Quantitative conceptual analysis of bond patterns, bond breaking and bond forming through a density and energy resolution in terms of oriented quasi-atomic orbitals that are intrinsic to ab initio wave functions

Aaron C. West, Michael W. Schmidt, Mark S. Gordon, Klaus Ruedenberg
Department of Chemistry and Ames Laboratory USDOE, Iowa State University, Ames, Iowa 50011

A rigorous energy decomposition analysis (EDA) for *ab initio* wave functions in terms of atoms is developed and implemented.

It is achieved by means of a set of orthogonal orbitals that possess the following qualities: (i) The orbitals are *quasi-atomic*, i.e. they typically have very large overlaps with corresponding accurate free atom orbitals; (ii) nonetheless the *ab initio* wave function can be expressed in terms of determinants formed from these orbitals; (iii) the orbitals are basis set independent. To obtain orbitals with these features, the molecular orbital space is resolved by means of a singular value decomposition into a valence internal space of minimal basis set dimension and an external space. In the internal space, *oriented quasi-atomic orbitals* are determined by further singular value decompositions and chemical adaptations.

The first and second order density matrices are then resolved in terms of the oriented quasi-atomic orbitals. Concrete molecular applications show that these resolutions exhibit the bonding patterns between atoms in molecules as well as the changes of these patterns along reaction paths. The resolution of the molecular energy in terms of quasi-atomic orbitals leads to a decomposition in terms of intra-atomic, two-center coulombic, two-center interference, three-center interference, and four-center interference energy contributions. The localized bonding and antibonding molecular orbitals derived from the bonding quasi-atomic orbitals moreover yield the rigorous *ab initio* quantification of HOMOs and LUMOs.

The quasi-atomic orbital determinants can be divided into three groups: group I contains all determinants in which, for each atom, the quasi-atomic population equals the population of the free atom; group II consists of determinants that generate covalent bonding through electron sharing; and group III consists of determinants that contribute to charge transfer.

The determinants of group I describe the assembly of atoms (at the molecular geometry) between which no electron migrations occur so that only coulombic type interactions exist. These determinants contain the atomic valence states that are embedded in the molecular wave function. Since the intra-atomic deformations ("promotions") in the valence states contribute unavoidable nontrivial antibonding energy increases to the bonding energies, the quantification of these "quasi-atoms" in the molecule is essential. It has arguably remained the most serious unsolved problem of bonding analyses.

While the determinants of group I unambiguously identify all quasi-atoms in a molecular wave function, the sizes of full molecular configuration spaces in quasi-atomic bases exceed available computer capabilities. This limitation is overcome by generating, separately for each given atom, a simpler local wave function facsimile that encompasses only the bonding interactions that are relevant for this atom with its molecular environment. This is accomplished by fitting to the actual local density matrices, which are readily available. The group I determinants of this reduced determinant expansion yield the atomic valence state and its energy.

References

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Work supported by the National Science Foundation (Grant CHE-1147446) and the US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences (Contract DE-AC02-07CH11358).