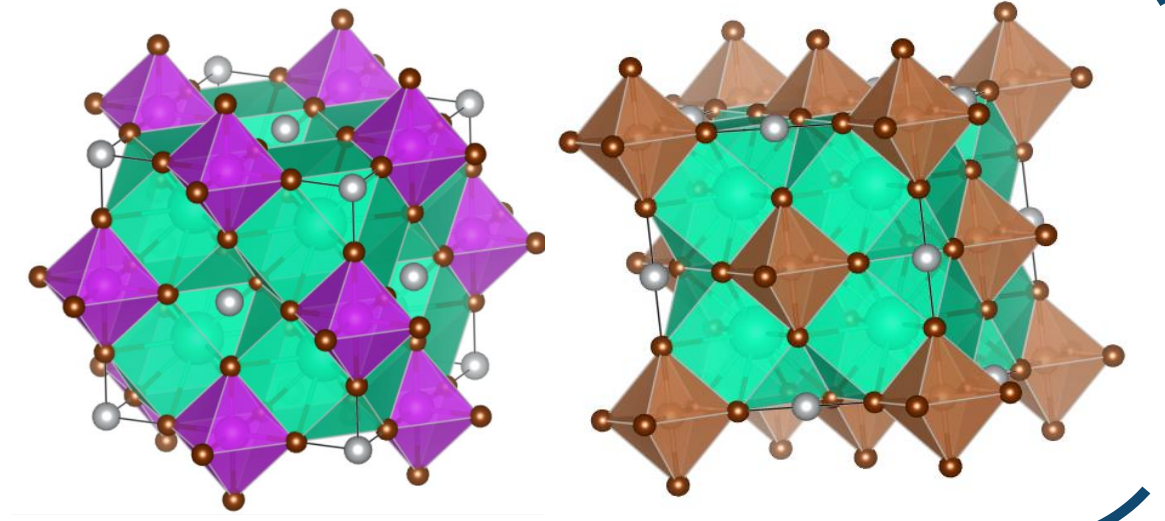


Abstract: Double perovskites are promising candidate materials for next-generation photovoltaic solar technology, which do not suffer from the stability and toxicity issues of their lead-containing counterparts. Using fully-relativistic hybrid density functional theory, we probe the electronic structure of two exciting members of this material class. Our investigations reveal the chemical origin of unusual band alignment behaviour, yielding pathways to band gap engineering in double perovskite alloys for efficient solar photovoltaic energy generation. Ongoing experimental validation with the group of Robert Hoyer.



Electronic Structure

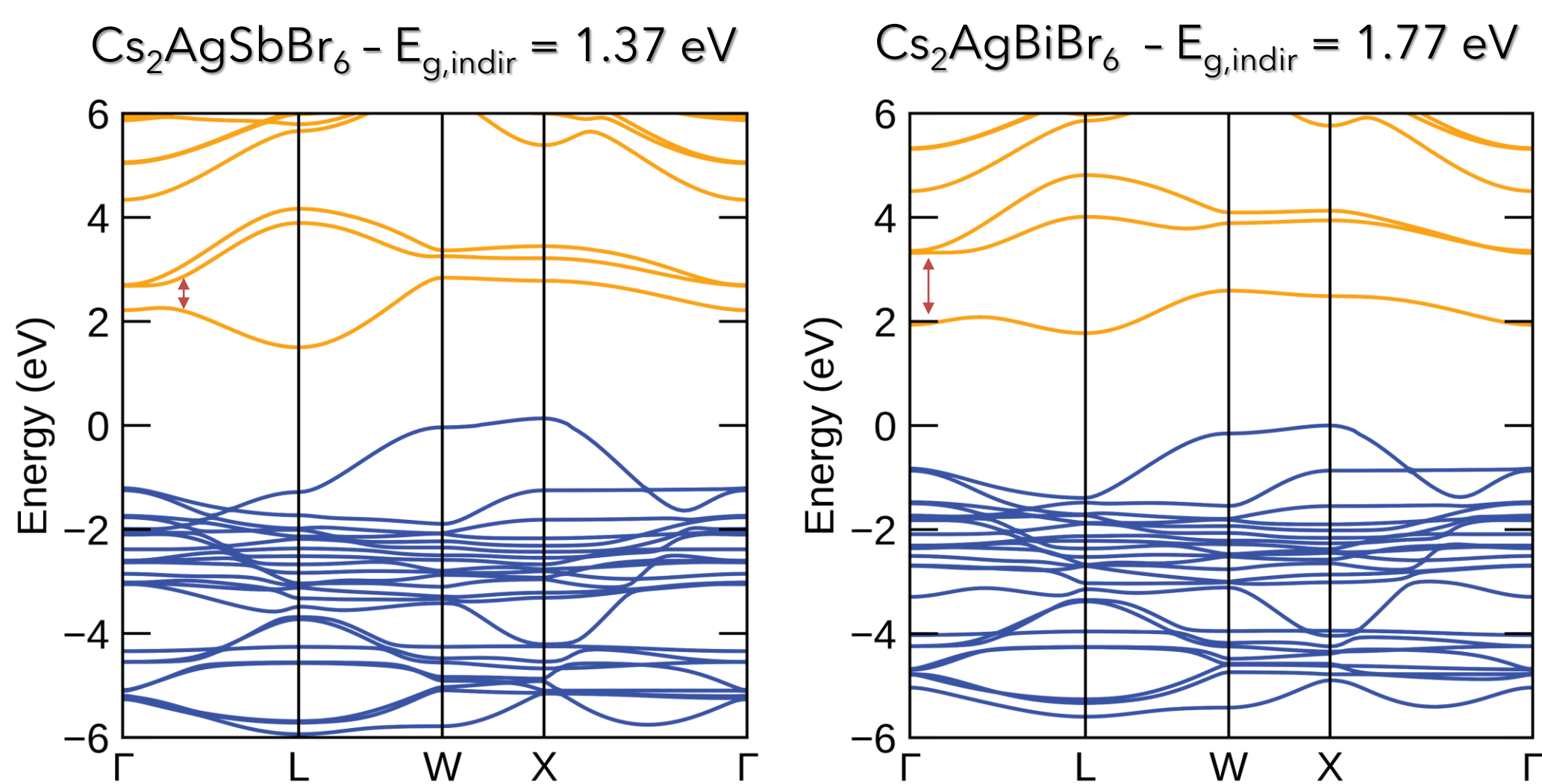


Figure 1 – Electronic band structures of $\text{Cs}_2\text{AgSbBr}_6$ and $\text{Cs}_2\text{AgBiBr}_6$, demonstrating spin-orbit splitting of the conduction band (red arrows), particularly in the case of $\text{Cs}_2\text{AgBiBr}_6$. Valence band coloured blue, conduction band coloured orange. VBM set to 0 eV.

Both materials are found to have indirect gaps, with the valence band maximum (VBM) located at $\mathbf{X}=(0.5,0,0.5)$ and the conduction band minimum (CBM) at $\mathbf{L}=(0.5,0.5,0.5)$. The CBM is primarily composed of anti-bonding Sb/Bi 5p - Br 4p interactions, while the valence band states arise from Br p, Ag d, Sb/Bi s and p orbital interactions. The Cs^+ cations act as spectator ions.

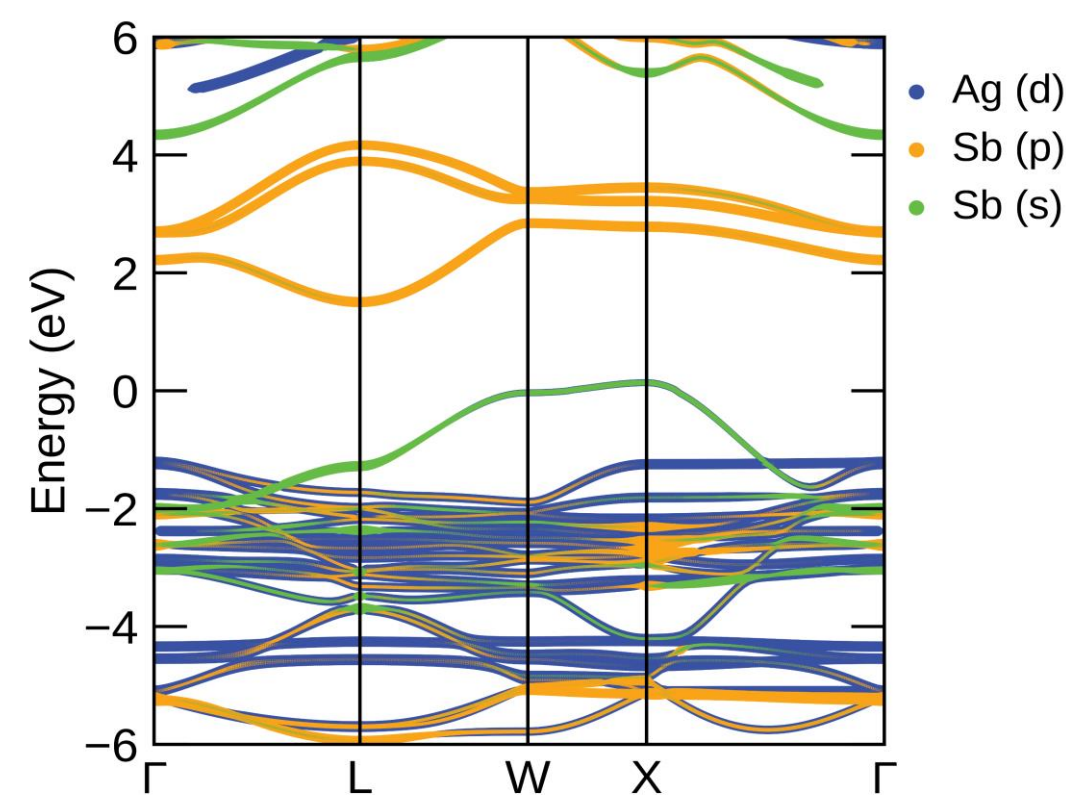
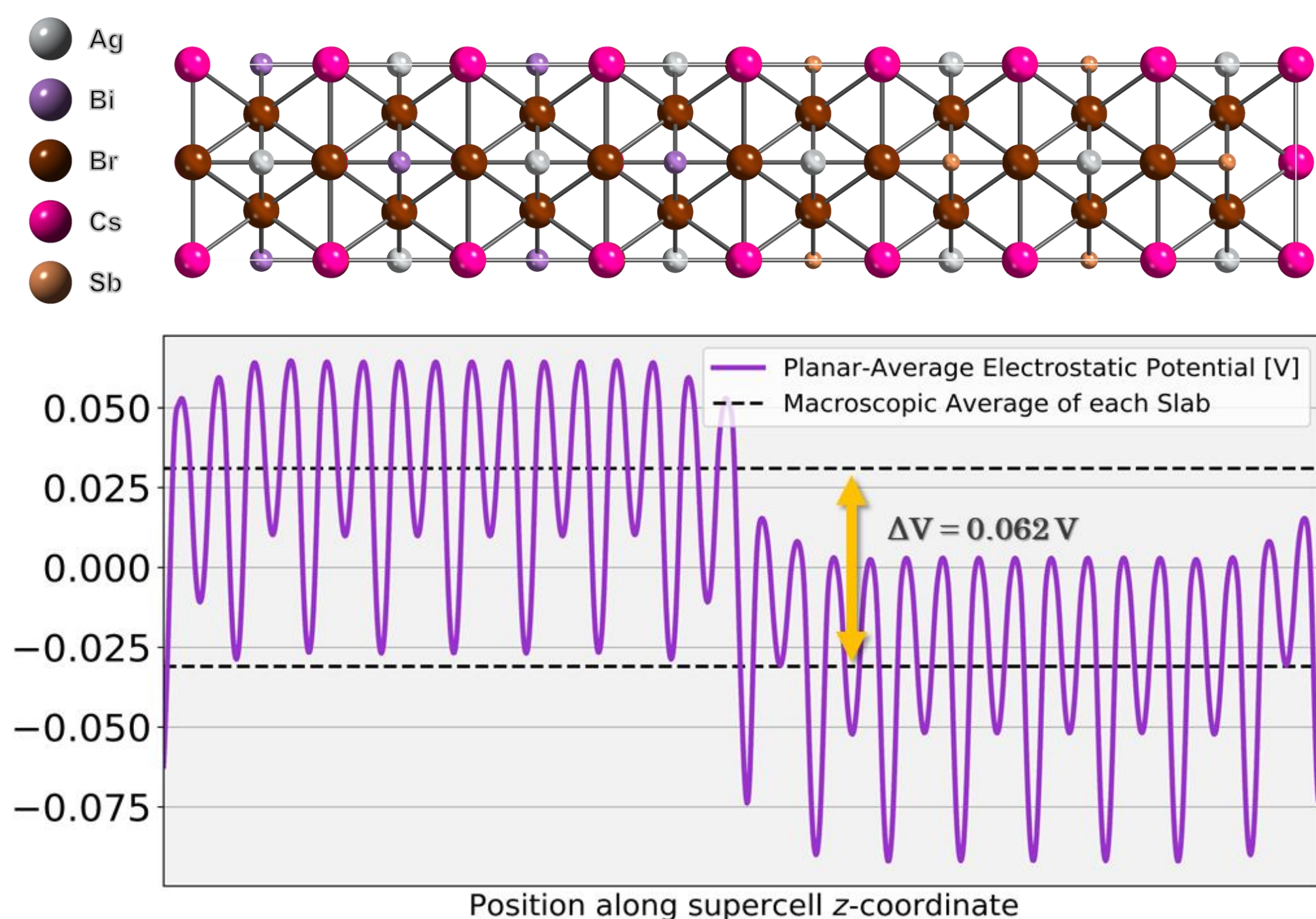


Figure 2 – $\text{Cs}_2\text{AgSbBr}_6$ orbital-projected band structure

Reference Potential Alignment

Due to the long-ranged nature of the Coulomb interaction in an infinitely periodic structure, there is no absolute reference potential. Therefore, to align the electron band energies between two crystalline materials, a supercell calculation is required, in which the offset in average electrostatic potential between the two materials is determined.



Material	$E_{g,dir}$	ϵ_{static}	ϵ_{optic}	c (Cubic Lattice Constant)
$\text{Cs}_2\text{AgSbBr}_6$	2.60 eV	8.78	4.52	11.082 Å
$\text{Cs}_2\text{AgBiBr}_6$	2.49 eV	7.99	4.44	11.187 Å

Electronic Band Alignment

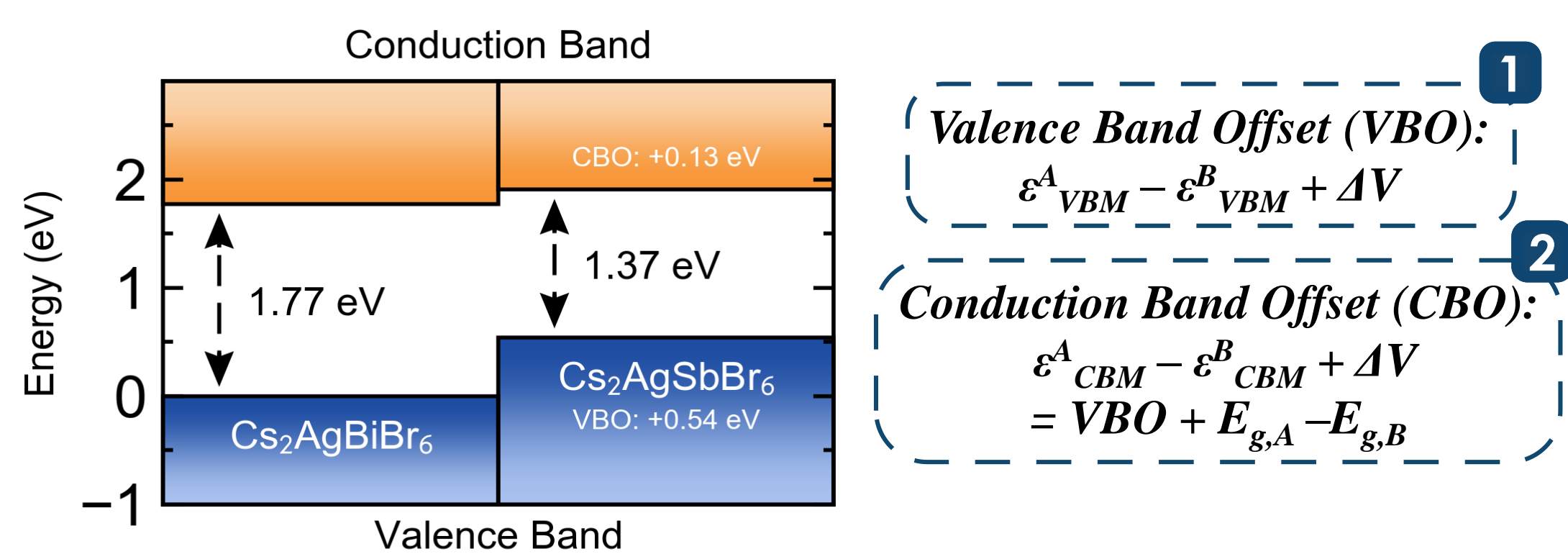


Figure 3 – Electron band offset of $\text{Cs}_2\text{AgSbBr}_6$ and $\text{Cs}_2\text{AgBiBr}_6$, and corresponding equations.

Chemical Origin of Band Offset

Standard molecular orbital theory suggests that atomic substitution with heavier members of a group in the periodic table yields a decrease in band gap. In the case of these materials, we witness an interesting contradiction to this trend. From analysis of the electronic density of states and orbital character of the VBM, the reduced band gap of $\text{Cs}_2\text{AgSbBr}_6$ can be attributed to a stronger interaction of the Sb 5s orbitals with the Ag 4d - Br 4p states.

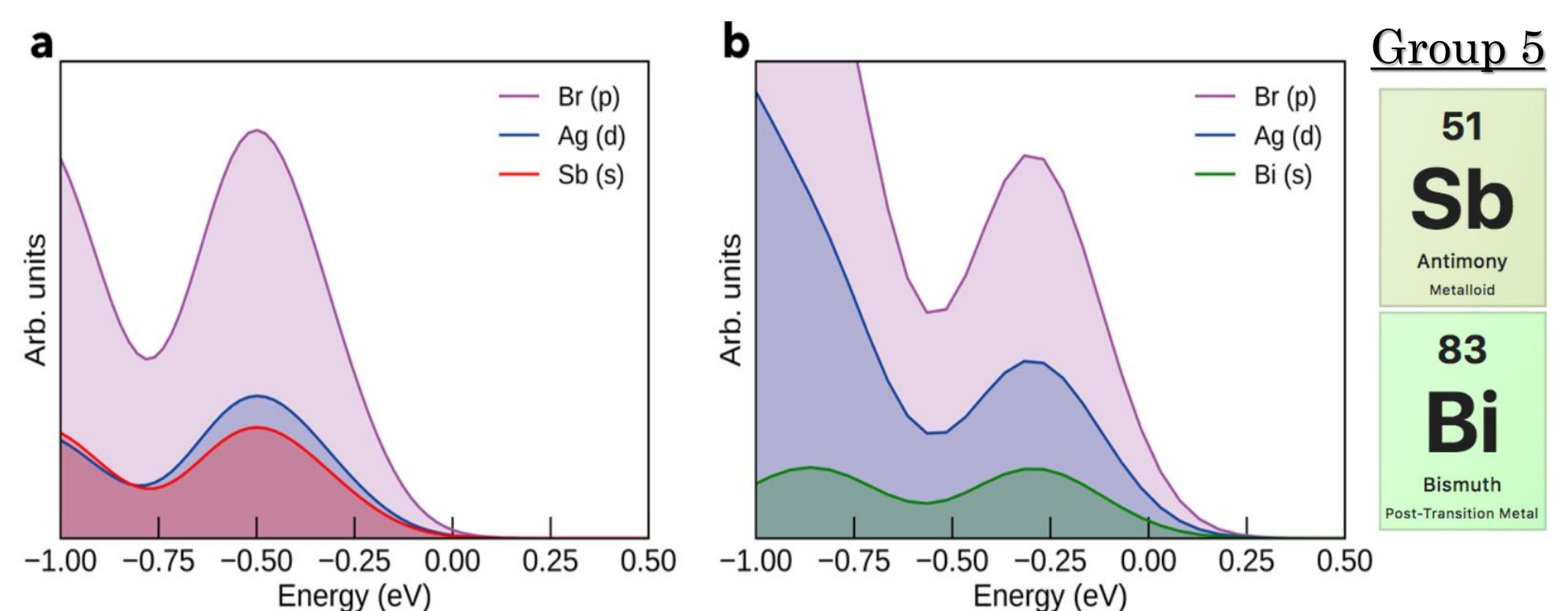


Figure 4 – Electronic density of states for (a) $\text{Cs}_2\text{AgSbBr}_6$ and (b) $\text{Cs}_2\text{AgBiBr}_6$ at the respective valence band maxima. VBM set to 0 eV. (c) Relative position of Sb and Bi on the periodic table.

Typically, ionisation energies decrease as one moves down a group in the periodic table. However, due to the heavy-atom nature of Bi, a relativistic contraction of the 6s² lone-pair occurs, lowering the electron energy and reducing the interaction with the Ag 4d - Br 4p states. This is also evidenced by the greater dispersion in the VB of $\text{Cs}_2\text{AgSbBr}_6$ (Figure 1).

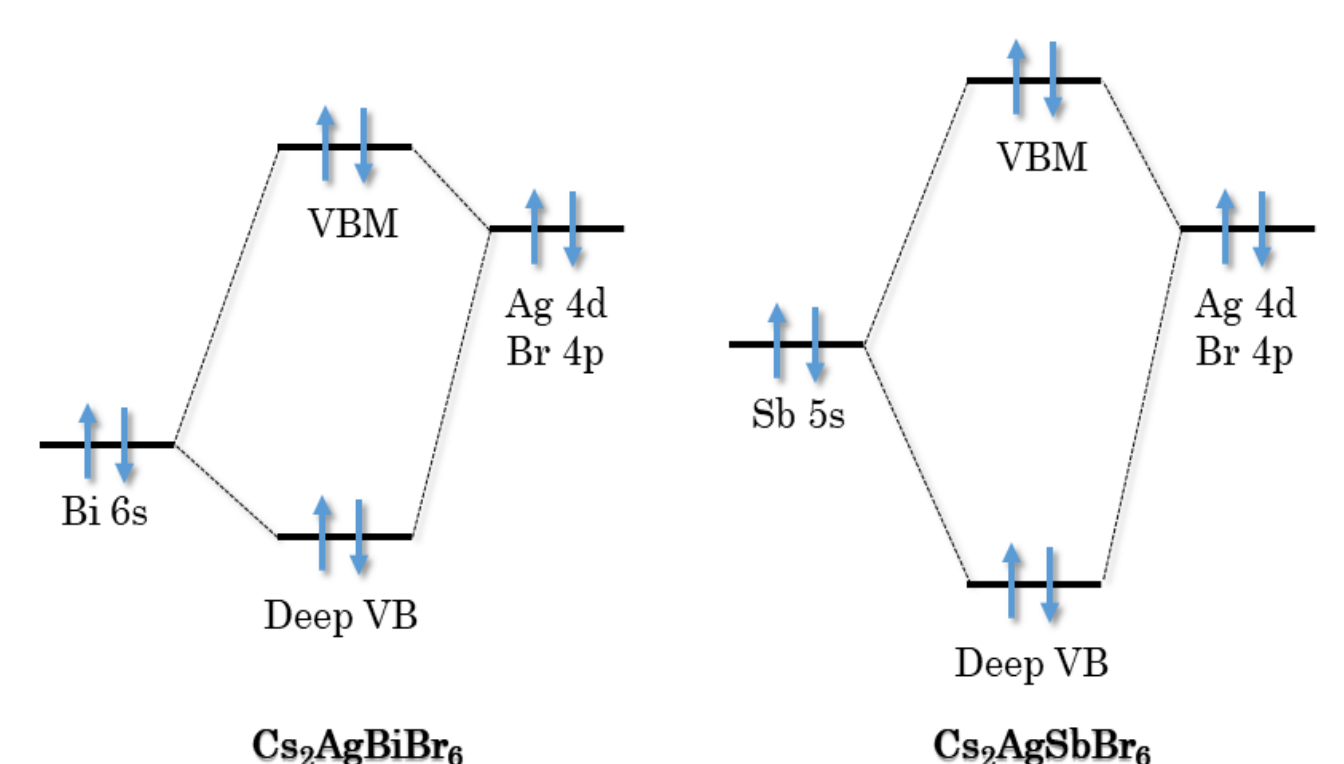


Figure 5 – Schematic molecular orbital diagram demonstrating the effect of cationic lone-pair interactions on the VBM position.

Acknowledgements

Electronic structure diagrams generated using **sumo** (Adam Jackson, Alex Ganose, Seán Kavanagh), **bapt** (Alex Ganose, Seán Kavanagh) and **MacroDensity** (Keith Butler), all of which are open-source and available on **GitHub**.