Theoretical studies of water oxidation in PSII.

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Hybrid density functional theory has been used for the past decade to study the mechanisms of a large number of transition metal containing enzymes. In the present talk the mechanism for dioxygen formation in PSII will be described. It will be concluded that these studies have now reached a level of convergence. After the first X-ray structures of PSII appeared five years ago, the understanding has improved significantly. A detailed mechanistic proposal will be presented including a complete energy diagram. During the past years major progress has also been made concerning the structure of the oxygen evolving complex. It will be argued that the theoretical prediction of the structure is at present more accurate than, and even qualitatively different from, what is obtained by X-ray crystallography or EXAFS. It is also quite different from what has been obtained with other theoretical approaches. Recent progress of calculating polarized EXAFS and spin spectra will be reported. Finally, a comparison of the calculated structure and the recent high-resolution structure by Shen et al will be given.