Probing the Singlet and Triplet State in Oxyhemoglobin with μSR: a First-Principles Study

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Hemoglobin is one of the most important proteins in the body, being responsible for the transport of oxygen. For a quantitative understanding of the efficiency of attachment and detachment of oxygen and the influence on these processes from the environment (e.g., varying pH level in different parts of the body), an accurate understanding of the electronic structures of both deoxyhemoglobin and oxyhemoglobin is very important. The present work focuses on oxyhemoglobin and especially the impact on the understanding of its electronic structure by muon spin rotation and relaxation (μSR) measurements.

The electronic state of oxyhemoglobin has been a subject of interest and controversy for several decades. It was believed at various times to exist in a singlet state or an antiferromagnetic state with spin coupling between Fe and O_2on the heme. However, susceptibility measurements in the late 1970's in oxyhemoglobin suggested paramagnetic character and a subsequent theoretical investigation indicated that there was a low-lying triplet state with an excitation energy above the singlet ground state corresponding to 216 K. This suggested that there can be a significant admixture of populations in singlet and triplet states in oxyhemoglobin at room temperature and somewhat lower temperatures.

This expectation of significant mixture of singlet and triplet populations has recently been augmented at a microscopic level by the observation of a significant and unique relaxation pattern in μSR measurements on oxyhemoglobin by K. Nagamine and collaborators (Proc. Japanese Academy, Ser. B83 (2007) 120). In view of this situation it is imperative to both demonstrate quantitatively by first-principles Hartree-Fock procedure (without any approximation to the exchange interaction) combined with many-body perturbation theory the existence of the low-lying excited triplet state above the ground singlet state and secondly make predictions about the hyperfine interaction parameter at the muon (μ) site in the triplet state.

With this aim in mind, we are investigating: (a) the total energy of the singlet state and the electric field gradient tensor at the Fe nucleus to compare with the quadrupole coupling constant and asymmetry parameter from experimental Mössbauer data, (b) trapping sites in the singlet state for muon (μ) and muonium (Mu) and associated muon hyperfine constants for Mu, (c) the total energy of the triplet state and the associated excitation energy from the singlet state, and (d) trapping sites for μ and Mu in the triplet state and associated hyperfine constants for muon at the trapped sites.

Results will be presented from our investigations on items (a), (b), (c) and (d).