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

Daniele Meggiolaro,^{a,b*} Filippo De Angelis^{a,b}

^a Computational Laboratory for Hybrid/Organic Photovoltaics (CLHYO), CNR-ISTM, Via Elce di Sotto 8, 06123, Perugia, Italy.

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

AUTHOR INFORMATION

Corresponding Author

*e-mail: daniele.meggiolaro@iit.it

ABSTRACT

Lead-halide perovskites are outstanding materials for photovoltaics, showing long lifetimes of photo-generated carriers which induce high conversion efficiencies in solar cell and light-emitting devices. Native defects can severely limit the efficiency of optoelectronic devices by acting as carrier recombination centers. The study of defects in lead halide perovskites thus assumes a prominent role in further advancing the exploitation of this class of materials. The perovskites defect chemistry has been mainly investigated by computational methods based on Density Functional Theory. The complex electronic structure of perovskites, however, poses challenges to the accuracy of such calculations. In this work we review the state of the art of defects calculations in lead halide perovskites, discussing the major technical issues commonly encountered and what we believe to be the best practices. By keeping as a test case the prototype MAPbI_3 compound, we discuss the impact of exchange-correlation functional on the electronic structure and on the defect

formation energies (DFEs), by comparing semi-local and hybrid functionals, with and without spin-orbit coupling corrections. The convergence of calculated defects structures and their DFEs with respect to the simulation supercell size and the performance of commonly employed charge corrections is thus discussed. A summary of results concerning the defect chemistry of MAPbI₃ is provided, providing hints onto the so called defect tolerance of this material class and casting possible scenarios to be addressed by experimental investigations.

TOC graphics

Metal-halide perovskites are among the most promising materials for photovoltaics¹ due to their attractive optoelectronic properties, such as direct band gap,^{2, 3} large absorption coefficient and low recombination rate of photo-generated charge carriers⁴⁻⁷ coupled to a fairly high mobility.⁸ The high efficiencies of these materials in solar cells, exceeding 22%, are mainly related to the very long lifetimes of photogenerated carriers,⁸⁻¹⁰ even in the presence of moderate-high defects density.¹¹⁻¹³

As for any semiconductor, native defects assume a prominent role in the optoelectronic properties of perovskites due to their ability to trap photo-generated carriers and to promote their recombination on the defects sites, leading to solar cell efficiency loss, which is especially manifested as open circuit voltage losses.¹⁴ According to the Schokley-Read-Hall theory,¹⁵ the charge trapping rate R of carriers on a defect center is defined by

$$R = \frac{np - n_i^2}{\tau_p(n + n_1) + \tau_n(p + p_1)} \quad (1)$$

where n , p , and n_i are the electron/hole carrier densities and intrinsic carriers density, respectively; $\tau_{p,n}$ are the holes and electrons lifetimes; $n_1 = N_C \exp(-\frac{E_C - E_T}{kT})$ and $p_1 = N_V \exp(-\frac{E_T - E_V}{kT})$; and E_T is the energy of the considered trap (E_C and E_V are the conduction and valence band energies, with related N_C and N_V density of states). Based on Eq. 1, trap states with ionization levels placed in the middle of the band gap show an increased trapping activity compared with shallow charge traps.¹⁵

Despite the limited lattice stability of perovskites compared to traditional semiconductors, only low to moderate trap densities of $\sim 10^{11}$ - 10^{16} cm⁻³ for single crystals and polycrystalline samples have been reported, respectively.¹⁶⁻²⁰ Such densities are comparable to those usually reported in conventional semiconductors like polycrystalline Si (10^{13} - 10^{14} cm⁻³),²¹ CdTe (10^{13} - 10^{15} cm⁻³)²² and CIGS (10^{13} cm⁻³).²³ Nevertheless, the efficiencies of perovskites in solar cells are only slightly affected.^{17, 24} Although the high dielectric screening of the organic/inorganic lattice can increase the lifetimes of charge carriers through the formation of large polarons,²⁵⁻²⁸ the origin of the apparent defect tolerance in this class of materials is still under debate and several studies aimed

to unveil the nature and the photophysics of charge traps in lead-halides perovskites have been performed.^{12, 13, 16-19, 29-42, 46-64, 67-80} Adinolfi et al., by using temperature dependent space charge limited current techniques, reported the presence of two broad distributions of charge traps in single crystal MAPbI₃ spanning ~0.2-0.3 eV below and above the conduction (CB) and valence band (VB), respectively, with estimated densities of 10¹¹ cm⁻³.¹⁶ These two distributions are compatible with the presence of both electron and hole traps in MAPbI₃. On the other hand, deep level transient spectroscopy experiments performed on polycrystalline MAPbI₃ showed the presence of charge traps placed in the middle of the band gap, with densities of 10¹⁵-10¹⁶ cm⁻³.²⁹ Sub band-gap photocurrent experiments on mixed MAPbI_{3-x}Br_x perovskites films confirmed the presence of trap states for three different compositions of the mixed phases, with the emergence of multiple defect states in Br-rich perovskites.³⁰

The chemical nature of charge traps and the charge carriers dynamics in this class of systems has been widely studied, mainly by spectroscopic techniques. In situ X-ray photoelectron spectroscopy (XPS) experiments revealed the high tendency of MAPbI₃ to release MAI from the lattice through the formation of vacancies couples, such as V_{MA} and V_I, with only limited impact on the photoluminescence (PL) properties of the perovskite.³¹ On the other hand, further XPS studies by Sadoughi et al. highlighted the presence of Pb metal clusters in the bulk of MAPbI₃, showing that the Pb sublattice is also largely involved in the defect chemistry, by forming vacancies in the lattice, with potentially harmful impact on the overall PL properties.³² Spatially resolved PL experiments performed on polycrystalline films of MAPbI₃ showed that I-rich surfaces are less emissive than Pb-rich surfaces, suggesting that most of the charge traps forms in I-rich portions of the perovskite.^{33, 34} This result is related to the study by Minns et al., who showed that high structural disorder in bulk MAPbI₃ is associated to iodine interstitials, through X-ray and neutron diffraction techniques.³⁵ The charge carriers dynamics has been also investigated in order to figure out the origin of the apparent defects tolerance. PL and transient absorption experiments performed

by Leijtens et al. confirmed the existence of electron traps in polycrystalline MAPbI₃, with higher densities compared to single crystals, i.e. $\sim 10^{16} \text{ cm}^{-3}$.¹⁷ Further insights in the photophysics of defects have been also provided by the same authors, by showing that after the initial trapping of electrons on the defects centers, filled traps become essentially inactive for very long times, of the order of μs . This largely limits the non-radiative recombination on these centers and leads to a predominant hole conductivity.¹⁷

Indirect hints concerning the nature of charge traps in lead-halide perovskites have been provided by investigating PL properties under different environment conditions. Exposure of MAPbI₃ to low pressures of gaseous I₂ was found to induce a quenching of the PL quantum yield (PLQY),³⁶ accelerating the degradation of the perovskite through the formation of metallic lead, as revealed by XPS experiments.³⁷ An irreversible p-doping of the perovskite associated to a decreasing of ionic conductivity was also reported.^{38, 39} These results confirm that iodine-rich environment likely tends to increase the density of charge traps in the material, with iodine vacancies likely playing a marginal role in PLQY quenching. This result has been indirectly confirmed by Zhang et al., who reported that purification of excess iodine from precursors (from MAI) effectively decreases the final density of traps in the perovskite, with beneficial impact on the efficiency of solar cells.⁴⁰ Isovalent halide doping with Br or Cl has been also showed to effectively enhance the PL properties of MAPbI₃.^{19, 41, 42} Similarly, the exposure of perovskites to low oxygen pressures improves reversibly the associated PLQY,⁴³⁻⁴⁹ highlighting a passivating action on the charge traps. This paves the way to post-synthesis treatment processes of the perovskites aimed to improve their optoelectronic efficiencies and large effort in order to improve permanently the PL enhancement is now performed.⁵⁰

An important topic still lacking general consensus is the effect of light irradiation on perovskite defects. The reversible photo-induced formation of charge traps in lead-halide perovskites in controlled atmosphere has been reported by Motti et al.,⁴⁹ while a photo-

decomposition under ambient conditions due to the loss of iodine has been reported by Kim et al.⁵¹ On the other hand, beneficial effects of light irradiation have been reported by several other authors.^{46, 47, 52, 53}

The experimental picture discussed above highlights the prominent role played by defects in the optoelectronic properties of perovskites, both in the intrinsic material and in its interactions with the environment. Experiments, however, cannot provide a microscopic picture of the observed phenomena. In this regard, computational modelling is a complementary tool for rationalizing experimental results, particularly regarding the nature of the defects involved in the aforementioned processes. Several computational studies have been carried on native defects in perovskites, mainly employing Density Functional Theory (DFT).^{12,13,54-65,67-80} Yin et al. performed calculations on the cubic phase of MAPbI₃ reporting that only shallow defect states exist in this phase, with a predominance of lead vacancies (V_{Pb}) and methylammonium interstitial (MA_i) defects.¹² Buin et al. carried out an extensive investigation of the defects stabilities in different halides comparing MAPbX₃ perovskites with X= I, Br and Cl. In this work calculations confirmed the high stability of V_{Pb} , MA_i and iodine vacancies (V_I) in all three phases and in all conditions of growth, by highlighting the emergence of I and Pb (I_i and Pb_i) interstitials as sources of charge trapping.^{54, 55} Similar conclusions have been also reported for formamidinium (FA) lead-iodide and inorganic perovskites.⁵⁶⁻⁵⁸ Agiorgousis et al., through MD simulations, discussed the possible role played by iodine vacancies in the trapping of electrons in MAPbI₃.⁵⁹ The migration barriers associated to the diffusion of defects within the lattice have been also studied by DFT methods, with a general consensus about iodine moving faster than methylammonium, faster than lead. Barriers of ~0.1 eV, 0.2-0.5 eV and > 0.8-1 eV have been reported for migration of I-, MA- and Pb-related defects, respectively.⁶⁰⁻⁶³ Based on these studies, the origin of the apparent defect tolerance of lead-halide perovskites has been ascribed to the shallow nature of the most stable native defects in the material, with the possible formation of Schottky defects couples, e.g. V_{MA} and V_I , further limiting the

electronic disorder in MAPbI₃ and avoiding trapping on single charged defects, as discussed by Walsh and coworkers.⁶⁴ The large part of these studies, however, have been carried out by using semi-local exchange correlation functionals, such as the Perdew-Burke-Ernzerhof (PBE) functional.⁶⁵ The use of such semi-local functionals, although usually providing a good approximation to defect geometrical structures and lattice energies, may lead to unsatisfactory results for the calculations of defects formation energies (DFEs) and thermodynamic ionization levels when both spin-orbit coupling (SOC) and self-interactions corrections are neglected.^{66, 67} Du discussed this point by comparing thermodynamic ionization levels of native defects in MAPbI₃ calculated with PBE and hybrid DFT functionals (SOC included).^{61, 67} It was shown that the overestimate of the valence and conduction band energies delivered by PBE (and similarly by other semi-local functionals) tends to underestimate the positions of the levels in the band gap. As a result, several shallow transitions at the PBE level occur deep in the band gap in hybrid HSE06+SOC⁶⁸ calculations, as reported for instance for iodine interstitials.⁶⁷ Hybrid DFT calculations have been also carried out on PbI₂ and MAI terminated surfaces of MAPbI₃, among the most stable and abundant surfaces in nanocrystals,⁶⁹ by reporting an increased trapping activity of the surface compared to the bulk with the emergence of several traps states deep in the band gaps.⁷⁰ By performing HSE06+SOC calculations Meggiolaro et al. investigated DFEs and thermodynamic ionization levels of native defects in MAPbI₃, by showing that iodine interstitials, and to a minor extent lead vacancies, are the main responsible of the charge trapping processes in the perovskite, while other stable defects are essentially shallow traps.¹³ This study also confirmed the existence long-lived electrons traps and short-lived holes traps in MAPbI₃, providing a possible interpretation of the apparent defect tolerance of lead-halide perovskite in connection with spectroscopic observations.^{13, 17} The activity of V_k and H-centers (iodine interstitials) in trapping holes in bulk MAPbI₃, typical of alkali halides compounds,^{71, 72} has also been discussed by Whalley et al.⁷³ Wei Li et al., through non-adiabatic MD (NAMD) simulations focussed on the carrier dynamics in presence of neutral interstitial iodines, by showing that such defect can easily exchange trapped

holes with the valence band at room temperature, further limiting the recombination of opposite charge carriers on the center.⁷⁴ Similar studies based on NAMD simulations reported increased electron-hole recombination rates on MAI-rich surfaces of MAPbI₃.⁷⁵ Changes in chemical and PL properties of perovskites upon doping and when interacting with the environment have been also studied computationally. Shi et al. performed a wide DFT study aimed to evaluate the doping activity of several extrinsic elements in MAPbI₃, by concluding that the p-type doping with Na, K, Rb, Cu, and O elements is easier than n-type doping, the last possible only in non-equilibrium growth of the perovskite.⁷⁶ Mosconi et al. showed that the PL quenching observed in Bi-doped lead perovskites is due to the introductions of deep electrons recombination centers in the band-gap.⁷⁷ On the other hand, other DFT works investigated the beneficial effects of isovalent halide doping with Br and Cl, by showing that these elements can effectively passivate charge traps and increase the lifetimes of charge carriers in MAPbI₃, both in the bulk and at the perovskite-TiO₂ interface.^{13, 78, 79} The PL quenching of MAPbI₃ due to the exposure to I₂ gas has been studied by Meggiolaro et al., by concluding that the high chemical potential of iodine in the gas phase leads to an increased density of iodine interstitials charge traps in the perovskite, with consequent p-doping and detrimental effects on the PLQY.⁸⁰ On the other hand, the beneficial effect of exposition to low pressures of O₂ has been showed to passivate such traps leading to an enhancement of the PL properties of MAPbI₃.⁸¹ By DFT calculations, an oxygen induced mechanism of photo-degradation of MAPbI₃ has been proposed by Aristidou et al., where the inclusion of oxygen within the perovskite can take place through the formation of superoxides species, whose formation is assisted by light.⁸²

Due to the importance of defects in determining the outstanding optoelectronic properties of lead-halide perovskites, in this work we summarize some of the most important technical issues commonly encountered in the computational modeling of defects in this materials class, keeping as a test case the prototype MAPbI₃ perovskite. We first discuss the effects of the level of theory

employed in DFT calculations on the defects formation energies and the thermodynamic ionization levels, with particular emphasis on the combined effect of spin orbit coupling (SOC) and quality of the DFT functional. The Defect Formation Energies (DFEs), which are the central quantity to estimate the defect abundance, calculated by using a semi-local approximation to the exchange correlation functional are compared and discussed with results obtained by using the hybrid functionals (HSE06 and PBE0) as a function of the amount of exact exchange, with and without including SOC. This analysis shows that sizable deviations in the thermodynamics and electronic properties of defects in perovskites are obtained at different levels of theory. The large deviations in the electronic properties of MAPbI₃ obtained with semi-local and hybrid functionals also induce remarkable energies differences between the calculated lattice defects equilibrium geometries. While, as expected, semi-local functionals, such as PBE, give satisfactory results in the search of geometrical minima, the large corrections on the band edges induced by the SOC and the self-interaction error may severely alter the calculated stability of different equilibrium configurations. This issue can be at the origin of the large deviations on the calculated DFEs reported by several authors in the literature. An in depth technical discussion about the charge corrections in the supercell approach for this class of materials is then presented, where various commonly employed methods for the corrections of images charge interactions are compared and discussed for two defects of increasing charge. Finally, a summary of calculated defect properties of MAPbI₃ is reported, with connection to available experimental observables.

1. Defects formation energies: computational protocol

The stability of native defects in solids is commonly evaluated by calculating the associated DFE through DFT calculations in the supercell approach following the equation:⁸³⁻⁸⁵

$$DFE(X^q) = E(X^q) - E(bulk) - \sum_i n_i \mu_i + q(E_F + VBM + \Delta V) + E^q \quad (2)$$

where $E(X^q)$ is the energy of the defect supercell of charge q , $E(bulk)$ the energy of the pristine supercell, n and μ are the number and the chemical potentials of the species added or subtracted to the perfect bulk in order to form the defect. The fourth term represents the energy associated to the exchange of charges with the electrons reservoir (the Fermi level of the system E_F), referenced to the valence band maximum (VBM) of the pristine crystal. Adopting this convention, the energy of the VBM explicitly contributes to the DFE. The absolute VBM energy should also be corrected for the electrostatic potential shift ΔV induced by the defect in the supercell calculation compared to the bulk reference potential, from which the VBM is taken. Finally, the last term in Eq. 2, E^q , is introduced to correct the electrostatic interaction between charged point defects in the periodically repeated supercells.

As expressed by Eq. 2, DFEs are function of the chemical potentials of the elements constituting the lattice μ_i ($i = \text{MA, Pb, I}$) and of the Fermi level of the system E_F . By fixing the chemical potentials, DFEs show a linear dependence on the Fermi level in the system which is allowed to vary within the material band gap, whose slope is determined by the charge of the defect. By the analysis of DFEs and of their variation as a function of the Fermi level it is possible to predict the stable states of charge of native defects with the associated ionization levels in the band gap, as well as their density in the system. The thermodynamic ionization levels between different charge state q/q' of a defect are defined as the Fermi energies (E_F) where the associated DFEs are equal, *i.e.* those which satisfy the condition $\text{DFE}(q', E_F) = \text{DFE}(q, E_F)$, with the Fermi energy range restricted to the band gap of the crystal. These quantities are calculated by applying the general expression:

$$\varepsilon(q/q') = \frac{\text{DFE}(D^q, E_F=0) - \text{DFE}(D^{q'}, E_F=0)}{q' - q} \quad (3)$$

Where $\text{DFE}(D^q, E_F=0)$ are the formation energies of defects in state of charge q calculated for $E_F=0$, *i.e.* coinciding with the VB maximum (VBM).⁸³ The relative concentration $c(D^q)$ of defects can

be estimated by the calculated DFE by applying the Boltzmann law $c(D^q) = N_s \exp(-\frac{DFE(D^q, E_F)}{kT})$, where N_s is the density of the defects sites in the modelled supercell, T is the absolute temperature and k the Boltzmann constant. Furthermore, from the calculated defect density it is possible to predict the position of the native Fermi level in the system, thus whether the material will be n- or p-doped (or intrinsic) by solving the associated electro-neutrality equation:⁸³

$$p - n + \sum_{Xi} q_i C_{Xi}(E_F) = 0 \quad (4)$$

where p and n are the intrinsic densities of electrons and holes.

Based on the above framework, three terms affect the accuracy of calculated DFEs and charge transitions: *i*) the relative energies of the bulk and defective systems; *ii*) the electronic term accounting for the exchange of charges between the defect site and the Fermi level, *i.e.* the absolute VBM value of the bulk reference phase; and *iii*) the electrostatic corrections need to account for the presence of charged defects. In the following, our analysis will focus on the computational methods applicable in order to accurately predict these terms.

2. Stability and electronic properties of bulk MAPbI₃

To simulate the defect chemistry of MAPbI₃ in different environments, appropriate values of the chemical potentials to the constituting species should be assigned. The energy ranges of chemical potentials are set in order to preserve the thermodynamic stability of the perovskite, by simulating halide rich (metal poor) or halide poor (metal rich) conditions. The field of thermodynamic stability of MAPbI₃ is defined by the following relations for the chemical potentials μ :

$$\mu(MA) + \mu(Pb) + 3\mu(I) = \mu(MAPbI_3) \quad (5)$$

$$\mu(MA) + \mu(I) < \mu(MAI) \quad (6)$$

$$\mu(Pb) + 2\mu(I) < \mu(PbI_2) \quad (7)$$

These relations express the stability of the three relevant compounds in equilibrium, i.e. MAPbI₃ with its constituents (Eq. 5), MAI (Eq. 6) and PbI₂ (Eq. 7); they are commonly expressed by referring the chemical potentials of the species to their respective values in the standard state. While the definition of standard states of iodine and lead is straightforward, by using the chemical potentials of molecular iodine and of bulk metallic lead, a difficulty clearly arises in assigning a definite standard state to the charged MA molecule.¹² The definition of a MA standard state is however not essential in the simulation of I-rich or I-poor conditions and its value can be evaluated by solving Eq. 5-7. In Table 1 the expression of chemical potentials simulating MAPbI₃ in equilibrium with PbI₂ and MAI in I-rich and I-poor conditions are reported for clarity.

Table 1. Expressions of the chemical potentials for the elemental species in MAPbI₃ in equilibrium with PbI₂ and MAI phases. Points A and C in the thermodynamic diagram are showed in Figure 1.

Equilibrium with PbI ₂	Equilibrium with MAI
I-rich (point A) $\mu(I) = \frac{1}{2} \mu(I_2^{mol})$ $\mu(Pb) = \mu(PbI_2) - \mu(I_2^{mol})$ $\mu(MA) = \mu(MAPbI_3) - \mu(PbI_2) - \frac{1}{2} \mu(I_2^{mol})$	I-rich $\mu(I) = \frac{1}{2} \mu(I_2^{mol})$ $\mu(Pb) = \mu(MAPbI_3) - \mu(MAI) - \frac{1}{2} \mu(I_2^{mol})$ $\mu(MA) = \mu(MAI) - \frac{1}{2} \mu(I_2^{mol})$
I-poor (point C) $\mu(I) = [\mu(PbI_2) - \mu(Pb^{bulk})]/2$ $\mu(Pb) = \mu(Pb^{bulk})$ $\mu(MA) = \mu(MAPbI_3) - \frac{3}{2} \mu(PbI_2) + \frac{1}{2} \mu(Pb^{bulk})$	I-poor $\mu(I) = [\mu(MAPbI_3) - \mu(MAI) - \mu(Pb^{bulk})]/2$ $\mu(Pb) = \mu(Pb^{bulk})$ $\mu(MA) = [3\mu(MAI) - \mu(MAPbI_3) + \mu(Pb^{bulk})]/2$

In Table 1 halide rich conditions are simulated by setting the chemical potential of I to that of the I₂ molecule (I_2^{mol}), while halide poor conditions can be simulated by setting the chemical potential of

Pb to that of the metallic lead, Pb^{bulk} . Although the standard state of iodine at room temperature is the I_2 molecule in the orthorhombic solid phase, we consider hereafter as a standard state the iodine molecule in the gas phase. This assumption is justified by considering the high vapor pressure of iodine at the temperature usually employed in the synthesis and annealing of $MAPbI_3$, *i.e.* above 100 °C.

By calculating chemical potentials according to expressions in Table 1, it is possible to define the thermodynamic field of stability of $MAPbI_3$, as illustrated in Figure 1a. Notably, the perovskite is stable only in a limited area of I and Pb chemical potentials, in equilibrium with the PbI_2 and MAI phases, whose width is the enthalpy of formation of the perovskite starting from PbI_2 and MAI, *i.e.* -0.11 eV as calculated at the PBE level.

Figure 1. a) Thermodynamic field of stability of the tetragonal $MAPbI_3$ phase calculated at the PBE level; b) Band edges energies of $MAPbI_3$ calculated at different level of theories: asterisks * denote calculations including spin-orbit corrections.

Similarly important to the rational definition of the chemical potentials for the elements, a quantitative prediction of the band edges is essential in order to estimate accurately the electronic

term in Eq. 2, since a possible inaccuracy in this term can have dramatic effects on the calculated DFEs.

Semi-local exchange correlation functionals, such as PBE⁶⁵ and PBEsol,⁸⁶ usually provide accurate geometries and lattice energies, but are not sufficiently accurate in the description of the electronic properties of semiconductors, neither for the band-gap nor for the energy of the band edges. The PBE functional predicts a MAPbI₃ band gap of 1.56 eV, in good agreement with experiments (see Figure 1b). However, as previously discussed, such matching is only fortuitous.⁸⁷
⁸⁸ The inclusion of SOC strongly narrows the band gap to 0.55 eV (see Figure 1b).^{89, 90} Notably, this is the correct band-gap predicted by semi-local functionals, retrieving the typical band-gap underestimate known for most of semiconductors. By using GW calculations including SOC on tetragonal MAPbI₃, a band gap of 1.64 eV was obtained,⁸⁷ in good agreement with experiments. A remarkable downshift of both the VBM and CBM of the perovskites, by about 0.5 eV compared to the PBE calculation, is also reported, Figure 1b. This result highlights that a reliable estimation of the electronic term in the calculation of DFEs requires a more accurate treatment of the electronic structure than semi-local exchange correlation functional. The GW approximation, although providing a good description of the electronic properties, is currently limited to the calculation of quasi-particle energies at fixed geometries, although promising procedures aimed to combine the GW addition/removal electrons energies with lattice relaxation energies obtained by DFT methods have been recently proposed.⁹¹ The high computational cost of the GW technique, however, currently limits its application to small/medium systems. A good compromise for an accurate treatment of both lattice and electronic energies is represented by hybrid exchange correlation functionals which employ a fraction of the exact Hartree-Fock exchange in their formulations in order to partially correct the self-interaction error of semi-local functionals. The advantage of using hybrid functionals, such as PBE0⁹² and HSE06⁶⁸ is that, beside a quantitative estimation of the electronic band edges energies, they also provide accurate lattice energies, generally improving

upon semi-local functionals. The fraction of exact exchange (α) included in the hybrid functional is a tunable parameter and is set to a value of 0.25 for both PBE0 and for the screened HSE06 functional, an optimal value for low-medium band gap semiconductors.⁹³ Such fraction of exact exchange turns out to be insufficient to reproduce the experimental MAPbI₃ band-gap when SOC is included. As an example, the standard HSE06 functional with $\alpha = 0.25$ provides a band gap of ~ 1.1 eV for MAPbI₃, Figure 1b. By using PBE0-SOC with the same $\alpha=0.25$ a band-gap of 1.64 eV is obtained, in good keeping with GW results. Increasing α to 0.43 with HSE06, as proposed by Du,⁶⁷ allows one to correctly reproduce the experimental band gap of MAPbI₃, with a calculated estimate of 1.58 eV. The calculated electronic structure consistently delivers a downshift of the MAPbI₃ VB and CB of ~ 0.5 eV compared to the PBE functional, in good agreement with GW calculations, Figure 1b. The use of increased fractions of exchange ($\alpha > 0.25$) in order to accurately describe the electronic properties of the perovskites in the HSE06 functional only slightly modifies the thermodynamic properties of the elementary phases, as showed by Table S1, Supporting Information, where a list of properties of MAPbI₃, PbI₂ and I₂ have been compared as calculated by using two different values of exchange fractions. Notice that while in PBE0 the exact exchange-multiplied by α - is used for any inter-electronic distance, in HSE06 the same exchange terms is used within a radius of inter-electronic distances, to switch to the semi-local exchange term at long range. As we will show below, this has important consequences for the calculation accuracy.

In the calculations of solids it is customary to remove core (and semi-core) electrons from the actual electronic structure problem, for computational convenience. This is either afforded by replacing the core electronic states by a pseudo-potential (PP)^{94, 95} or by freezing such states at those of the isolated atom, as in the Projector Augmented Wave (PAW) approach.⁹⁶ Notably, the use of PPs can be more computationally effective, but we found that PPs in combination with hybrid functionals can lead to unsatisfactory results in hybrid calculations if partially incomplete valence shells are considered in the pseudopotentials. This is (unfortunately) the case of Pb when the semi-

core $n=5$ valence shell is excluded in the pseudopotential construction, leaving only the 5d, 6s and 6p electrons in the valence, the most common pseudopotentials usually employed in calculations. The exclusion of the semi-core 5s and 5p electrons in the calculation of exact exchange leads to an unphysical down shift of the CB band edge by increasing the fraction of exchange with large underestimations of the calculated band gaps, see Figure S1, Supporting Information. The origin of this behavior resides in the exclusion of the 5s and 5p electrons in the calculations of the exact exchange which bring a sizable contribution to the exchange term due to the overlap with the 5d orbitals of the metal.⁹⁷ The inclusion of these states through the construction of a 22 valence electrons Pb pseudopotential allows us to retrieve an accurate description of the electronic properties, comparable to the results of PAW calculations which are not affected by this problem, retaining the full space of atomic levels for the calculation of exact exchange. To visualize this effect we investigate the band edge energies and band-gap behavior calculated for three fractions of exact exchange by HSE06 and PBE0 using two different Pb pseudopotentials, with 14 and 22 valence electrons. For simplicity, we neglect SOC in these test calculations so the reported band-gaps have only a comparative value. As shown in Figure S1, Supporting Information, increasing the fraction of exact exchange by using 14 electrons pseudopotentials leads to a relatively modest band-gap increase with HSE06, due to an unphysical CB down-shift. Similarly, PBE0 delivers a reduced band-gap opening with the 14 electrons PP. Both functionals instead show the expected (and correct) band-gap opening with 22 electrons PP upon increasing α .

3. Effects of self-interaction and spin-orbit coupling on defect properties

The terms affecting the accuracy of calculated DFEs in Eq. 2 are the energies of the bulk and defective supercells and the electronic term accounting for the charges exchange with the Fermi level. In this section we discuss the influence of the self-interaction error and spin-orbit coupling on these terms.

The accuracy in the calculation of the energies of the defective supercells, *i.e.* first term in Eq. 2, is intrinsically related to the accuracy in the determination of the equilibrium geometries of the defects systems. Due to the fairly high computational cost of hybrid functionals, the relaxation of defects supercells is commonly carried out by using semi-local exchange correlation functional, *e.g.* PBE, which usually provide fairly accurate equilibrium geometries at a comparatively low computational cost. The self-interaction error intrinsic to the semi-local functionals is however responsible of both the band-gap underestimate and of the limited localization of the charge density on the defects sites. Basically, (defects) charges tend to be over-delocalized by semi-local functionals, which may affect the energies and the equilibrium geometries of the defective supercells.

To highlight the possible issues related to the use of the PBE functional in the prediction of lattice energies, we discuss the configurational energies of two relevant defects in MAPbI₃, *i.e.* V_I and I_i, in two different charge states, as calculated in the 2x2x1 supercell. Here we want to focus directly on the energies of the defects along fixed configuration coordinates as calculated at the PBE and hybrid levels of theory, in order to make the discussion independent from chemical potentials.

I_i has been recently indicated as one of the potential active hole trap in MAPbI₃ through the (0/-) transition placed ~0.30 eV above the VB at hybrid level.^{67, 81} In the stable negative configuration, I_i⁻, the defect is characterized by two iodine atoms coordinated by two Pb ions in a double-bridged geometry with a I-I distance > 3.80 Å, Figure 2a. By looking at Figures 2b-d this configuration is the energy minimum at PBE, PBE-SOC and HSE06-SOC levels. On the other hand, the neutral form of I_i⁰, representing the product of the hole trapping on the defect, induces a shortening of the I-I bond to form the analogous of a coordinated I₂⁻ specie. We studied the potential energy profile along the I-I bond length coordinate at the PBE, PBE-SOC and HSE06-SOC level in a range of distances corresponding to the two minima of the charged and neutral defect states.

While PBE and PBE-SOC predict for I_i^0 essentially the same minimum structure than for I_i^- , showing an overall flat energy profile, the same path calculated by HSE06-SOC clearly shows an increasing stability of the bound I_2^- species at an I-I distance of 3.26 Å, with a calculated stabilization energy of 0.33 eV with respect to the PBE minimum. The discrepancy between PBE or PBE-SOC and HSE06-SOC is ascribed to the larger stabilization of the hole localized on the I_2^- center obtained at the hybrid level due to the down-shift of the band edges with respect to the PBE calculation.

The iodine vacancy (V_I), a typical donor defect, shows a somehow similar behavior. At the PBE level V_I is stable in the positive and negative charge states as observed for iodine interstitials. Moving from the positive to the negative charged vacancy, a progressive shortening of the vicinal Pb ions is found, with the formation of a Pb-Pb dimer in the negative charged state observed at the PBE level, Figure 2e, consistent with the results of Argiourgos et al.⁵⁹.

Figure 2. Effect of spin-orbit and self-interaction on the energies of iodine interstitial and vacancy defects in their negative and neutral forms. a) Structure of I_i^- (PBE negative configuration), the

explored I-I distance is marked by red arrow; b-d) Profile energy for the neutral and negative interstitials calculated at the PBE, PBE-SOC and HSE06-SOC ($\alpha=0.43$) levels respectively; e) Structure of V_I^- (Pb-dimer, PBE negative configuration) the explored Pb-Pb distance is marked by red arrow; f-h) Profile energy for the neutral and negative V_I calculated at the PBE, PBE-SOC and HSE06-SOC ($\alpha=0.43$) levels respectively. Energy minima are marked with asterisks.

By introducing SOC both at the PBE and HSE06 levels we found that the Pb-Pb dimer is no more the energy minimum, with the dimer being less stable than the unbound configuration by 0.29 eV at the hybrid level for the negatively charged vacancy, Figures 2f-h. In this case the dominating effect is that of SOC, which profoundly alters the electronic structure of the Pb states, leading to a destabilization of the Pb-Pb dimer. Taken together, these results call for the use of hybrid+SOC geometry optimizations for an accurate description of defects in MAPbI₃. While this may turn out to be computationally impracticable, the use of properly tailored GGA+U+SOC methods may represent a viable tool.⁹⁸ In any case, it is advised to check the obtained PBE structures by single point hybrid+SOC calculations at different geometries to avoid possible artifacts.

The combined effects of spin-orbit coupling and exact exchange over the DFEs of several defects are reported in Figure 3a-b. A summary of the calculated DFEs at different levels of theory in I-rich conditions have been also reported in Table 2.

Table 2. Influence of the spin-orbit coupling and the electronic exchange on the DFEs of neutral and charged defects ($E_F=0$) in I-rich conditions (point A in Figure 1a). PBE and PBE-SOC calculations have been carried out in the 2x2x1 supercell by using US pseudopotentials (Pb 14 electrons) and a cutoff on PWs of 40 Ryd (320 Ryd for the charge density). HSE06-SOC ($\alpha=0.43$) calculations have been carried out by using norm-conserving pseudopotentials (22 electrons Pb pseudo) and a cutoff of 40 Ryd on the PWs. Van der Waals dispersion corrections (vdW) have been

added a-posteriori by using the DFT-D3 scheme. Both the potential alignment and Makov-Payne corrections ($\epsilon=24.0$) have been applied to the DFEs.

DFE (eV)	V_I	I_i	V_{Pb}	Pb_i	V_{MA}	MA_i
PBE	2.14	0.80	0.01	4.13	0.13	2.93
PBE-SOC	1.17	0.71	-0.07	3.37	-0.06	2.02
HSE06-SOC	1.87	0.93	0.19	4.19	0.67	2.59
HSE06-SOC-vdW	2.44	0.31	-0.32	4.59	0.99	2.16
DFE (eV) , $E_F=0$	V_I^+	I_i^-	V_{Pb}^{2-}	Pb_i^{2+}	V_{MA}^-	MA_i^+
PBE	0.58	0.76	0.33	1.56	0.18	1.41
PBE-SOC	0.67	0.58	-0.09	1.71	-0.02	1.52
HSE06-SOC	0.29	1.24	1.16	0.75	0.76	1.01
HSE06-SOC-vdW	0.87	0.61	0.66	1.16	1.06	0.57

By the analysis of results in Table 2, strong variations in the calculated DFEs of neutral defects at PBE and PBE-SOC levels of theory are reported for donor defects, such as V_I , Pb_i and MA_i , while limited deviations for the other defects are reported. Donor defects can ionize through the general reaction $D^0 = D^+ + 1e^-$ (CB), with V_I and MA_i in their neutral state leading to partially occupied CB states. SOC largely stabilizes the unoccupied 6p orbitals of lead, leading to a CB stabilization of ~ 0.8 eV compared to scalar relativistic results. Such stabilization is responsible of the DFEs decrease calculated for these defects when SOC is included. On the other hand, the limited SOC-

Figure 3. Calculated DFEs with different functionals in I-rich conditions in the 2x2x1 supercell: a) PBE; b) HSE06-SOC; c) HSE06-SOC including D3 dispersions; d) Thermodynamic ionization levels calculated at the PBE, HSE06-SOC and PBE0-SOC levels of theory for the most stable defects. The ionization levels of the pristine supercell (P^*) has been also reported in order to show the effects of PBE0 functional on shallow defects. In all cases both the potential alignment and Makov-Payne corrections ($\epsilon=24.0$) have been applied to the DFEs.

induced destabilization of 0.19 eV reported for 5p orbitals of iodine, determining the electronic structure of the top of the VB, only slightly affects the calculated DFEs of defects with acceptor character, like I_i , V_{MA} and V_{Pb} , which introduce holes in the VB following the general reaction $A^0 = A^- + 1h^+$.

Concerning charged defects, the rigid down-shifts of the VB and CB after the introduction of SOC and self-interaction corrections through hybrid functionals leads to a stabilization/destabilization of positive/negative defects compared to the PBE results. By looking for instance to the iodine interstitial, calculated DFEs for $E_F=0$, left side of the Fermi level range in the two diagrams in Figure 3a-b, a stabilization of positive interstitial of 0.23 eV and a destabilization of the negative interstitial of 0.48 eV is found. For charged defects the relation between the DFEs and the position of the VBM is explicitly formalized in Eq. 2.

The VBM downshift obtained at the HSE06-SOC level with respect to the PBE functional is responsible of the destabilization/stabilization of the negative/positive defects, due to the energy decrease of the E_F term, as calculated at the VBM. The extent of DFEs deviation cannot be easily predicted due to the contribution of the exact exchange to the lattice energies (see for instance change of DFE for neutral interstitial), but deviations almost proportional to the band edges shifts are reported.

The effects on the DFEs induced by the hybrid functional has a dramatic impact on the thermodynamic ionization levels, Figure 3d, whose levels shift in the band gap compared with the PBE case. As a consequence, the (0/-) transition of interstitial iodine, shallow in the PBE analysis, becomes 0.30 eV deep in the band gap by HSE06-SOC. Similar effects are reported for all the defects showing localized spin densities at the PBE level, such as the I_{MA} and Pb_I antisite defects. An overview of the thermodynamic ionization levels of native defects in $MAPbI_3$ at different levels of theory are reported in Figure S2, Supporting Information.

It is worth mentioning that HSE06 functional provides more accurate results than PBE0 for thermodynamic ionization levels of shallow defects. Inaccuracies of the PBE0 functional in the prediction of shallow transition levels have been reported in the literature.⁹⁹ We illustrate this point in Figure 3d, where the thermodynamic ionization levels of the pristine phase P*, iodine interstitial (deep) and shallow defects, *i.e.* V_{MA} and V_I , are reported as calculated by PBE0-SOC. While this approach delivers thermodynamic ionization levels comparable to HSE06 results for deep levels, such as in the case of the (0/-), (+/-) and (+/0) transitions of interstitial iodine, the long tail of the bare Coulomb kernel in the PBE0 functional causes an over-stabilization of partially filled electronic states almost resonant with the CBM and VBM, leading to an artificial deepening of the associated thermodynamic ionization levels in the band gap.

Beside the effects of the functional and SOC, also the inclusion of Van der Waals dispersions has a sizable impact on the defects formation energies, with a different behavior between Pb and I-related defects, Figure 3c. While in the case of iodine-related defects interstitials and vacancies are stabilized and destabilized respectively, in the case of Pb-related defects the opposite trend is reported. The negligible dispersions contributions to the chemical potential of the I_2 molecule in the gas phase destabilize the iodine in such form by favoring interstitials iodine in the perovskites lattice, where dispersions contributions are larger. On the other hand, dispersion corrections, as calculated in the Pb metal, tend to over-stabilize Pb ions in the metallic phase compared to Pb in the perovskite, by stabilizing vacancies (the opposite is reported for interstitials). The impact of dispersion corrections on the calculated DFEs is also related to the choice of chemical potentials references. As a comparison, in Figure S3 of the SI we report the effects of dispersion corrections on the DFEs of $MAPbI_3$ in I-rich conditions by using as chemical potential reference for iodine the I_2 gas molecule and the I_2 in the orthorhombic solid phase. In the last case the impact on the DFEs is less dramatic than in the former and an overall trend to stabilize/destabilize interstitials/vacancies is observed.

4. Charge corrections and elastic effects

Within the supercell approach the simulation of charged defects is limited by periodic interactions of the charges in periodic boundary conditions (PBC). The calculation of charged systems in PBC is problematic due to the divergence of the $G=0$ term in the Hartree potential. This term is usually neglected in the Hartree summation, as in the case of neutral systems where the term is formally null. In the case of charged systems, this is physically consistent with the introduction of a background of opposite charge in order to maintain the electroneutrality of the cell. Within this approach, both the background-charge and charge-charge electrostatic interactions require ad-hoc corrections in order to recover the infinite dilute limit, where the charges are non-interacting. Furthermore, in order to accurately predict the charges exchange contribution to the DFEs, *i.e.* the term $q\Delta V$ in Eq. 2, a potential alignment procedure is commonly adopted between the defects and pristine supercells in order to align the Fermi reservoir in the two calculations. The introduction of the defect into the pristine supercell in fact may shift the average electrostatic of the pristine lattice even in regions far away from the defect and this should be taken in account when the energy of the VBM of the bulk phase is used in the calculation of the electrons exchange term. The shift of the average electrostatic potential is induced by the change in the number and type of pseudopotentials in the supercell simulation due to the introduction of the defect, as well as by the electrostatic pinning due to the localized defect charge. Due to the slow convergence of the potential term in charged calculations, usually the alignment term $q\Delta V_{0/b}$ is used as calculated in the shift of the potential in the neutral defect and pristine supercells.⁸⁴ In order to correct the calculated DFEs of charge defects, several correction schemes have been proposed and in this section the accuracy of the most common methods, specifically the Makov-Payne¹⁰⁰ (MP), Freysoldt-Neugebauer-Van de Walle (FNV),¹⁰¹ and the Lany-Zunger (LZ)⁸⁵ methods is discussed by focusing on two native defects in MAPbI₃ in two different states of charge, namely V_{Pb}^{2-} and I_i^+ .

In the Makov-Payne approach the correction term is an extension of the Madelung energy for localized charge q in a periodically repeated cubic lattice of length L , whose expression is

$$E_{corr}^{MP} = \frac{q^2 \alpha}{2\epsilon L} - \frac{2\pi q Q}{3\epsilon \Omega L^3} \quad (8)$$

where α is the Madelung constant, ϵ the dielectric constant of the pristine bulk, Q the quadrupole moment of the charge distribution and Ω the volume of the cell. The first term in Eq. 8 represents the Madelung energy of an ideal point charge within a neutralizing background, while the second term represents the interaction of the quadrupole moment of the charge with the background. Due to the different scaling behavior of the two terms in Eq. 8, i.e. the first and second terms scale with L^{-1} and L^{-3} respectively, the second term has a minor (although sizable) contribution to the total energy correction term and is rarely applied. The difficulty in the definition of the quadrupole moment of a periodic system and of the localized charge density shape around the defect further limit its use and thus in our discussion it is neglected. In the LZ approach the Madelung term is further reduced to a fraction of 0.65 of the first MP term. Such an approach is formally justified in the original work by showing a better accuracy compared to the original MP correction.⁸⁵ Both the MP and LZ corrections are the simplest correction that can be applied in the calculation of DFEs of charged defects, in conjunction to the shift correction $\Delta V_{0/b}$ of the potential induced by the defect. This last term is evaluated by averaging the electrostatic potentials of the neutral defect and pristine supercells in a region sufficiently distant from the defect. The partial ambiguity of this approach is removed in the FNV approach, where an exact formulation of the electrostatic corrections and potential shift in periodic lattices is formalized through the introduction of a model charge potential and its comparison with the DFT potential calculated in the supercell. The FNV correction is expressed as¹⁰¹

$$E_{corr}^{FNV} = E_{lat} - q\Delta V_{q/b} \quad (9)$$

where E_{lat} corresponds to the MP electrostatic correction for the model charge distribution, usually a gaussian charge, and

$$\Delta V_{q/b} = (V_q^{\text{DFT}} - V_{\text{bulk}}^{\text{DFT}}) - V^{\text{mod}} \quad (10)$$

is the difference between the DFT potential difference of the charged and pristine system ($V^{\text{DFT}} = V_q^{\text{DFT}} - V_{\text{bulk}}^{\text{DFT}}$) and the potential of the model charge V^{mod} in a region far away from the defect in the supercell. Compared to the MP corrections, the FNV scheme allows one to tune the model charge expression in order to reproduce the long range behavior of the charged defect in a dielectric medium depending on the localization nature of the defect, by providing more accurate results. The FNV scheme also provides a formally exact definition of the potential alignment term ΔV of charged defects in Eq. 2, although its use is limited due to the difficulty in the determination of the V_{DFT} term due to the noise introduced by structural relaxation of the lattice.

All the methods described above require the definition of the dielectric constant of material, which is a critical parameter to estimate the screening of the defect charge by the electronic and lattice polarization. As discussed below, the application of these schemes to the corrections of DFEs of frozen defects, *i.e.* without relaxing the structure upon defect formation, is straightforward and the use of the high frequency dielectric constant, $\epsilon(\infty)$, leads to satisfactory results. The high frequency dielectric constant can be calculated by density functional perturbation theory (DFPT)¹⁰² or by applying finite field perturbation methods. On the other hand, the use of the static dielectric constant $\epsilon(0)$, where the contribution of the relaxation of the lattice to the dielectric constant is taken in account,¹⁰³ is more appropriate for the corrections of DFEs in the case of practical interest in which the structure is also relaxed.⁸⁴

In Figure 4b-c and 4e-f the accuracy of the above mentioned methods in the corrections of the defects formation energies of V_{Pb}^{2-} and I_i^+ defects, both in the unrelaxed (NR) and relaxed cases (R), is illustrated. The DFEs of these defects have been calculated in increasing size supercells:

Figure 4. a) Potential profile of the DFT potentials difference V^{DFT} , of a model Gaussian charge V^{mod} and the respective difference $\Delta V_{q/b}$ for the unrelaxed V_{Pb}^{2-} ; Electrostatic corrections within different corrections schemes for b) Unrelaxed V_{Pb}^{2-} (NR); c) Relaxed V_{Pb}^{2-} (R); d) Potentials profile of the frozen I_i^+ defect; e-f) Correction for unrelaxed and relaxed I_i^+ , respectively; f) (w/o = non corrected, PA = potential alignment, MPPA= Makov Payne with PA, FNV=Freysoldt-Neugebauer - Van de Walle, LZ = Lany-Zunger).

2x1x1, 2x2x1, 2x2x2, 3x2x2 and 3x3x2 supercells, with 96, 192, 384, 586 and 764 atoms respectively and by using k-points grids of 2x4x2, 2x2x2, 2x2x1, 1x2x2 and Γ in the Brillouin zone (BZ), respectively. In the diagrams the uncorrected formation energies have been compared with corrected energies following the different schemes, in order: potential alignment (PA), MP + PA (MPPA), LZ and FNV. In all cases the relative variations of the DFEs with respect to the

smallest supercells are reported *vs.* $1/V^{1/3}$, where V is the volume of the supercells. The infinite dilute limit to the corrections have been evaluated by fitting the values of uncorrected formation energies with functions of the form $L^{-1} + L^{-3}$. Here, the extrapolation procedure is complicated by the non-cubic symmetry of the tetragonal MAPbI₃ cell and by the non-isotropic change of the Madelung constant across the differently shaped supercells. In the case of relaxed defects elastic contributions across different sized supercells may also affect extrapolated values, although only minor effects are expected (see discussion below). In order to avoid elastic effects, we extrapolated only the last four points in the case of relaxed V_{Pb}^{2-} (see Figure 4c), while we did not apply the extrapolation procedure in the case of relaxed I_i^+ (see Figure 4f) where the last three points are indicative of a converged energy of formation (within the limits of accuracy of the functional).

By looking at Figure 4, a slow convergence of the electrostatic potential by increasing supercells size is reported for both frozen and relaxed defects. The origin of such behavior is not trivial and likely resides in the electronic structure of the modelled defects and in the number and nature of the pseudopotentials added or removed in order to form it. PA corrected results are underestimated with respect to the extrapolated value in frozen defects, while for relaxed defects the potential alignment procedure provides sufficiently converged results starting from the 2x2x2 supercell. The MP, LZ and FNV corrections have been applied to frozen defects by using the infinite frequency dielectric constant ϵ_∞ of MAPbI₃ calculated by the DFPT method at the PBE level, *i.e.* 5.7. In order to show the adequacy of this approach we report in Figure 4a-d the plot of the calculated potential difference between the frozen charged defect and pristine supercells V^{DFT} , the potential of a Gaussian model charge in a dielectric medium with $\epsilon=5.7$ V^{mod} and their difference $\Delta V_{q/b}$. This procedure is adopted in the FNV scheme in order to verify the goodness of the modelled charge in the electrostatic correction and to estimate an accurate value of the potential shift between the charged and pristine supercell. As it can be seen, in the two cases the long range part of the calculated DFT potential is well reproduced by the model charge and their difference

simply provides the shift in the electrostatic potential not directly induced by the charge, *i.e.* $\Delta V_{q/b}$. This last term is then used in order to align the Fermi energy between the defect and pristine calculation.

Among the MPPA, LZ and FNV schemes, the last two schemes show a faster convergence toward the extrapolated value by increasing the supercell size, while a slower convergence and an overestimation of the DFEs are reported for the MPPA scheme. The calculations of the DFEs of unrelaxed defects are however useless and the relaxation of the lattice upon formation of the defect should be accounted in order to provide accurate values. In this regard the application of the FNV corrections is somehow limited, due to the difficulty in the determination of the DFT potential difference far away from the defects which appears noisy due to the relaxation of the ions. In our approach the potential alignment term $\Delta V_{q/b}$ has been evaluated by averaging the potential difference in a region far from the defect. By looking at Figure 4c and 4f, it is shown that the corrections to the DFEs of relaxed defects through the MP schemes are largely overestimated when the $\epsilon(\infty)$ dielectric constant is used, due to the contribution to the dielectric constant introduced by the relaxation of the lattice. The use of the static dielectric constant $\epsilon(0)=24.0$, although improving the quality of the corrected energies with respect to extrapolated results, tends to overestimate the energy correction, particularly in small supercells. In the cases of relaxed defects the better agreement between corrected and extrapolated values is achieved by only adopting the potential alignment term, taking care of performing calculations in the $2 \times 2 \times 2$ supercell. Beside charge corrections, elastic effects may also have a large impact on the calculated DFE in supercells smaller than $2 \times 2 \times 2$. In order to show these effects in Table 3 the DFEs of a selected list of neutral defects calculated at the PBE level in I-rich conditions have been reported as calculated in the $2 \times 2 \times 1$ and $2 \times 2 \times 2$ supercells.

Table 3. DFEs of a selected list of relaxed neutral defects calculated at the PBE level (no dispersions) in I-rich conditions in the 2x2x1 and 2x2x2 supercells. For I_i in parenthesis the value calculated in the 3x3x2 supercell is reported.

DFE(eV)	V_{Pb}	I_i	V_I	MA_i
2x2x1	0.01	0.80	2.14	2.93
2x2x2	0.01	0.49 (0.54)	2.09	2.91

While most of the defects show converged values already in the 2x2x1 supercell, in the most critical case, the I_i interstitial is stabilized by ~ 0.31 eV going from the 2x2x1 to 2x2x2 supercell. This suggests that in order to avoid elastic effects in the evaluation of DFEs, calculations should be performed at least in 2x2x2 supercells of the tetragonal phase or in comparable supercells for cubic and orthorhombic phases.

5.1 Defect chemistry of $MAPbI_3$

Summarizing the previous results, an accurate estimation of DFEs in lead halide perovskites requires: i) high level DFT calculations based on hybrid functionals with the inclusion of spin-orbit corrections; ii) the use of fairly large supercells, *e.g.* 2x2x2 supercells. Technical precaution i) allows to correctly estimate both lattice energies and the electronic exchange terms in Eq. 2 due to a quantitative description of the electronic structure of the perovskite. On the other hand, precaution ii) provides sufficiently converged results after applying PA and electrostatic corrections to the DFEs and avoid elastic effects related to lattice relaxation in the defects supercells. Electrostatic corrections based on the MP, LZ and FNV schemes in combination with PA corrections only slightly improve results in large supercells due to the high static dielectric constant of the perovskite ($\epsilon=24.0$), while they tend to overestimate corrections in small/medium supercells. The use of PA corrections alone provides sufficiently converged results starting from the 2x2x2 supercell.

Based on these considerations, in this last section we provide an overview of the main defects properties of the MAPbI₃ perovskite, as calculated in the 2x2x2 tetragonal supercell by using the HSE06-SOC functional ($\alpha=0.43$) and by only applying the potential alignment term. Dispersion corrections have been also added a-posteriori according to the DFT-D3 method of Grimme.¹⁰⁴ In Figure 5a-c we report the calculated DFEs in I-rich, I-medium and I-poor conditions; the thermodynamic ionization levels diagram is shown in Figure 5d; and the optimized structures of a selected list of defects are reported in Figure 5e.

Figure 5. a) Calculated DFEs at the HSE06-SOC ($\alpha=0.43$) level by including dispersion corrections through the DFT-D3 method (a posteriori correction) in a) I-rich (point A); b) I-medium (point B) and c) I-poor (point C) conditions. DFEs have been calculated in the 2x2x2 supercell by

applying PA corrections. d) Thermodynamic ionization levels of the most stable defects. e) Structures of a selected list of defects.

Under I-rich conditions conditions the most stable defects in the perovskite are positive I_i^+ interstitials and lead vacancies, which pin the Fermi level at 0.27 eV above the VBM. In its positive charged state I_i^+ is bonded to other two iodines to form a trimer with bond lengths of 2.95 Å, Figure 5e. This defect is stable in the p-region of the diagram and can trap electrons through the (+/0) deep transition placed at 0.86 eV above the VBM, Figure 5d. Upon the electron trapping process the positive trimer undergoes a large lattice relaxation by forming the neutral I_i , where two iodines are bonded at a distance of 3.26 Å in a I_2^- dimer. The neutral trapped interstitial is however metastable, by showing a barrier to recombination.¹³ Lead vacancies are stable in the neutral and doubly negative charged forms and are among the most stable defects in all conditions of growth of the perovskite. Although the migration barrier for this defect is relatively high (> 1 eV),⁶⁰ the low energy of formation in all environment conditions highlights the tendency of the perovskite to release metal lead under intense irradiation or at high temperature, as already observed in XPS experiments.³² In the negative vacancy, the Pb ion leaves its lattice position with a consequent outwards relaxation of halide ions at distances > 6 Å, Figure 5e. Interestingly, at low Fermi energies lead vacancies decompose to give a positive interstitial and an halide vacancy, following the reaction $V_{Pb}^{2-} + 2h^+ = V_{Pb}^0 = V_{Pb}^{2-} + I_i^+ + V_I^+$, Figure 5e. The (0/2-) thermodynamic transition is placed at 0.30 eV above the VBM, while a shallow (-/2-) and deep (0/-) transitions are reported in the thermodynamic ionization diagram for this defect. The (0/2-) and (0/-) transitions, although deep in the band gap have only a limited trapping activity: the first due to the low cross section of the two-electron trapping process, while the second transitions can act by charge trap only in heavily p-doped conditions, where the neutral V_{Pb} (I trimer) is stable.

In I-medium conditions of growth the most stable defects are methylammonium interstitials MA_i^+ and lead vacancies $\text{V}_{\text{Pb}}^{2-}$, as well as negative I_i^- , which pin the Fermi level of the system at 0.61 eV above the VBM. The calculated native Fermi value for MAPbI_3 highlights that the perovskite tends to growth mightly p-doped. Methylammonium cations are stable only in the positive charged states along the overall Fermi level range, by showing a shallow (+/0) transition occuring within the CB. The cation occupies interstitials positions on the facets of the Pb-I_6 octahedra in the lattice, Figure 5e, with relatively low energies of formation, 0.49 eV. Negative iodine interstitials I_i^- are weakly bonded to form iodine dimers at distances $> 3.80 \text{ \AA}$, Figure 5e. Such defects can trap holes through the (0/-) transition placed at 0.18 eV above the VBM, by providing neutral interstitials in the form of I_2^- dimers. In this case however, the small lattice rearrangement within the trapping process and the overlap between vibronic states of the negative and neutral interstitials favor a relatively fast emissive decay of the hole from the defects.¹³ Similarly to I-medium conditions, also in I-poor conditions the most stable defects are MA_i^+ , $\text{V}_{\text{Pb}}^{2-}$ and I_i^- , which pin the Fermi level to the n-region of the diagram. Other defects such as V_I^+ , Pb_i^{2+} and V_{MA}^- show higher formation energies in all conditions of growth with shallow ionization levels and likely play a minor role in the defects chemistry of bulk MAPbI_3 .

The analysis of the defects formation energies and thermodynamic ionization levels diagrams of MAPbI_3 highlights that potential recombination centers in the perovskite are related to iodine defects, in the form of interstitials I_i (+ and -) and, to minor extent, lead vacancies. These defects introduce deep levels in the band gap with calculated densities in I-medium conditions of 10^{10} - 10^{13} cm^{-3} , in good agreement with experiments performed on single crystal MAPbI_3 .¹⁶ Antisites defects I_{MA} also show similar trapping properties of iodine interstitials and lead vacancies (see Figure S2 in SI), with the neutral charged form assuming the configuration of the iodine trimer and the 2- negative charged state a configuration similar to I_i^- . The intermediate charged forms of these three defects being always the I_2^- dimer.

The similar configurations assumed by iodines in I_i , V_{Pb} and I_{MA} defects centers in their different oxidation states highlight that the photo-chemistry of charge traps in $MAPbI_3$ is dominated by the redox chemistry of iodine.^{13, 105} Furthermore, the large lattice rearrangements involved in the conversions among the different oxidation states, as a consequence of charge trapping processes, may lead to the formation of metastable trapped centers, partially inactivating non-radiative recombination channels in the perovskites, as discussed by us in the case of positive iodine interstitial.¹³

5.2 Effects of the environment

The calculated DFEs and ionization levels also deepens our knowledge of the defects chemistry when the perovskite interacts with the environment, particularly regarding the activity of charge traps. As an example, in Figure 6, a schematic of two possible mechanisms of PL quenching (PLQ) and enhancement (PLE) induced by exposure of $MAPbI_3$ to I_2 and O_2 gas, respectively, is reported.^{80, 81}

The exposure of $MAPbI_3$ to moderate pressure of I_2 gas induces: i) the formation of metallic Pb, as revealed by XPS experiments;³⁷ ii) a PL quenching;³⁶ iii) an irreversible p-doping of the perovskite with an increased holes conductivity.^{38, 39} A microscopic interpretation of these effects is possible by the analysis of the energetics of incorporation of I_2 within the $MAPbI_3$ lattice and the study of the DFE diagram of the perovskite in equilibrium with gaseous I_2 .

Based on DFT calculations, a general instability of the I_2 molecule both in the bulk and on the surface of $MAPbI_3$ is reported.⁸⁰ Specifically, I_2 spontaneously dissociates on iodine vacancies to form positive interstitials, following the reaction $I_2 + V_I^+ = I_I^+ + I_i^+$, with a favored energy of -0.39 eV (PBE) in the bulk $MAPbI_3$. Besides the vacancies saturation path, further interactions with lattice iodines leads to the dissociation of the molecule to form I_i^+ / I_i^- couple interstitials, i.e. $I_2 = I_i^+ + I_i^-$ (see Figure 6a-b), with calculated PBE energies of 0.40 eV and -0.73 eV in the bulk and on the PbI_2 -terminated (001) surface, respectively.⁸⁰ The analysis of the DFE diagram calculated in I-rich

Figure 6. Two proposed mechanism of PL quenching (PLQ) and enhancement (PLE), involving defects of MAPbI₃ in interaction with I₂ and O₂ gas.^{80, 81} a) Initial structure of the I₂ molecule in the bulk MAPbI₃ lattice and b) equilibrium geometry configuration showing the formation of I_i⁺ / I_i⁻ couple; c) DFE diagram of MAPbI₃ in equilibrium with I₂ gas, i.e. $\mu_I = 1/2 \mu(\text{I}_2)$, calculated in the 2x2x1 supercell at the HSE06-SOC level, by including dispersion corrections and translational entropy in the iodine chemical potential at room temperature; d) Equilibrium geometry of negative iodine interstitial and e) geometry of the IO₃⁻ species, the product of oxidation of interstitial in the bulk MAPbI₃; f) the thermodynamic ionization levels of the I_i⁻ and IO₃⁻ defects calculated in the 2x2x1 supercell at the HSE06-SOC level, dispersion included.

conditions (Figure 6c), simulating MAPbI₃ in equilibrium with I₂ gas at room temperature, also confirms this picture by indicating that most stable defects in these conditions are I_i⁺ and V_{Pb}²⁻, which pin the Fermi level to lower values compared to the intrinsic perovskite, indicating a p-

doping.⁸⁰ These results confirm that the exposure of MAPbI₃ to I₂-rich environment leads to the spontaneous incorporation of iodine into the perovskite to form positive interstitials I_i⁺ and lead vacancies V_{Pb}²⁻, with parallel nucleation of metallic Pb. The observed PL quenching is thus induced by the increased densities of I_i⁺ charge traps in the perovskite and the irreversible p-doping likely associated to the formation of compensating V_{Pb}²⁻ defects. Interestingly, the I_i⁺ / I_i⁻ couple is not stable under light irradiation conditions, when both electrons and holes are trapped on the center. By simulating the lowest triplet state of the couple on the (001) surface of MAPbI₃, a release of I₂ from the surface is observed, with a spontaneous energy of -0.19 eV (PBE). This may represent an additional path of defects curing in the perovskite.⁸⁰

The exposure of MAPbI₃ to moderate quantities of dry oxygen, on the other hand, leads to an enhancement of the PL (PLE), as reported by several experiments.⁴³⁻⁴⁹ The reversibility of the process suggests a weak interaction of O₂ with the charge traps of the perovskite, likely leading to their passivation. The interaction with O₂ however is a complex process, and can also induce a degradation of the perovskite through the formation of superoxides species assisted by light.⁸²

The beneficial effect of oxygen on the PL can be investigated by simulating its interaction with charge traps, in particular negative iodine interstitials which can trap holes through the (0/-) transition, leading to radiative recombination processes. The oxidation of negative iodine interstitials I_i⁻ mainly leads to the formation of typical hypoiodite, iodite and iodate compounds, i.e. IO⁻, IO₂⁻ and IO₃⁻. The formation of these species is only slightly thermodynamically favored, with calculated PBE energies of 0.02, 0.13 -0.05 eV, respectively, highlighting that such reactions are partially reversible.⁸¹ Furthermore, besides the oxidation of interstitials, oxidation of the lattice iodines can also take place, although this process is less favored than the former.⁸¹ Among the aforementioned reactions, the formation of iodate, i.e. I_i⁻ + 3/2 O₂ = IO₃⁻ (see Figure 6e) is the most favored reaction and likely IO₃⁻ is the most stable defect product forming upon exposition of MAPbI₃ to O₂-rich environment. The effect of the oxidation of interstitials defects on the PL

properties can be investigated by the analysis of the deep (0/-) transition responsible of the charge trapping on the center. The oxidation of iodine interstitial to form IO_n^- induces a shallowing of the (0/-) transition, that shifts down 0.25 eV toward the VB as reported for the IO_3^- defect (see Figure 6f), by reducing the trapping activity of the defect.⁸¹ By our model thus we predict a reversible passivation of iodine traps through the formation of iodate species in the lattice associated to an increase of the PLQY of the perovskite.

6. Concluding remarks

In summary, an analysis of the technical issues commonly encountered in the DFT modelling of defects in lead halide perovskites has been carried out. Our discussion, focused on the prototype MAPbI_3 perovskite, highlights that for an accurate prediction of the defects properties of these materials traditional semi-local functionals, such as PBE, are largely insufficient and high level DFT calculations with hybrid functionals and SOC corrections are required. These methods, besides providing a more accurate electronic structure of the perovskite, also have a large impact on the defects geometries. In this regard, while full hybrid functional relaxation procedures are computationally impractical, the use of opportunely tailored LDA+U+SOC procedures or a careful check of the geometries at the hybrid level by performing single points calculations at different geometries can be the solution.

Among hybrid functionals, the use of screened coulomb kernel functionals, such as HSE06, should be the preferred choice over full coulomb kernel functionals such as PBE0, particularly for shallow defects. The use of screened hybrid functionals in their original implementation however can lead to unsatisfactory results in the electronic description of perovskites, and the exchange fraction should be increased in order to retrieve a band gap more comparable with benchmark GW calculations (and experiments). While an increased fraction of exchange does not affects the basic thermodynamics of perovskites, a problem arises when extrinsic elements are modelled within the perovskites, such as in the case of extrinsic doping. In these cases, the overall effects of the

increased exchange on the thermodynamics of formation is not clear and further studies aimed to confirm the goodness of this approach should be performed. Furthermore, the use of hybrid functionals in conjunction with norm-conserving pseudopotentials and plane waves can lead to unsatisfactory results if partially complete semi-core states are included in the valence. These results suggest the use of norm-conserving pseudopotentials with complete semi-core shells in the valence or, where possible, the use of all-electrons or PAW methods.

We also discussed convergence issues in the calculation of the defects formation energies, by comparing the performance of commonly employed correction schemes. In this regard, the high dielectric screening of the lattice strongly reduces the periodic interactions of charged defects in the supercell approach and potential alignment procedures are sufficient in order to have accurate DFEs, provided that calculations are performed in medium/large supercells.

Finally, we discussed the defect properties of MAPbI₃ by using a converged computational strategy. The results show that the defect chemistry of MAPbI₃ is dominated by the typical iodine redox chemistry, as exemplified by the defect properties of interstitial iodine. As such, we expect quantitative differences by changing the halide in *e.g.* MAPbBr₃, although the underlying chemistry should remain similar. The lack of strong directional preference for lead-halide bonds makes Pb-based defects less relevant for trapping.

We believe this study will serve as useful reference for further defect calculations on lead-halide perovskites.

Computational details

All defects calculations throughout the work have been carried out in the tetragonal phase of MAPbI₃, by fixing the cell parameters to the experimental values, i.e. $a = b = 8.849 \text{ \AA}$, $c = 12.642 \text{ \AA}$.² PBE calculations have been performed by using ultrasoft pseudopotentials with a cutoff on plane waves of 40 Ryd (320 Ryd on the charge density), while hybrid calculations were performed at the

PBE geometries by using norm-conserving pseudopotentials and a cutoff of 40 Ryd on the wavefunctions (160 Ryd on the charge density). To reduce the computational effort the cutoff on the Fock grid has been reduced to 80 Ryd, without sizable impact on the total energies and preserving the good convergence of calculations. 1x1x2 and Γ -only k-points grids in Brillouin zone were used for the 2x2x1 and 2x2x2 supercells, respectively. All calculations have been carried out by using the Quantum Espresso package.¹⁰⁶ Dispersion corrections have been applied to defects formation energies a-posteriori on the PBE geometries by using the DFT-D3 code of Grimme.¹⁰⁴ The 22 electrons norm-conserving pseudopotential used in hybrid calculations has been generated by using the ONCV code,¹⁰⁷ while FNV corrections to the DFEs have been applied by using Freysoldt's code.¹⁰¹

Supporting Information available: The Supporting Information is available free of charge on the ACS Publications website.

Band edges and band gaps of MAPbI₃ calculated at the hybrid level with norm-conserving pseudopotentials and PAW method; effects of increased exchange fraction on a selected list of thermodynamic quantities; comparison of thermodynamic ionization levels of native defects in MAPbI₃ at different levels of theory; effects of the iodine chemical potentials on the DFEs with and w/o dispersion corrections.

Authors Biographies:

Daniele Meggiolaro received his PhD in Chemistry at 'La Sapienza' University of Rome (Italy) in 2015. Currently he is working as a postdoctoral researcher at Istituto Italiano di Tecnologia (IIT) of Genova (Italy). His research activity is focussed on the computational modelling of innovative materials for photovoltaics and energy storage, such as perovskites solar cells and Li-ion batteries.

Filippo De Angelis is Senior Researcher at Consiglio Nazionale delle Ricerche CNR-ISTM of Perugia (Italy) and leader of the Computational Laboratory for Hybrid/Organic Photovoltaics

(CLHYO - www.clhyo.org). Most of his recent research includes the computational modelling of solar energy materials, with emphasis on water splitting, dye-sensitized and perovskite solar cells.

Acknowledgment:

The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No. 763977 of the PerTPV project.

References

- (1) Green, M. A.; Ho-Baillie, A.; Snaith, H. J. The Emergence of Perovskite Solar Cells. *Nat. Photon.* **2014**, 8, 506-514.
- (2) Stoumpos, C. C.; Malliakas, C. D.; Kanatzidis, M. G. Semiconducting Tin and Lead Iodide Perovskites with Organic Cations: Phase Transitions, High Mobilities, and near-Infrared Photoluminescent Properties. *Inorg. Chem.* **2013**, 52, 9019-9038.
- (3) Mosconi, E.; Amat, A.; Nazeeruddin, K.; Grätzel, M.; De Angelis, F. First-Principles Modeling of Mixed Halide Organometal Perovskites for Photovoltaic Applications. *J. Phys. Chem. C* **2013**, 117.
- (4) Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J. P.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J. Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber. *Science* **2013**, 342, 341-344.
- (5) Miyata, A.; Mitoglu, A.; Plochocka, P.; Portugall, O.; Wang, J. T.-W.; Stranks, S. D.; Snaith, H. J.; Nicholas, R. J. Direct Measurement of the Exciton Binding Energy and Effective Masses for Charge Carriers in Organic-Inorganic Tri-Halide Perovskites. *Nat. Phys.* **2015**, 11, 582-587.
- (6) Lin, Q.; Armin, A.; Nagiri, R. C. R.; Burn, P. L.; Meredith, P. Electro-Optics of Perovskite Solar Cells. *Nat. Photon.* **2015**, 9, 106-112.
- (7) Srimath Kandada, A. R.; Petrozza, A. Photophysics of Hybrid Lead Halide Perovskites: The Role of Microstructure. *Acc. Chem. Res.* **2016**, 49, 536-544.
- (8) Wehrenfennig, C.; Eperon, G. E.; Johnston, M. B.; Snaith, H. J.; Herz, L. M. High Charge Carrier Mobilities and Lifetimes in Organolead Trihalide Perovskites. *Adv. Mater.* **2014**, 26, 1584-1589.
- (9) Jeon, N. J.; Noh, J. H.; Yang, W. S.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. I. Compositional Engineering of Perovskite Materials for High-Performance Solar Cells. *Nature* **2015**, 517, 476-480.
- (10) Zhou, H.; Chen, Q.; Li, G.; Luo, S.; Song, T.-b.; Duan, H.-S.; Hong, Z.; You, J.; Liu, Y.; Yang, Y. Interface Engineering of Highly Efficient Perovskite Solar Cells. *Science* **2014**, 345, 542-546.
- (11) Shi, D.; Adinolfi, V.; Comin, R.; Yuan, M.; Alarousu, E.; Buin, A.; Chen, Y.; Hoogland, S.; Rothenberger, A.; Katsiev, K., et al. Low Trap-State Density and Long Carrier Diffusion in Organolead Trihalide Perovskite Single Crystals. *Science* **2015**, 347, 519-522.

- (12) Yin, W.-J.; Shi, T.; Yan, Y. Unusual Defect Physics in CH₃NH₃PbI₃ Perovskite Solar Cell Absorber. *Appl. Phys. Lett.* **2014**, 104, 063903.
- (13) Meggiolaro, D.; Motti, S. G.; Mosconi, E.; Barker, A. J.; Ball, J.; Andrea Riccardo Perini, C.; Deschler, F.; Petrozza, A.; De Angelis, F. Iodine Chemistry Determines the Defect Tolerance of Lead-Halide Perovskites. *Energy Environ. Sci.* **2018**, 11, 702-713.
- (14) Tress, W. Perovskite Solar Cells on the Way to Their Radiative Efficiency Limit – Insights into a Success Story of High Open-Circuit Voltage and Low Recombination. *Adv. Energy Mater.* **2017**, 7, 1602358-n/a.
- (15) Shockley, W.; Read, W. T. Statistics of the Recombinations of Holes and Electrons. *Phys. Rev.* **1952**, 87, 835-842.
- (16) Adinolfi, V.; Yuan, M.; Comin, R.; Thibau, E. S.; Shi, D.; Saidaminov, M. I.; Kanjanaboos, P.; Kopilovic, D.; Hoogland, S.; Lu, Z.-H., et al. The in-Gap Electronic State Spectrum of Methylammonium Lead Iodide Single-Crystal Perovskites. *Adv. Mater.* **2016**, 28, 3406-3410.
- (17) Leijtens, T.; Eperon, G. E.; Barker, A. J.; Grancini, G.; Zhang, W.; Ball, J. M.; Kandada, A. R. S.; Snaith, H. J.; Petrozza, A. Carrier Trapping and Recombination: The Role of Defect Physics in Enhancing the Open Circuit Voltage of Metal Halide Perovskite Solar Cells. *Energy Environ. Sci.* **2016**, 9, 3472-3481.
- (18) Chen, Y.; Yi, H. T.; Wu, X.; Haroldson, R.; Gartstein, Y. N.; Rodionov, Y. I.; Tikhonov, K. S.; Zakhidov, A.; Zhu, X. Y.; Podzorov, V. Extended Carrier Lifetimes and Diffusion in Hybrid Perovskites Revealed by Hall Effect and Photoconductivity Measurements. *Nat. Commun.* **2016**, 7, 12253.
- (19) deQuilettes, D. W.; Vorpahl, S. M.; Stranks, S. D.; Nagaoka, H.; Eperon, G. E.; Ziffer, M. E.; Snaith, H. J.; Ginger, D. S. Impact of Microstructure on Local Carrier Lifetime in Perovskite Solar Cells. *Science* **2015**, 348, 683-686.
- (20) Blancon, J.-C.; Nie, W.; Neukirch, A. J.; Gupta, G.; Tretiak, S.; Cognet, L.; Mohite, A. D.; Crochet, J. J. The Effects of Electronic Impurities and Electron–Hole Recombination Dynamics on Large-Grain Organic–Inorganic Perovskite Photovoltaic Efficiencies. *Adv. Funct. Mater.* **2016**, 26, 4283-4292.
- (21) Ayres, J. R. Characterization of Trapping States in Polycrystalline-Silicon Thin Film Transistors by Deep Level Transient Spectroscopy. *J. Appl. Phys.* **1993**, 74, 1787-1792.
- (22) Balcioglu, A.; Ahrenkiel, R. K.; Hasoon, F. Deep-Level Impurities in CdTe/Cds Thin-Film Solar Cells. *J. Appl. Phys.* **2000**, 88, 7175-7178.
- (23) Kerr, L. L.; Li, S. S.; Johnston, S. W.; Anderson, T. J.; Crisalle, O. D.; Kim, W. K.; Abushama, J.; Noufi, R. N. Investigation of Defect Properties in Cu(In,Ga)Se₂ Solar Cells by Deep-Level Transient Spectroscopy. *Solid-State Electron.* **2004**, 48, 1579-1586.
- (24) Zhang, W.; Saliba, M.; Moore, D. T.; Pathak, S. K.; Hörantner, M. T.; Stergiopoulos, T.; Stranks, S. D.; Eperon, G. E.; Alexander-Webber, J. A.; Abate, A., et al. Ultrasoft Organic–Inorganic Perovskite Thin-Film Formation and Crystallization for Efficient Planar Heterojunction Solar Cells. *Nat. Commun.* **2015**, 6, 6142.
- (25) Zhu, H.; Miyata, K.; Fu, Y.; Wang, J.; Joshi, P. P.; Niesner, D.; Williams, K. W.; Jin, S.; Zhu, X.-Y. Screening in Crystalline Liquids Protects Energetic Carriers in Hybrid Perovskites. *Science* **2016**, 353, 1409-1413.
- (26) Miyata, K.; Meggiolaro, D.; Trinh, M. T.; Joshi, P. P.; Mosconi, E.; Jones, S. C.; De Angelis, F.; Zhu, X. Y. Large Polarons in Lead Halide Perovskites. *Sci. Adv.* **2017**, 3, e1701217.
- (27) Neukirch, A. J.; Nie, W.; Blancon, J.-C.; Appavoo, K.; Tsai, H.; Sfeir, M. Y.; Katan, C.; Pedesseau, L.; Even, J.; Crochet, J. J., et al. Polaron Stabilization by Cooperative Lattice Distortion and Cation Rotations in Hybrid Perovskite Materials. *Nano Lett.* **2016**, 16, 3809-3816.
- (28) Ambrosio, F.; Wiktor, J.; De Angelis, F.; Pasquarello, A. Origin of Low Electron-Hole Recombination Rate in Metal Halide Perovskites. *Energy & Environ. Sci.* **2018**, 11, 101-105.

- (29) Heo, S.; Seo, G.; Lee, Y.; Lee, D.; Seol, M.; Lee, J.; Park, J.-B.; Kim, K.; Yun, D.-J.; Kim, Y. S., et al. Deep Level Trapped Defect Analysis in CH₃NH₃PbI₃ Perovskite Solar Cells by Deep Level Transient Spectroscopy. *Energy & Environ. Sci.* **2017**, 10, 1128-1133.
- (30) Sutter-Fella, C. M.; Miller, D. W.; Ngo, Q. P.; Roe, E. T.; Toma, F. M.; Sharp, I. D.; Lonergan, M. C.; Javey, A. Band Tailing and Deep Defect States in CH₃NH₃Pb(I₁-XBr_x)₃ Perovskites as Revealed by Sub-Bandgap Photocurrent. *ACS Energy Lett.* **2017**, 2, 709-715.
- (31) Steirer, K. X.; Schulz, P.; Teeter, G.; Stevanovic, V.; Yang, M.; Zhu, K.; Berry, J. J. Defect Tolerance in Methylammonium Lead Triiodide Perovskite. *ACS Energy Lett.* **2016**, 1, 360-366.
- (32) Sadoughi, G.; Starr, D. E.; Handick, E.; Stranks, S. D.; Gorgoi, M.; Wilks, R. G.; Bär, M.; Snaith, H. J. Observation and Mediation of the Presence of Metallic Lead in Organic-Inorganic Perovskite Films. *ACS Appl. Mater. Interfaces* **2015**, 7, 13440-13444.
- (33) Kong, W.; Ding, T.; Bi, G.; Wu, H. Optical Characterizations of the Surface States in Hybrid Lead-Halide Perovskites. *Phys. Chem. Chem. Phys.* **2016**, 18, 12626-12632.
- (34) Chen, S.; Wen, X.; Yun, J. S.; Huang, S.; Green, M.; Jeon, N. J.; Yang, W. S.; Noh, J. H.; Seo, J.; Seok, S. I., et al. Spatial Distribution of Lead Iodide and Local Passivation on Organo-Lead Halide Perovskite. *ACS Appl. Mater. Interfaces* **2017**, 9, 6072-6078.
- (35) Minns, J. L.; Zajdel, P.; Chernyshov, D.; van Beek, W.; Green, M. A. Structure and Interstitial Iodide Migration in Hybrid Perovskite Methylammonium Lead Iodide. *Nat. Commun.* **2017**, 8, 15152.
- (36) Li, C.; Guerrero, A.; Zhong, Y.; Gräser, A.; Luna, C. A. M.; Köhler, J.; Bisquert, J.; Hildner, R.; Huettner, S. Real-Time Observation of Iodide Ion Migration in Methylammonium Lead Halide Perovskites. *Small* **2017**, 13, 1701711-n/a.
- (37) Wang, S.; Jiang, Y.; Juarez-Perez, Emilio J.; Ono, Luis K.; Qi, Y. Accelerated Degradation of Methylammonium Lead Iodide Perovskites Induced by Exposure to Iodine Vapour. *Nat. Energy* **2016**, 2, 16195.
- (38) Zohar, A.; Levine, I.; Gupta, S.; Davidson, O.; Azulay, D.; Millo, O.; Balberg, I.; Hodes, G.; Cahen, D. What Is the Mechanism of Mapbi₃ P-Doping by I₂? Insights from Optoelectronic Properties. *ACS Energy Lett.* **2017**, 2, 2408-2414.
- (39) Senocrate, A.; Moudrakovski, I.; Kim, G. Y.; Yang, T.-Y.; Gregori, G.; Grätzel, M.; Maier, J. The Nature of Ion Conduction in Methylammonium Lead Iodide: A Multimethod Approach. *Angew. Chem. Int. Ed.* **2017**, 56, 7755-7759.
- (40) Zhang, D.; Cui, B.-B.; Zhou, C.; Li, L.; Chen, Y.; Zhou, N.; Xu, Z.; Li, Y.; Zhou, H.; Chen, Q. Reduction of Intrinsic Defects in Hybrid Perovskite Films Via Precursor Purification. *Chem. Commun.* **2017**, 53, 10548-10551.
- (41) Noh, J. H.; Im, S. H.; Heo, J. H.; Mandal, T. N.; Seok, S. I. Chemical Management for Colorful, Efficient, and Stable Inorganic-Organic Hybrid Nanostructured Solar Cells. *Nano Lett.* **2013**, 13, 1764-1769.
- (42) Kiermasch, D.; Rieder, P.; Tvingstedt, K.; Baumann, A.; Dyakonov, V. Improved Charge Carrier Lifetime in Planar Perovskite Solar Cells by Bromine Doping. *Sci. Rep.* **2016**, 6, 39333.
- (43) Tian, Y.; Merdasa, A.; Unger, E.; Abdellah, M.; Zheng, K.; McKibbin, S.; Mikkelsen, A.; Pullerits, T.; Yartsev, A.; Sundström, V., et al. Enhanced Organo-Metal Halide Perovskite Photoluminescence from Nanosized Defect-Free Crystallites and Emitting Sites. *J. Phys. Chem. Lett.* **2015**, 6, 4171-4177.
- (44) Galisteo-López, J. F.; Anaya, M.; Calvo, M. E.; Míguez, H. Environmental Effects on the Photophysics of Organic-Inorganic Halide Perovskites. *J. Phys. Chem. Lett.* **2015**, 6, 2200-2205.
- (45) Tian, Y.; Peter, M.; Unger, E.; Abdellah, M.; Zheng, K.; Pullerits, T.; Yartsev, A.; Sundstrom, V.; Scheblykin, I. G. Mechanistic Insights into Perovskite Photoluminescence Enhancement: Light Curing with Oxygen Can Boost Yield Thousandfold. *Phys. Chem. Chem. Phys.* **2015**, 17, 24978-24987.

- (46) Stranks, S. D.; Burlakov, V. M.; Leijtens, T.; Ball, J. M.; Goriely, A.; Snaith, H. J. Recombination Kinetics in Organic-Inorganic Perovskites: Excitons, Free Charge, and Subgap States. *Phys. Rev. Applied* **2014**, 2, 034007.
- (47) deQuilettes, D. W.; Zhang, W.; Burlakov, V. M.; Graham, D. J.; Leijtens, T.; Osherov, A.; Bulovic, V.; Snaith, H. J.; Ginger, D. S.; Stranks, S. D. Photo-Induced Halide Redistribution in Organic-Inorganic Perovskite Films. *Nat. Commun.* **2016**, 7, 11683.
- (48) Lorenzon, M.; Sortino, L.; Akkerman, Q.; Accornero, S.; Pedrini, J.; Prato, M.; Pinchetti, V.; Meinardi, F.; Manna, L.; Brovelli, S. Role of Nonradiative Defects and Environmental Oxygen on Exciton Recombination Processes in CsPbBr₃ Perovskite Nanocrystals. *Nano Lett.* **2017**, 17, 3844-3853.
- (49) Motti, S. G.; Gandini, M.; Barker, A. J.; Ball, J. M.; Srimath Kandada, A. R.; Petrozza, A. Photoinduced Emissive Trap States in Lead Halide Perovskite Semiconductors. *ACS Energy Lett.* **2016**, 1, 726-730.
- (50) Brenes, R.; Guo, D.; Osherov, A.; Noel, N. K.; Eames, C.; Hutter, E. M.; Pathak, S. K.; Niroui, F.; Friend, R. H.; Islam, M. S., et al. Metal Halide Perovskite Polycrystalline Films Exhibiting Properties of Single Crystals. *Joule* **2017**, 1, 155-167.
- (51) Kim, G. Y.; Senocrate, A.; Yang, T.-Y.; Gregori, G.; Grätzel, M.; Maier, J. Large Tunable Photoeffect on Ion Conduction in Halide Perovskites and Implications for Photodecomposition. *Nat. Mater.* **2018**, 17, 445-449.
- (52) Mosconi, E.; Meggiolaro, D.; Snaith, H. J.; Stranks, S.D.; De Angelis, F. Light-Induced Annihilation of Frenkel Defects in Organo-Lead Halide Perovskites. *Energy Environ. Sci.* **2016**, 9, 3180-3187.
- (53) Tsai, H.; Asadpour, R.; Blancon, J.-C.; Stoumpos, C. C.; Durand, O.; Strzalka, J. W.; Chen, B.; Verduzco, R.; Ajayan, P. M.; Tretiak, S., et al. Light-Induced Lattice Expansion Leads to High-Efficiency Perovskite Solar Cells. *Science* **2018**, 360, 67-70.
- (54) Buin, A.; Comin, R.; Xu, J.; Ip, A. H.; Sargent, E. H. Halide-Dependent Electronic Structure of Organolead Perovskite Materials. *Chem. Mater.* **2015**, 27, 4405-4412.
- (55) Buin, A.; Pietsch, P.; Xu, J.; Voznyy, O.; Ip, A. H.; Comin, R.; Sargent, E. H. Materials Processing Routes to Trap-Free Halide Perovskites. *Nano Lett.* **2014**, 14, 6281-6286.
- (56) Liu, N.; Yam, C. First-Principles Study of Intrinsic Defects in Formamidinium Lead Triiodide Perovskite Solar Cell Absorbers. *Phys. Chem. Chem. Phys.* **2018**, 20, 6800-6804.
- (57) Kang, J.; Wang, L.-W. High Defect Tolerance in Lead Halide Perovskite CsPbBr₃. *J. Phys. Chem. Lett.* **2017**, 8, 489-493.
- (58) Li, Y.; Zhang, C.; Zhang, X.; Huang, D.; Shen, Q.; Cheng, Y.; Huang, W. Intrinsic Point Defects in Inorganic Perovskite CsPbI₃ from First-Principles Prediction. *Appl. Phys. Lett.* **2017**, 111, 162106.
- (59) Agiorgousis, M. L.; Sun, Y.-Y.; Zeng, H.; Zhang, S. Strong Covalency-Induced Recombination Centers in Perovskite Solar Cell Material CH₃NH₃PbI₃. *J. Am. Chem. Soc.* **2014**, 136, 14570-14575.
- (60) Azpiroz, J. M.; Mosconi, E.; Bisquert, J.; De Angelis, F. Defect Migration in Methylammonium Lead Iodide and Its Role in Perovskite Solar Cell Operation. *Energy Environ. Sci.* **2015**, 8, 2118-2127.
- (61) Ming, W.; Chen, S.; Du, M.-H. Chemical Instability Leads to Unusual Chemical-Potential-Independent Defect Formation and Diffusion in Perovskite Solar Cell Material CH₃NH₃PbI₃. *J. Mater. Chem. A* **2016**, 4, 16975-16981.
- (62) Eames, C.; Frost, J. M.; Barnes, P. R. F.; O'Regan, B. C.; Walsh, A.; Islam, M. S. Ionic Transport in Hybrid Lead Iodide Perovskite Solar Cells. *Nat. Commun.* **2015**, 6, 7497.
- (63) Yang, J.-H.; Yin, W.-J.; Park, J.-S.; Wei, S.-H. Fast Self-Diffusion of Ions in CH₃NH₃PbI₃: The Interstitially Mechanism Versus Vacancy-Assisted Mechanism. *J. Mater. Chem. A* **2016**, 4, 13105-13112.

- (64) Walsh, A.; Scanlon, D. O.; Chen, S.; Gong, X. G.; Wei, S.-H. Self-Regulation Mechanism for Charged Point Defects in Hybrid Halide Perovskites. *Angew. Chem. Int. Ed.* **2014**, 53, 1-5.
- (65) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77, 3865-3868.
- (66) Alkauskas, A.; Pasquarello, A. Band-Edge Problem in the Theoretical Determination of Defect Energy Levels: The O Vacancy in ZnO as a Benchmark Case. *Phys. Rev. B* **2011**, 84, 125206.
- (67) Du, M.-H. Density Functional Calculations of Native Defects in CH₃NH₃PbI₃: Effects of Spin–Orbit Coupling and Self-Interaction Error. *J. Phys. Chem. Lett.* **2015**, 6, 1461-1466.
- (68) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid Functionals Based on a Screened Coulomb Potential. *J. Chem. Phys.* **2003**, 118, 8207-8215.
- (69) Haruyama, J.; Sodeyama, K.; Han, L.; Tateyama, Y. Termination Dependence of Tetragonal CH₃NH₃PbI₃ Surfaces for Perovskite Solar Cells. *J. Phys. Chem. Lett.* **2014**, 5, 2903-2909.
- (70) Uratani, H.; Yamashita, K. Charge Carrier Trapping at Surface Defects of Perovskite Solar Cell Absorbers: A First-Principles Study. *J. Phys. Chem. Lett.* **2017**, 8, 742-746.
- (71) Stoneham, A. M. Theory of Defects in Solids. *OUP, Oxford* **1975**.
- (72) Castner, T. G.; Känzig, W. The Electronic Structure of V-Centers. *J. Phys. Chem. Solids* **1957**, 3, 178-195.
- (73) Whalley, L. D.; Crespo-Otero, R.; Walsh, A. H-Center and V-Center Defects in Hybrid Halide Perovskites. *ACS Energy Lett.* **2017**, 2, 2713-2714.
- (74) Li, W.; Liu, J.; Bai, F.-Q.; Zhang, H.-X.; Prezhdo, O. V. Hole Trapping by Iodine Interstitial Defects Decreases Free Carrier Losses in Perovskite Solar Cells: A Time-Domain Ab Initio Study. *ACS Energy Lett.* **2017**, 2, 1270-1278.
- (75) Tong, C.-J.; Li, L.; Liu, L.-M.; Prezhdo, O. V. Long Carrier Lifetimes in PbI₂-Rich Perovskites Rationalized by Ab Initio Nonadiabatic Molecular Dynamics. *ACS Energy Lett.* **2018**, 1868-1874.
- (76) Shi, T.; Yin, W.-J.; Yan, Y. Predictions for P-Type CH₃NH₃PbI₃ Perovskites. *J. Phys. Chem. C* **2014**, 118, 25350-25354.
- (77) Mosconi, E.; Merabet, B.; Meggiolaro, D.; Zaoui, A.; De Angelis, F. First-Principles Modeling of Bismuth Doping in the MapbI₃ Perovskite. *J. Phys. Chem. C* DOI:10.1021/acs.jpcc.8b01307 **2018**.
- (78) Liu, J.; Prezhdo, O. V. Chlorine Doping Reduces Electron–Hole Recombination in Lead Iodide Perovskites: Time-Domain Ab Initio Analysis. *J. Phys. Chem. Lett.* **2015**, 6, 4463-4469.
- (79) Long, R.; Prezhdo, O. V. Dopants Control Electron–Hole Recombination at Perovskite–TiO₂ Interfaces: Ab Initio Time-Domain Study. *ACS Nano* **2015**, 9, 11143-11155.
- (80) Meggiolaro, D.; Mosconi, E.; De Angelis, F. Modeling the Interaction of Molecular Iodine with MapbI₃: A Probe of Lead-Halide Perovskites Defect Chemistry. *ACS Energy Lett.* **2018**, 3, 447-451.
- (81) Meggiolaro, D.; Mosconi, E.; De Angelis, F. Mechanism of Reversible Trap Passivation by Molecular Oxygen in Lead-Halide Perovskites. *ACS Energy Lett.* **2017**, 2794-2798.
- (82) Aristidou, N.; Eames, C.; Sanchez-Molina, I.; Bu, X.; Kosco, J.; Islam, M. S.; Haque, S. A. Fast Oxygen Diffusion and Iodide Defects Mediate Oxygen-Induced Degradation of Perovskite Solar Cells. *Nat. Commun.* **2017**, 8, 15218.
- (83) Van de Walle, C. G.; Neugebauer, J. First-Principles Calculations for Defects and Impurities: Applications to III-Nitrides. *J. Appl. Phys.* **2004**, 95, 3851-3879.
- (84) Komsa, H.-P.; Rantala, T. T.; Pasquarello, A. Finite-Size Supercell Correction Schemes for Charged Defect Calculations. *Phys. Rev. B* **2012**, 86, 045112.
- (85) Lany, S.; Zunger, A. Assessment of Correction Methods for the Band-Gap Problem and for Finite-Size Effects in Supercell Defect Calculations: Case Studies for ZnO and GaAs. *Phys. Rev. B* **2008**, 78, 235104.

- (86) Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E.; Constantin, L. A.; Zhou, X.; Burke, K. Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces. *Phys. Rev. Lett.* **2008**, 100, 136406.
- (87) Umari, P.; Mosconi, E.; De Angelis, F. Relativistic Gw Calculations on $\text{CH}_3\text{NH}_3\text{PbI}_3$ and $\text{CH}_3\text{NH}_3\text{SnI}_3$ Perovskites for Solar Cell Applications. *Sci. Rep.* **2014**, 4, 4467.
- (88) Filip, M. R.; Giustino, F. GW Quasiparticle Band Gap of the Hybrid Organic-Inorganic Perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$: Effect of Spin-Orbit Interaction, Semicore Electrons, and Self-Consistency. *Phys. Rev. B* **2014**, 90, 245145.
- (89) Even, J.; Pedesseau, L.; Jancu, J.-M.; Katan, C. Importance of Spin–Orbit Coupling in Hybrid Organic/Inorganic Perovskites for Photovoltaic Applications. *J. Phys. Chem. Lett.* **2013**, 4, 2999–3005.
- (90) Giorgi, G.; Fujisawa, J.-I.; Segawa, H.; Yamashita, K. Small Photocarrier Effective Masses Featuring Ambipolar Transport in Methylammonium Lead Iodide Perovskite: A Density Functional Analysis. *J. Phys. Chem. Lett.* **2013**, 4, 4213–4216.
- (91) Rinke, P.; Janotti, A.; Scheffler, M.; Van de Walle, C. G. Defect Formation Energies without the Band-Gap Problem: Combining Density-Functional Theory and the GW Approach for the Silicon Self-Interstitial. *Phys. Rev. Lett.* **2009**, 102, 026402.
- (92) Perdew, J. P.; Ernzerhof, M.; Burke, K. Rationale for Mixing Exact Exchange with Density Functional Approximations. *J. Chem. Phys.* **1996**, 105, 9982–9985.
- (93) Paier, J.; Marsman, M.; Hummer, K.; Kresse, G.; Gerber, I. C.; Ángyán, J. G. Screened Hybrid Density Functionals Applied to Solids. *J. Chem. Phys.* **2006**, 124, 154709.
- (94) Hamann, D. R.; Schlüter, M.; Chiang, C. Norm-Conserving Pseudopotentials. *Phys. Rev. Lett.* **1979**, 43, 1494–1497.
- (95) Vanderbilt, D. Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism. *Phys. Rev. B* **1990**, 41, 7892–7895.
- (96) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, 59, 1758–1775.
- (97) Umari, P.; Fabris, S. Importance of Semicore States in GW Calculations for Simulating Accurately the Photoemission Spectra of Metal Phthalocyanine Molecules. *J. Chem. Phys.* **2012**, 136, 174310.
- (98) Welch, E.; Scolfaro, L.; Zakhidov, A. Density Functional Theory + U Modeling of Polarons in Organohalide Lead Perovskites. *AIP Adv.* **2016**, 6, 125037.
- (99) Bang, J.; Sun, Y. Y.; Abtew, T. A.; Samanta, A.; Zhang, P.; Zhang, S. B. Difficulty in Predicting Shallow Defects with Hybrid Functionals: Implication of the Long-Range Exchange Interaction. *Phys. Rev. B* **2013**, 88, 035134.
- (100) Makov, G.; Payne, M. C. Periodic Boundary Conditions in Ab Initio Calculations. *Phys. Rev. B* **1995**, 51, 4014–4022.
- (101) Freysoldt, C.; Neugebauer, J.; Van de Walle, C. G. Fully Ab Initio Finite-Size Corrections for Charged-Defect Supercell Calculations. *Phys. Rev. Lett.* **2009**, 102, 016402.
- (102) Baroni, S.; de Gironcoli, S.; Dal Corso, A.; Giannozzi, P. Phonons and Related Crystal Properties from Density-Functional Perturbation Theory. *Rev. Mod. Phys.* **2001**, 73, 515–562.
- (103) Umari, P.; Pasquarello, A. Ab Initio Molecular Dynamics in a Finite Homogeneous Electric Field. *Phys. Rev. Lett.* **2002**, 89, 157602.
- (104) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (Dft-D) for the 94 Elements H–Pu. *J. Chem. Phys.* **2010**, 132, 154104.
- (105) Boschloo, G.; Hagfeldt, A. Characteristics of the Iodide/Triiodide Redox Mediator in Dye-Sensitized Solar Cells. *Acc. Chem. Res.* **2009**, 42, 1819–1826.
- (106) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cocconi, M.; Dabo, I., et al. Quantum Espresso: A Modular and Open-Source

Software Project for Quantum Simulations of Materials. *Journal of Physics: Condensed Matter* **2009**, 21, 395502.

(107) Hamann, D. R. Optimized Norm-Conserving Vanderbilt Pseudopotentials. *Phys. Rev. B* **2013**, 88, 085117.

Quotes to highlight in paper:

“a quantitative prediction of the band edges is essential in order to estimate accurately the electronic term in Eq. 2”

“The effects on the DFEs induced by the hybrid functional has a dramatic impact on the thermodynamic ionization levels, whose levels shift in the band gap compared with the PBE case.”

“an accurate estimation of DFEs in lead halide perovskites requires: i) high level DFT calculations based on hybrid functionals with the inclusion of spin-orbit corrections; ii) the use of fairly large supercells”

“the photo-chemistry of charge traps in MAPbI₃ is dominated by the redox chemistry of iodine.”