Analyzing Complex Electronic Structure Calculations on Large Molecules in Simple Chemical Terms

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In this talk we shall introduce a new scheme for chemical bond analysis [*J. Chem. Theory Comput.*, 2009] by combining the Extended Transition State (ETS) method [Theor.Chim.Acta 1977,46,1] with the Natural Orbitals for Chemical Valence (NOCV) theory [J.Phys.Chem.A. 2008,112,1933]. The ETS-NOCV charge and energy decomposition scheme makes it not only possible to decompose the 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 from these components.

Thus, the ETS-NOCV scheme offers a compact, qualitative and quantitative, picture of the chemical bond formation within one common theoretical framework. Although, the ETS-NOCV approach contains a certain arbitrariness in the definition of the molecular subsystems that constitute the whole molecule, it can be widely used for the description of different types of chemical bonds. The applicability of the ETS-NOCV scheme is demonstrated for single (H_3X-XH_3, for X = C, Si, Ge, Sn) and multiple (H_2X=XH_2, H_3CXXCH_3, for X = C, Ge) covalent bonds between main group elements, for sextuple and quadruple bonds between metal centers (Cr_2, Mo_2, W_2, $[Cl_4CrCrCl_4]^{4-}$) and for double bonds between a metal and a main group element ($(CO)_5Cr$=XH_2, for X = C, Si, Ge, Sn). Applications are also given to hydrogen- and agostic bonds as well as the interaction between adsorbates and metal surfaces. The scheme is finally used to explain the trans-effect in square planar platimum complexes.

References.

1. S. Nambuki and T.Ziegler "An Analysis of the Putative Cr-Cr Quintuple Bond in Ar´CrCrAr´ (Ar´=C_6H_3-2,6(C_6H_3-2,6-Pr^i_2)$_2$ Based on the Combined Natural Orbitals for Chemical Valence and Extended Transition State (NOCV-ETS) Method Inorg.Chem. **2012**,51,7794.

2. S.Nambuki and T.Ziegler "An Analysis of Unsupported Triple and Quadruple Metal-Metal Bonds Based on the ETS-NOCV Method" Int. J.Quant. Chem. 2012, DOI:10.1002/qua.24068.

3. S.Nambuki and T. Ziegler "A Theoretical Analysis of Supported Quintuple and Quadruple Chromium-Chromium Bonds" Inorg.Chem. 2013, submitted.

4. I.Seidu and T.Ziegler "A Theoretical Analysis of the Putative Triple Bond in Ar'EEAr' (E=Si, Ge, Sn; Ar'=C_6H_3-2,6(C_6H_3-2,6-Pr^i_2)$_2$) and Ar*PbPbAr* (Ar*=C_6H_3-2,6(C_6H_2-2,4,6-Pr^i_3)$_2$)" Inorg.Chem. 2013,submitted