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A theoretical study of two local minima for the structures of [4Fe–4S] clusters

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The accuracy of geometries is important for predicting the electronic properties of molecular systems using computational methods. A previous investigation has indicated that there exist two local minima for [4Fe–4S] clusters in proteins when optimized with a density functional theory (DFT) method [1]. In this work, we performed a detailed study of two distinct local minima for [4Fe–4S] clusters in five proteins and two oxidation states, using combined quantum mechanical and molecular mechanical (QM/MM) methods. The MM part of the QM/MM calculations was performed with the Amber software [2], using the Amber ff14SB force fields. In the QM part, we employed nine different DFT methods, PBE, BP86, BLYP, B97D, TPSS, r^{2}SCAN, TPSSh, B3LYP, and B3LYP*. All the functionals were combined with def2-SV(P) or def2-TZVPD basis sets. The QM system consisted of the Fe and S ions and the directly coordinated Cys groups modeled by $CH_3CH_2S^-$, for the whole cluster (cf. Figure 1). We indicated that one local minimum (L state) has longer Fe–Fe distances than the other (S state) and that the L state is more stable for all cases studied. Also, our results showed that some DFT methods may only obtain the L state, while others may obtain both states. We recommend r^{2}SCAN for optimizing [4Fe-4S] clusters in proteins, which gives the most accurate structures.

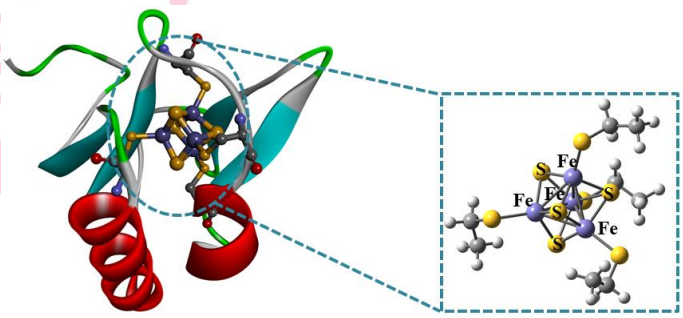


Figure 1. The close-up of the QM system we used in the calculations.

Keywords: Iron-Sulfur Cluster, Protein, DFT, Geometry, QM/MM

References

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