

book reviews

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Molecular Clusters. A Bridge to Solid-State Chemistry. By Thomas P. Fehlner, Jean-François Halet and Jean-Yves Saillard. Pp. xii + 378. Cambridge University Press, 2007. Price £70. ISBN 978-0-521-85236-4

'Chemical Bonding in Molecular Clusters' would be a more appropriate title because that is the sole subject of this book. This curtailment makes it a costly investment. Therefore, although it is intended as a text for advanced students of chemistry, I can only recommend it for research workers in the field. Synthesis, reactivity, chemical and physical properties, applications, and crystallographic aspects are absent topics.

The book is well understandable, provided the reader has previous knowledge of basic chemistry, chemical-bonding and ligand-field theories, symmetry, irreducible representations, and the terminology and jargon of chemists. Familiarity with computer programs to calculate molecular-orbital energies is advantageous.

Many molecular-orbital-energy diagrams are depicted and conclusions about the structures of the clusters are drawn from them in the qualitative manner that is common practice in chemistry. The reader is not burdened with calculations or mathematical formulae.

Electron-counting rules are the thread that runs all through the book. Two kinds of electron counts are used: (i) the number of valence-electron pairs that connect the cluster atoms with each other, called sep (skeletal-electron pairs); (ii) the total number of valence electrons of the atoms of the cluster, including the 'external' electrons in lone pairs and in bonds with ligands, called cve (cluster valence electrons). The text calls for frequent mental calculations of these numbers, otherwise the reading is futile. Exceptions to the counting rules receive much attention; the sheer number of the exceptions produces the bewildering impression that the exceptions are the rule.

Chapter 1 presents simple molecular-orbital models. The Wade-Mingos electron-counting rules are introduced in Chapter 2, using boron hydrides as examples. A convenient recipe is developed, showing how to mentally build up a cluster from simple building blocks that have only two-center or three-center bonds. These ideas then are extended to transition-metal clusters (Chapters 3-5), including the consideration of external ligands using isolobal relationships. The first five chapters are devoted mainly to single-shell clusters.

The treatment of delocalized bonds in solids in Chapter 6 closely follows the treatises by Roald Hoffmann. It includes electronic bands, densities of states, crystal overlap populations and Peierls distortions. Chapter 7 extends this to the

derivation of electronic structures of solids starting from clusters and other molecular entities (instead of atoms).

Numerous worked-out examples within the text and problems at the ends of the chapters with solutions in the appendix enhance the understanding.

Some annoying features have to be noted. The figures have no captions. Degenerate levels in orbital-energy diagrams are drawn one on top of the other; often it is not obvious whether the lines in a stack of lines represent levels of the same or of differing energies. In the text referring to Fig. 1.3 pairs of degenerate orbitals are counted as one, but in Table 1.1 the same orbitals are given separate numbers. What do the coordinates in Table 1.2 mean? The 'bonding edges' on p. 41 do not refer to bonds. The 'six diamond-square-diamond rearrangements' on page 71 cannot be discerned. In the figure to Exercise 3.1 it is not clear which of the vertices are occupied by the Rh atoms. The text on page 117 refers to cve counts in Fig. 3.22 which are missing in the figure. In Exercise 3.3 it remains unclear where to place the 16th CO group. Where are the CO groups in Fig. 3.7? Fig. 4.10 is supposed to show a square-pyramidal arrangement which is not present. Nothing can be recognized in Fig. 6.17M. It should be mentioned that Section 7.3.1 deals with the K_2PtCl_6 structure type.

In a book intended for students, incorrect and inaccurate expressions should be taboo. However, we find lots of them, e.g. 'stoichiometry' meaning composition; 'nuclearity' meaning the number of skeleton atoms of a cluster; 'localized compounds' (Section 1.3.3); polyhedral clusters are termed 'spherical'; 'dimension' for the number of polyhedron vertices (p. 95). A dimer always has twice the number of atoms of the monomer; but the monomer on p. 127 has 31 Pd atoms and the 'dimer' has 56; the 'dimer' on page 304 has seven Ga atoms and it remains obscure what the monomer could be. In Table 3.1 it is not clear what 'dimer' and 'trimer' refer to. By definition, an electron in a band is delocalized; how can it be 'localized in a band' (p. 269)? The vogue word 'center' abounds, and in some cases it is not quite clear whether an atom or the center of a cluster is meant. A 'planar center' is nonsense (p. 285). 'Mononuclear center' (p. 297). Many people say 'geometry' or 'architecture' when they mean shape, arrangement or structure; this is no excuse for the wrong usage of these terms (geometry is a mathematical discipline and nothing else).

The style of writing, of course, is a matter of taste. However, in a scientific book, idle remarks seem out of place, e.g. 'shoe-horning the stoichiometry' (p. 18); 'rear their ugly heads' (p. 56); 'three strikes and you're out' (p. 78); 'gritting your teeth' (p. 126); 'its better to smile than cry' (p. 182); 'OK, fine you say' (p. 212); 'aren't you impressed?' (p. 235); 'hey, a little suspense always helps the story line' (p. 336).

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The number of misprints is pleasingly low. A few are: the wrong perspective of one orbital in Fig. 1.3; four instead of six bonds in P_4 (p. 38); net-like instead of nest-like (p. 45); CO instead of PMe_3 (p. 53); missing arrows in Fig. 2.21; wrong formula in Fig. 8.4.

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