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Book review

A Pictorial Approach to Molecular Bonding; By J.G. Verkade, Springer Verlag Berlin etc, 1986, xiii + 282 pages, DM 125. ISBN 3-540-96271-9.

The aims are admirable; for the non-theoretically oriented chemist to appreciate the underlying principles governing molecular orbital formation and to be able to deduce results of general validity without esoteric mathematics. There will be few to disagree. Indeed to teach an undergraduate chemistry course on chemical bonding with other aims would be, except for the rare student, a waste of time. It is, however, not an easy matter to decide how this is best done, and books will differ both in the order in which concepts are introduced and in the level of mathematical support given to these concepts.

No one can leave mathematics out altogether because on the bottom line electronic wave functions are derived from the Schrödinger equation by the imposition of boundary conditions, and hand-waving from models of vibrating strings and surfaces will not get one far in understanding orbital energies. In my view, the book is not significantly less mathematical than many others that are aimed at the beginning student, but it does take a different set of mathematics, and different models, from those usually adopted. It is a new approach, which is refreshing, but I am sorry to say that I think it fails.

At the heart of the book is the concept of the generator orbital, a concept which was introduced by the author and his collaborators in the 1970's, but which has its origins in the united atom limit used by Mulliken in the early years of quantum chemistry to construct molecular orbital correlation diagrams.

Molecular orbitals are normally constructed by taking linear combinations of the atomic orbitals of all the atoms in the molecule. A generator orbital is an imaginary atomic orbital placed at the centre of the molecule whose only role is as an aid in deducing these atomic orbital combinations. The recommended procedure is to take the generator orbitals in succession, with increasing numbers of nodal surfaces (s, p, d, etc.) and to pick out combinations which have the same nodal pattern, more properly one would say the same symmetry, as the generator orbital. The book takes one through many examples starting with diatomic molecules.

For example, the valence molecular orbitals of O_2 are formed by taking linear combinations of the $2s$, and $2p$ atomic orbitals of each oxygen atom (a and b). What are the correct combinations? There are simple symmetry arguments, or more mathematical procedures, from which one can deduce that they are $2s_a + 2s_b$, $2s_a - 2s_b$, etc. These combinations can also be obtained using the generator orbital. A $1s$ orbital in the centre of the bond generates (has the same symmetry as) $2s_a + 2s_b$, it also generates $2pz_a + 2pz_b$ (z being the intermolecular axis). A $2s$ generator orbital has the same symmetry as $1s$ and therefore adds nothing new, but the $2px$, $2py$ and $2pz$ generator orbitals produce the other molecular orbital combinations, $2s_a - 2s_b$, etc.

Now in a few words I cannot do justice to the analysis by the author, but I am personally doubtful that students will easily see that the 1s generator orbital has a similar nodal pattern to $2pz_a + 2pz_b$; or if they do then they are already thinking in terms of the symmetry operations of the molecular point group and they might as well use these to calculate the molecular orbitals directly. I also believe that molecular orbital "shapes" are not the core of molecular orbital theory; that place is held by molecular orbital energies — for it is from these that one answers such questions as why is the ground state of O_2 a triplet and why does the first photoelectron band of H_2O show no vibrational structure? Generator orbitals will not tell you that $2s_a - 2s_b$ is below $2pz_a + 2pz_b$. To be fair to the author he makes no claim that they do, hence after the molecular orbital shapes or symmetries have been generated, traditional arguments have to be used to deduce energies.

Although the book contains a very large number of examples of the use of generator orbitals they are all cases where the molecule has a clearly defined centre or where there is one heavy atom which provides a central focus. There are chapters on linear triatomics, polygonal molecules, octahedral and tetrahedral molecules, bipyramidal and prismatic molecules. There is also a short chapter on bent triatomics which deals with H_2O and NO_2. There are two treatments of H_2O, one a delocalized molecular orbital scheme and the other a localized orbital scheme. Unfortunatly, neither of these is helpful for explaining the photoelectron spectrum of water because in the former the highest occupied orbital is OH bonding and in the latter it is a doubly denerate sp^3 lone pair. Photoelectron spectroscopy shows that the highest occupied molecular orbital should be a non-bonding oxygen 2p orbital.

The book does not contain a description of Hückel Theory nor does it discuss ethylene or butadiene. The cyclic polyenes are discussed and the $4n + 2$ aromaticity rule is stated; I hesitate to use the word derived because there was no proof that I could understand. I suppose a good test of the generator orbital concept would be to derive the π molecular orbitals of benzene. The book actually deals with C_6H_6. $C_7H_7^+$ and $C_8H_8^{2-}$ in one paragraph as being entirely analogous to $C_5H_5^-$ (which receives heavy treatment), so readers get little help in deducing that for benzene they need to employ, pz, dxz, dyz, a pair of f orbitals called $f2'$ and $f2''$ and a g orbital called $g3'$. Readers needs to have a good grasp of f and g orbitals and must also be able to see that dxz and dyz generate degenerate π orbitals otherwise the $4n + 2$ rule will be lost. Unfortunately it is not at all obvious that the x-axis (passing through atoms) is equivalent to the y-axis (passing through bonds) in a hexagon. A little bit of group theory does, I think, make the job easier.

I certainly think the book is worth reading by all who teach elementary courses on chemical bonding for they will find plenty of points which stimulate thought. They will presumably make up their own minds whether it is a good course book.

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