Electron Transport in Biomolecular Junctions Studied by DFT and Tight Binding Approaches

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INTRODUCTION

Biomolecular juntions can be nowadays almost routinely prepared and studied by scanning tunneling microscopy (STM) or atomic force microscopy (AFM) techniques. From theoretical point of view, the transport phenomena there can be described by quantum tunneling effects. However, the situation is more complex, when large redox-active biomolecules are investigated. While in a native aqueous environment, the electron flow through the system of redox sites proceeds by the thermally activated hopping mechanism, the temperature-independent currents of relatively high magnitudes were detected on protein/metal junctions, suggesting atypical long-range tunneling behavior. [1], [2]

METHODOLOGY

We investigate these electron-transport phenomena by means of computer simulations based on classical molecular dynamics (MD) as well as the first-principles description within the framework of density functional theory (DFT). [3], [4] While the incoherent hopping could be studied by combined quantum-mechanical/molecular-mechanical (QM/MM) techniques, [5] the coherent tunneling requires a quantum description of the whole interface models. Special care is taken to electronic–state alignment on the bio/metallic interfaces for which we apply the DFT+Σ scheme.

RESULTS

We systematically investigate these biomolecular junctions by quantum calculations based on tight-binding potentials (TB) and DFT. Different types of molecular junctions (benzene-1,4-diamine, benzene-1,4-dithiolate, Zn-porphyrin, Fe-heme) were investigated using non-equilibrium Green's function method (NEGF) and approximative approaches on the basis of Landauer formalism. Besides, electron transport properties of small redox proteins (STC, Cytochrome c, Cytochrome b_{562}, Azurin) in contact with gold electrodes were studied to elucidate the electronic states and transport conduction channels in such systems. [6]–[8] We show importance of the energy-level alignment on the bio/metallic contacts and discuss accuracy of different approaches to capture the transport phenomena.

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