Atoms and interactions between atoms in molecular electronic wave functions

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The quantum chemical concepts developed by the pioneers of the 1930's identified fundamental physical synergisms that create chemical bonds. Basic qualitative insights were that atoms in molecules differ from free atoms and that the interatomic interactions are of two kinds: 'classical' coulombic and 'nonclassical' resulting from the sharing of electrons between atoms. Understanding bonding requires therefore understanding the energy increases due to the formation of 'quasi-atoms' as well as the larger energy decreases due to the interactions between the quasi-atoms.

Accurate molecular electronic wave functions have complex structures. As a consequence, complex analyses are required in order to distill, from quantitative ab initio calculations, theoretically valid conceptual interpretations for qualitative chemical reasoning. Notably challenging has been the identification of quasi-atoms in molecular electronic wave functions. This issue has been universally sidestepped by *postulating* certain atomic valence states in molecules.

The foundation of the present analysis is the demonstration that, without introducing any postulated intermediate wave functions, a quasi-atomic organization of the electronic structure can be identified that is embedded in the electronic wave function of a molecule. The characteristics of the quasi-atoms that are intrinsic to the wave function can be determined. The relative roles of the intra-atomic energy changes and the interatomic interactions in bond formation can be deduced from the actual wave function. An essential prerequisite is the demonstration that molecular electronic wave functions can be exactly expressed in terms of quasi-atomic orbitals, which are slightly deformed free atom orbitals. When a molecular electronic wave function is expressed in terms of its quasi-atomic orbitals, its energy can be additively resolved in terms of contributions from the quasi-atoms, from coulombic interactions, from interactions due to electron sharing, and from interactions due to interatomic entanglements. The ab initio analysis quantifies and extends the early qualitative concepts mentioned at the outset. In many instances, the quasi-atomic orbitals represent ab initio quantifications of the dots in the Lewis electron structure symbolism.

The quasi-atomic orbitals and the energy resolution are illustrated by applying the analysis to clarify the bonding patterns in a series of molecules.

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