The structure of the water oxidizing complex in photosystem II

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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. The present strategy for treating these systems using larger and larger clusters, entirely treated quantum mechanically, will be briefly outlined. DFT studies on the mechanism for dioxygen formation in photosystem II are then described, and it will be concluded that these studies have now reached a level of convergence. After the first X-ray structures of PSII appeared a few years ago, the understanding of this fundamental reaction 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. I have previously argued that the theoretical prediction of the structure was more accurate than, and even qualitatively different from, what had been obtained by X-ray crystallography or EXAFS. It was also quite different from what had been obtained with other theoretical approaches. Very recently (Shen et al, Nature, 2011), a new X-ray structure with much higher resolution than before (1.9 Å) has been described. The structure is very similar to the one predicted by theory.