Excited state dynamics in 1D thermoelectric materials

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A fundamental postulate of quantum mechanics is if an isolated quantum system is excited optically or thermally from the ground state to an excited eigenstate, it will remain there for an infinitely long time. However, in an open system an excited state eventually returns to the ground state via nonadiabatic coupling. Therefore, nonadiabatic coupling computations are critical in understanding photo-induced charge transfer, photocatalysis, and thermally activated charge transfer. Nonadiabatic calculations are in increasing demand for time-dependent and nonequilibrium phenomena (1) Here, nonadiabatic computations are used to study the thermoelectric effect and evaluate electron relaxation rates in lead telluride nanowires. $K_e = 1/\tau_{el}$ is defined as the *electron relaxation rate*. It is directly connected to the thermoelectric figure of merit in a material. This work provides computational evidence in support of the proceeding hypothesis. **The hypothesis is the electron relaxation rates will comply with the following band gap law: $Ke = Aexp(-\alpha\Delta E)$,** where Ke is the electronic relaxation rate, A and α are constants, and ΔE is the energy difference between the initial and final states. This work reports results on PbTe (lead telluride) atomistic models doped with sodium and iodine that contain approximately 300 atoms in simulation cells with periodic boundary conditions. The calculations are performed in the basis of ground state DFT with PBE functional, under the VASP software.(2) The transitions between states are modeled in terms of Redfield equation of motion(3) parameterized by on-the-fly nonadiabatic couplings along thermalized molecular dynamics trajectory.(4) The initial excited states are approximated by promotion of an electron from occupied to unoccupied Kohn-Sham orbital. An index of occupied orbital is e=referred by a label iH representing HOMO-iH+1 for electron hole and by label iE representing LUMO+iE-1 for electron. Four orbital transitions were studied: iH1-iE8, iH5-iE10, iH3-iE20, and iH12-iE15. In 6each scenario, the change of energy and position with respect to time was graphically calculated (5)(6). More importantly, the electron and hole relaxation rates were calculated. Thereafter the decay constants were extrapolated.

References:

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