1 Introduction

In 1973, Bill Jorgensen and Lionel Salem published a small paperback that was to become the constant companion of many physical organic chemists for years to come. The *Organic Chemist's Book of Orbitals* was delightful in its simplicity and clarity of presentation of the concepts of group orbitals and qualitative molecular orbital theory in general. For many of us, it was symbolic of a chemical era. Sadly, it went out of print far too early. Now, 25 years later, the concepts presented by Jorgensen and Salem are as valid as ever and have advanced to become the major interpretational tool of organic and inorganic chemists. However, the technical possibilities for presenting this material have changed beyond recognition. We have therefore revived the idea of the *Organic Chemist's Book of Orbitals* and given it a new form that allows the reader (or is the "reader" now the "user"?) to rotate and zoom the molecular orbital (MO) plots, which are stored as three-dimensional objects. As in the original, the MO-plots are preceded by a short text section on the principles of qualitative MO-theory, although we have also added a short introduction to elementary symmetry considerations in order for the reader to be able to understand the symmetry designations of the individual orbitals. We have also added MO-plots for some of the more important organic compounds that are commonly used as ligands for transition metal complexes.

    Chapter 2 presents the principles of the *L*inear *C*ombination of *A*tomic *O*rbitals (*LCAO*) approximation. This is the dominant approximation of qualitative (and 99 % of quantitative) MO-theory. It has become so established that we very often lose sight of the fact that it is an approximation and there have been many controversial discussions about methods for analysing the properties of individual atoms within molecules over the last 25 years. Chapter 2 also describes the effects of the electronegativities of the individual elements and introduces the Walsh diagram approach to analysing the structures of small molecules and fragments.

Chapter 3 extends these concepts to larger molecules. The MOs of one-heavy-atom fragments can be used as group orbitals to build up the MOs of larger molecules. This concept of group orbitals often provides the basis for the interpretation of MO-effects in larger molecules. Chapter 3 then moves on to treat π-systems, which are involved in much of the reactivity that we seek to explain using MO-concepts, and hyperconjugation.

Chapter 4 extends the qualitative MO-concepts to reactions and gives a very short treatment of the Woodward-Hoffman rules. The treatment of concerted electrocyclic reations, cycloadditions and sigmatropic rearrangements provided the impetus for the adoption of MO-treatments, rather than the more traditional resonance theory, in organic chemistry. We now have a rather unsatisfactory situation in which elementary mechanistic organic chemistry is treated using valence-bond and resonance arguments (because they work and are easy to explain) but that for the above processes we change to MO-theory. There have been many heroic attempts to resolve this dichotomy in organic textbooks in the last 20 years, but an ideal solution remains elusive.

Chapter 5 gives a short introduction to molecular symmetry, symmetry elements, point groups, Mulliken symbols and character tables. It is not intended to provide a complete treatment of the subject, but rather to help the non-specialist understand the symbols and perhaps to prepare students for more specialised textbooks on symmetry. The final section of this chapter treats degenerate MOs. The MO-plots for these orbitals used moelcular structures that were slightly distorted from the full molecular symmetry so that the degenerate MOs appear in their usual forms with nodal planes corresponding to molecular mirror planes. It is, however, important to realise that real MO-calculations using the full symmetry may give different, equivalent sets of MOs.

Chapter 6 contains the MO-plots themselves. The printed version simply contains the table of the molecules available with their point groups and molecular formulae. In the CD-ROM version, this table is linked to the MO-plots themselves, which are available as *V*irtual *R*eality *M*arkup *La*nguage (*VRML*) objects that can be rotated, zoomed and printed in the desired orientation. It may be necessary to install the appropriate VRML-viewer from the CD if your Web browser is not already equipped for VRML. The MO-plots themselves were all produced using AM1 semiempirical MO-theory at the AM1-optimised geometries. Generally, the differences between orbitals plotted at this level of theory and those given by high level large basis set ab initio calculations are hardly visible, so that we

have chosen the fast, efficient semiempirical method that has become so popular for large organic molecules. The geometries may, however sometimes deviate significantly from those given by higher levels of theory.

We intend this edition to be the beginning of a continuous development that will take advantage of new technologies to provide more interactive multimedia features in the text and additional ways for the user to interact with the MO-plots. Time will tell whether the format that we have chosen will survive long into the future, but we have tried to make the CD-ROM as platform-independent as possible so that it can be used by PC, Mac and Unix users equally well without the need to buy additional software.