

Quantitative analysis of interactions between atoms in molecules through a resolution of the ab initio energy

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From the very beginning it was a goal of quantum chemistry to gain an understanding of energy changes along reaction paths on potential energy surfaces in terms of synergisms of various physical interactions between atoms and between molecules. Already in the 1930s, insightful examinations of quantum mechanical energy expressions led to qualitative distinctions such as covalent bonding, ionic bonding, hydrogen bonding, van der Waals interactions and many others. This approach proved seminaly fruitful in creating fundamental concepts that explained, organized and predicted many phenomena and, moreover, could be intuitively assimilated by non-theorists.

However, even though all bonding effects derive from the same basic quantum mechanical energy expression, a comprehensive formulation that meshes the various synergistic as well as competitive interactions through a quantitative integration was not achieved. The first attempt at a general formula for bond energies may have been Mulliken's "Magic Formula" of 1952. Since then, the problem of finding such a general "energy decomposition analysis" has become even more challenging because the theoretical and computational advances that, over recent decades, have brought accurate quantitative theoretical predictions of many chemical properties and reactions within reach, have led to increasingly complex wave functions and energy expressions.

By virtue of these increased complexities, the qualitative argumentations of the earlier period can only provide very tenuous rationalizations of ab initio results. One would hope that the quantitative advances that have been made would also lead to a sharpening and broadening of the concepts regarding the physical interactions that are embedded in ab initio wave functions. Manifestly, there exists no basis for the expectation that the extraction of information regarding these interactions from ab initio wave functions should involve only the simplest mathematical formalisms, even if the resulting information can be simply interpreted.

An integrated approach to this problem has been developed.

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).