Supporting Information

Role of Inorganic Cations in the Excitonic Properties of Lead Halide Perovskites

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SUPPLEMENTARY RESULTS

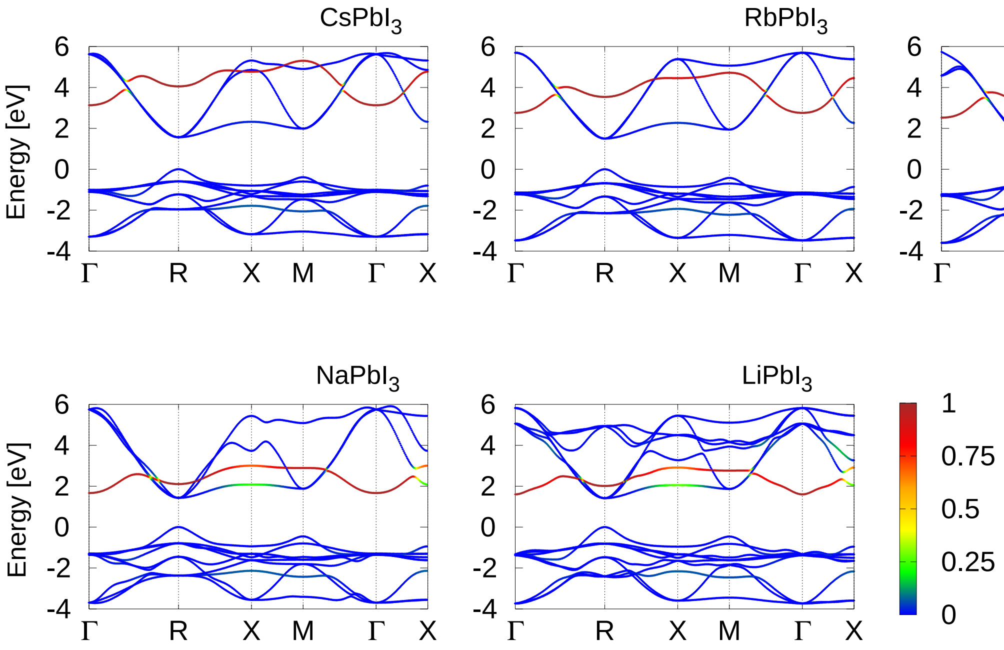

FIG. S1. DFT band structures of $APbI_3$ perovskites with A = Cs, Rb, K, Na, Li. Bands projected at MLWFs located at the A^+ cation empty states are in red according to the legend, which is common for all cases.

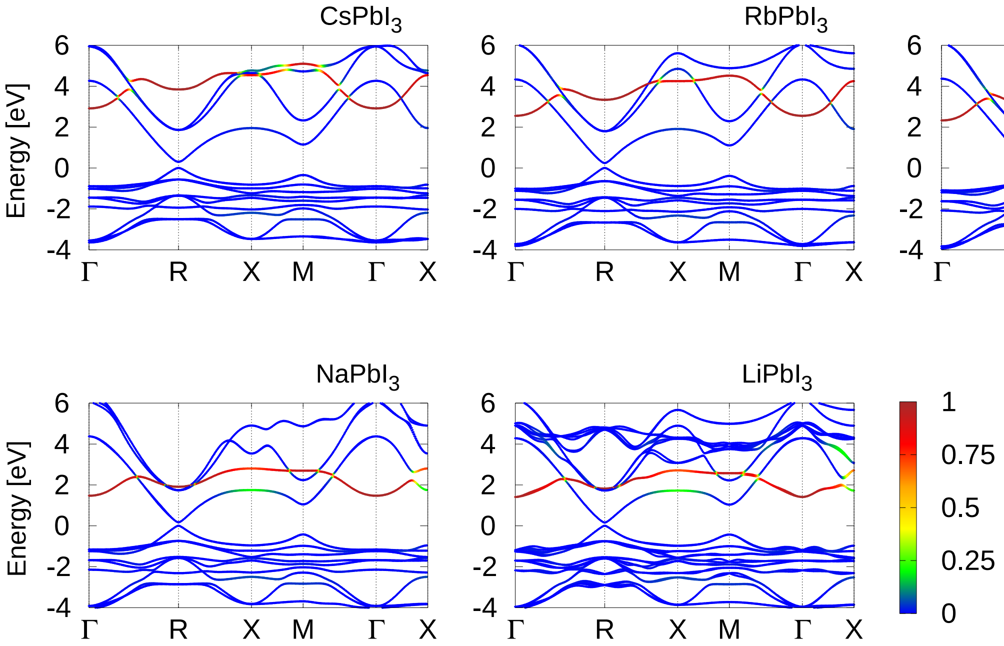

FIG. S2. Same as Fig. S1 within DFT+SOC

TABLE S1. Characterization of the DFT and DFT+SOC band structures for APbI$_3$ with A = Cs, Rb, K, Na and Li. E_g^R and E_g^Γ are the bandgaps at R and Γ, respectively, Δ^{CBM-R} and $\Delta^{CBM-\Gamma}$ are the differences between the CBM and the A$^+$-band at R and Γ, respectively, W_A is the band width of the A$^+$ cation empty states and a is the optimized lattice constant (in Å). All energies are given in eV.

A	E_g^R	E_g^Γ	Δ^{CBM-R}	$\Delta^{CBM-\Gamma}$	W_A	a
			DFT			
Cs	1.57	4.14	-2.48	-1.56	2.10	6.379
Rb	1.50	3.90	-2.03	-1.25	1.86	6.327
K	1.46	3.75	-1.77	-1.06	1.77	6.295
Na	1.43	2.96	-0.67	-0.23	1.34	6.279
Li	1.42	2.93	-0.60	-0.19	1.31	6.259
			DFT+SOC			
Cs	0.30	3.81	-3.54	-2.61	2.10	6.379
Rb	0.24	3.57	-2.94	-2.31	1.86	6.327
K	0.20	3.42	-2.82	-2.12	1.74	6.295
Na	0.17	2.63	-1.73	-1.30	1.33	6.279
Li	0.16	2.60	-1.66	-1.25	1.30	6.259

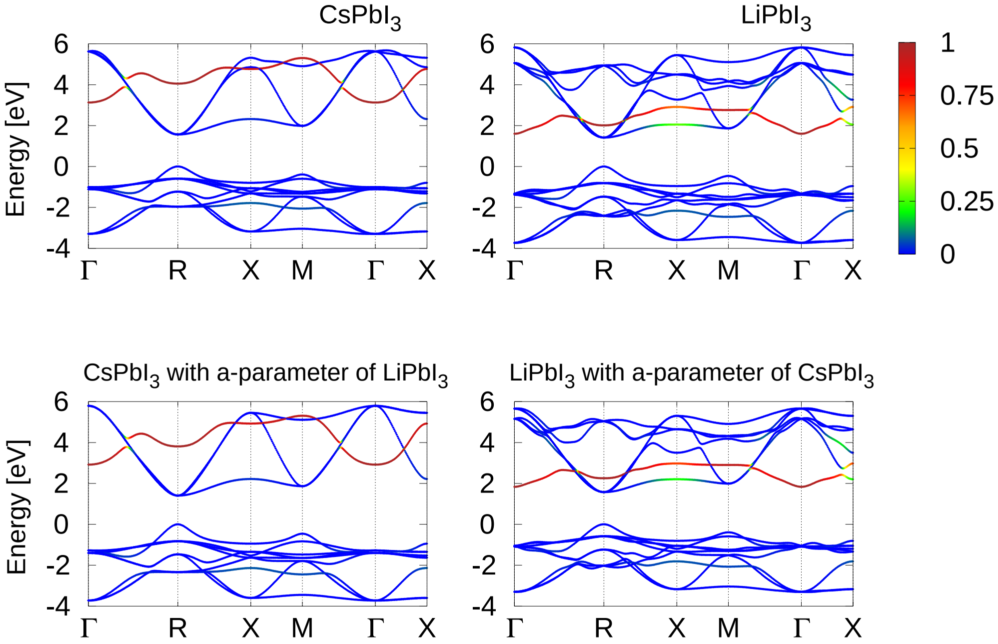

FIG. S3. DFT band structures of $\mathrm{APbI_3}$ perovskite with A = Cs and Li, in their optimized geometries, are compared with bands of the same cases calculated with the lattice constants of the opposite case. As before, bands projected at MLWFs located at the $\mathrm{A^+}$ cation empty states are in red, according to the legend.

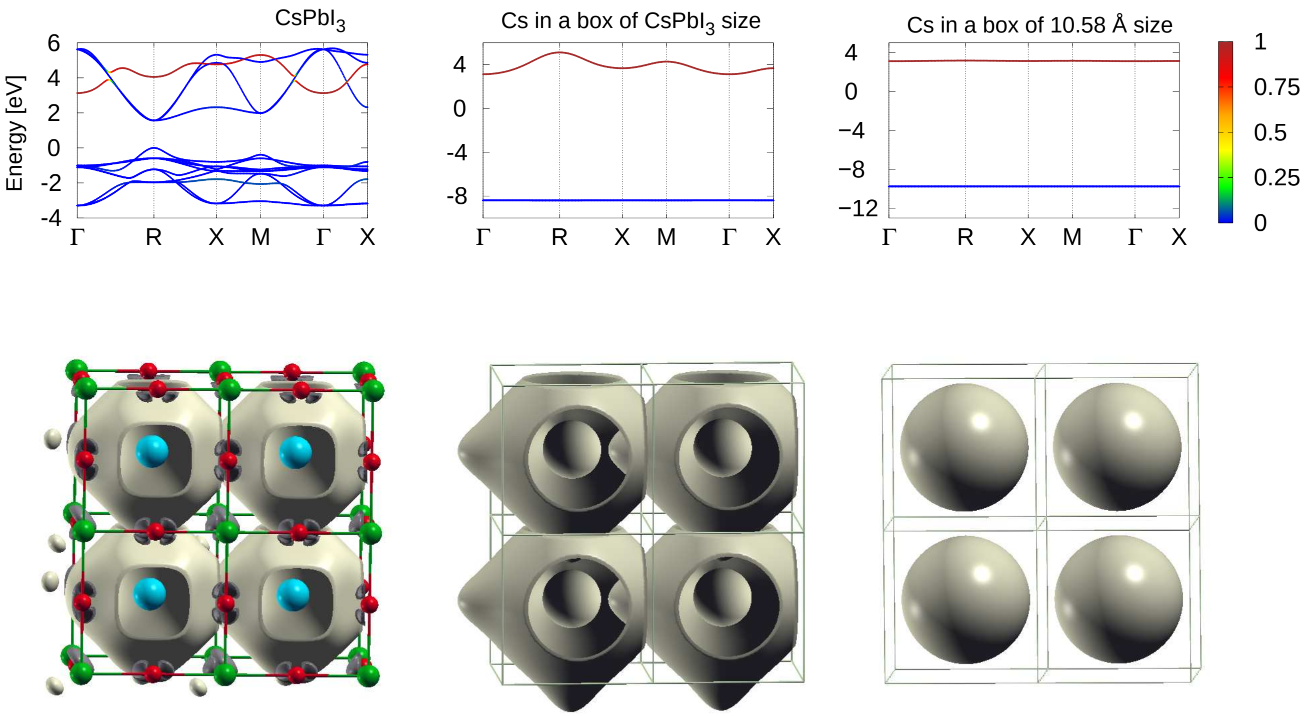

FIG. S4. DFT band structures for $\mathrm{CsPbI_3}$ (left) and isolated $\mathrm{Cs^+}$ in periodic structures with lattice constants 6.38 Å (equal to that of $\mathrm{CsPbI_3}$, center) and 10.58 Å (right). Bands are projected onto the s-type MLWF located at the $\mathrm{Cs^+}$ cation. For the calculations for pure cations, a compensating negative charge background has been used. Below each case, the MLWFs used for the bands projection are plotted; the isosurface is set to 5 for all cases. The MLWFs spreading for $\mathrm{CsPbI_3}$ and $\mathrm{Cs^+}$ in the small and large lattices are 9.91, 10.07 and 7.11 Å^2, respectively.

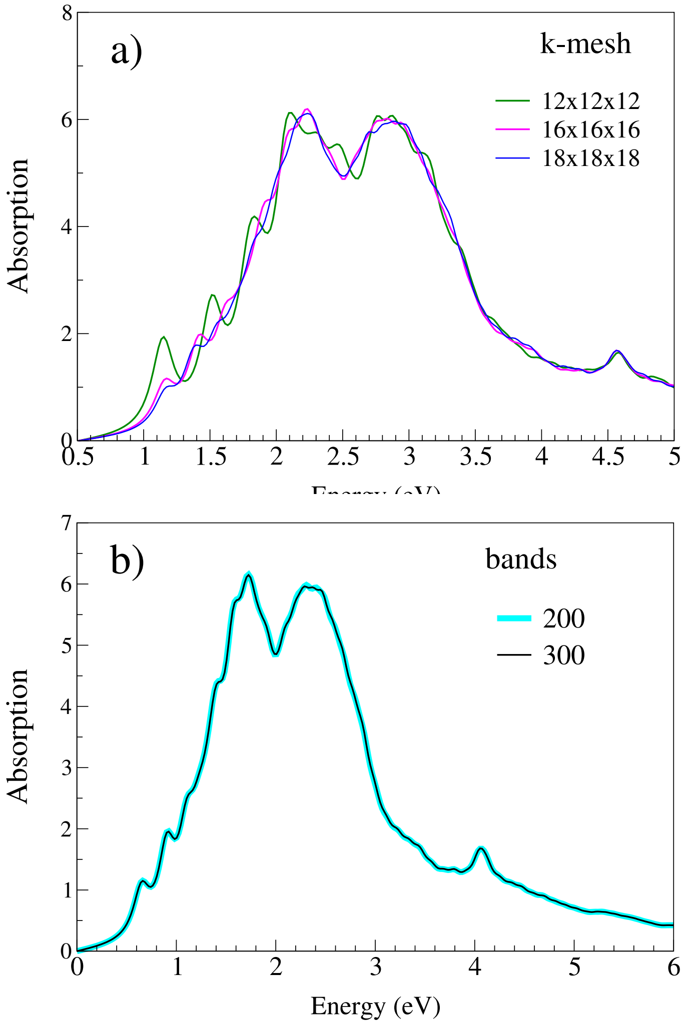

FIG. S5. *a*) Absorption spectra of $CsPbI_3$ calculated from the BSE using different samplings of the BZ. *b*) Convergence test of the BSE solution with respect to the number of bands (using k-mesh 16×16×16).