

Partition theory; further developments

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While it is straightforward to identify the subset of nuclei belonging to each natural component of a molecule or material --individual atoms, bases, acids, sugars, nucleotides, etc., as the case may be, how to allocate electron density to each component is not. In its simplest form, this is the "Atoms in Molecules" problem. The evident broad utility of a solution to the problem has called forth many proposals over the last half century, none of which is objection free. In recent papers with collaborators, I have developed Partition Theory (PT), a method for the exact decomposition of the electron density and spin density based on the constrained minimization of the energies of the parts treated as though they were independent. We have shown that 1.) the method does not add to the computational complexity of obtaining the atomic and electronic structure of a system; 2.) it eliminates the fundamental inconsistencies between previous density-functional-theory-based (DFT) formulations of chemical reactivity theory and DFT itself; and 3.) it is capable of clarifying many important questions, e.g. the sign reversal of molecular dipoles, charge localization upon molecular fragmentation, the ionic to covalent transition, how to partition a large molecule into quantum mechanically treated and classically treated parts as in QM-MM methods, etc. In the present talk, I shall motivate the development of PT, summarize its formalism briefly, and illustrate some of its concepts and applications via extremely simple one dimensional examples which can be treated analytically.