Molecules in Molecules as Complementary Approach to Quantum Theory of Atoms in Molecules

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In the present lecture a new scheme for bonding analysis will be presented; it originates from combining the Extended Transition State (ETS) energy decomposition method with the Natural Orbitals for Chemical Valence (NOCV). [1a] This approach is based on the concept which considers formation of a molecule from smaller fragments (i.e. another molecules bonded to each other). The associated change in electron density of fragments (so called deformation density, $\Delta\rho=\rho_{molecule}-\rho_{fragments}$) shows specific areas of charge depletion and accumulation due to molecule formation. The ETS-NOCV charge and energy decomposition scheme makes it not only possible to decompose the total deformation density, $\Delta\rho$, into the different components (such as σ, π, δ, etc.) of the chemical bond, but it also provides the corresponding energy contributions to the total bond energy. Thus, the ETS-NOCV scheme offers a compact, qualitative and quantitative, picture of the chemical bond formation within one common theoretical framework. It will be presented that ETS-NOCV results are not only fully in line with the outcomes based on the Quantum Theory of Atoms in Molecules by Richard Bader [2], but they can also be complementary. [3] Hence, ETS-NOCV and QTAIM when used together provide very deep insight into bonding phenomenon at atomistic level.
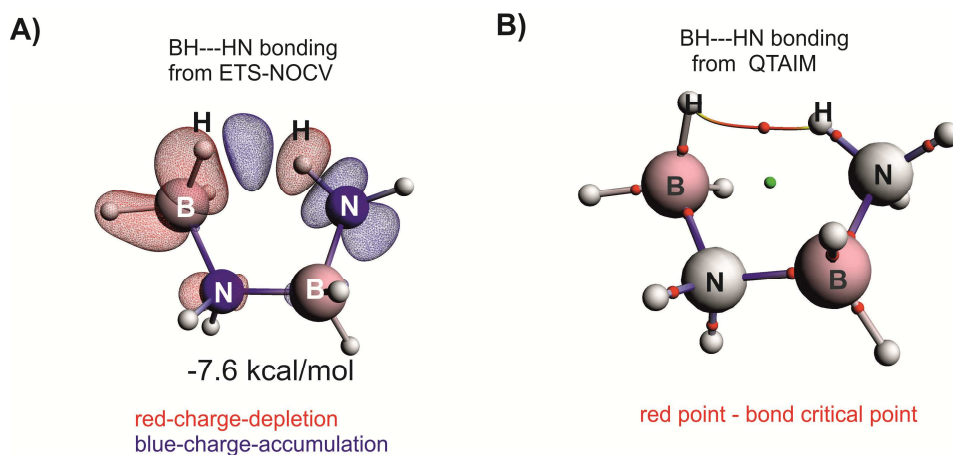

Figure 1. The contour of NOCV-deformation density contribution describing dihydrogen bonding NH---HB (part A) together with the QTAIM molecular graph (part B). In addition the corresponding energies are shown.

The applicability of the ETS-NOCV scheme will be demonstrated for various donor-acceptor bonds. It will be also included the applications involving strong covalent bonds as well

as inter- and intra-molecular weak interactions (agostic, hydrogen, halogen, polar and non-polar dihydrogen bonds). As example, formation of dihydrogen BH---HN bonding in *cis*-BN-buthane is presented in Figure 1 together with QTAIM results. [1c]

Finally, it will be shown that ETS-NOCV can be used not only to analyze the stationary points on PES, but it is also able to describe the changes in electronic structure along the reaction paths. Decomposition of energetic reaction barrier into the stabilizing (electronic and electrostatic) and destabilizing (Pauli repulsion and geometry reorganization) components will be discussed in a detailed way for the examples of reactions of industrial importance (see Figure below presenting the mechanism of activation of dihydrogen H_2 by Mo-complex). [1b]
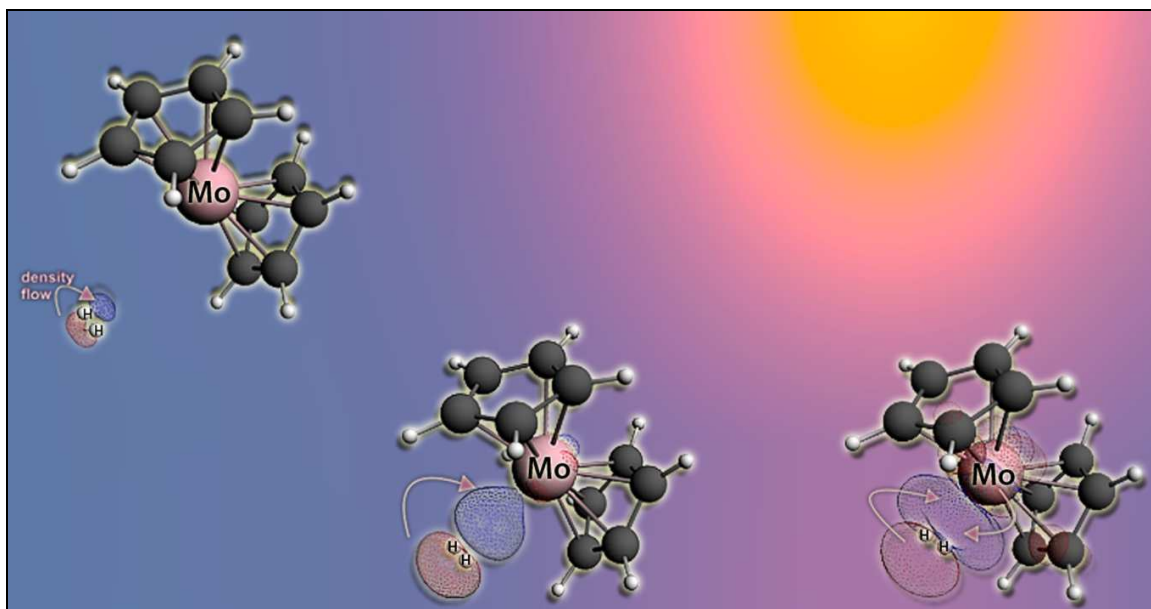

Figure 2. Subsequent stages (from the left to the right) of breaking of dihydrogen molecule by molybdenum complex obtained from ETS-NOCV scheme.

References:

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2. Bader, R. F. W. Atoms in Molecules: A Quantum Theory; Oxford University Press: Oxford, 1990.
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