

Electron Transfer Pathway in Biomolecules: FMO-LCMO and Tunneling Current Analysis

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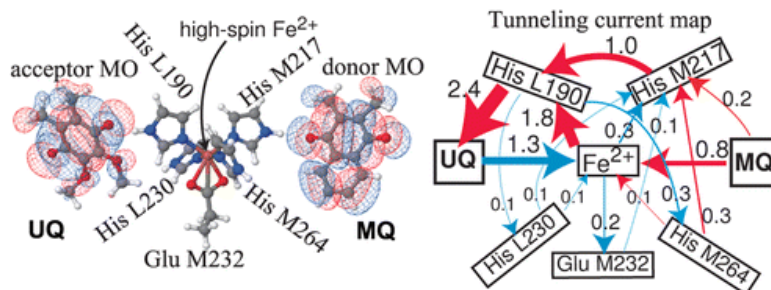
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Biological energy conversions such as photosynthesis and respiration involve long-distance electron transfers (ETs) as key processes. However, the role of protein environment has not been fully elucidated; that is, it is unclear whether they are simply holding the redox centers at appropriate locations, or they play some specific roles to mediate the long-distance ETs. While biological long-distance ETs are basically single-electron processes, the effective one-electron potentials or orbitals should be derived via many-electron calculations, which is apparently formidable for realistic large proteins. To address this, we deploy the linear combinations of fragment molecular orbitals (FMO-LCMO) [1]. We then compute the electronic coupling energy of ETs by the generalized Mulliken-Hush and bridge Green function methods, as well as the tunneling current pathways at atomic or fragment resolution.

The scheme has been applied to ET steps in the reaction center of photosynthetic bacteria *Blastochloris viridis*. Figure shows the molecules involved in the ET step from menaquinone (MQ) to ubiquinone (UQ) via Fe^{2+} complex with four histidines (His) and one glutamate (Glu). The right panel shows the result of tunneling current analysis. In contrast with the previously prevailing suppositions from mutagenesis experiments that exhibit weak dependence of the ET rate on metal substitution and depletion, a major pathway involves Fe^{2+} ion and one of the His ligands (L190). When the metal ion is replaced by Zn^{2+} , another pathway via two His ligands (M217 and L190) opens. These two His ligands take up the major role when the metal ion is depleted. The computed values of electronic coupling are consistent with experiments.



[1] Tsuneyuki, S., Kobori, T., Akagi, K., Sodeyama, K., Terakura, K., Fukuyama, H. *Chem. Phys. Lett.* 476:104, 2009.

[2] Nishioka, H., Ando, K. *J. Chem. Phys.* 134:204109, 2011; Kito-Nishioka, H., Ando, K. *J. Phys. Chem. B* 116:12933, 2012