Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

Shallow Trapping *vs*. Deep Polarons in Hybrid Lead Halide Perovskite, $CH_3NH_3PbI_3$

*Byungkyun Kang and Koushik Biswas**

Department of Chemistry and Physics**,** Arkansas State University, State University, AR 72467, United States

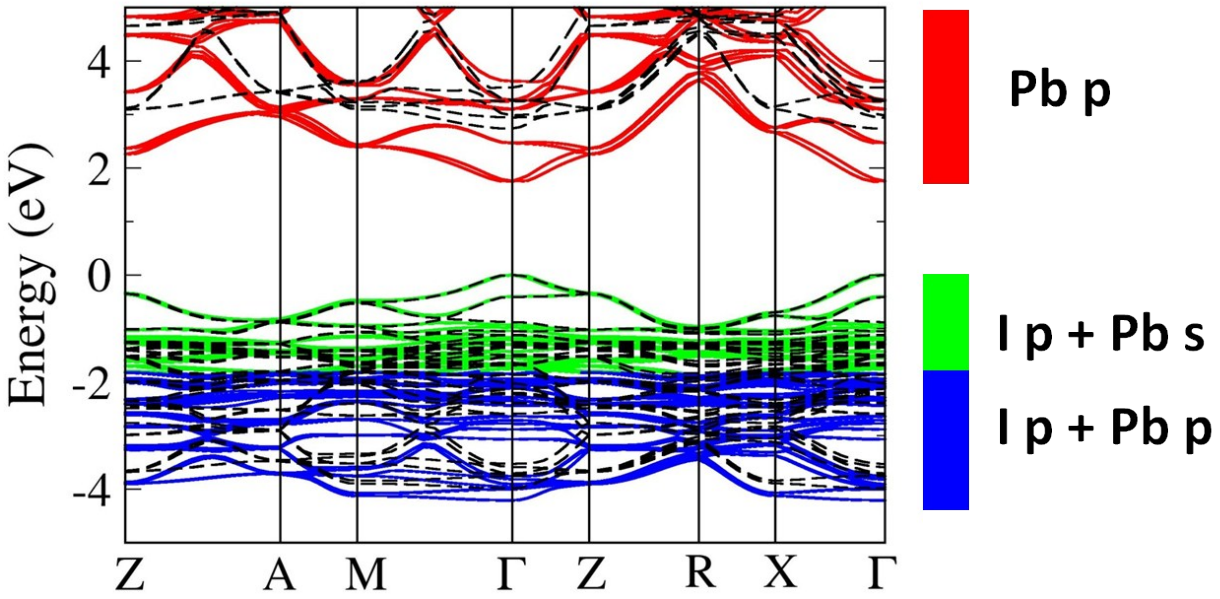

Fig. S1 Calculated band structure (solid lines) of tetragonal $CH_3NH_3PbI_3$ using PBE0-SOC. The energy of the valence band maximum is set to zero. The dashed (black) lines show corresponding bands obtained using PBE0, without spin-orbit interaction. The solid lines are colored according to their primary orbital character.

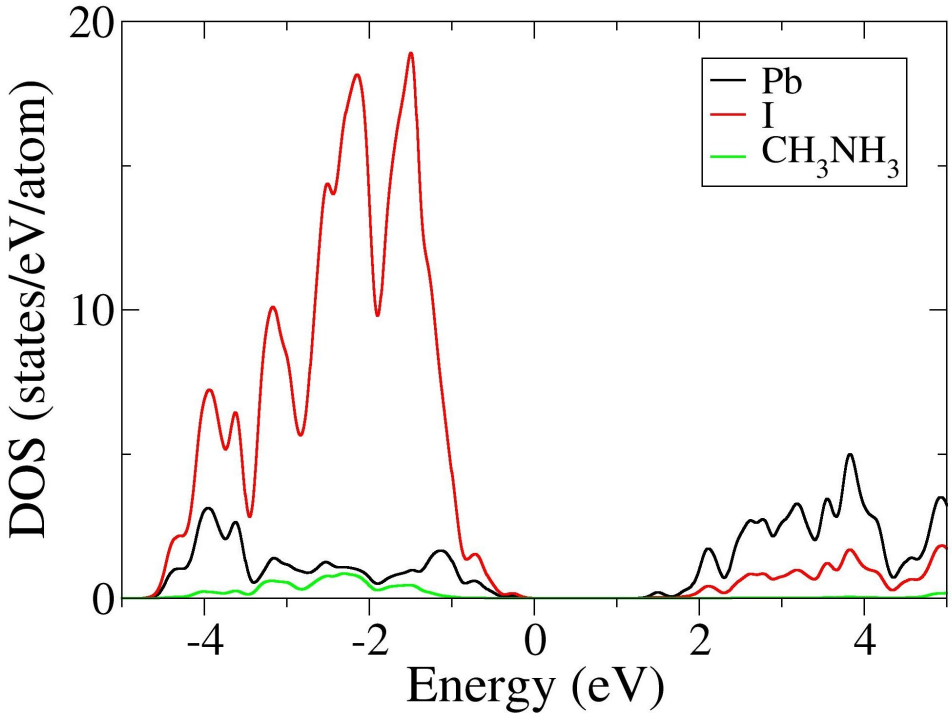

Fig. S2 Calculated density of states of tetragonal $CH_3NH_3PbI_3$ using PBE0-SOC functional. The bottom of the conduction bands have primarily Pb 6p character, while the top of the valence bands are derived mostly from I 5p. It should be noted that some contribution from Pb 6s and 6p can also be found near the top of the valence bands.

Table S1 Calculated band gap (E_g) of tetragonal $CH_3NH_3PbI_3$ obtained with various functionals is compared with experiment.

	E_g (eV) {Functional}
Experiment[1-4]	1.55 - 1.6
This work	1.75 {PBE0-SOC} 2.74 {PBE0}
Gao et al.[5]	1.67 - 1.73 {GW+SOC} 1.68 - 1.76 {PBE}
Umari et al.[6]	1.67 {SOC-GW} 0.60 {SOC-DFT} 2.68 {SR-GW} 1.68 {SR-DFT}
Quarti et al.[7]	1.34 - 1.82 {Scalar Relativistic} 0.30 - 0.80 {SOC-DFT}
Geng et al.[8]	1.6, 1.82 {vdW-DF}
Du et al.[9]	0.6 {PBE-SOC} 1.5 {HSE-SOC}
Zhou et al.[10]	1.27 - 1.42 {PBESol}
Wang et al.[11]	1.27 {PBE-SOC}

Table S2 Calculated lattice constants (LC) of tetragonal $CH_3NH_3PbI_3$ obtained with various functionals is compared with experiment.

	LC (Å) {Functional}
Experiment[12]	a = b = 8.849, c = 12.642
Experiment[13]	a = b = 8.855, c = 12.659
Experiment[14]	a = b = 8.8, c = 12.685
This work	a=8.84, b=8.85, c=13.03 {PBE}
Brivio et al.[15]	a =8.70, b = 8.72, c = 12.83 {PBEsol}
Mosconi et al.[16]	a =8.783, b = 8.746, c = 12.699 {PBE}
Zhou et al.[10]	a =9.074, b = 9.029, c = 13.175 {PBE} a =9.007, b = 9.015, c = 13.010 {optPBE-vdW} a =8.891, b = 8.869, c = 12.811 {optB86b-vdW} a =8.868, b = 8.802, c = 12.806 {PBE-vdW} a =8.880, b = 8.816, c = 12.723 {PBEsol}

References

1 Y. Yang, M. Yang, Z. Li, R. Crisp, K. Zhu and M. C. Beard, *J. Phys. Chem. Lett*. 2015, **6**, 4688-4692.

2 Y. Yang, D. P. Ostrowski, R. M. France, K. Zhu, J. van de Lagemaat, J. M. Luther and M. C. Beard, *Nat. Photon.* 2016,**10**, 53-59.

3 X. Wu, T M. T. rinh, D. Niesner, H. Zhu, Z. Norman, Z. S. Owen, O. Yaffe, B. J.Kudisch and X. -Y. Zhu, *J. Am. Chem. Soc*. 2015, **137**, 2089−2096.

4 Y. Yamada, T. Nakamura, M. Endo, A. Wakamiya and Y. Kanemitsu. *Appl. Phys. Express* 2014, **7**, 032302.

5 W. Gao, X. Gao, T. A. Abtew, Y.-Y. Sun, S. Zhang and P. Zhang, *Phys. Rev. B: Condens. Matter Mater. Phys.* 2016, **93**, 085202.

6 P. Umari, E. Mosconi and F. De Angelis, *Sci. Rep*. 2014, **4**, 4467.

7 C. Quarti, E. Mosconi and F. De Angelis, *Chem. Mater.* 2014, **26**, 6557-6569.

8 W. Geng, L. Zhang, Y. N. Zhang, W. M. Lau and L. M. Liu, *J. Phys. Chem. C* 2014, **118**, 19565−19571.

9 M.-H. Du, *J. Mater. Chem. A* 2014, **2***,* 9091-9098.

10 Y. Zhou, F. Huang, Y. B. Cheng and A. Gray-Weale, *Phys. Chem. Chem. Phys*. 2015, **17**, 22604-22615.

11 Y. Wang, Y. Zhang, P. Zhang and W. Zhang, *Phys. Chem. Chem. Phys*. 2015, **17**, 11516-11520.

12 C. C. Stoumpos, C. D. Malliakas and M. G. Kanatzidis, *Inorg. Chem.,* 2013, **52**, 9019-9038.

13 A. Poglitsch and D. Weber, *J. Chem. Phys*., 1987, **87**, 6373-6378.

14 Y. Kawamura, H. Mashiyama and K. Hasebe, *Phys. Soc. Jpn*. 2002, **71**, 1694-1697.

15 F. Brivio, J. M. Frost, J. M. Skelton, A. J. Jackson, O. J. Weber, M. T. Weller, A. R. Goni, A. M. A. Leguy, P. R. F. Barners and A. Walsh, *Phys. Rev. B: Condens. Matter Mater. Phys*., 2015, **92**, 144308.

16 E. Mosconi, C. Quarti, T. Ivanovska, G. Ruani and F. De Angelis, *Phys. Chem. Chem. Phys*., 2014, **16**, 16137–16144.