Competing relaxation mechanisms for improving quantum efficiency in methylammonium lead iodide perovskite quantum dots

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Many methods for increasing quantum efficiencies (QE) within photovoltaic and optoelectronic processes have been developed such as material interfacing, modified device architecture, and physical constraints to the photoactive material. One such process harnessed by size confinement of the light absorbing material is multi-exciton generation (MEG). This processes applied to small bandgap semiconductor quantum dots (QD) has achieved QE over 1.[1] Methylammonium lead iodide perovskite ($MAPbI_3$) materials have successfully been applied in photovoltaic devices with high solar energy conversion efficiencies driving research to reach an understanding of material behavior.[2] Here we provide a computational approach to studying electronic relaxation processes within a $MAPbI_3$ QD. Understanding which electronic relaxation mechanisms and their corresponding timescales will allow for a clearer picture into which relaxation processes are of greatest importance and can be harnessed for maximum efficiency. Non-radiative (NR) relaxation rates calculated by nonadiabatic dynamics and density matrix formalism produce rates on the scale of 10^{12} s^{-1}. Radiative (R) relaxation rates computed by estimating oscillator strengths in the independent orbital approximation[3] are on the scale of 10^{11} s^{-1}. MEG relaxation rates computed with many-body perturbation theory are found to be on the scale of 10^{14} s^{-1}. From the computed relaxation rates, the mechanism timescales trend in the order of MEG > NR > R. From these results one expects MEG to be a highly probable relaxation process in the $MAPbI_3$ QD. The rates of NR relaxation within the MAPbI3 QD are also compared to 3D bulk $MAPbI_3$ materials, showing a decreased relaxation rate due to the effects of size confinement.

1. Nozik, A. J., Multiple Exciton Generation in Semiconductor Quantum Dots. *Chem Phys Lett* **2008**, *457*, 3-11.
2. Nie, W., et al., High-Efficiency Solution-Processed Perovskite Solar Cells with Millimeter-Scale Grains. *Science* **2015**, *347*, 522-525.
3. Vogel, D. J.; Kilin, D. S., First-Principles Treatment of Photoluminescence in Semiconductors. *The Journal of Physical Chemistry C* **2015**, *119*, 27954-27964.

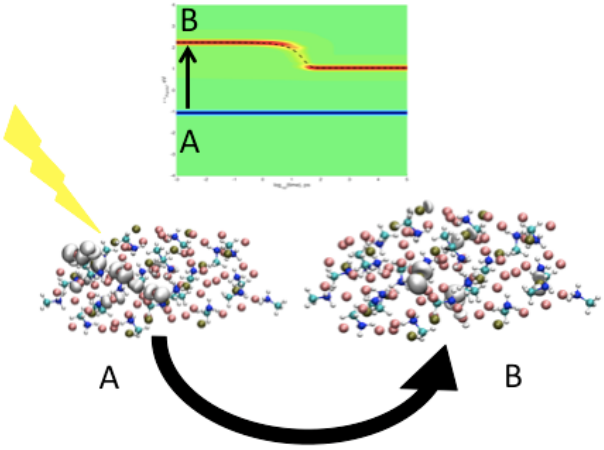

Figure 1
The figure shows the computed electronic orbitals and charge carrier relaxation dynamics following the strongest photoexcited transition. Models represented by **A** and **B** show the MAPbI3 QD with initial and excited state electron densities represented by white clouds, respectively. The green image represents the computed charge carrier dynamics following photoexcitation from state A → B, as shown by a vertical arrow at time zero. The electron (red) and hole (blue) migrate in time to the band edges, allowing for calculation of non-radiative relaxation rates.