

Theory of Chemical Bonds in Metalloenzymes XX: Confinements of Hole- and Electron-Doped Strongly Correlated Electron Systems for Catalytic Reactions in Chemistry and Biology

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In this series of papers [1, 2] we have performed broken-symmetry (BS) DFT [3] calculations of transition-metalloenzymes in biological systems. Accumulated computational results have elucidated basic concepts for understanding of quantum-mechanical (QM)/molecular mechanics (MM) descriptions of active sites of the enzymes; namely “confinements of hole- and electron-doped strongly correlated electron systems (SCES) [4-6] with proteins and other materials for catalytic reactions in chemistry and biology”. Labile nature of chemical bonds in the enzymes have been elucidated on the basis of the orbital, spin and charge degrees of freedoms in hole- and electron-doped SCES that are actively controlled by confinements. As an example of hole-doped SCES, electronic (orbital and charge) and spin states of the CaMn₄O₅ cluster [7-9] in oxygen evolving complex (OEC) of photosystem II have been investigated to obtain guiding principles for design of possible artificial 3d electron systems (Fe, Co, Ni, Cu) for water oxidation by the use of sunlight [2]. Roles of divalent ions (Ca, Sr, Ba, Mg, Zn) are also discussed in relation to hole-doping and charge degree of freedom.

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