DELOCALIZED BONDING AND ITS PECULIAR CONCEQUENCES IN CHEMISTRY

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Chemists usually tend to consider a chemical compound as a single classical structure, where its bonding is represented as a combination of lone pairs and two-electron two-center (2c-2e) bond, so called Lewis bonding model. However, this model could not properly describe bonding in aromatic molecules. Thus, chemists introduced the concept of resonance of a few classical structures. Chemical bonding in benzene can be represented by a resonance of two Kekulé structures. The resonance is simply another way of saying that π-bonding in benzene is delocalized. Of course canonical molecular orbitals, which are always available from Hartee-Fock or density functional calculations are delocalized over the whole molecule and thus could be used to describe delocalized bonding in aromatic molecules. However, chemists believe that σ-bonding in organic aromatic molecules is localized. Thus, we have a dilemma which description to chose: localized bonding with resonance or completely delocalized bonding with canonical MOs.

We recently proposed a new tool, which we call Adaptive Natural Density Partitioning (AdNDP) method, which allows for the first time to reconcile localized and delocalized bonding elements in one molecular bonding model. The AdNDP method is an extension of the Natural Bond Orbital (NBO) analysis developed by Weinhold. In the AdNDP analysis the search is initially performed for localized 1c-2e (lone pairs) and 2c-2e bonding elements similar to the NBO analysis. The electron density responsible for localized bonding is removed at both steps. Then the search is performed for the delocalized bonding elements (*n*c-2e bonds with *n* ranging from 3 to the total number of atoms in the system) with removal of the corresponding density. The localized and multicenter bonding elements when superimposed onto the molecular framework are always consistent with the point group symmetry of the system. Like in the NBO analysis, all the bonding elements are accepted if their occupation numbers (ON) are close to 2.00 |e|. Because of that, the Lewis idea of an electron pair as the essential element of chemical bonding is preserved.

I will show how our cluster/molecular and solid state AdNDP methods can help to rationalize bonding in organic aromatic molecules, most stable form of two-dimensional boron, so called α-sheet, boron clusters, a remarkable new sandwich complex $[Pd_4(\mu_4\text{-}C_9H_9)(\mu_4\text{-}C_8H_8)][BAr^f{}_4]$ with a four atomic Pd cluster as the "meat", the nano-molecular wheel TaB_{10}^- with the highest coordination number 10 in two dimensional compounds. In all these cases delocalized bonding is essential for understanding structure, stability and some unusual properties of these new chemical species.