

Supplementary Information for

Electronic Structure of Two Dimensional Lead (II) Iodide Perovskites: An Experimental and Theoretical Study

Dibya Phuyal^{a‡}, Majid Safdari^{b‡}, Meysam Pazoki^c, Peng Liu^b, Bertrand Philippe^a, Kristina O. Kvashni-
na^{d, e}, Olof Karis^a, Sergei M. Butorin^a, Håkan Rensmo^{*a}, Tomas Edvinsson^c, Lars Kloo^b, and James M.
Gardner^{*b}

^a Dept. of Physics and Astronomy, Uppsala Univ., Box 516, SE-75121, Uppsala, Sweden.

^b Division of Applied Physical Chemistry, Department of Chemistry, KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden. E-mail: jgardner@kth.se.

^c Department of Engineering Sciences, Solid state Physics, Ångström laboratory, Uppsala University, Uppsala, Sweden.

^d Rossendorf Beamline at ESRF – The European Synchrotron, CS40220, 38043 Grenoble Cedex 9, France

^e Helmholtz Zentrum Dresden-Rossendorf (HZDR), Institute of Resource Ecology, PO Box 510119, 01314 Dresden, Germany

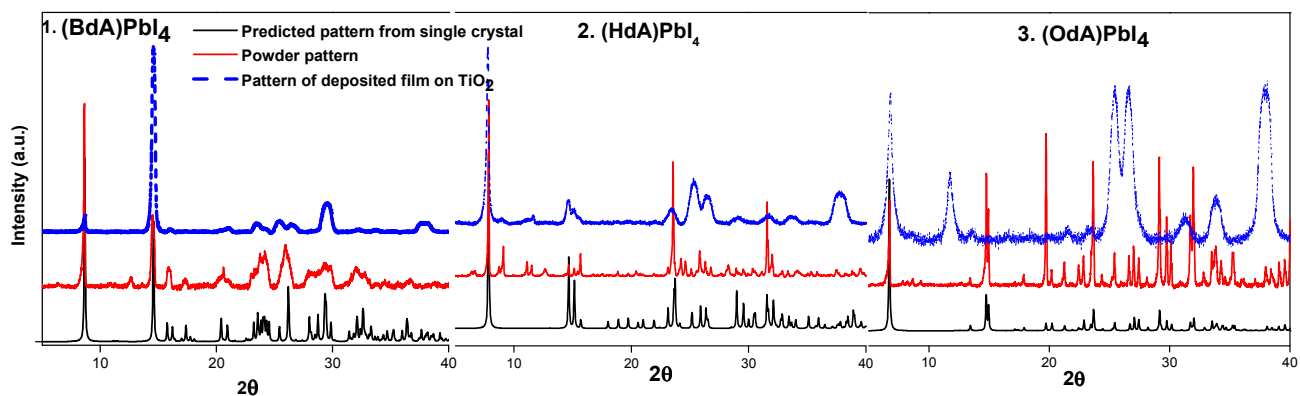


Figure S1 XRD pattern of the three 2D perovskite materials. The patterns were compared with the powder patterns and single crystal data.

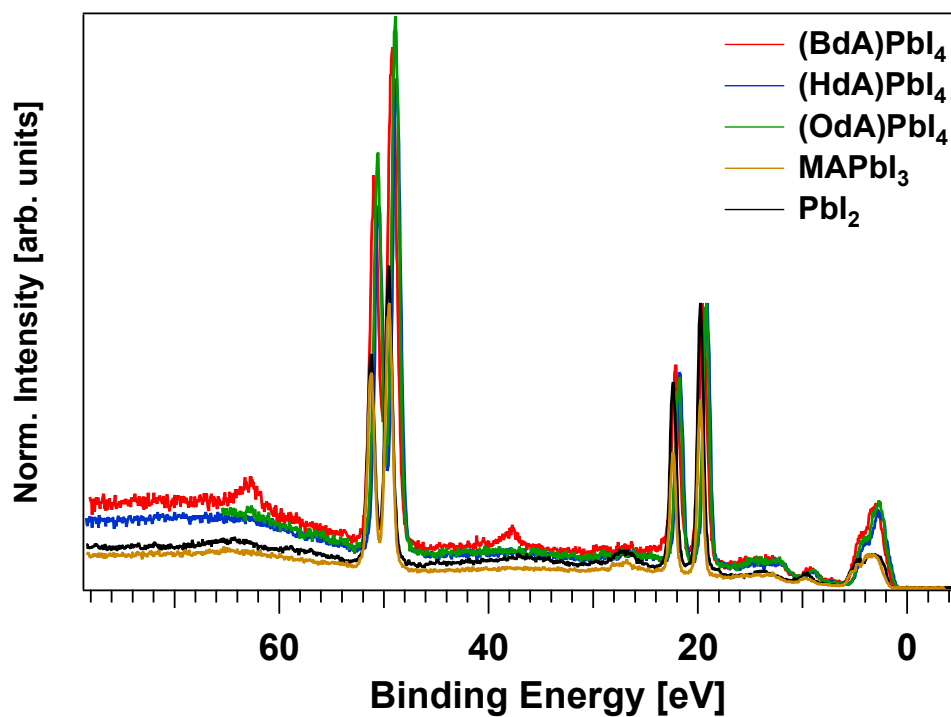


Figure S2 Experimental HAXPES spectra showing the shallow core I 4d (~ 50 eV) and Pb 5d (~ 20 eV) binding energy levels. Estimation on the material stoichiometry for iodine and lead has been made utilizing these two peaks.

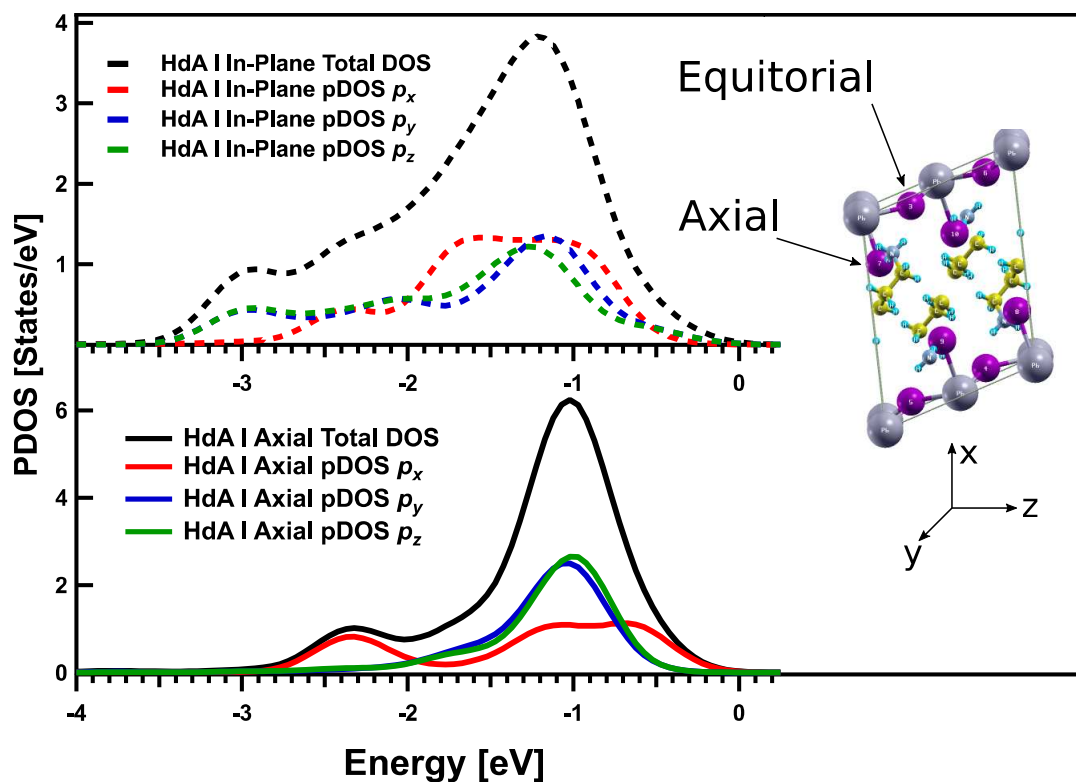
Table S1. Obtained binding energies for Pb 4*f* and I 3*d* orbitals and their relative difference.

	Binding Energy for I 3 <i>d</i> (eV)	Binding Energy for Pb 4 <i>f</i> (eV)	Difference Between Pb 4 <i>f</i> & I 3 <i>d</i>
BdAPbI ₄	619.17	138.41	480.76
HdAPbI ₄	618.87	138.07	480.80
OdAPbI ₄	619.11	138.31	480.80
MAPbI ₃	619.5	138.59	480.91
PbI ₂	619.57	138.62	480.95

Table S2. Recorded valence band offset for different samples via Hard X-ray PES.

Sample	VB offset
BdAPbI ₄	1.46 eV
HdAPbI ₄	1.31 eV
OdAPbI ₄	1.33 eV
PbI ₂	1.69 eV
TiO ₂	3.65 eV

Figure S3 Partial and total DOS for iodine in (HdA)PbI₄ showing the contribution to from both axial and equatorial iodine atoms. The effect of dimensionality clearly has an effect on the orbital narrowing for iodine in the axial direction.



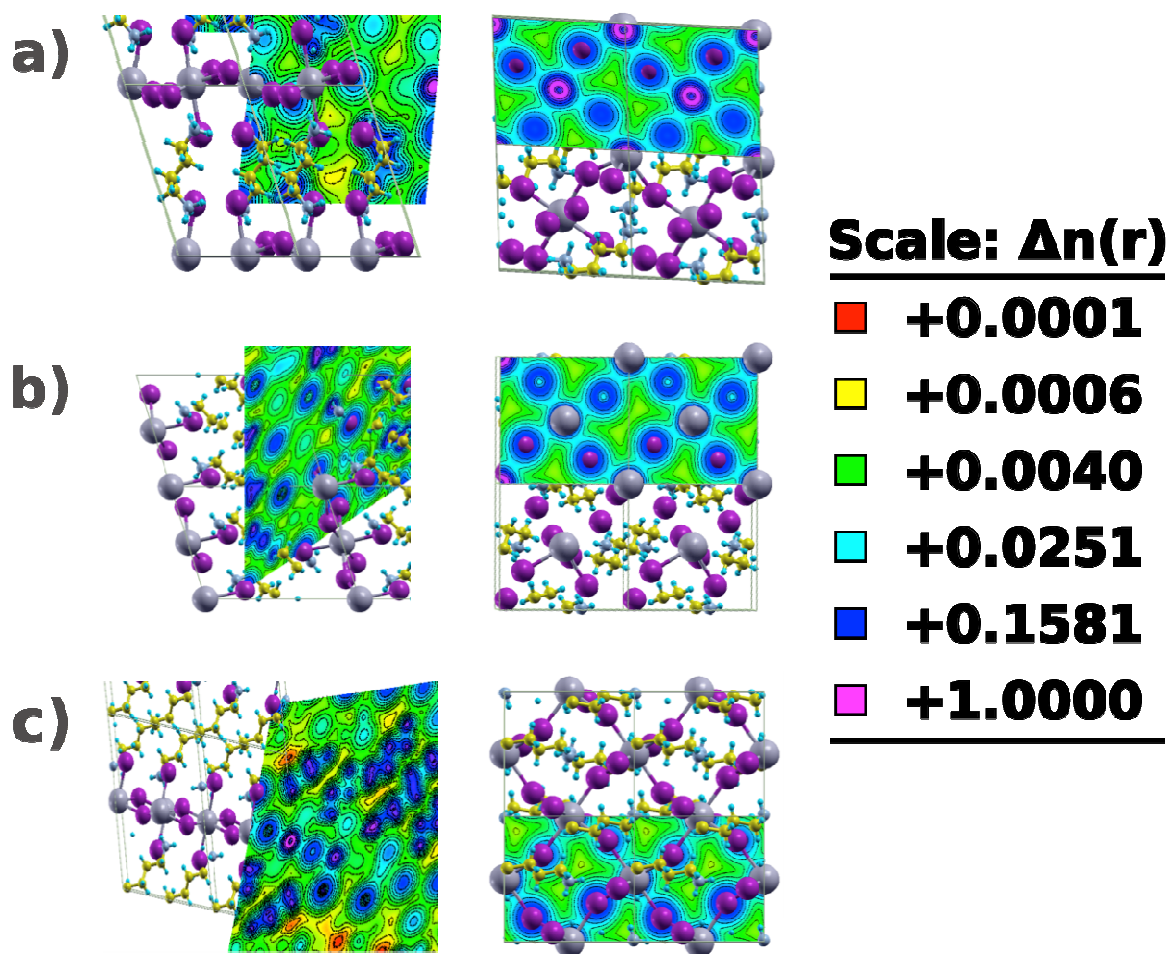


Figure S4 Charge density plots of the 2D perovskites a. (BdA)PbI₄, b. (HdA)PbI₄, and c. (OdA)PbI₄ along the organic cations (Pb, I, C atoms are shown as gray, purple and yellow balls). The maximum electron density is around Pb and I planes, which are spatially separated due to the presence of the organic cations. The high electron density zones are shown in blue and purple, which clearly connect and facilitate charge movement in the lattice.

Table S3. Bond lengths and angles between lead and iodide for three 2D perovskite materials. The detailed data are obtained from single crystal data.

	(BdA)PbI ₄				(HdA)PbI ₄	(OdA)PbI ₄
Angle I-Pb-I (90) in the plane (equatorial)	89.23		89.69		88.22	87.72
	89.38		89.78		91.78	92.28
	90.63		90.18		88.22	87.72
	90.76		90.35		91.78	92.28
Average \pm STDEV	90.00 \pm 0.57				90.00 \pm 2.05	90.00 \pm 2.63
Angle I-Pb-I (90) Out of plane (Axial)	86.76	91.37	89.42	90.18	87.67	93.82
	87.09	91.51	89.69	90.23	89.7	91.18
	88.55	92.91	89.72	90.35	92.33	88.82
	88.57	93.24	89.78	90.60	90.3	86.18
Average \pm STDEV	90.00 \pm 1.78				90.00 \pm 1.92	90.00 \pm 3.26
Angle I-Pb-I (180)	179.92				180	180
	179.90					
Average \pm STDEV	179.91 \pm 0.02				180 \pm 0	180 \pm 0
Angle Pb-I-Pb	146.37					
	146.48					
	147.46				148.47	147.44
	147.9					
Average \pm STDEV	147.05 \pm 0.75				148.47 \pm 0	147.44 \pm 0
Distance (Å) I-Pb (90) in the plane (equatorial)	3.181		3.202		3.213	3.202
	3.183		3.203		3.213	3.202
	3.186		3.205		3.220	3.192
	3.191		3.211		3.220	3.192
Average \pm STDEV	3.195 \pm 0.011				3.216 \pm 0.004	3.197 \pm 0.006
Distance (Å) I-Pb (180) out of the plane (Axial)	3.170					
	3.181					
	3.192				3.180	3.187
	3.189					
Average \pm STDEV	3.183 \pm 0.001				-	-

Additional Computation Methods:

The details of the GGA calculations have been described in the main text. The implemented pseudopotential for the calculations presented in this section is a norm-conserving GGA including scalar relativistic effects. SOC calculations are based on the GGA pseudopotential including fully relativistic effects. (SOC considered just for lead element here.) The typical cut-off energy for the wave function and charge density is 45 and 450 Rydberg respectively. The hybrid functional calculations are based on HSE without considering SOC effects with different contributions from Fock exchange i.e. 25% and 43%. The k-point samplings were done in a grid of 2x2x4 in the first Brillouin zone.

Additional Computational Results:

In Table S4, we show the different functionals used in the new calculations and the obtained bandgap. The value of the theoretical bandgap can be tuned to the experiment value by choosing SOC and different levels of hybrid functionals. To clarify this effect, we have calculated for (HdA)PbI₄ with different levels of theory. The HSE-SOC method is currently unavailable in the QUANTUM ESPRESSO package without changing the previously used pseudo potentials and would the incorporate an unknown error. To resolve this, we have calculated the different contributions separately where the results expected for the different functionals and SOC can be extended for the HSE-SOC, according to our data.

Table S4. Estimated bandgap values for (HdA)PbI₄ for the different functionals used.

(HdA)PbI ₄	
Functional	Bandgap (E _g)
GGA SOC	1.59 eV
HSE (25% Hartree-Fock)	2.67 eV
HSE (43% Hartree-Fock)	3.08 eV
GGA + Scalar Relativistic	2.14 eV
Experimental	2.55 eV

We also present the structural changes such as the distance between nearest iodine atoms for (HdA)PbI₄ using several different approaches as shown in Table S5.

Table S5. Distance between nearest iodine atoms, separated by organic cation for HdAPbI₄.

(HdA)PbI ₄				
Functional	I-I Distance	I-Pb-I Angle	Pb-I Bond Vertical	Pb-I Horizontal
GGA SOC	6.02 Å	198.88 °	3.20 Å	3.23 Å
HSE (0.25 Hartree-Fock)	6.03 Å	179.8°	3.18 Å	3.22 Å
HSE (0.43 Hartree-Fock)	6.05 Å	179.6°	3.16 Å	3.21 Å
GGA + Scalar Relativistic	6.05 Å	180°	3.18 Å	3.21 Å
Experimental	6.05 Å	180°	3.18 Å	3.22 Å

In Figure S5, we present the calculated partial density of states (pDOS) for (HdA)PbI₄ using spin-orbit coupling and a 43% HSE+SOC calculations. Note that a slightly lower smearing of the density of states has been used compared to the main manuscript to enable more specific details in the supporting information.

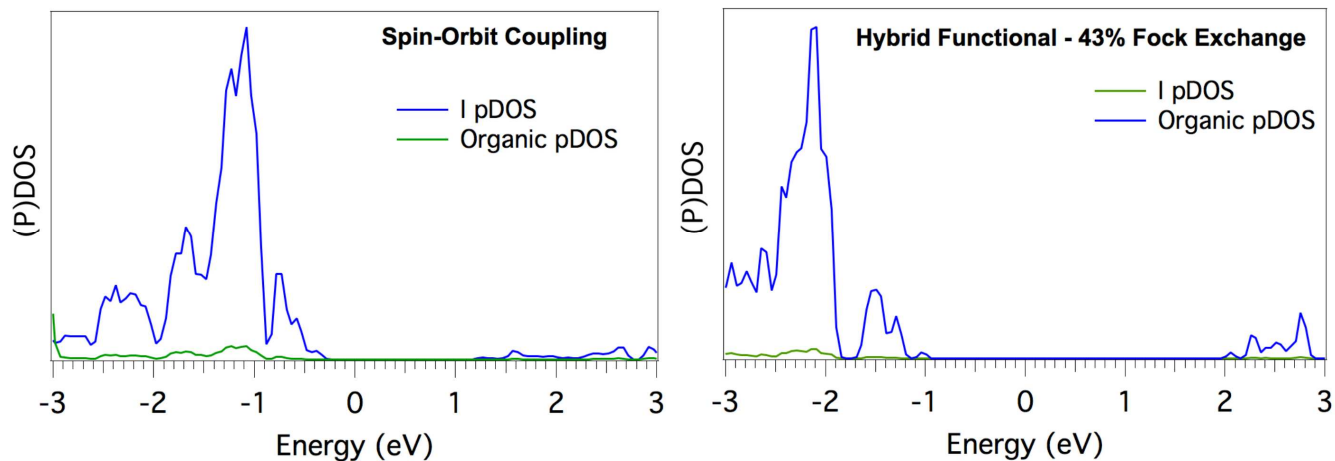


Figure S5 – Partial density of states (pDOS) for a GGA + SOC (*left*) and a hybrid functional with 43% Fock exchange (*right*). The energy alignment has been calibrated against the GGA calculations in the main text, in which the top most Iodine states in the VB was set to 0 eV.

In Figure S6, the different degree of Fock exchange are compared as well as the total DOS using SOC, HSE-43%, and a GGA with a norm-conserving scalar relativistic calculations for (HdA)PbI₄.

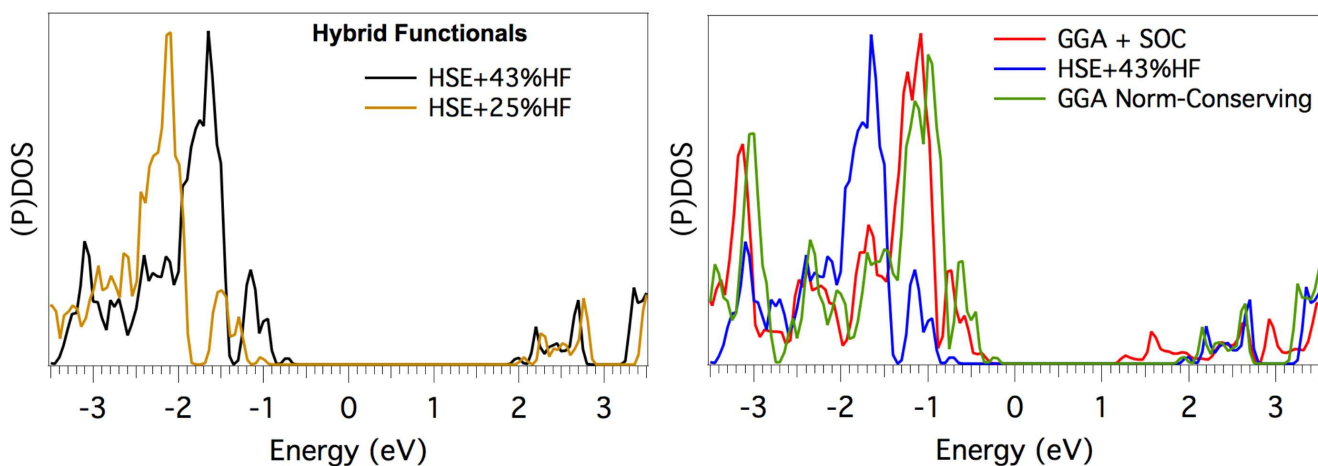


Figure S6 - Total density of states for the two different hybrid functionals used (HSE-43% HF and HSE – 25% HF (*left*), and DOS with the different levels of theory for comparison.

We have performed spin orbit coupling (SOC), a HSE+25%HF exchange contribution and HSE+0.43% HF exchange contribution. The net effect is mainly shifting (pushing/pulling) the bands by different levels of implemented theory (SOC/HSE). As we do not aim at an absolute determination of the band gap

or the exact value for electron/hole effective masses, the shift has no impact in the interpretations of the experimental results, where the final results and conclusions are based on GGA and scalar relativistic calculations. There is a minor change in the band structure, the shape and slope of the bands as well as geometrical factors (see above) but again, this do not alter the conclusions that can be drawn from the GGA based calculations. We refer the reader to the work by Wang and colleagues¹ for further details, in the case that the absolute value of the bandgap is important in the calculations.

In addition to the calculations, we provide the band structure plot for MAPbI₃.

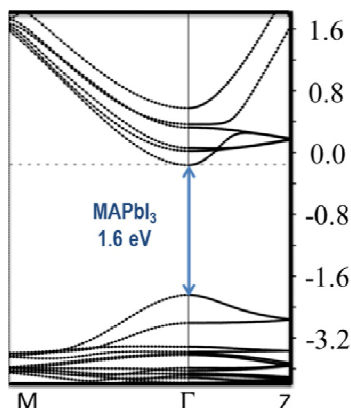


Figure S7 - Calculated band structure for MAPbI₃.

REFERENCES

¹ Wang, Z.; Ganose, A.M.; Niu, C.; Scanlon, D.O. First-principles insights into tin-based two-dimensional hybrid halide perovskites for photovoltaics. *J. Mater. Chem. A* **2018**, *6*, 5652-5660.