On the electronic properties of metal halide perovskites

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hole

electron

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Metal halide perovskite, who art thou?

General formula $\text{ABX}_3$

- Easily synthesized
- Highly tunable electronic properties
- Numerous possible applications

- A-site cation ($\text{Cs, CH}_3\text{NH}_3^+$...)
- $X$ Alogen ($\text{I, Cl, Br}$)
- $B$ Metal ($\text{Pb, Sn}$)
Metal halide perovskites for photovoltaics...why?

First answer: unprecedented growth!
Ok, but again...why? Let’s talk about recombination

Both charge loss mechanisms are very slow in MHPs!

Ehm...But why?
Large polarons in metal halide perovskites

2015

Charge Carriers in Hybrid Organic–Inorganic Lead Halide Perovskites Might Be Protected as Large Polarons

2016

Extended carrier lifetimes and diffusion in hybrid perovskites revealed by Hall effect and photoconductivity measurements

2017

Large polarons in lead halide perovskites
Meanwhile somewhere else...

Advanced techniques to simulate polarons in different materials
e.g. the solvated electron

Let’s develop these techniques for perovskites!

J. Phys. Chem. Lett. 2017 89 2055-2059
Polarons in MAPbI$_3$ from advanced simulations

Polarons are localized in different regions of the materials following structural distortions in the organic sublattice.

Different spatial localization of the charges reducing bimolecular recombination!
Polarons and the chemistry of Iodine in MAPbI$_3$

MHPs are generally found to be defect-tolerant

But again...why?

Let’s consider the typical Iodine interstitial defect in MAPbI$_3$

...but the barrier is not enough to explain it!

Reduced interaction between the hole polaron and the interstitial
Distortions in the inorganic sub-lattice can form polarons only in presence of a net dipole field of the A-site cations.
On the origin of polaron formation and hopping

Barrier is related to MA

The random reorientation of MA cations determines polaron hopping
Conclusions and perspective

• Spatial separation of polarons in MAPbI$_3$ explains slow bimolecular and monomolecular recombination.
• Polaron formation is a synergistic process in which distortions in the inorganic sub-lattice are induced by the A-site cations’ dipole field.
• Polaron hopping is induced by the random reorientation of A-site cations.

...but what about surfaces?

Charge loss at the surface and interface is one of the main issues for the development of perovskite solar cells
Acknowledgements

...and thank you for your attention!