Atomistic Simulation of Charge Transfer at Functionalized Semiconductor Surfaces

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We model dynamics of photo-excitations in functionalized semiconductor nanostructures. The modeling is performed by reduced density operator method in the basis of Kohn-Sham orbital's. Thermalized lattice vibrations are modeled through ab initio molecular dynamics of nuclei, forming a time-dependent trajectory. Non-adiabatic couplings in the basis of Kohn-Sham orbital's are computed in a course of molecular dynamics, and are utilized to build autocorrelation functions and the Redfield dissipative part of the equation of motion for the reduced density operator. The latter one is solved in the frequency domain (i) and time domain (ii): (i) In the frequency domain, the steady state solution illustrates formation of the density of an excited non-equilibrium state with contributions of multiple electron-hole pairs. (ii) Time domain solution for non-equilibrium initial state of the model shows how the energy of photo-excitation is dissipating due to interaction with lattice vibrations with the electron/hole part of an excitation relaxing to the bottom of conduction band /top of valence band. [1] The methodology is applied to surfaces of silicon and titanium dioxide, functionalized by minimalistic metal nano-clusters or doped. Solution for nonequilibrium density of electrons is used for determining the dynamics of formation of charge transfer state on the surface, computing surface photo-voltage, and rates of energy and charge transfer. Simulations of these models demonstrate the formation of charge transfer state. [2] These results are of the importance for an optimal design of nano-materials for photo-catalytic water splitting and solar energy harvesting.[3]

[1] D.S.Kilin, D.A.Micha, J. Phys. Chem. Lett. 1(2010) 1073.
[2] D.S.Kilin, D.A.Micha, J. Phys. Chem. C 115 (2011) 770.
[3] T. Inerbaev, J. Hoefelmeyer, D. Kilin, (2012, in preparation)

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