict the symmetry of vibrational normal modes. By 1936, the character tables compiled by Rosenthal and Murphy *(6)* included all of the 32 point groups that commonly appear in crystallographic applications.

The earliest set of point group character tables published in books in English are those in *Quantum Chemistry* by Henry Eyring, John Walter, and George Kimball *(7)* in 1944, followed closely by *Infrared and Raman Spectra* by Gerhard Herzberg *(8)* published in 1945. Eyring et al. include 39 tables. For each of the irreducible representations of the group, these tables include not only the characters for each of the classes of symmetry operations but, in separate columns, a list of common bases that transform according to the irreducible representation. The assigned bases include x, y, and z translations of the molecular center of mass (which are also the symmetries of the components of the dipole moment vector and of p_x, p_y, and p_z orbitals) rotations about the x, y, and z axes (usually denoted R_x, R_y, and R_z, having the same symmetries as components of the angular momentum axial vector) and the components of the polarizability tensor (which have the same symmetries as atomic d orbitals). Most subsequent publications have followed this same format. Another early set of character tables is in the 1955 book *Molecular Vibrations* by Wilson, Decius, and Cross *(9).* They include tables for 40 groups, expanding to include, among others, a table for the S_8 group.

Character tables can be easily calculated. Two computer programs that do so for any group are Magma *(10),* marketed by the University of Sydney, and GAP 4 *(11),* available as a free download from the University of St. Andrews. These tables, however, are for abstract groups and are independent of the physical interpretation of the group operations. Again, the errors discussed here are not in the tabulated characters but in the physical interpretation of the classes and in the assignment of the symmetries of basis functions of physical interest.

Error 1

In the S_8 character table in Wilson, Decius, and Cross, *Molecular Vibrations (9),* in the last columns of the E_1 representation, the pairs (x, y) and (R_x, R_y) appear together. The pair (x, y) correctly appears here, but the (R_x, R_y) should actually appear in the row for the E_3 representation. An earlier appearance of this error is unknown, but it may have been copied from an earlier, yet undiscovered, table. It may have been a typographical or transcriptional error, or it may have been an actual mistake. However, this error has continued to appear in almost every published set of character tables since 1955. Only three known sets of character tables are correct on this assignment: David Schonland, *Molecular Symmetry*, 1965 *(12)*; J. A. Salthouse and M. J. Ware, *Point Group Character Tables and Related Data (13)*; and Gerald Burns, *Introduction to Group Theory with Applications*, 1977 *(14).*

The correct assignment can be justified by at least three methods:

1. **Direct product tables:** Rotations about the x and y axes transform as the x and y components of the angular momentum axial vector, $\mathbf{r} \times \mathbf{p}$. This vector product is antisymmetric with respect to interchanging **r** and **p**. The vector **r** transforms according to $E_1 \oplus B$, as does the vector **p**. The vector product $\mathbf{r} \times \mathbf{p}$ thus transforms according to the antisymmetric components of $(E_1 \oplus B) \otimes (E_1 \oplus B) = (E_1 \otimes E_1) \oplus (B \otimes E_1) \oplus (E_1 \otimes B) \oplus (B \otimes B) = (A \oplus [A] \oplus E_2) \oplus 2E_3 \oplus A$, using direct product tables (e.g., ref *15*) or reducing direct products manually. The $[A]$ in brackets in the first direct product indicates an antisymmetric product of A symmetry, and it can be shown to be $(xp_y - yp_x)$, identified as R_z. Symmetric and antisymmetric combinations of the two pairs of E_3 functions can be formed. The antisymmetric pair is $(yp_z - zp_y, zp_x - xp_z)$, which is (R_x, R_y). The correct direct product results have been known and published at least since 1937 *(16).*
2. **Class Characters:** The character for x and y rotations under a rotation through angle θ about the z axis is $+2 \cos \theta$ for proper rotations and $-2 \cos \theta$ for improper rotations. These values are consistent with characters of E_3 for each of value of $\cos \theta$ for the four improper rotations in the S_8 group ($\theta = n\pi/4$ for S_n^8, n = 1, 3, 5, 7) but not with the characters of E_1.
3. **Group Correlation Chains:** In point group D_{4d}, with which S_8 correlates, (R_x, R_y) has always been correctly listed under E_3 rather than E_1.

Why did this error occur? One reason might be that the Abelian groups C_8 and S_8 are isomorphous, so it might be expected that the assignment of translations and rotations would be equivalent. However, the different geometrical nature of the S_8^n operations for odd n requires that (R_x, R_y) be assigned to different irreducible representations in the two groups. In several point groups, (x, y) and (R_x, R_y) transform according to the same irreducible representation. These include the groups C_n for n = 3, 4, 5, 6, 8; D_n for n = 3, 4, 5, 6; C_{nv} for n = 3, 4, 5, 6, ∞; D_{nd} for n = 2, 3; and S_4. Thus, the erroneous assignment is not obvious. In any case, S_8 is a rare group, and so there is little reason that this error should have been discovered. In fact, most sets of character tables do not include the S_8 point group at all.

The Appendix contains a, probably incomplete, list of books having character tables that propagate the 1955 error in the S_8 point group assignments. These were found by searching two large university libraries. The books are listed in alphabetical order by first author. Authors and publishers of books such as these are encouraged to correct this error in subsequent editions. The owners of already published books should pencil in the correct assignment for (R_x, R_y) as E_3 rather than E_1.

Error 2

Another error, this one in the character table for the D_{8h} group, appears in Cotton's *Chemical Applications of Group Theory*, 2nd edition, 1971 *(17).* The D_{8h} group character table was not included in the first edition of this popular text, and this is the first known publication of the character table for this group. The column labels on the columns labeled $2S_8$ and $2S_8^3$ should be reversed. The correct column labeling can be understood by identifying the D_{8h} group as a direct product group of D_8 and C_i. The first 16 group operations are those of D_8, and the last 16 group operations should be the products of those same operations with inversion—in the same order. It is easy to verify that $C_8 i = S_8^5$, which is in the same class as S_8^3, and $C_8^3 i = S_8^7$, which is in the same class as S_8. The third edition of the Cotton book continues this error, as does nearly every book that has included the D_{8h} character table. The lone known exception is the booklet by Salthouse and Ware *(13).*

This error appears to result from a desire to maintain a simple and logical operator ordering in the columns. It seems natural to have C_8, C_8^3, and C_4 in the first half of the table be followed by S_8, S_8^3, and S_4 in the last half of the table. However, this ordering is incorrect if the direct product arrangement of the table is preserved.

The Appendix contains a list of books having character tables that propagate the 1971 error. Other than ref *13,* they are the only ones known to have included the D_{8h} group character table. Authors and publishers of books such as those below are encouraged to correct this error in future editions. The owners of these books should pencil in the correct assignment for the 9th and 10th classes as $2S_8^3$ followed by $2S_8$ rather than the reverse.

Conclusion

These two errors are unlikely to have caused serious problems for researchers or teachers since they are minor errors in two rarely used point groups. The errors have gone undetected for so long because of this obscurity. In fact, most published tables exclude both of these groups as unimportant. Even so, educators should seek to eliminate even minor errors from their materials.

Acknowledgment

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Literature Cited

1. Bethe, H. *Ann. Phys. (Leipzig)* **1929,** *3,* 133–208.
2. Wigner, E. *Nach. Akad. Wissen. Göttingen Math.-Phys.* **1930,** 133ff.
3. Tisza, L. *Z. Phys.* **1933,** *82,* 48–72.
4. Mulliken, R. S. *Phys. Rev.* **1933,** *43,* 279–302.
5. Wilson, E. B., Jr. *J. Chem. Phys.* **1934,** *2,* 432–439.
6. Rosenthal, J. E.; Murphy, G. M. *Rev. Mod. Phys.* **1936,** *8,* 317–346.
7. Eyring, H.; Walter, J.; Kimball, G. E. *Quantum Chemistry;* Wiley: New York, 1944; pp 383–388.
8. Herzberg, G. *Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules;* Van Nostrand Reinhold: New York, 1945; pp 105–123.
9. Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations, The Theory of Infrared and Raman Vibrational Spectra;* McGraw-Hill: New York, 1955; pp 323–330. Republished as a Dover paperback, Dover: New York, 1980.
10. Magma Computational Algebra System Home Page. *http://magma.maths.usyd.edu.au/magma/* (accessed Jul 2007).

11. GAP System for Computational Discrete Algebra. *http://www-gap.mcs.st-andrews.ac.uk/~gap/index.html* (accessed Jul 2007).
12. Schonland, D. S. *Molecular Symmetry, An Introduction to Group Theory and its Uses in Chemistry;* D. Van Nostrand: London, 1965.
13. Salthouse, J. A.; Ware, M. J. *Point Group Character Tables and Related Data;* Cambridge University Press: Cambridge, 1972.
14. Burns, G. *Introduction to Group Theory with Applications;* Academic: New York, 1977.
15. Atkins, P. W.; Child, M. S.; Phillips, C. S. C. *Tables for Group Theory;* Oxford University: Oxford, 1970; pp 13–17.
16. Jahn, H. A.; Teller, E. *Proc. Roy. Soc. London* **1937,** *A161,* 220–235.
17. Cotton, F. A. *Chemical Applications of Group Theory,* 2nd ed.; Wiley: New York, 1971; p 360.

Appendix

Book List for Error 1

Atkins, P. W.; Child, M. S.; Phillips, C. S. C. *Tables for Group Theory;* Oxford University: Oxford, 1970.

Bishop, David M. *Group Theory and Chemistry;* Clarendon Press: Oxford, 1973; reprinted by Dover, 1993 (in error despite the acknowledged use Schonland's tables, whose S_8 table is correct).

Carter, Robert L. *Molecular Symmetry and Group Theory;* Wiley: New York, 1998.

Cotton, F. Albert. *Chemical Applications of Group Theory,* 1st ed.; Wiley: New York, 1963; 2nd ed., 1971; 3rd ed., 1990.

Davidson, George. *Group Theory for Chemists;* MacMillan: Basingstoke, United Kingdom, 1991.

Diem, Max. *Introduction to Modern Vibrational Spectroscopy;* Wiley: New York, 1993.

Drago, Russell S. *Physical Methods in Chemistry;* Saunders: New York, 1977.

Ferraro, John R.; Ziomek, Joseph S. *Introduction to Group Theory and Its Application to Molecular Structure,* 1st ed.; Plenum: New York, 1969; 2nd ed., 1975.

Guillory, William A. *Introduction to Molecular Structure and Spectroscopy;* Allyn and Bacon: Boston, 1977.

Hall, Lowell H. *Group Theory and Symmetry in Chemistry;* McGraw-Hill: New York, 1969.

Harris, Daniel C.; Bertolucci, Michael D. *Symmetry and Spectroscopy;* Oxford University Press: Oxford, 1978 (in error despite having the correct $B \otimes E_1 = E_3$ in the direct product tables).

Hochstrasser, Robin M. *Molecular Aspects of Symmetry;* W. A. Benjamin: New York, 1966.

Hollas, J. Michael. *Symmetry in Molecules;* Chapman and Hall: London, 1972.

Jacobs, Patrick W. M. *Group Theory with Applications in Chemical Physics;* Cambridge University Press: Cambridge, 2005.

Liboff, Richard L. *Primer for Point and Space Groups;* Springer-Verlag: New York, 2003.

Lowe, John P. *Quantum Chemistry,* 1st ed.; Academic Press: New York, 1978; 2nd ed., 1993.

Ohrn, Yngve. *Elements of Molecular Symmetry;* Wiley: New York, 2000.

Schutte, Caspar J. H. *Theory of Molecular Spectroscopy;* North-Holland: Amsterdam, 1976.

Urch, D. S. *Orbitals and Symmetry;* Penguin: Baltimore, 1970.

Vincent, Alan. *Molecular Symmetry and Group Theory;* Wiley: London, 1977.

Book List for Error 2

Carter, Robert L. *Molecular Symmetry and Group Theory;* Wiley: New York, 1998.

Cotton, F. Albert. *Chemical Applications of Group Theory,* 2nd ed.; Wiley: New York, 1971; 3rd ed., 1990.

Diem, Max. *Introduction to Modern Vibrational Spectroscopy;* Wiley: New York, 1993.

Drago, Russell S. *Physical Methods in Chemistry;* Saunders: New York, 1977.

Harris, Daniel C.; Bertolucci, Michael D. *Symmetry and Spectroscopy;* Oxford University Press: Oxford, 1978

Lowe, John P. *Quantum Chemistry,* 1st ed.; Academic Press: New York, 1978; 2nd ed., 1993.

Vincent, Alan. *Molecular Symmetry and Group Theory;* Wiley: London, 1977.