Molecular energy decompositions

István Mayer

Chemical Research Center, Hungarian Academy of Sciences
H-1525 Budapest, P.O. Box 17
Hungary
mayer@chemres.hu

The understanding and interpretation of the results obtained in a quantum chemical calculation can be much facilitated by presenting the total energy as a sum of chemically meaningful components. In the era of semiempirical quantum chemistry, this aim could be achieved trivially, as the semiempirical model Hamiltonians contained only one- and two-center integrals, so the different terms could be allocated to the atoms or pairs of atoms involved in a quite trivial manner. In *ab initio* theory, however, there are three- and four-center integrals, too, and in the straightforward energy component analysis of Clementi they led to the appearance of significant three- and four-atomic energy contributions, in sharp contradiction with the chemist's way of thinking of molecule as consisting of atoms exhibiting pairwise interactions.

The solution of this problem is difficult because we are lacking a unique definition of an atom *within* a molecule: one can perform the analysis either in the Hilbert space of the atomic basis orbitals or in the physical 3-dimensional (3D) space.

In the talk I am going to summarize some of our results obtained in the last decade—partly in the cooperation with the Girona group. First I will show the conceptually very important 3D result, according to which in the framework of Bader's "topological" AIM analysis, the SCF energy spontaneously decomposes into sum of atomic and diatomic contributions. In the Hilbert-space case the emphasis will be on the approximate CECA ("chemical energy component analysis") scheme, in which the the three- and four-center effects are compressed into one- and two-center ones as much as it is possible by performing appropriate projections. The further developments leading to an exact version of CECA and some other schemes will be briefly discussed, and a brand new energy decomposition method—which is yet under publication—will be presented, which contains some conceptually new elements permitting to overcome the difficulties connected with the previous schemes.