Valence excited states of an iron-porphyrin complex: multireference wavefunction calculations

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The singlet valence excited states of an iron-porphyrin-pyrazine-carbonyl complex are investigated up to the Soret band (about 3.eV) using Multi-State Complete Active Space with Perturbation at the Second Order (MS-CASPT2). This complex is a model for the active site of carboxy-hemoglobin/myoglobin. The spectrum of the excited states is rather dense, comprising states of different nature: d→π* transitions, d→d states, π→π* excitations of the porphyrin and doubly excited states involving simultaneous intra-porphyrin π→π* and d→d transitions. Specific features of the MS-CASPT2 method are investigated. The effect of varying the number of roots in the state average calculation is quantified as well as the consequence of targeted modifications of the active space. The effect of inclusion of standard Ionization Potential-Electron Affinity (IPEA) shift in the perturbation treatment is also investigated.

Preliminary calculations performed using Restricted Active Space with Perturbation at the Second Order (RASPT2) are also presented.

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