Models of the photosynthetic oxygen-evolving center and electronic structure of Mn clusters

GABRIEL DROBNY, MICHAL BAJDICH, LUBOS MITAS, Center for High Performance Simulation and Department of Physics, North Carolina State University — It is known that the oxidation of water to $O_2$ in green plants is associated with a tetramanganese complex of the photosystem II (PSII) protein-cofactor complex but the exact structure of the oxygen-evolving center (OEC) remains unknown. The recent X-ray spectroscopic studies suggest that the OEC contains a cubane-like $\text{Mn}_3\text{CaO}_4$ center linked to a forth Mn by an oxo-bridge. Using ab-initio methods we carry out geometry optimizations for a few models of the OEC and study their electronic properties. We consider the cubane-like $\text{Mn}_3\text{CaO}_4$ center, a funnel-like $\text{Mn}_4$ core with Ca ligand and a synthetic $\text{Mn}_4\text{O}_6$ core structure. Possibilities for binding sites and eventual reaction paths of the water splitting are explored. Manganese clusters are recognized also as single-molecule magnets. Therefore we investigate spin properties of ground and excited states of these clusters. High spin ground states of $\text{Mn}_2\text{O}_2$ and $\text{Mn}_4$ compared to a low spin ground state of $\text{Mn}_4\text{O}_4$ illustrate a competition between ferromagnetic and antiferromagnetic ordering.

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