First Principle Polaron Modeling in Hybrid Perovskites Using the GGA+U Method

Eric Welch1,\*, Amanda Neukirch2, Sergei Tretiak2, , Petr Obraztsov4,5, Dmitry Lyashenko1, Pavel Chizhov4, Kuniaki Konishi6, Natsuki Nemoto7, Makoto Kuwata-Gonokami7, Alexander Obraztsov4,8, Alex Zakhidov1,3

1 Department of Material Science, Engineering and Commericialization, Texas State University (\*email: eww9@txstate.edu); 2 Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM, 87545; 3 Department of Physics, Texas State University, San Marcos, TX, 78666; 4 A. M. Prokhorov General Physics Institute, Moscow, Russia, 119991; 5 Department of Physics and Mathematics, University of Eastern Finland, Joensuu, Finland, 80101; 6 Institute for Photon Science and Technology, The University of Tokyo, Tokyo, Japan, 113-0033; 7 Department of Physics, The University of Tokyo, Tokyo, Japan, 113-0033; 8 Department of Physics, M.V. Lomonsov Moscow State University, Moscow, Russia, 119991

Hybrid perovskite based solar cells have reached over 23% efficiency in just over five years, causing research in this area to thrive. With optimum photovoltaic properties like a VOC > 1 V, JSC > 25 $\frac{mA}{cm^{2}}$, inexpensive, solution-processable precursors and low temperature processing temperatures, devices using the light harvesting material CH3NH3PbI3 promises to fill the need for large-scale, commercial, renewable energy sources. However, anomalous device behavior (e.g. JV hysteresis) and device stability still prevent these materials from becoming the next generation solar cells in the market. Ab initio calculations are abundant concerning electronic and optical properties of these materials in a search for an underlying theory to explain the adverse behaviors seen in hybrid perovskite solar cells. This study uses Hubbard corrected local potentials (GGA+U) to study polarons in the benchmark hybrid perovskite light harvesting material CH3NH3PbI3. Spin-orbit coupling (SOC) occurs in elements with valence electrons residing in d/f-orbitals, and relativistic effects must be taken into account. The heavy lead and iodine atoms in CH3NH3PbI3 require SOC corrections which result in the lifting of degeneracies near the HOMO-LUMO gap. Polarons are still present with SOC corrections while the lifting of degeneracies results in momentum-dependent Rashba splitting of the electronic band edges. These results were tested experimentally using THz emission spectroscopy which confirmed the presence of the circular photogalvanic effect in a solar cell device. With these theoretical and experimental results, CH3NH3PbI3 is realized as a robust material for multiple spin-controlled opto-electronic applications e.g. spintronics, ultra-fast photodetectors, tunable THz emitters, etc.