Resonance theory of catalytic action of transition-metal complexes.

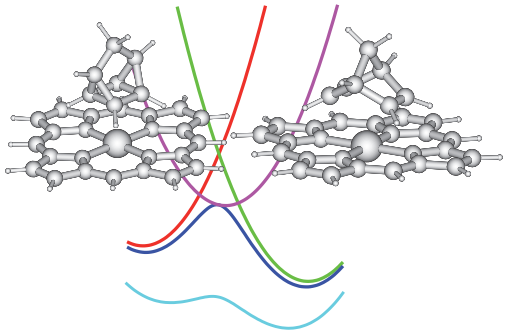
A.L. Tchougréeff[1], A.M. Tokmachev[2], R. Dronskowski[1].

[1] Institut für Anorganische Chemie, RWTH Aachen University, Aachen, Germany
[2] NBICS Centre, NRC "Kurchatov Institute", Moscow, Russia

A Google "catalysis theory" search results in dull entries like "DF *Theory* application to *catalysis* of ... by ..." rather than "theory of catalysis". We, instead, provide a general theory of catalysis of Woodward-Hoffmann restricted reactions by transition-metal complexes based on a) valence-bond ideas of chemical reactivity, b) entanglement of electronic states of reactants, and catalyst described by c) an effective Hamiltonian for the reaction center. In development of our previous works [1–3] where the potential energy surface of a catalytic reaction was expressed through the eigenstates of the free reactants Φ_r^i and catalyst Φ_d^k:

$$E = \sum_{k,i} \left(A_{ki}\right)^2 \left(E_d^k + E_r^i\right) + \sum_{k.i} \sum_{k',i'} A_{ki} A_{k'i'} \left\langle \Phi_d^k \otimes \Phi_r^i \right| \mathbf{H}_{int} \left| \Phi_d^{k'} \otimes \Phi_r^{i'} \right\rangle . \quad (1)$$

we apply the program suit catal [4] based on eq. (1) to the catalytic transformation of quadricyclane to norbornadiene:



We confirm the qualitative explanation of contrasting catalytic behavior of Mn- and Co-porphyrins obtained previously [1–3] from the analysis of the spectra of local many-electron states of free catalysts and the reactant/product. A new four-state qualitative model of this catalytic isomerization is proposed [5] as based on the results of this numerical study.

[1] Tchougréeff, A.L., Misurkin, I.A., *DAN USSR*, 291:1177, 1986 [in Russian].

[2] Tchougréeff, A.L., Misurkin, I.A., *Theor. Exp. Chem.*, 24:398, 1988 [in Russian].

[3] Tchougréeff, A.L., Misurkin, I.A., *Chem. Phys.*, 133:77, 1989.

[4] Tokmachev, A.M., Tchougréeff, A.L., Misurkin, I.A., *Int. J. Quantum Chem.*, 84:99, 2001; Tokmachev, A.M., Tchougréeff, A.L., *Zh. Fiz. Khim.*, 74:66, 2000 [in Russian].

[5] A.L. Tchougréeff, A.M. Tokmachev, R. Dronskowski. *Int. J. Quant. Chem.* Accepted. DOI: 10.1002/qua.24386.