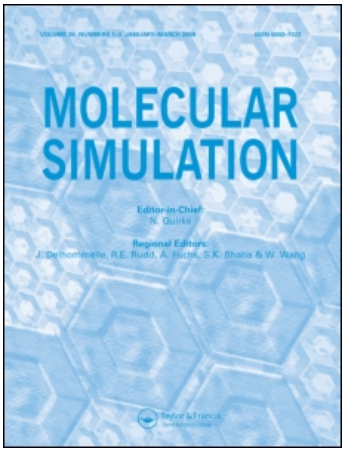

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Guest editorial: Electron transfer

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Guest editorial: Electron transfer

Electron transfer reactions lie at the heart of the molecular sciences, with applications throughout biology, chemistry, physics, and engineering. This volume contains a sampling of contributions from the frontiers of this research field. The papers reflect a broad range of experimental systems and theoretical–computational approaches. The contributions are divided into three topical areas: organic and organometallic electron transfer, biological electron transfer and bioenergetics, and electron transfer through molecular junctions and at surfaces.

1. Organic and organometallic electron transfer

Studies of electron transfer in organometallic systems by Pheasant, Kouzelos, Van Ryswyk, and Cave compare *ab initio* and semiempirical methods for computing electronic coupling elements in ruthenium porphyrin dimer systems. Also, they explore the effects of orientation and ligation on the coupling interactions. Interestingly, they find a strong dependence of the coupling interactions on ligand binding, even when the ligands do not directly perturb coupling pathways. Prins, Grozema, and Siebbeles use quantum methods to explore the effects of torsional fluctuations on the charge mobility in poly-phenylenevinylene (PPV) molecular wires. The authors find a correlation between charge mobility and torsional fluctuations: the slower fluctuations lead to reduced mobility. The model reproduces experimental mobility data on PPV systems. Troisi examines the influence of structural fluctuations on electron transport in the small- and large-polaron regimes for pi-stacked systems, with emphasis on organic crystals. Fluctuations have distinct effects in the two regimes. In the small-polaron case, fluctuations lead to small dynamical corrections to the static electron transfer rate. For large polarons, fluctuations cause dynamic localization of the electron and thus determine the transport mechanism.

2. Biological electron transfer and bioenergetics

Goychuk describes an analytical model for biological electron-transfer pumps. The electron-transfer molecule has two interconverting conformations with different donor and acceptor energies and electronic matrix elements. He demonstrates how it is possible to drive uphill electron transfer for a wide range of model parameters. If the conformational transitions are associated with ATP binding and hydrolysis, the model may describe the physics of biological electron transfer pumps. Nishioka, Yamato, and Kakitani explore the influence of a fluctuating electronic coupling matrix element on electron transfer and the link to inelastic electron tunneling. They present an extensive computational study of electronic coupling fluctuation effects on the electron transfer reaction between the bacteriochlorophyll anion and the primary quinone in the bacterial photosynthetic reaction center. Medvedev, Kotelnikov, Goryachev, Psikha, Ortega, and Stuchebrukhov describe a theoretical–experimental approach to probe protein dynamics on the microsecond timescale by analysing the temperature dependence of electron transfer kinetics. Their strategy allows the estimation of parameters related to the activated dynamics of microsecond protein motions, including activation energies and pre-exponential factors. Applications are made to the electron transfer reaction from the proximal heme of the cytochrome to the special pair in the bacterial photosynthetic reaction center.

3. Electron through molecular junctions and at surfaces

Muralidharan, Ghosh, and Data present a critical analysis of nonequilibrium Green's function DFT methods that are often used to compute molecular conductance. A Hubbard

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Hamiltonian is used and the limitations of mean-field approximations are explored. This contribution also discusses the rich physics associated with the conductance in molecular Coulomb-blockade structures. Starikov, Fujita, Watanabe, Sengoku, Tanaka, and Wenzel describe a computational study of the influence of molecular motion and base-pair mismatches on DNA conductance. Their computational approach combines molecular dynamics simulations with quantum chemical computations of the conductance for each molecular dynamics snapshot. They assign DNA transmission channels based on the analysis. Wang, Willig, and May present a comprehensive theory for ultrafast heterogeneous electron transfer between a molecule and a semiconductor surface. The theory accounts for the vibrational degrees of freedom of the molecule and is applied to photoinduced electron transfer between perylene and TiO_2.

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