Electron transfer and transport through multi-heme proteins

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Multi-heme cytochromes are proteins that bind several redox-active heme cofactors in very close proximity, facilitating biological electron transport over nanometers. These proteins are sometimes referred to as biological nanowires. Understanding their conductive electronic properties is currently of very high interest due to many promising potential revolutionizing bionanotechnological applications.

In this presentation, I will discuss our computational study of the electron transfer and transport mechanisms in multi-heme cytochromes, both in solvent and in solid-state gold junctions. Our findings show that the heme chains allow for efficient electron transfer via incoherent hopping in solvent [1], whereas in solid-state heme protein/gold junctions, electron transport occurs via a coherent mechanism, leading to exceptionally high temperature-independent currents. This coherent transport mechanism contradicts the expectation of long-range transport over the multi-layer protein contacts, where incoherent hopping would be more probable. To gain a better understanding of these findings, we conducted classical molecular dynamics (MD) and density functional theory (DFT+Σ) simulations to investigate the distance and band-alignment dependencies of these two mechanisms[2]. We show that the alignment between protein states and Fermi level could drastically affect how electronic charges pass through the heme protein junction.

[1], J. van Wonderen, K. Adamczyk, X. Wu, X. Jiang, S. E. H. and Piper, C. R. Hall, T. A. Clarke, I. Sazanovich, M. Towrie, J. Blumberger, S. R. Meech, and J. N. Butt. *Proc. Nat. Acad. Sci*. 2021, 118 (39), e210793911
[2], Z. Futera, X. Wu, J. Blumberger. J. *Phys. Chem. Lett*. 2023, 14, 445-452