Delocalized Bonding in Molecules, Clusters, Two-Dimensional Materials and Solids

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Canonical Molecular Orbitals (CMO) obtained by either the Hartree-Fock method or by the Density Functional Theory are completely delocalized over the whole chemical system. When systems are getting larger it is hard to interpret CMOs. Chemist on the other side prefer to use localized bonding based on Lewis model which operates with lone pairs and two-center two-electron (2c-2e) bonds. When Lewis model works, interpretation of chemical bonding is simple. However, more and more new chemical systems cannot be represented by Lewis model. The resonance description may be used in those cases, but it becomes very challenging for structurally complex chemical species. We recently introduced two new theoretical methods: Adaptive Natural Density Partitioning (AdNDP)[1] and Solid State Adaptive Natural Density Partitioning (SAdNDP)[2], which allow to express chemical bonding in terms of localized (1c-2e and 2c-2e) and delocalized (multi-center nc-2e) bonds. We initially search for all lone pairs, core electrons and 2c-2e bonds with good occupation numbers. In the ideal Lewis model occupation numbers correspond to 2 (an electron pair). After that we look for multicenter bonds still trying to use as small number of centers as possible, though in principle delocalized bonds can be delocalized over the whole chemical system. In my talk I will show how AdNDP and SSAdNDP methods allow us to use both localized and delocalized bonding elements for rationalization of chemical bonding in difficult cases of organic molecules, bare and embedded clusters, two-dimensional sheets and solids. I will discuss examples of delocalized bonding with 3c-2e bonds in supertetrahedral aluminum − a new allotropic ultralight crystalline form of aluminum, 4c-2e bonds in two-dimensional borane BH, 9c-2e and 10c-2e bonds in the transition metal centered boron wheel clusters, 8c-2e bonds in sodium vacancies in the high-pressure Na_2He compound, 6c-2e and 5c-2e bonds in oxygen vacancies in the bulk and on the surface of MgO crystal. AdNDP and SSAdNDP both provide a very efficient and visual approach to represent chemical bonding and could be used for research and for teaching chemistry.

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References

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