New Theoretical Method to Determine and Visualize the Electron Tunneling Route in Protein Media

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In biological systems, long-range electron transfer reactions between protein cofactors take place via a superexchange mechanism where the electron tunnels with use of virtual states provided by protein environments. The protein environment has the heterogeneous and intrinsic structure. It has been a significant subject to elucidate how these protein structures contribute to regulate the long-range electron tunneling (ET).

In this paper, we developed a new theoretical method to determine and visualize the ET route in protein media. [1] In accordance with thermal fluctuation of protein conformation, the ET pathway which is obtained by the combination of interatomic tunneling currents (ITCs) is largely fluctuated. [2] As a result, the electronic factor T_{DA}^2 of the electron transfer rate is fluctuated by 4 or 5 orders of magnitude with time. [2] To treat this fluctuation effect in the ET route, we took the thermal average of the square of the ITCs and multiplied a quantum interference factor to it. As a result, we obtained the modified mean square interatomic tunneling current (MMSIATC). The sum of MMSIATC in any plane which cuts the line connecting donor and acceptor correctly becomes mean square T_{DA}^2. We draw the map of the MMSIATC onto the protein conformation by a pipe model in which the pipe width is proportional to the value of MMSIATC. We can assign that the connection of the bonds or space whose MMSIATC has a very large value constitutes the average ET route including the quantum interference effect.

We applied this method to the electron transfer from the bacteriopheophytin anion to the primary quinone in the bacterial photosynthetic reaction center of *Rhodobacter sphaeroides*. We calculated the time-dependent ITCs by a combined method of molecular dynamics simulations and quantum chemical calculations. We found that the average electron tunneling route is composed of only few pathways in the Pathways model [3] and the global shape of the route is nearly straight.

[1]. H. Nishioka, T. Kakitani J. Phys.Chem. B **112**, 9948 (2008).

[2]. H. Nishioka *et al.* J. Phys. Chem. B **109**, 1978 (2005)

[3]. Beratan *et al.* Science **252**, 1285(1991)