

## Developments of Broken Symmetry Methods Application to the $\text{CaMn}_4\text{O}_5$ Cluster at OEC of PSII Refined to 1.9 Å X-Ray Resolution

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In this lecture historical developments of broken symmetry methods at Osaka [1-4] have been briefly reviewed, particularly, in relation to electronic and spin structures of organic polydiradicals and transition-metal oxides with local spins. Past decades, manganese-oxo ( $\text{Mn}=\text{O}$ ) and related manganese-oxides species [3,4] have been received great interest concerning with water splitting reaction at oxygen evolving complex (OEC) of photosynthesis II (PSII). Here, we present our recent BS UB3LYP computational results [5] on the  $\text{CaMn}_4\text{O}_5$  cluster of PSII refined to 1.9 Å X-ray resolution [6] reported by Shen and Kamiya and their collaborators.

Possible electronic and spin structures of the  $\text{CaMn}_4\text{O}_5$  cluster have been investigated by UB3LYP assuming the X-ray structure [6]. All the BS configurations feasible for the valence configurations of the cluster,  $\text{Mn(III)}_x\text{Mn(IV)}_y$  ( $x,y = 0-4$ ), have been constructed by the HOMO-LUMO mixing and other techniques. The spin and charge populations obtained by UB3LYP are consistent with BS configurations available. The effective exchange interactions ( $J$ ) between manganese ions in the cluster are determined by our computational procedures based on the approximate projection (AP). Full geometry optimizations of the antiferromagnetic exchange-coupled states of the cluster have been performed for comparison with the X-ray result [4]. The nature of chemical bonds of the cluster is also investigated by the natural orbital analysis of the BS solutions to elucidate possible mechanisms of water splitting reaction. Implications of the present computational results are also discussed briefly.

[1] K. Yamaguchi, T. Fueno and H. Fukutome, *Chem. Phys. Lett.* 22, 461 (1973).

[2] K. Yamaguchi, *Chem. Phys. Lett.* 33, 330 (1975); 35, 230 (1975); 66, 395 (1979).

[3] K. Yamaguchi, Y. Takahara and T. Fueno, *Appl. Quant. Chem.* p155-p184 (1986).

[4] K. Yamaguchi et al, in *Organic Peroxides* (W. Ando Ed., Wiley, 1992) p1-p100.

[5] K. Kanda et al, *Chem. Phys. Lett.* 506, 98 (2011)

[6] Y. Umena, K. Kawakami, J. R. Shen, N. Kamiya, *Nature* 473, 55 (2011).