Supporting Informations

First-Principles Modeling of Defects in Lead-Halide Perovskites: Best Practices and Open Issues

Daniele Meggiolaro,[a,b*] , Filippo De Angelis[a,b]

[a] ComputationalLaboratory for Hybrid/OrganicPhotovoltaics (CLHYO), CNR-ISTM, Via Elce di Sotto 8, 06123, Perugia, Italy.

[b]CompuNet, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy.

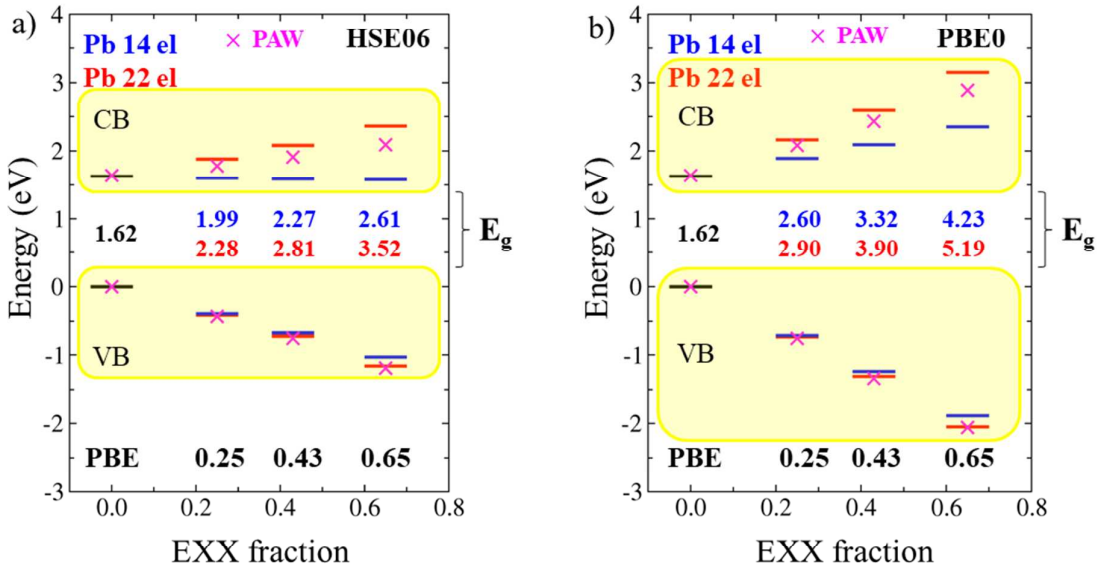

Figure S1. Calculated band edges energies and relative band gaps of $MAPbI_3$ at the a) HSE06 and b) PBE0 level of theory by using Norm-conserving pseudopotentials and, for lead, two different pseudopotentials with 14 valence ($5d^{10}$ $6s^2$ $6p^2$) electrons in blue, and 22 valence ($5s^2$ $5p^6$ $5d^{10}$ $6s^2$ $6p^2$) electrons in red. In the central regions of the diagrams the calculated band gaps with these two

pseudopotentials are reported. Calculated band edges by using Projected Augmented Wave (PAW)[1] approach as implemented in the VASP code[2] have been also reported for comparison.

Table S1. Influence of the fraction of exact exchange (EXX) α on a selected list of thermodynamic and electronic properties of the $MAPbI_3$, PbI_2 and I_2 phases and on the defect formation energy of the iodine interstitials as calculated by the HSE06 functional and including spin orbit corrections.

System	Quantity	EXX α=0.25	EXX α=0.43
$MAPbI_3$	Heat of formation (kJ/mol)	-0.10	-0.06
	Band gap (eV) [exp. 1.60]	1.09	1.58
PbI_2	Heat of formation (kJ/mol)	-209.8	-215.4
	Band gap (eV) [exp. ~2.49]	1.87	2.44
I_2	Binding energy (eV) [exp. 1.57]	1.58	1.49
I_i^-	DFE (E_F=0, I-rich, eV)	0.94	1.24
I_i	DFE (E_F=0, I-rich, eV)	0.87	0.93
	(0/-) transition (eV)	0.07	0.30

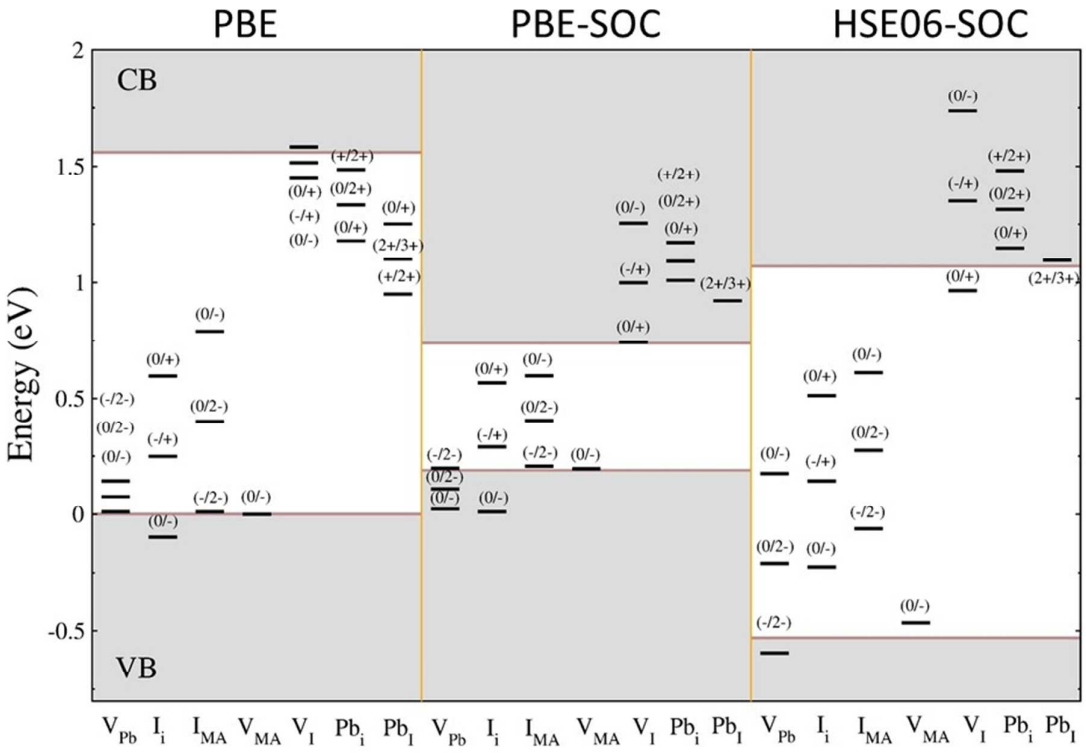

Figure S2. Comparison of the thermodynamic ionization levels of several native defects in $MAPbI_3$, as calculated at different level of theory, i.e. PBE, PBE-SOC and HSE06-SOC (α=0.43) in the 2x2x1 supercell. Only potential alignment corrections have been applied.

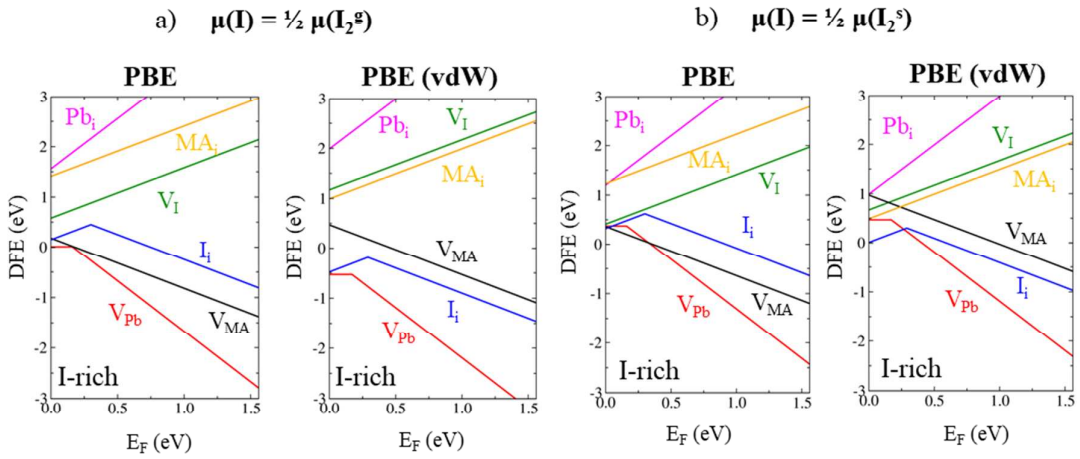

Figure S3. Defects formation energies of $MAPbI_3$ calculated at the PBE level with and without dispersion corrections by using the chemical potential of a) I_2 gas molecule and b) I_2 solid (orthorhombic cell) for iodine.

References

1. Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, 59, 1758-1775.
2. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, 54, 11169-11186.