Abstract

Ph.D. thesis of Peter Scheurer: „Theoretische Beiträge zum Konzept der lokalisierten Orbitale mit Anwendungen an ungewöhnlichen Valenzzuständen“ („Theoretical contributions to the concept of localized orbitals with applications to unusual valence states“), University of Siegen, Germany, 2000.

After a discussion of standard quantum chemical methods (chapter 1) and the concept of localized orbitals (first part of chapter 2), a new algorithm of unitarily transforming a set of occupied molecular orbitals into an equivalent set of localized molecular orbitals (LMO's), which optimally resembles a set of guess LMO's, is presented in the second part of chapter 2. The new approach is applied to investigate degeneracy among LMO sets in highly symmetric molecules. Several counter examples are found to a LMO–theorem in the literature. The correct symmetry and occupation conditions for continuous LMO degeneracy are derived in chapter 3.

A step towards systematizing the bonding situations of metastable nitrogen clusters (N_{2n}–systems) is undertaken in chapter 4. LMO's are useful for rationalizing the energies and bonding situations of these clusters.

With the help of LMO's the electronic structure of several molecules (XeF_2, NF_5, PF_5, H_2CYN (Y = N, P, As)) belonging to the class of so–called “hypervalent“ compounds is analyzed in the first part of chapter 5. It is found that the bonds in the molecules under study have highly polar character, and the analysis demonstrates that there is no valence shell expansion and the octet rule is not violated. In the second part of chapter 5 the bonding situations of the [n]phenylenes and a number of trisannelated benzenes (aromatic or olefinic) is analyzed with the help of their π–LMO's, the bond alternation index, the NICS-value and the reactivity of these compounds. These systems show various degrees of bond alternation in the six–membered ring. Their structures are discussed in terms of ring strain and cyclic π effects.