

# Preface

Electronic structure and relaxation of photoexcitations in nano-size materials, such as carbon nanotubes (CNTs) and quantum dots (QDs), are strongly affected by interaction with phonons. We use a wide arsenal of theoretical tools to approach these phenomena. In order to investigate the intricate details of phonon-induced dynamics in QDs, this study uses a novel state-of-the-art quantum-classical approach that combines a molecular dynamics formalism based on density functional theory with a trajectory surface hopping approach. Applying this method, we calculate electronic structure and real-time atomistic relaxation dynamics of charge carriers in QDs made from different materials, such as PbSe and CdSe, that are widely used in nanotechnology. While the sizes of the systems we study are close in size to the typical experimentally investigated QDs, our numeric calculations have an accuracy similar to first-principle quantum mechanical methods. Using this approach, we provide information about the mechanisms that occur on the atomic level and that are extremely difficult – if not impossible – to probe experimentally. We specifically focus on the phonon bottleneck effect in strongly confined QDs – a mysterious phenomenon predicted theoretically but not observed experimentally. We show that PbSe and CdSe have drastically different electronic band structures. Despite this difference, both QDs demonstrate fast subpicosecond relaxation and the absence of the phonon bottleneck, which agree with experiments. We present two rationalizations for such fast relaxation. First, a surface reconstruction and the deviation from the absolute spherical symmetry of the QD lead to a dense distribution of electronic states near the band edges. Most of these states are optically dark; however, they can still help the relaxation process avoiding the phonon bottleneck. Second, localization of wave functions and strong nonadiabatic electron-phonon coupling in small QDs both

enhance the probability of multiphonon processes opening a new channel of relaxation and increasing relaxation rates.

In the second part of the thesis we address excited state phenomena in CNTs using the excited-state molecular dynamics methodology that is based on the time-dependent Hartree-Fock approach. This method incorporates electron-hole interactions (excitonic effects), which are essential in CNTs, and makes simulations of exciton-vibrational dynamics in very large systems (up to one thousand atoms in size) possible, while retaining the necessary quantitative accuracy. Based on this approach, we analyze in detail the nature of the strongly bound first and second excitons in CNTs for a number of different tubes, emphasizing emerging size-scaling laws. Characteristic delocalization properties of excited states are identified by the underlying photoinduced changes in charge densities and bond orders. We also estimate the exciton-phonon coupling and its size-scaling law in different CNTs by calculating Huang-Rhys factors, vibrational relaxation and Stokes shift energies, which increase with increasing tube diameter. Due to the rigid structure, exciton-phonon coupling is much weaker in SWCNTs compared to QDs and to typical molecular materials. Yet in the ground state, a CNT surface experiences the corrugation associated with electron-phonon interactions. Vibrational relaxation following photoexcitation reduces this corrugation, leading to a local distortion of the tube surface, which is similar to the formation of self-trapped excitons in conjugated polymers.

Both numerical approaches provide observables, such as relaxation rates in QDs and Huang-Rhys factors and Stokes shift energies in CNTs, that are possible to detect experimentally. Thus, our results allow for better understanding of photoinduced electronic dynamics in nanomaterials, guiding design of new experimental probes, and, potentially may lead to new nanotechnological applications.

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