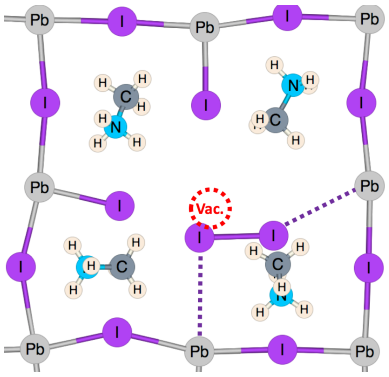
Defect and Confinement: Directing Methylammonium Lead Iodide Perovskite Photophysics

Dayton J. Vogel
Department of Chemistry, University of South Dakota, Vermillion, SD, USA

Recent development of Methylammonium lead iodide perovskite ($MAPbI_3$) materials has produced high efficiency photovoltaic devices. Overall device efficiency may be enhanced through fundamental understanding of the photophysics of $MAPbI_3$. To achieve maximum efficiency and direct specific relaxation mechanisms, one needs to explore the role of both material defects and spatial confinement. This work presents the effect a neutral and charged Pb point defect, in bulk $MAPbI_3$, has on optoelectronic properties. The role of spatial confinement, and the direct effect on relaxation mechanism time scales, is illustrated for the example of a $MAPbI_3$ quantum dot. This work presents spin-polarized and noncollinear spin ground-state electronic structures and nonradiative rates of charge-carrier relaxation and introduces an extension to a novel procedure to compute photoluminescence spectra for open-shell models.[1,2,3] The vacancy of a Pb ion introduces a new energy state within the unblemished material band gap region. This additional unoccupied state is expected to increase the nonradiative relaxation lifetime of the excited electron, allowing for a longer lifetime of the charge carrier and increased opportunity for secondary relaxation mechanisms or collection to take place. Photoexcited dynamic processes in a $MAPbI_3$ quantum dot (QD) have been modeled by many-body perturbation theory and nonadiabatic dynamics. Within the $MAPbI_3$ QD electron relaxation mechanisms include exciton cooling (EC), radiative (RR) or nonradiative recombination (NRR), and multiexciton generation (MEG) processes. Computed times of these processes fall in the order of MEG < EC < RR < NRR, where MEG is on the order of a few femtoseconds, EC is in the picosecond range, while RR and NRR are on the order of nanoseconds.[4]

1. Vogel, D. J.; Inerbaev, T. M.; Kilin, D. S., Role of Lead Vacancies for Optoelectronic Properties of Lead-Halide Perovskites. *J. Phys. Chem. C* **2017**.
2. Vogel, D. J.; Kilin, D. S., First-Principles Treatment of Photoluminescence in Semiconductors. *J. Phys. Chem. C* **2015**, *119*, 27954-27964.
3. Han, Y.; Vogel, D. J.; Inerbaev, T. M.; May, P. S.; Berry, M. T.; Kilin, D. S., Photoinduced Dynamics to Photoluminescence in Ln3+ (Ln = Ce, Pr) Doped B-Nayf4 Nanocrystals Computed in Basis of Non-Collinear Spin Dft with Spin-Orbit Coupling. *Mol. Phys.* **2017**, 1-11.
4. Vogel, D. J.; Kryjevski, A.; Inerbaev, T. M.; Kilin, D. S., Photoinduced Single- and Multiple- Electron Dynamics Processes Enhanced by Quantum Confinement in Lead Halide Perovskite Quantum Dots. *J. Phys. Chem. Lett.* **2017**.

V_{Pb} in Bulk $MAPbI_3$



MAPbI3 QD