The atomic orbitals of the topological atom

Pedro Salvador, Eloy Ramos-Cordoba and István Mayer

The concept of *atom in a molecule* has always craved for proper unambiguous definition. Over the last decades a vast number of schemes or formalisms have been devised to identify the atom within a molecule. Within the LCAO approach, the atom may be identified by its nucleus and the subspace of the basis functions attached to it. A more general strategy is to subdivide the physical 3D space into atomic regions or domains (either disjoint like in in Bader's atoms in molecule theory or "fuzzy") which identify the atom. But, what do we mean by *atom in a molecule*? Clearly, the mere subdivision of the 3D space would not render any property that could be associated to the atoms -other than their volume.

Probably, the most appropriate quantities that serve to characterize the state of the atom within the molecule are the so-called effective atomic orbitals (eff-AOs). With this formalism one obtains (for each atom) a decomposition of the atoms net population in terms of a set of orthogonal atomic hybrids and their respective occupations, adding up to the *net* population of the atom. A remarkable feature of this scheme is that, for a given molecular system, irrespective of the atomic basis set size, one obtains the same number of significantly populated atomic hybrids that closely mimic the core and valence shells of the atom, *even if no basis functions are included in the calculation.* This formalism was introduced long ago in the framework of Hilbert-space analysis, and was generalized to the case of "fuzzy" atoms a few years ago. It had also been formulated in the context of Bader's QTAIM, but it was never actually realized until now.

This talk aims at showing that when the atoms are associated with non-overlapping domains, as in QTAIM, the eff-AOs have special properties that make them very appealing from both conceptual and practical point of view. Remarkably, the Mulliken-type population analysis of the density carried out on the basis of eff-AOs exactly reproduces the original QTAIM atomic populations of the atoms. That is, the eff-AOs can be seen as the genuine atomic orbitals of Bader's theory, perhaps one of the few ingredients missing in QTAIM's toolbox. We will also illustrate their applicability to the determination of oxidation states of transition metal systems.