Spin Unrestricted Excited State Relaxation Dynamics in Semiconducting Systems

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Atomistic modeling of light driven electron dynamics is important in studies of photoactive materials. Spin-resolved electronic structure calculations become necessary when dealing with transition metal, magnetic, and even some carbon materials, intermediates, and radicals. An approximate treatment can be pursued in the basis of spin-collinear density functional theory. Most transition-metal compounds exhibit open shell nonsinglet configurations, necessitating special treatment of electrons with α/β spin projections. By separate treatment of electronic states with the *α/β* spin components one is able to describe a broader range of materials, identify new channels of relaxation and charge transfer, and provide knowledge for rational design of new materials in solar energy harvesting and information storage. For this methodology, named spin-resolved electron dynamics, spin- polarized DFT is used as the basis to implement nonadiabatic molecular dynamics. At ambient temperatures, the thermal lattice vibrations results in orbital and energy fluctuations with time. Nonadiabatic couplings are then calculated, which control the dissipative dynamics of the spin resolved density matrix. Different initial excitations are then analyzed and used to calculate relaxation dynamics. Spin-resolved electronic dynamics approach is applied to study vanadium (IV) substitutionally doped bulk anatase in a doublet ground state. Spin-resolved charge transfer dynamics at the interface of a $Co(NH_3)_2$ -doped (001) anatase TiO_2 nanowire and liquid water calculations based on density functional theory and density matrix formalism are considered. Three models with the same stoichiometry but different electronic structure are explored. While one model had no change to electron count and spin count (neutral model), the other two models were assigned a charge of 2+, one in a doublet and the other a quartet spin configuration. Co^{2+} is the most probable state for dopant in all models and Co acts as an electron acceptor. The results show that a difference in the electronic structure for *α* and *β* spin components determines consequences in optical excitations and electronic dynamics pathways experienced by electrons with *α* and *β* spin projections. The slower non-radiative relaxation rate of α-excitations is rationally explained as a consequence of difference of electronic structure for α and β spin projections and specific pattern of energy levels contributed by doping. Specifically, excitations involving orbitals with α-projection of spin experience transitions through larger sub-gaps in the conduction band compared to the ones experienced by similar excitations involving orbitals with *β*-projection of spin.