Dynamics of electron transfer at nanostructured semiconductor surfaces: ab initio calculations and the reduced density matrix

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A combination of time dependent density matrix and *ab initio* electronic structure methods provides details of the dynamics of photoinduced charge redistribution at nanostructured semiconductor surfaces. Properties of electronically excited states in periodic slab models of semiconductor surfaces are obtained using basis sets of plane waves and energies generated with density functional theory. Transfer processes can be understood and calculated in terms of numerical solutions of equations of motion (EOM) for the reduced density matrix (RDM). The EOM of the RDM are treated in a secular approximation, where population dynamics and coherence undergo relaxation and dephasing. The relaxation and dephasing rates are obtained from the Fermi golden rule and calculated with ab initio data: vibrational density of states and electronic state couplings induced by fluctuations of local polarization. Thus, electron transfer at the surfaces involves interactions with a thermal bath of lattice vibrations, which promote relaxation of electrons and holes, and electronic rearrangement at the surface. Applications have been done to clusters of silver atoms on silicon surfaces. Specifically, silver clusters adsorbed on the (111) surface add surface-localized states that enhance electron transfer and the surface photovoltaic effect by more than one order of magnitude. The EOM are solved with initial condition corresponding to instantaneous photo-excitation. Solutions are presented in terms of the evolution of populations in energy space, showing inter- and intra- band relaxation so that populations of electron and hole orbitals explore the energy band landscape of a Si slab and end up in a charge-separated state, with a hole in the Si slab and an electron in the Ag-cluster adsorbate.

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