Modeling of water oxidation in photosystem II and proton pumping in cytochrome oxidase

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Hybrid density functional theory has been used to study the mechanisms of a large number of transition metal containing enzymes. The present strategy for treating these systems will be described, with comparison of large DFT and QM/MM models. DFT studies on the mechanism for dioxygen formation in photosystem II is then described. 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 year 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. Finally, a mechanism for proton pumping across the membrane for cytochrome c oxidase will be presented. Quantitative reasoning, rather than large calculations, has been particularly fruitful in this case.