

**Extended Hartree-Fock Theory of Chemical Reactions IX.**  
**Symmetry and Multireference Approaches to**  
**Hydroxylation Reactions by P450 model complexes.**

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**Abstract**

The energy levels and energy gaps for the ground and lower excited states of the iso-electronic species, O, O<sub>2</sub> and Fe(IV)=O cores in the ligand fields have been investigated on the basis of the broken-symmetry (BS) methods; unrestricted Hartree-Fock (UHF), UHF Møller-Plesset (UMP), UHF coupled-cluster (UCCSD), BS hybrid DFT (HDFT), and multi-reference methods; CASCI, CASSCF and MRMP2 [1]. The UCCSD and MRMP2 with large CAS space are found to be necessary for reasonable calculations of the energy gaps. The HDFT is tunable so as to reproduce the computational results by these reliable methods for applications to relatively large systems. The relative stabilities among the different electronic and spin states of the Fe(IV)=O cores are found to be highly dependent on the configuration mixing of the zwitterionic and/or charge-transfer configurations, which is a key facet in the P450-catalyzed oxygenation reactions. Implications of the computational results are discussed in relation to various BS HDFT calculations of the transition structures and intermediates of hydroxylation reactions of alkanes by P450.

**Reference**

[1] H. Isobe et al., *Int. J. Quant. Chem.*, 108, 2991 (2008).