Theoretical studies on chemical bonding between Cu(II) and oxygen molecule in type 3 copper proteins

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Abstract

Type 3 copper proteins, which contain the Cu_2O_2 core in their active sites have attracted attention from both experimental and theoretical aspects. In this study, we focused on the active site of oxyhemocyanin (oxyHc) and constructed model complexes corresponding to both deoxy form (PDB code: 1LLA) and oxy form (PDB code: 1OXY) as shown in Fig. 1.

We investigated the effect of exact exchange in broken-symmetry (BS) hybrid DFT functional on the most stable coordination of O_2 binding in the Cu_2O_2 core. We used five hybrid GGA functionals that contain different proportion of exact exchange in a range of 20–50%. In order to evaluate their net accuracy rigorously, the spin contamination errors caused by the triplet state for energy and energy gradient in BS state were replaced by our approximate spin projection (AP) method. In addition to the equilibrium structure, we also compared O-O stretch vibrational frequencies and solvation free energies to each functional.

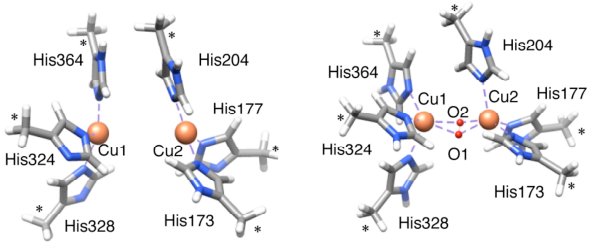

Fig. 1. Calculated model. The atoms marked by an asterisk are fixed in the X-ray crystallography geometry.

References

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