Supplemental Information

Role of Pb2+ Adsorbents on the Opto-Electronic Properties of a CsPbBr3 Nanocrystal: A DFT Study

Aaron Forde1, Erik Hobbie1, Dmitri Kilin2

1 Department of Materials Science and Nanotechnology, North Dakota State University, Fargo, North Dakota 58102, United States

2Department of Chemistry and Biochemistry, North Dakota State University, Fargo, North Dakota 58102, United States

Methods

Theory:

To accurately describe the electronic structure of CsPbBr3 NCs spin-orbit coupling (SOC) interaction has to be considered due to Pb2+ having large angular momentum which mixes spin states. Within DFT this requires using the non-collinear spin (NCS) framework 1 2.

= (2)

For equations (1)-(2), is the Kroenecker-delta function, and define spin projections or , is the spin-dependent external potential, and is a spin-dependent KSO. The solution to the set of noncollinear spin DFT equations is represented as a superposition of spin- and spin- states and with spatially dependent coefficents and . These solutions are commonly referred to as spinor KSOs (SKSOs) shown in equation (3).

(3)

The large angular momentum of the Pb2+ atoms mix the spin components which giving rise to a large SOC interaction. SOC is treated as a 2nd order correction to the relativistic Hamiltonian and is represented in equation (4) as

(*4*)

where is composed of Pauli spin matrices.

From the SKSOs observables, such as density of states (DOS) and absorption spectra, can be computed. DOS is computed as

(*5*)

where is the band energy for each SKSO.

Absorption spectrum is computed from transition dipoles between two SKSOs within the independent orbital approximation (IOA) 3 4 which is represented in equation (6) as

(6)

From transition dipoles the oscillator strength (probability) of an optical transition is computed as equation (7)

(7)

where is the transition frequency between SKSO and , is the mass of an electron, and the other symbols represent the familiar fundamental constants. Then the absorption spectrum can be computed as

(8)

where is the transition energy of the optical excitation.

References

1. U.v. Barth and L. Hedin: A local exchange-correlation potential for the spin polarized case. i. *J. of Phys. C: Solid State Physics* **5**, 1629 (1972).

2. J. Kubler, K.-H. Hock, J. Sticht and A.R. Williams: Density functional theory of non-collinear magnetism. *J. of Phys. F: Metal Physics* **18**, 469 (1988).

3. A. Forde, T. Inerbaev and D. Kilin: Spinor Dynamics in Pristine and Mn2+-Doped CsPbBr3 NC: Role of Spin–Orbit Coupling in Ground- and Excited-State Dynamics. *J. Phys. Chem. C* **122**, 26196 (2018).

4. Y. Han, D.J. Vogel, T.M. Inerbaev, P.S. May, M.T. Berry and D.S. Kilin: Photoinduced dynamics to photoluminescence in Ln3+ (Ln = Ce, Pr) doped β-NaYF4 nanocrystals computed in basis of non-collinear spin DFT with spin-orbit coupling. *Mol. Phys.* **116**, 697 (2018).

.