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Recensiones

Molecular Aspects of Symmetry, ROBIN M. HOCHSTRASSER, 355 pages, New York-Amsterdam: W. A. Benjamin, Inc. 1966.

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"The principal aim of this book is to provide, in a single volume, the background, formalism, and application of group theoretical notions as they relate to molecular problems". These lines from Professor HOCHSTRASSER's preface to "Molecular Aspects of Symmetry" indicate the best intentions, and the material treated in the book has in fact been well selected to serve the author's purpose, with the applications taken from some of the most interesting fields of modern chemistry.

It is therefore deplorable that Professor HOCHSTRASSER has been unable to treat this important material with sufficient care. The number of misprints, errors, and false statements in the book is incredibly large; cross referencing is in general misleading, and the notation on the figures is often different from the one used in the text.

The first half of the book gives an account of groups and their representations. At the defining stage we learn on page 8 that "transformations which interchange identical framework particles are called point symmetry operations of the system", and on page 15 the author defines "1. Point symmetry transformations that take the system into itself", and "2. Permutation operations that interchange identical particles". This provides a single example of the many casual definitions proposed in the book. On the elementary mathematical level one encounters statements like "the commutator of a matrix with its Hermitian conjugate is equal to the null matrix", page 39, and "the associative rule applies to the scalar product of vectors", page 41.

Such assertions are annoying enough from a pedagogical point of view. More serious, however, is the fact that the author is inconsistent in the way he transforms functions under symmetry transformations. It is apparently quite at random whether an operator or its inverse is applied to a function. An example is provided by the sections dealing with angular momentum: The commutator relations (3.32) for the infinitesimal operators come out wrong, because one of the rotation matrices ($\boldsymbol{I}_y$) corresponds to the inverse rotation. In section 7.4 it is the rotation about x which is in error. As a result the final relation in section 7.12 between the rotation operators and the angular momentum operators is incorrect. (Incidentally, the reader will observe that the differential expressions in sections 7.5 and Eqs. (7.28), 7.165) for the linear and angular momentum operators are wrong).

When a set of functions $\psi_1, \psi_2 \ldots, \psi_n$ are transformed into each other under a symmetry transformation R, one may write

$$R\,\psi_i = \sum_{j=1}^{n} D_{ij}(R)\,\psi_j$$

or

$$R\,\psi_i = \sum_{j=1}^{n} D'_{ij}(R)\,\psi_j \,.$$

However, it is only the matrices $\boldsymbol{D}(R)$ that form a representation of the group of operators R such that $\boldsymbol{D}(RS) = \boldsymbol{D}(R)\boldsymbol{D}(S)$. This is not realized by the author who uses the matrices $\boldsymbol{D}(R)$ and $\boldsymbol{D}'(R)$ indiscriminately. The consequences of such carelessness are the more difficult to sort out, as the outhor uses wrong expressions for the projection operators throughout the book [the derivation of these operators in section 5.4 introduces errors in the order of indices, Eq. (5.51), or in complex conjugation, Eq. (5.55)]. These inconsistencies make the reading of, for instance, section 7.8 "The Use of Symmetry in Molecular Orbital Theory", a sad experience.

The second half of the book deals with the application of group theory to molecular problems. This part of the book is marred, not only by inconsistencies in the application of representation theory, but also by bad physics. Thus it is claimed in section 7.9 that permutation symmetry (of the electrons) has no influence in accounting for the fact that the ground state wave function for benzene is totally symmetric. The author then proceeds to discuss the excited states of benzene and formaldehyde without antisymmetrizing the wave functions involved. When the permutation symmetry eventually is taken into account, section 9.3, it is asserted that only antisymmetric wave functions will satisfy the Schrödinger equation for a four electron system. From section 9.5 the reader must get the impression that unless spin-orbit coupling is taken into account, the wave function is separable in a space and a spin part. Unfortunately, many electron theory is not as simple as Professor HOCHSTRASSER seems to imply.

Section 8.6 "Vibrational Electronic Coupling" contains some unclear remarks about the Born-Oppenheimer approximation (page 232), and it is not made clear to which state the equilibrium nuclear configuration Q_0 refers. This section is perhaps one of the best in the book, after all, when some proper sign changes are made in the listed formulae.

The stability of nuclear configurations is treated in section 8.7. It is here claimed that a Π_u state of a linear molecule must necessarily be stable to distortions, but this does not prevent the author from showing an unstable Π_u state in Fig. 8.5. The brief discussion of the Jahn-Teller effect is accompanied by Fig. 8.3 (reproduced on the cover of the book), with inappropriate notation for the vibrational species.

It is hardly surprising that chapter 10, which deals with applications of symmetry to organic molecular crystals and aggregates, is also unprecise. The important expression (10.34) for a Bloch function ought to be the complex conjugated; the error stems from an application of the erroneous projection operator (5.55). On page 294 the star of Δ is claimed to consist of seven "branches", and the point M is believed to be equivalent to the point Γ. In section 10.3 an attempt is made to prove a case of the reciprocity theorem due to Frobenius. The author proves first, Eq. (10.51), that $a = a$, from which he then concludes that $a = b$, Eq. (10.52). For a correct proof the reader is referred to H. WINSTON, J. chem. Physics **19**, 156 (1951). Section 10.5 "Factor Group Character Tables" has an irrelevant title and contains only misrepresented material.

Only a few of the errors in this book have been touched upon here. There are far too many of them for the book to be of any value to the research worker, and in the education of the youth there is no place for it.

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J. N. Murrell, S. F. A. Kettle and J. M. Tedder, Valence Theory, XIII + 101 p., John Wiley & Sons, London, New York, Sydney 1965, 50/-.

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The task of writing a book for nonspecialists is inevitably an extremely difficult one. The level of sophistication and the selection of topics risk to be considered as individual and arbitrary. According to my opinion, the book of MURRELL, KETTLE and TEDDER represents a very reasonable – even if certainly not the only possible – solution of this delicate problem. The level of the presentation is not too difficult and it allows students, who do not have a deeper training in mathematics and physics, to understand the text. The treatment, nevertheless, is not limited to the explanation of simple ideas and models of quantum chemistry. Also, the book shows many useful applications. The topics concerning organic chemistry and inorganic chemistry are well balanced. On the other hand, the intended omission even of the simplest version of the theory of spectroscopic properties of organic compounds is somewhat disturbing. (The corresponding paragraph for complexes is in the chapter on ligand-field theory.) The use of the spectroscopic properties of conjugated hydrocarbons in the critique of the Hückel theory can not be convincing without a broader discussion of the theory of electronic spectra of alternant hydrocarbons. The systematic comparison of the MO and VB approach is a very positive feature of the book.

The authors did not try, for obvious reasons, to go too deep into the discussion of the difficulties and shortcomings of various methods of quantum chemistry. But it is very helpful for the orientation of the reader and for the student's training in a scientific attitude that some criticism is included. However, in the case of the Hückel theory (Paragraph 15.8) it seems to me that statements are not precise enough.

A relatively extended discussion of the Dewar numbers N_μ is given in paragraph 17.3 on "Localization theory". It seems strange to me that the original derivation of the Dewar numbers is generally still accepted – as it is shown by the presentation in this book. This derivation is concerned with the interaction of the odd alternant fragment R with the single atom S giving the even alternant hydrocarbon RS. The following two assumptions are accepted: a) The main contribution to the energy difference between RS and $R + S$ arises from the energy difference between the non-bonding orbitals of R and S and the highest occupied orbital of RS. b) First order perturbation theory is applied for the calculation of the difference mentioned. But the energy difference $E(RS) - E(R) - E(S) = \Delta E(RS)$ is independent of the selection of R. The differences between the N_μ for different positions (different μ) are due, therefore, only to the inaccuracy of the assumption b. The real meaning of the Dewar numbers lies in their functional connection with other reactivity indices.

There are some misprints in the book (e.g. Eqs 13.15, 15.50, table on the p. 144 etc.).

The book contains many problems which are surely very helpful for the active understanding of the topics discussed. The book can be recommended for the use of the nonspecialists in quantum chemistry and as a basis of lectures for students not specializing in theoretical chemistry.

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