Capturing Excitonic Effects in Lead Iodide Perovskites from Many-Body Perturbation Theory

Pooja Basera*, Arunima Singh, Deepika Gill, Saswata Bhattacharya*

Dept. of Physics, Indian Institute of Technology Delhi, New Delhi 110016

E-mail: Pooja.Basera@physics.iitd.ac.in[PB], saswata@physics.iitd.ac.in[SB]
Phone: +91-2659 1359. Fax: +91-2658 2037

Abstract

Lead iodide perovskites have attracted considerable interest in the upcoming photovoltaic technologies and optoelectronic devices. Therefore, an accurate theoretical description of the electronic and optical properties especially to understand the excitonic effects in this class of materials is of scientific and practical interest. However, despite several theoretical research endeavours in past, the most accurate analysis of the key electronic parameters for solar cell performance, such as optical properties, effective mass, exciton binding energy ($E_B$) and the radiative exciton lifetime are still largely unknown. Here, we employ an integrated approach with several state-of-the-art first-principles based methodologies viz. hybrid Density Functional Theory (DFT) combined with spin-orbit coupling (SOC), many-body perturbation theory (GW, BSE), model-BSE (mBSE), Wannier-Mott and Density Functional Perturbation Theory (DFPT). By taking a prototypical model system viz. APbI$_3$ ($A =$ Formamidinium (FA), methylammonium (MA), and Cs), an exhaustive analysis is presented on the theoretical
understanding of the optical, electronic and excitonic properties. We show that tuning of exact exchange parameter ($\alpha$) in hybrid density functional calculations (HSE06) incorporating SOC, followed by single shot GW, and BSE play a pivotal role in obtaining a reliable predictions for the experimental bandgap, which helps to resolve an inconsistency observed in previously reported GW calculations. We demonstrate that model-BSE (mBSE) approach improves the feature of optical spectra w.r.t experiments. Furthermore, Wannier-Mott approach and ionic contribution to dielectric screening (i.e. optical phonon modes below 16 meV) ameliorate the exciton binding energy. Our results reveal that the direct-indirect band gap transition (Rashba-Dresselhaus splitting) may be a factor responsible for the reduced charge carrier recombination rate in MAPbI$_3$ and FAPbI$_3$. The role of cation “A” for procuring the long-lived exciton lifetime is well understood. This proposed methodology allows to design new materials with tailored excitonic properties.

TOC graphic
Introduction

Lead iodide perovskites (APbI$_3$), have received considerable interest as energy materials,$^{1-12}$ in particular to optoelectronic devices by virtue of its remarkable phenomena, illustrated as ambipolar charge transport,$^{1,2}$ collection and recombination of charge carriers,$^5$ and multivalley nature of the bandstructure.$^6$ Rapid developments in the field of perovskite cells have led to a dramatic increase in the power conversion efficiency from 3.8%$^7$ to 25.2%$^8$ in less than 10 years. Amongst the lead iodide perovskites, MAPbI$_3$ and FAPbI$_3$ are the most studied systems that come under the category of hybrid inorganic-organic perovskites (HIOPs).$^7,9,10,12$ Long charge carrier lifetimes, high carrier mobility, low trap density, and potentially low manufacturing costs have made them excellent candidates for solar cells.$^{13-16}$

Likewise HIOPs, inorganic perovskites are also rich in practical applications because of its long carrier diffusion lengths$^{17}$ and high fluorescence quantum yields.$^{18}$ For example, CsPbI$_3$ is one of the highly studied systems under inorganic perovskites. Since, these systems have been widely studied in past, they act as a best prototype for studying new theoretical methodologies that can provide significant scientific insights.

To date, the reliable theoretical methods to comprehend the optical, electronic and the excitonic properties of APbI$_3$ (A = FA, MA and Cs) perovskites have not been discussed, to the best of our knowledge. These properties explicitly include effective mass, electronic as well as ionic dielectric screening, and exciton parameters such as exciton binding energy and exciton lifetime, which have been scarcely reported in the literature.$^{19,20}$ Thus, despite the wide study of the properties like transport phenomena, defects, thermodynamic stability, formation energy of APbI$_3$ system,$^{1,2,5,21-24}$ the accurate methodology in determining the exciton parameters is hitherto unknown. Therefore, revisiting the analytical methodologies is crucial in the present scenario, for accurate correlation with the experimental studies.

At the theoretical level (here Density Functional Theory (DFT)$^{25,26}$), it has never been easy to understand these properties as the exchange-correlation ($\epsilon_{xc}$) functional needs to be carefully analyzed in the light of electron’s self-interaction error and spin-orbit coupling
(SOC) effect. Note that, for the case of MAPbI$_3$ and FAPbI$_3$, GGA (PBE) provides a bandgap in fortuitous agreement with the experimental results, because of lucky error cancellation, which persuades researchers to use GGA (PBE) functionals for these systems. However, local/semi-local functionals (viz. LDA or GGA) are not sufficient to determine the correct band edge positions and also incapable to discern the excitonic peaks. In principle, the decent way to calculate the optical properties is to determine the accurate position of the quasiparticle peak in the spectra by evaluating the quasiparticle energies, in particular, the bandgap. Thus, the sole motivation of this work is to correctly predict the quasiparticle bandgap and henceforth, their optical spectra using Many-Body Perturbation Theory (MBPT) approach.

It should be noted here, with the development of perovskite solar cells, the mechanism behind the efficiency of perovskites to convert solar energy to power has become a topic of capital interest. In this regard, a relatively large exciton binding energy [6 - 55 meV] has been reported. Therefore, the extreme challenge is to compute accurately the exciton binding energy and following that the optical gap.

The accuracy of the optical gap and excitonic peak can be further used to circumvent the problem of determination of exciton lifetime of the charge carriers. Recently, Jana et al. has demonstrated that the organic cations (MA, FA) carry a fundamental advantage over the inorganic cations (Cs) for achieving the long-lived exciton lifetime. Since, the band edges are primarily contributed by Pb and I, we intend to understand how the cations affect the excited state lifetime in APbI$_3$ perovskite. Hence, it is interesting to understand the role of cations in determining the exciton lifetime.

In this article, using state-of-the-art first-principles based methodology under the framework of DFT (with PBE and hybrid functionals (HSE06) combined with SOC), MBPT, model-BSE (mBSE), Wannier-Mott and Density Functional Perturbation Theory (DFPT) approaches, we present an exhaustive study on the theoretical understanding of the optical, electronic and excitonic properties of APbI$_3$ perovskites. We have carefully analyzed the
starting point by tuning exact exchange parameter $\alpha$ in HSE06+SOC calculations, in order to have an accurate estimation of GW bandgap in APbI$_3$ perovskites. Furthermore, by the quantitative description of the optical spectra, we have shown that relativistic BSE calculation with SOC is not sufficient. This is due to the fact that it requires extremely high k-grid sampling, which is indeed computationally very demanding task. Subsequently, mBSE approach has been used to sample the Brillouin zone with sufficient accuracy. This approach derives the experimental features of the optical spectra. Further, we have used Wannier-Mott and DFPT approach, to explore the effective mass, electronic and ionic contribution to dielectric screening and the exciton parameters including exciton binding energy, exciton energy, and exciton radius. The role of Rashba-Dresselhaus splitting is also addressed in APbI$_3$ perovskites. Finally, we have done qualitative as well as quantitative analysis of the radiative lifetime of excitons, where the cation A’s role is well investigated via IR spectra.

Results and Discussions

**Determination of accurate quasiparticle peak position: GW bandgap**

We have determined the optical response of APbI$_3$ perovskites by computing the imaginary part of dielectric function ($\text{Im } (\varepsilon)$). Initially, we have started with basic GGA (PBE) functional for the optical spectra of the cubic phase of MAPbI$_3$ perovskite, without incorporating SOC (see Fig 1(a)). Then, we have performed the single shot GW calculations. It is well known that single shot GW calculation is very much dependent on its starting point. Hence, it is crucial to obtain a pertinent starting point for the GW calculations. Therefore, from PBE calculation, we have obtained first peak at 1.55 eV, which is very close to the reported experimental value (1.57–1.69 eV).\textsuperscript{46–49}
Here, in our case, this matching is just the outcome of error cancellation due to self interaction error and non inclusion of SOC. Notably, this is not true for all the perovskites. We have shown in our recent work on FAPbBr$_3$, that the electron’s self interaction error and SOC counter each other by unequal amount, thereby resulting in bandgap with PBE functional (1.72 eV) not in agreement with experimental value (2.23 eV).\textsuperscript{50} However, we have tried to further improve the optical peak of MAPbI$_3$, by performing GW@PBE calculations. This results in a large discrepancy in optical peak (2.37 eV) with respect to the experiments (see Fig 1(a)). To correct it, we have explored BSE@GW calculation, that takes into account the e-h interactions. This leads to the reduction in the bandgap. Although BSE has reduced the GW bandgap, the achieved gap (2.12 eV) via BSE@GW@PBE is still far from the experimental value (see Fig 1(a)). However, a sharp peak is observed for BSE calculations.

Figure 1: Imaginary part of dielectric function of the cubic phase of MAPbI$_3$ calculated using single shot GW and BSE, where several $\epsilon_{xc}$ functional are used as a starting point ($i$): (a) PBE (b) PBE+SOC (c) HSE06 ($\alpha = 25\%$) (d) HSE06+SOC ($\alpha = 25\%$) (e) HSE06+SOC ($\alpha = 50\%$).
which signifies the excitonic effect.

It is important to include the SOC effect in the APbI$_3$ perovskites, because of the presence of heavier elements like Pb and I. The role of SOC can be easily observed from the comparative analysis of bandstructures computed with and without SOC. The conduction band levels are significantly affected by SOC (see SI, Fig S3). Therefore, SOC should not be omitted in the calculations, even though PBE calculations yield the correct bandgap for MAPbI$_3$. The inclusion of SOC in PBE calculation tends to reduce the bandgap significantly by almost 1 eV. Here, we have observed a peak at 0.49 eV (see Fig 1(b)). Then, we have performed GW@PBE+SOC calculations, hoping an improvement in the peak or bandgap, as it has a tendency to overestimate the bandgap. Unfortunately, GW@PBE+SOC calculation gives a peak value at 1.16 eV (see Fig 1(b)). This value is in agreement with the previous theoretical calculations based on GW.$^{46,51}$ Note that, the value obtained from GW@PBE+SOC (1.16 eV) is still better, comparing the same with GW@PBE (2.37 eV). However, the BSE@GW@PBE+SOC gives the peak value at 0.88 eV which does not correlate well with the experimental value. Hence, we rationalize that, to perform single shot GW on the top of PBE (with or without SOC) is not a good choice. This is the main reason behind the deviation of the GW bandgap as reported in literature with the experimental values. Therefore, a theoretical approach is needed, which would better reproduce the experimental bandgap and peak position.

Hybrid functionals have emerged as an effective method, considering the agreement between theoretical calculations and experiments, at an affordable increase in the computational cost.$^{52}$ In HSE06 calculations, the exact exchange term from Hartree Fock (HF) is mixed with the semi-local $\epsilon_{xc}$ part of the DFT in a ratio ($\alpha$). This ratio can be further adjusted in order to reproduce the experimental bandgap of the material. We have started with the default parameters of the HSE06 with a fraction of exact exchange of 25%, and screening parameter of 0.2 Å$^{-1}$. The peak position is obtained at 2.2 eV i.e far away from the experimental results. Hence, there is no use to perform GW@HSE06 and BSE@GW, because the
peak value will be in any case overestimated due to poor starting point (see Fig 1(c)). Therefore, incorporation of SOC is important even for the hybrid functional HSE06. Initially, we have used standard parameter ($\alpha = 25\%$) of HSE06 with SOC, the peak position is obtained at 0.95 eV. Then, we have performed GW@HSE06+SOC with 25% $\alpha$, that gives the first peak position at 1.37 eV. This peak position is closer to the experimental value, whereas, the subsequent BSE peak position at 1.11 eV deviates from the former (see Fig 1(d)). Nevertheless, there is a possibility to further improve the peak position and the optical spectra. In view of this, we have increased the exact exchange parameter $\alpha$ and finally, the convergence is reached at $\alpha = 50\%$ for MAPbI$_3$. Hence, the optical peak or bandgap obtained using HSE06+SOC with $\alpha = 50\%$ is 1.55 eV, which is in close agreement with the experiments (1.57 - 1.69 eV). Therefore, we conclude that, HSE06+SOC ($\alpha = 50\%$) is a prominent choice as a starting point for the GW in our calculations. GW@HSE06+SOC with ($\alpha = 50\%$) gives rise to a peak value at 1.67 eV (see Fig 1(e)) (i.e. in good agreement with the experiments). On comparing Fig 1(a) and (e), we can see that PBE and HSE06+SOC ($\alpha = 50\%$) tend to give the same value of the bandgap (1.55 eV), however, the first peak obtained from GW and BSE in both the cases are totally different. The above analysis highlights the crucial three factors for considering the initial point: (i) inclusion of SOC, (ii) inclusion of more HF exact exchange to reduce electron’s self-interaction error (in HSE06 $\epsilon_{xc}$ functional), and (iii) the converged value of $\alpha$.

Note that in earlier studies, people have tuned exact exchange parameter $\alpha$ to get correct bandgap from the hybrid calculations. Surprisingly, controversies for bandgap obtained from GW calculations are not fully discussed in details. In view of this, here we present these benchmark results to establish that by a systematic analysis of the starting point, with single shot GW, one can predict the exact fundamental gap. This not only helps to improve the GW bandgap, but also resolves the controversies that are pre-existent in literature. The corresponding analysis of BSE result (underestimated peak at 1.29 eV) is discussed in the next section. We have benchmarked two more systems viz. FAPbI$_3$ and CsPbI$_3$ to ensure
that the above approach is not just an artifact or responsive only for MAPbI\textsubscript{3} perovskites. The tuning of the exact exchange parameter $\alpha$ by 53\% in HSE06+SOC followed by GW works very well for FAPbI\textsubscript{3} and CsPbI\textsubscript{3}. The first peak position (bandgap) is obtained at 1.45 eV and 1.73 eV for FAPbI\textsubscript{3} and CsPbI\textsubscript{3}, respectively. These values are in exact agreement with the experiments.\textsuperscript{57–61} A detailed discussion is given in SI (see Fig S4 and S5).

**Exciton binding energy (E\textsubscript{B})**

Until now, we have delivered fairly accurate electronic bandgap (GW bandgap) by tuning exact exchange parameter ($\alpha$). However, in order to obtain correct optical gap and absorption spectra, one needs to look upon the Bethe-Salpeter equation (BSE). The accuracy related to BSE peak position has not been yet achieved or benchmarked well. This tends to mislead the BSE exciton peak position, and consequently the exciton binding energy. Using the above method, the obtained BSE peak position (optical gap) for MAPbI\textsubscript{3} (see Fig 1), FAPbI\textsubscript{3} (see Fig S4) and CsPbI\textsubscript{3} (see Fig S5) perovskites are 1.29 eV, 1.08 eV and 1.34 eV, respectively. Notably, the exciton binding energy (E\textsubscript{B}) is defined as the difference between the energy of an unbound non-interacting e-h pair (electronic gap (GW)) and the exciton energy, where the e-h are bound by a screened Coulomb interaction (optical gap (BSE)). Therefore, a discrepancy in BSE peak position consequently leads to incorrect exciton binding energy E\textsubscript{B} i.e., 0.38 eV, 0.37 eV and 0.39 eV for MAPbI\textsubscript{3}, FAPbI\textsubscript{3} and CsPbI\textsubscript{3} perovskites, respectively. Note that, low E\textsubscript{B} ($E_B < kT = 26$ meV at room temperature) values are desirable, so that exciton will dissociate easily to form free charge carriers. In this regard, a low but non vanishing E\textsubscript{B} value will be congenial for solar cell material to retain its partial excitonic character without having any energy loss in the formation of free carriers.
model-BSE (mBSE) approach

To compute the optical spectra or optical gap, the conventional BSE@GW approach is a reliable and an exemplary approach that mostly provides high quality results for exciton energy and $E_B$. However, the requirement of a large number of processors for high k-grid sampling (approx $12 \times 12 \times 12$), even for a unitcell is not affordable, and thus, results in inconsistency observed in BSE excitonic peak position or exciton energy. This attributes to the incorrect $E_B$ value as shown in previous section. Therefore, to tackle the BSE convergence, the only way is to sample the Brillouin zone with sufficient accuracy (high k-mesh is required). This motivates us to use a parameterized model for the dielectric screening i.e., model-BSE approach (mBSE). The convergence of the optical spectra as a function of the number of k-points (k-mesh) is performed within this model. This method is generally based on two approximations:

(i) The RPA static screening $W$ is replaced by a simple analytical model, given in Eq. 1; as the latter one is easier to compute. Here, the dielectric function is replaced by the local model function:

$$\varepsilon_{G,G}^{-1}(q) = 1 - (1 - \varepsilon_{\infty}^{-1})\exp\left(-\frac{|q+G|^2}{4\lambda^2}\right)$$

where $\varepsilon_{\infty}$ is the static ion-clamped dielectric function in the high frequency limit. $\varepsilon_{\infty}^{-1}$ is calculated either from DFPT or GW as shown in Table 1. $\lambda$ is the screening length parameter, obtained by fitting the screening $\varepsilon^{-1}$ at small wave vectors with respect to $|q+G|$ (see Fig 2(a)-(c)). $q$ and $G$ are defined as wave vector and lattice vector of the reciprocal cell, respectively. The parameters obtained for the APbI$_3$ perovskites are given in Table 1.
Table 1: Calculated inverse of the static ion-clamped dielectric function $\varepsilon_{\infty}^{-1}$ and the screening length parameter $\lambda$ used in mBSE.

|          | $\varepsilon_{\infty}^{-1}$ (GW) | $\lambda$ (GW) | $\varepsilon_{\infty}^{-1}$ (PBE+SOC) | $\lambda$ (PBE+SOC) |
|----------|-------------------------------|----------------|-------------------------------------|-------------------|
| APbI$_3$ | 0.196                         | 0.854         | 0.148                               | 0.827             |
| MAPbI$_3$| 0.186                         | 0.876         | 0.142                               | 0.856             |
| FAPbI$_3$| 0.206                         | 0.793         | 0.174                               | 0.778             |

(ii) PBE+SOC single particle eigenvalues are used as an input for the mBSE calculations, instead of GW+SOC quasiparticle energies. This approach requires scissor operator, which is calculated by taking the difference of GW bandgap and DFT band gap, including SOC.$^{62}$

![Figure 2](image_url)

Figure 2: Variation of parameter $\varepsilon^{-1}$ with respect to $|q+G|$ for (a) MAPbI$_3$, (b) FAPbI$_3$ and (c) CsPbI$_3$, respectively. The red curve is obtained by fitting Eq. 1. Imaginary part of dielectric function with k-mesh (4\times4, 6\times6, 8\times8, 10\times10\times10, 12\times12\times12) for (d) MAPbI$_3$, (e) FAPbI$_3$ and (f) CsPbI$_3$, respectively.

Fig 2(d)-(f) shows the optical spectra as predicted by mBSE approach. Here, we have done robust k-point sampling up to 12\times12\times12 k-mesh. We can see that the first peak is shifted with an increase in k-mesh (shown by arrow). It confirms that high k-point sampling is required to converge BSE calculations. The comparison of mBSE and BSE approach at
low k-point sampling ($4 \times 4 \times 4$) has been discussed in SI (Fig S6). However, with PBE+SOC, the convergence of optical peak can be achieved with few k-points only (see SI, Fig S1). Undoubtedly, the spectrum features are improved (see the sharp first peak describing excitonic effect as in Fig 2(d)-(f)) with an increase in k-mesh, but with an incorrect position of the same. The obvious reason is that, we have performed mBSE on the top of PBE+SOC. However, PBE+SOC is not a suitable choice as a starting point for the mBSE, that we have already confirmed in aforementioned section. Our motivation in this section is to present a qualitative analysis of how the k-grid affects the spectra, because to perform mBSE calculations on the top of HSE06 (with 50% or 53% $\alpha$ as applicable) incorporating SOC along with denser k-grid is computationally not only very expensive but also sometimes not feasible. Nevertheless, these calculations are of paramount importance in inferring the experimental features of the optical spectra. Henceforth, it’s justified assumption that a reduction in the exciton binding energy is expected with a denser k-grid. With this background and qualitative picture, in the following section our aim is to determine the exciton binding energy and the optical peak position quantitatively using Wannier-Mott approach.

**Wannier-Mott approach**

**Effective mass**  Excitons are bound e-h pairs attracted via electrostatic Coulomb force. There are mainly two types of excitons: (i) Frenkel exciton (tight bound exciton) and (ii) Wannier-Mott exciton (loosely bound or free exciton). Wannier-Mott excitons are characterized by small bandgaps and high dielectric constant, generally found in semiconductors.$^{63,64}$ The Bohr’s model is used for Wannier exciton by approximating e-h pairs as a hydrogenic atom. In order to extract the $E_B$, we have herein considered Wannier-Mott approach along with Fermi’s golden rule for APbI$_3$ perovskites.$^{44}$ As a first step, the effective mass of electrons and holes using the Wannier-Mott model are determined by the E-K dispersion curve. Therefore, we have performed bandstructure calculations using GW approximation on top of HSE06+SOC along with $\alpha = 50\%$, 53% and 53% for MAPbI$_3$, FAPbI$_3$ and CsPbI$_3$. 
respectively (see Fig 3(a)-(c)).

Figure 3: Bandstructure computed from GW@HSE06+SOC along with (a) $\alpha = 50\%$ for MAPbI$_3$, (b) 53% for FAPbI$_3$ and (c) 53% for CsPbI$_3$, respectively, using Wannier interpolation. (d) The Rashba-Dresselhaus splitting of the CBM in the $R \rightarrow X$ and $R \rightarrow \Gamma$ directions for (d) MAPbI$_3$ (e) FAPbI$_3$ and (f) CsPbI$_3$. (d) and (e) shows inset of zoomed section of the conduction bands.

The valence band maximum (VBM) and conduction band minimum (CBm) are obtained at high symmetry R (0.5, 0.5, 0.5) point, and their difference is defined as bandgap. The obtained bandgap for MAPbI$_3$, FAPbI$_3$ and CsPbI$_3$ are 1.67 eV, 1.45 eV and 1.73 eV, respectively, which are in excellent agreement with the experiments.$^{46,58,61}$ In addition, we have observed direct-indirect nature of the bandgap, due to splitting of bands. This is prominent in MAPbI$_3$, moderate in FAPbI$_3$, and completely vanished in CsPbI$_3$ (see Fig 3(d)-(f)). The splitting of bands due to SOC and lack of inversion symmetry results in the Rashba splitting of bands.$^{65–67}$

The Rashba effect is dominant near the CBm, because of the strong influence of SOC towards heavier atom Pb (main contributor at the CBm). The vertical energy difference ($E_R$) between slightly shifted CBm and the conduction band energy at R, leads to indirect
The nature of the bandgap (see inset of Fig 3(d)). The values of $E_R$ for MAPbI$_3$ along $R \rightarrow X$ and $R \rightarrow \Gamma$ directions are 22 meV in agreement with literature$^{68}$ and 12.8 meV, respectively. However, for FAPbI$_3$, the calculated values are 0.59 meV ($R \rightarrow X$) and 2 meV ($R \rightarrow \Gamma$), respectively. Notably, due to slight change from direct to indirect (in meV), the absorption spectrum is hardly affected by the presence of an indirect gap. The direct-indirect nature of the band gap allows photogenerated charge carriers to relax into indirect band, whereas direct bandgap allows strong absorption of light. The indirect bandgap may reduce the possibility of radiative recombination of e-h, on the contrary, which is active in direct bandgap semiconductors.

The strength of the Rashba effect can be obtained by the parameter $a = 2E_R/k$, where $E_R$ is the amplitude of the band splitting in a $R \rightarrow X$ and $R \rightarrow \Gamma$ directions$^{69}$ (see the inset of Fig 3(d)). For MAPbI$_3$, the estimated $a$ values in the $R \rightarrow X$ and $R \rightarrow \Gamma$ directions are 1.96 eVÅ and 1.01 eVÅ, respectively. For FAPbI$_3$, $a$ values in the $R \rightarrow X$ and $R \rightarrow \Gamma$ directions are 0.17 eVÅ and 0.77 eVÅ, respectively. Hence, MAPbI$_3$ and FAPbI$_3$, have significant Rashba splitting, which is completely absent in cubic CsPbI$_3$ (see Fig 3(d)-(f)).

The interplay of a low recombination rate (due to indirect gap) and strong absorption (direct gap) indicate the high solar efficiencies of HIOPs.

Next, we have extracted the effective mass of an exciton from the bandstructure. Following this, we have fitted the dispersion curves with a parabolic function at the valence band maximum and the conduction band minimum at point R (average along $R \rightarrow X$ and $R \rightarrow \Gamma$ directions), using the equation:

$$m^* = \frac{\hbar}{\frac{d^2E(K)}{dK^2}}$$  \hspace{1cm} (2)

where $m^*$, $E(K)$, $K$, and $\hbar$ are the effective mass, energy, wave vector and reduced Planck’s constant, respectively. The values of effective mass and reduced mass (see Table 2) are very well in agreement with previous experimental findings.$^{61,70-72}$ We have noticed that electron effective masses ($m^*_e$) are consistently smaller than the hole effective masses ($m^*_h$), thus, in agreement with previous trends reported in refs.$^{55,71,73}$ Following this, the exciton binding
Table 2: Effective mass of electron $m^*_e$, hole $m^*_h$ and reduced mass $\mu$. $m_0$ is rest mass of electron.

|       | $m^*_e/m_0$ | $m^*_h/m_0$ | $\mu/m_0$ |
|-------|-------------|-------------|-----------|
| APbI₃ | 0.210       | 0.220       | 0.107     |
| MAPbI₃| 0.195       | 0.216       | 0.102     |
| FAPbI₃| 0.190       | 0.252       | 0.108     |
| CsPbI₃| 0.190       | 0.252       | 0.108     |

energies for screened coulomb interacting e-h pairs in parabolic bands are calculated as:

$$E_B = (\frac{\mu}{\varepsilon_{\text{eff}}'}) R_\infty$$

where, $\mu$ is the reduced mass, $\varepsilon_{\text{eff}}$ is the effective dielectric constant and $R_\infty$ is the Rydberg constant. In the given formula, all the terms are known to us except $\varepsilon_{\text{eff}}$. Henceforth, our task is to determine $\varepsilon_{\text{eff}}$.

**Electronic and ionic contribution to dielectric screening** The early reports depended only on the static value of dielectric constant at high frequency $\varepsilon_e$ ($= \varepsilon_\infty$), which is based on the assumption that the dielectric screening occurs only when $E_B$ is larger than the optical phonon energy. However, recently it has been reported experimentally that optical phonon modes are observed from 8 to 16 meV. This infers that low frequency optical phonon modes also play an important role in dielectric screening. Therefore, for $\varepsilon_{\text{eff}}$, a value intermediate between the static ionic dielectric constant at low frequency i.e., $\varepsilon_i$, and the static electronic dielectric constant at high-frequency $\varepsilon_e$ should be used. The imaginary and real part of dielectric function are shown for MAPbI₃, FAPbI₃ and CsPbI₃, respectively. In Fig 4(a)-(c), we have shown the electronic contribution to the dielectric function. The static real part of electronic dielectric constant for MAPbI₃, FAPbI₃ and CsPbI₃ are 6.75, 7.02 and 5.74, respectively (indicated by the point in Fig 4(a)-(c)).
Figure 4: Electronic contribution to dielectric function (a) MAPbI$_3$ (b) FAPbI$_3$ and (c) CsPbI$_3$, respectively. Ionic contribution to dielectric function (d) MAPbI$_3$ (e) FAPbI$_3$ and (f) CsPbI$_3$. Variation of $E_B$ with respect to $\varepsilon$ is shown in (g) (h) and (i). All the calculations are performed using DFPT including SOC.

The ionic contribution to real and imaginary part of the dielectric function is shown in Fig 4(d)-(f). To obtain the ionic contributions of the dielectric function one needs to compute the force-constant matrices, which is defined as the Hessian (second derivative) of the total energy with respect to the ionic positions and internal strain tensors (strain fields). These parameters may be obtained from finite differences or from perturbation theory. Here, we have used DFPT for our calculations. The static real part of ionic dielectric constant for MAPbI$_3$, FAPbI$_3$ and CsPbI$_3$ are 30.4, 37.9, and 30.5, respectively.

On comparing the values, a sizable increase of the static low frequency ionic dielectric constant as compared to the static high frequency electronic dielectric constant is found.
The reason for this behavior is the increase in optically active phonon modes below 16 meV as shown within the shaded portion (see Fig 4(d)-(f)). This shows unequivocally the ionic nature of the perovskites. The electronic and ionic contribution of the dielectric constant will decide the upper and lower bound for the exciton binding energy by using Eq. 3. The robust theoretical methodology to compute the effective dielectric constant \( \varepsilon_{\text{eff}} \) for APbI\(_3\) perovskites is given in the literature.\(^{77}\)

\[
\varepsilon_{\text{eff}}^{-1} = 1 + \frac{2}{\pi} \int_{0}^{\infty} \frac{\text{Im}(\varepsilon^{-1}(\omega))}{\omega + E_B} d\omega
\]

(4)

On solving Eq. 4, we can determine \( \varepsilon_{\text{eff}} \) as a function of \( E_B \) i.e., \( \varepsilon_{\text{eff}}(E_B) \). \( \text{Im}(\varepsilon^{-1}(\omega)) \) is the energy loss function, which can be calculated from the real and imaginary part of the dielectric function. The intersection point of \( \varepsilon_{\text{eff}}(E_B) \) (from Eq. 4) and the \( E_B(\varepsilon_{\text{eff}}) \) (from Eq. 3 (shown in Fig 4(g)-(i))) will give the value of \( \varepsilon_{\text{eff}} \). The intersection point is directly taken from the literature\(^{77}\) here, marked by circle in Fig 4(g)-(i). The \( \varepsilon_{\text{eff}} \) values considered for MAPbI\(_3\), FAPbI\(_3\) and CsPbI\(_3\), are 9.5, 10.2 and 7.6, respectively. However, the reported values have satisfied the upper and lower bound for static electronic (at high frequency) and ionic dielectric constant (at low frequency), respectively.

Table 3: Electronic and ionic contribution to the dielectric constant. \( \varepsilon_e \) and \( \varepsilon_i \) are static value of electronic and ionic dielectric constant, respectively. \( E_{\text{Bu}} \) and \( E_{\text{Bl}} \) are upper and lower bound of exciton binding energy, respectively.

| APbI\(_3\) | \( \varepsilon_e \) | \( E_{\text{Bu}} \) (meV) | \( \varepsilon_i \) | \( E_{\text{Bl}} \) (meV) |
|------------|----------------|-----------------|----------------|----------------|
| MAPbI\(_3\) | 6.75          | 32              | 30.42          | 1.57           |
| FAPbI\(_3\) | 7.02          | 28              | 37.91          | 0.96           |
| CsPbI\(_3\) | 5.74          | 44              | 30.54          | 1.57           |

After the substitutions of \( \mu \) and \( \varepsilon_{\text{eff}} \) in Eq. 3, the obtained \( E_B \) (by taking into account full relativistic approach as well as ionic dielectric screening) for MAPbI\(_3\), FAPbI\(_3\) and CsPbI\(_3\) are 16.13 meV, 13.30 meV and 25.40 meV, respectively. These values are close in agreement with the recent experimental estimates.\(^{78-80}\) However, several large values of \( E_B \) exist in
previous theoretical and experimental studies.\textsuperscript{19,35,38–40} The obvious reason is the negligence of the optically active phonon modes (below 16 meV), that will contribute for the ionic dielectric screening. We have shown in Table 3, the variation of $E_B$ as per the electronic and the ionic dielectric constant. On the other hand, we have obtained the exciton binding energy of 14.60 meV corresponding to $\varepsilon_{\text{eff}} = 10^{61}$ for CsPbI$_3$. This is in agreement with that reported in experimental paper.\textsuperscript{61} The discrepancy observed in exciton binding energy from 14.60 meV to 25.40 meV is in agreement with recent reports,\textsuperscript{61,77} therefore it will be more justified to show the variation of dielectric constant with exciton binding energy (see Fig 4(g)-(i)). In this figure, we have shown the variation of $E_B$ from lower bound ($E_{B_l}$) to upper bound ($E_{B_u}$) of static dielectric constant.

**Exciton parameters for APbI$_3$ perovskites: exciton energy, exciton radius and exciton lifetime** By knowing the exciton binding energy, we can estimate the highest temperature, at which exciton will remain stable. The thermal energy needed to separate the exciton is $E_B = k_B T$, where $E_B = 16.13$ meV for MAPbI$_3$ and $k_B$ is Boltzmann constant. Therefore, exciton will be unstable above $T = 187$ K. The exciton energy is defined as the difference between GW bandgap and the exciton binding energy.\textsuperscript{77}

$$E_{\text{exc}} = E_g - E_B = 1.67 - 0.016 = 1.65 \text{ eV}$$

(5)

The exciton radius for MAPbI$_3$ perovskite with the orbital $n=1$ is given by,\textsuperscript{63,64}

$$r_{\text{exc}} = \frac{m_0}{\mu} \varepsilon_{\text{eff}} n^2 r_{\text{Ry}}$$

(6)

where, $r_{\text{Ry}} = 0.0529$ nm is Bohr’s radius. The exciton radius for MAPbI$_3$ comes out to be 4.57 nm.

In order to find the exciton lifetime, as a first step, we have to calculate the probability
of the wavefunction $|\phi_n(0)|^2$ for e-h pairs at zero separation.\textsuperscript{64,81}

$$|\phi_n(0)|^2 = \frac{1}{\pi \left( r_{\text{exc}} \right)^3 n^3} = 3.08 \times 10^{24} \text{m}^{-3} \quad (7)$$

Secondly, transition dipole matrix needs to be determined. The dipole matrix from $k.p$ model\textsuperscript{82} is defined as:

$$(\frac{m_0}{m^*})_{ij} = \delta_{ij} + \frac{2}{m_0} \sum_k |<v_k|p|c_k>|^2$$

where, $p = -i\hbar \frac{\partial}{\partial r}$ is a momentum operator. $v_k$ and $c_k$ are valence band and conduction band, respectively. $2|<v_k|p|c_k>|^2$ is defined as Kane energy without SOC. For perovskite case (see SI of Ref. \textsuperscript{83}), Kane energy is defined as $3 \times (2|<v_k|p|c_k>|^2)$.

In terms of reduced mass, Eq. 8 can be written as:

$$\frac{1}{\mu} = 4 \left| <v_k|p|c_k>|^2 \right.$$

Using Eq. 9, the value of transition dipole matrix $|<v_k|p|c_k>|^2$ for MAPbI$_3$ is $5.71 \times 10^{-49}$ Kg$^2$ m$^2$s$^{-2}$.

The above mentioned expressions will help us in determining the exciton lifetime, which is used to judge the efficiency of solar cells or photovoltaic devices. The long lived exciton lifetime infers that recombination is reduced, that leads to higher quantum yield and conversion efficiency. The exciton lifetime is the reciprocal of the transition rate, which is defined by Fermi’s golden rule. The transition rate is given by: \textsuperscript{84}

$$\gamma = \frac{2\pi e^2 \omega^2 A^2 \sum_k \left|<v_k|\hat{e}.r|c_k>|^2 \delta(E_f - E_i - \hbar\omega)\right.}{\hbar e^2} \quad (10)$$

The matrix elements of a momentum operator is related to the matrix elements of a position
operator:

$$\sum_{k} |<\mathbf{v}_k|\hat{\mathbf{e}}.\mathbf{r}|\mathbf{c}_k>|^2 \approx \frac{4}{3m_0^2\hbar^2} |<\mathbf{v}_k|\hat{\mathbf{e}}.\mathbf{p}|\mathbf{c}_k>|^2$$  (11)

On substituting Eq. 11 in Eq. 10,

$$\gamma \approx \frac{8\pi e^2 A_0^2}{3\hbar c^2 m_0^2} |<\mathbf{v}_k|\mathbf{p}|\mathbf{c}_k>|^2$$  (12)

This shows that transition rate is directly proportional to transition dipole matrix.

$$\gamma \approx t |<\mathbf{v}_k|\hat{\mathbf{e}}.\mathbf{p}|\mathbf{c}_k>|^2$$  (13)

where, $t = \frac{8\pi e^2 A_0^2}{3\hbar c^2 m_0^2}$

Finally, the lifetime of exciton:

$$\tau \propto \frac{1}{\gamma}$$  (14)

Hence, the lifetime of exciton for MAPbI$_3$:

$$\tau \propto \frac{1}{\gamma} \propto 0.18 \times 10^{49} t$$  (15)

where $t$ is in second. Similarly, we have determined the exciton parameter for FAPbI$_3$ and CsPbI$_3$. Table 4 provides comparison of the parameters for APbI$_3$ perovskites. From Table 4, we can conclude that, HIOPs (MAPbI$_3$ and FAPbI$_3$) have longer exciton lifetime than inorganic perovskite CsPbI$_3$. However, on comparing MAPbI$_3$ and FAPbI$_3$, FAPbI$_3$ has longer exciton lifetime than MAPbI$_3$. Note that, exciton lifetime is directly dependent on the inverse of transition dipole matrix value. Since, the proportionality constant would not affect the trend, the calculated values of the inverse of transition dipole matrix have been simply reported. These calculations also support the experimental observations that a perovskite containing larger A site cation favors a longer exciton lifetime. The ionic radii of the cation in APbI$_3$ perovskite are in the order FA > MA > Cs, and thus, the exciton
lifetimes also follow the same trend $\tau_{\text{FA}} > \tau_{\text{MA}} > \tau_{\text{Cs}}$.

Table 4: Exciton parameters for APbI$_3$ perovskites. $E_{\text{exc}}$, $T_{\text{exc}}$, $r_{\text{exc}}$, $|\phi_n(0)|^2$, $|<\mathbf{v}\mathbf{k}|\mathbf{p}|c\mathbf{k}>|^2$, $\tau$ are exciton energy, exciton temperature, exciton radius, probability of wavefunction for e-h pairs at zero separation, transition dipole matrix and exciton lifetime, respectively.

| Exciton parameters | MAPbI$_3$ | FAPbI$_3$ | CsPbI$_3$ |
|--------------------|-----------|------------|------------|
| $E_{\text{exc}}$ (eV) | 1.65      | 1.44       | 1.71       |
| $E_B$ (meV)         | 16.13     | 13.30      | 25.40      |
| $T_{\text{exc}}$ (K) | 187       | 154        | 294        |
| $r_{\text{exc}}$ (nm) | 4.69      | 5.30       | 3.72       |
| $|\phi_n(0)|^2$ (10$^{24}$ m$^{-3}$) | 3.08      | 2.13       | 6.18       |
| $|<\mathbf{v}\mathbf{k}|\mathbf{p}|c\mathbf{k}>|^2$ (10$^{-49}$Kg$^2$m$^2$s$^{-2}$) | 5.71      | 5.20       | 5.85       |
| $\tau$ (t $\times$ 10$^{49}$) | 0.18      | 0.19       | 0.17       |

Note that, there is also an alternative method to have a qualitative estimation of excited state lifetime of the excitons using mBSE approach. We already have an experimentally featured optical spectra of APbI$_3$ perovskite (obtained by 12$\times$12$\times$12 k-mesh) (see Fig 2(d)-(f)) and also the accurate exciton energy ($E_{\text{exc}}$) (see Table 4). We shift the optical spectra obtained via mBSE approach at exciton energy, and further calculate the broadening $\Gamma$ of the first exciton peak. Note that, exciton lifetime is inversely proportional to the broadening.

Figure 5: Qualitative analysis of exciton lifetime using mBSE exciton peak, where $\Gamma$ is broadening.
In order to calculate broadening, we have taken rms value of the exciton peak, and corresponding trend for broadening is as follows: $\Gamma_{Cs} > \Gamma_{MA} > \Gamma_{FA}$. Therefore, exciton lifetime follows the opposite trend $\tau_{FA} > \tau_{MA} > \tau_{Cs}$.

**Cations role via Infra-red spectra (IR)**

To understand the role of cations in the obtained exciton lifetime, we have further computed their Infra-red (IR) spectra.

![Infra-red spectra of MAPbI$_3$, FAPbI$_3$ and CsPbI$_3$, respectively.](image)

**Figure 6:** Infra-red spectra of MAPbI$_3$, FAPbI$_3$ and CsPbI$_3$, respectively.

IR spectra is used to determine the vibrational modes corresponding to the motion of atoms or molecules. IR spectra of APbI$_3$ perovskites show vibrational modes, particularly in three energetic regions of phonons: low frequency, mid frequency and high frequency band. To briefly explain the reason behind the observed sequence for exciton lifetime, we are interested here only in low frequency band (0 – 200 cm$^{-1}$) and the high frequency band (2900 – 3500 cm$^{-1}$) (see Fig 6). The large difference in atomic mass between the inorganic cage atoms (Pb, I) and the covalently bonded organic atoms (H, C, N), has anticipated that the low frequency modes are entirely comprised of PbI$_6$ octahedra. However, high frequency mode involves the A cation (mainly organic cation, because of the presence of light atoms H, C, N).

The reason for the observed trend in exciton lifetimes of the perovskites is carefully analyzed by comparing the individual role of the electron-phonon coupling and the size of
cation. Note that, cations do not have any contribution to the band edges (see SI, Fig S7), however, indirectly they do affect the inorganic cage Pb–I via electrostatic interaction. IR spectra of the lattice is associated with direct coupling of the photons to phonons. The excited photons have a tendency to induce dipole and the square of the dipole is proportional to IR intensity. The size of the cation, electron-phonon coupling and the IR intensity are strongly correlated. Note that electron-phonon coupling depends on free volume (unoccupied space). A large free volume (because of the small size of cation) provides more space for atomic motions, and as a result electron-phonon coupling will be enhanced. Also, the small size of cation will not suppress the vibrational modes of PbI cage. Consequently, this results in high intensity at low frequency mode. Hence, the intensity of IR spectra for low frequency modes is given as follows: CsPbI$_3$ > MAPbI$_3$ > FAPbI$_3$. The same trend is further followed by the electron-phonon coupling. On the other hand, the size of the cation is in the order FA > MA > Cs, which suppresses the vibrations of inorganic Pb-I cage on the same trend.

From Fig 6, we compare the low frequency bands, which comprise mainly of Pb-I cage. We have observed the strong intensity for CsPbI$_3$, because it has stronger electron-phonon coupling, due to more space for atomic fluctuations. Notably, the strong intensity observed for CsPbI$_3$ (frequency range 0 – 500 cm$^{-1}$) is not just because of Pb-I cage, it also involves the vibrational mode of Cs cation, due to its heavy size. Whereas, the low intensity peak of MAPbI$_3$, that signifies weak electron-phonon coupling, is due to the moderate space for atomic fluctuations. The intensity is lowest in the case of FAPbI$_3$ as the large size of FA cation has suppressed the Pb-I modes significantly. The electron-phonon coupling leads to very slow, moderate and very fast recombination process in perovskite containing FA, MA, and Cs. As a result, exciton lifetime will be enhanced in the order FAPbI$_3$ > MAPbI$_3$ > CsPbI$_3$. 


Conclusion

In summary, we have presented an exhaustive study for the accurate determination of the quasiparticle bandgap or optical peak of APbI$_3$ perovskites. All the calculations are well validated to avoid artefacts of numerical simulations. The experimental band gap is reproduced by using the tuned $\alpha$ of hybrid DFT calculations with the SOC, as an initial step for GW and BSE calculations. This methodology resolves the inconsistency observed in bandgap from previously reported GW calculations. Further, model-BSE (mBSE) approach is used for qualitative description, to improve the features of optical spectra, where the Brillouin zone is sampled with sufficiently high accuracy. The Wannier-Mott approach and ionic dielectric screening have been used to anticipate the accurate exciton binding energy. Our results show that ionic contribution to dielectric screening is extremely important, because of the presence of optically active phonon modes below 16 meV. We have observed significant Rashba splitting for MAPbI$_3$ and FAPbI$_3$, which tends to reduce the recombination rate (due to indirect gap) along with strong absorption of light (due to the direct gap). The exciton lifetime as determined by Wannier-Mott approach (k.p perturbation theory) is in agreement with the trend observed in broadening of exciton peak via mBSE approach. The role of cation “A” for achieving the long-lived exciton lifetime is well investigated via IR spectra. The detailed analysis and the theoretical framework presented in this work will serve as a reliable technique for future studies of the electronic, optical and excitonic properties of alloyed or defected systems.

Theoretical Methods and Computational Details

We have used several methods systematically (viz. DFT, MBPT, mBSE, DFPT, Wannier-Mott) to explore the most accurate one in addressing the experimentally obtained bandgap, optical and electronic properties of the APbI$_3$ perovskites. As a first step, DFT calculations are performed with PAW pseudopotential method$^{87}$ as implemented in Vienna ab initio
simulation package (VASP). We have used exchange-correlation functionals ($\epsilon_{xc}$) viz. generalized gradient approximation (GGA with PBE) for optimizing the atomic positions of the structures. We have started with the experimental lattice parameters of the unitcell for the cubic phases of APbI$_3$ perovskites. Conjugate gradient minimization algorithm is used to relax the atomic positions and lattice parameters of the structures with force convergence 0.001 eV/Å. The structures are optimized with $\Gamma$ centered 4×4×4 k-mesh sampling. The tolerance criteria for total energy is set to 0.001 meV for the energy calculations. The k-mesh is converged at 6×6×6 for simple PBE optical spectra calculations. The details of the validation of k-mesh for PBE calculations is given in Supplementary Information (SI) (see Fig S1). To obtain accurate electronic structure and optical properties, we have performed hybrid functional HSE06 calculations. In HSE06 method, the exchange potential is divided into two parts: short range [SR] and long range [LR]. A fraction of non-local Hartree-Fock exchange potential is mixed with the GGA exchange potential of PBE in short range part. The long range exchange part [LR] and the correlation potential are contributed by the PBE functional.

$$E_{xc}^{\text{HSE06}} = \alpha E_{x}^{\text{HF,SR}}(\omega) + (1 - \alpha) E_{x}^{\text{PBE,SR}}(\omega) + E_{x}^{\text{PBE,LR}}(\omega) + E_{c}^{\text{PBE}}$$  (16)

where, $\alpha$ is mixing coefficient and $\omega$ is screening length. We have tuned the $\alpha$ parameter from 25% to 53% and $\omega$ is 0.2 Å$^{-1}$ in hybrid calculations (HSE06) along with SOC, in order to have a reliable prediction of the starting point, for the single shot GW calculations. The number of bands in GW calculations are taken as three times the number of occupied orbitals. In order to determine the optical gap and excitonic effects, the Bethe-Salpeter equation is solved. Initially, we have used light 4×4×4 k-point sampling. The convergence criteria for the number of occupied and unoccupied bands in BSE calculations is given in SI (see Fig S2). To further improve the spectra, the model-BSE (mBSE) approach is used, which takes into account a denser k-point sampling. Following this, we have used DFPT
approach with k-grid $12 \times 12 \times 12$, in order to have the electronic as well as ionic contribution in dielectric function. The plane wave energy cut-off is set to 600 eV in our calculations. Note that, SOC effect is duly included in all our calculations.

**Supporting Information**

(I) PBE functional convergence with high k-grid. (II) Convergence of occupied and unoccupied bands in BSE calculations. (III) Effect of SOC on bandstructure. (IV) Determination of GW bandgap for FAPbI$_3$ and CsPbI$_3$ perovskites. (V) Comparison between model-BSE (mBSE) and BSE approach. (VI) Projected density of states (PDOS) of MAPbI$_3$, FAPbI$_3$ and CsPbI$_3$.

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Capturing Excitonic Effects in Lead Iodide Perovskites from Many-Body Perturbation Theory

Pooja Basera*, Arunima Singh, Deepika Gill, Saswata Bhattacharya*

Dept. of Physics, Indian Institute of Technology Delhi, New Delhi 110016

E-mail: Pooja.Basera@physics.iitd.ac.in[PB], saswata@physics.iitd.ac.in[SB]

Phone: +91-2659 1359. Fax: +91-2658 2037

Supporting Information

I. PBE functional convergence with high k-grid.
II. Convergence of occupied and unoccupied bands in BSE calculations.
III. Effect of SOC on bandstructure.
IV. Determination of GW bandgap for FAPbI$_3$ and CsPbI$_3$ perovskites.
V. Comparison between model-BSE (mBSE) and BSE approach.
VI. Projected density of states (PDOS) of MAPbI$_3$, FAPbI$_3$ and CsPbI$_3$. 

S1
I. PBE functional convergence with high k-grid

We have shown convergence of the imaginary part of the dielectric function using PBE functional for MAPbI$_3$, FAPbI$_3$ and CsPbI$_3$, respectively. We have used DFPT method in order to show high k-grid sampling. We have observed that with increase in k-mesh, first peak does not change (shown by arrow) for all the systems (MAPbI$_3$, FAPbI$_3$ and CsPbI$_3$), unlike the case of mBSE calculations. In case of mBSE calculations, the first peak position has been slightly changed with an increase in k-mesh (see Fig 2(d)-(f) in main manuscript). This observation reinforces that, for PBE functional, convergence (in terms of bandgap) can be achieved at low k-grid sampling. However, for BSE calculations, we need to go at high k-grid sampling. Notably, the optical features or shape of spectra require high k-grid sampling in order to validate the results with experiment in case of both PBE and mBSE approach.

![Figure S1: Variation of the imaginary part of dielectric function calculated using PBE functional with k-mesh.](image)

II. Convergence of occupied and unoccupied bands in BSE calculations

For BSE calculations, the real and imaginary parts of the dielectric function are carefully examined with respect to a different number of occupied (NO) and unoccupied (NV) bands.
The imaginary and real part of the dielectric function for different NO and NV [viz. NO = 4, NV = 8; NO = 20, NV = 20; NO = 22, NV = 22 etc.] are calculated for FAPbI$_3$ (see Fig S2). Fig S2(a) shows a slight change in the imaginary part of the dielectric function (only in the intensity of the peak), whereas it is clear from Fig S2(b) that there is significant change in the real part of the dielectric function. Here, we have observed that the static value of the real part of dielectric constant increases with an increase in NO, NV. The real and imaginary parts of the dielectric function are saturated at NO=NV=20. If we increase NO, NV beyond 20, no change in dielectric function is observed. Therefore, for rest of the calculations, we have set NO and NV at 20.

![Figure S2: Convergence of number of bands in BSE calculations.](image)

III. Effect of SOC on bandstructure

The bandgap calculated for MAPbI$_3$ from PBE and PBE+SOC are 1.54 eV and 0.49 eV, respectively. Here, we have observed that inclusion of SOC significantly reduces the bandgap by almost 1 eV. On comparing the bandstructure from PBE and PBE+SOC, we have discerned that, the valence and conduction band levels are significantly affected by SOC. The drastic changes mostly originate in the Pb-derived conduction band levels along with slight changes in the valence band levels.
IV. Determination of GW bandgap for FAPbI$_3$ and CsPbI$_3$ perovskites

The bandgap or first peak of optical spectra obtained from PBE for FAPbI$_3$ is 1.40 eV, which is very close to the experimental value 1.46 eV. However, GW@PBE and BSE@GW give the optical peak at 2.20 eV and 1.87 eV, respectively (see Fig S4(a)). Similarly, on the inclusion of SOC, the peaks are redshifted and the values are 0.25 eV, 0.96 eV and 0.65 eV corresponding to PBE+SOC, GW@PBE+SOC and BSE@GW, respectively (see Fig S4(b)). Likewise MAPbI$_3$, PBE+SOC is not appropriate to act as a starting point for GW calculations. We have shown in detail how all the peak positions (HSE06, GW@HSE06, BSE@GW) are shifted due to default value of $\alpha$ (25%) in HSE06 with and without SOC (see Fig S4(c) and (d)). In order to achieve an accurate peak position, tuning of the exact exchange parameter $\alpha$ by 53% works very well for FAPbI$_3$ perovskite. HSE06+SOC gives a peak position at 1.39 eV, whereas GW performed on the top of HSE06+SOC with $\alpha$=53% provides a peak position at 1.45 eV (see Fig S4(e)). This value is in exact agreement with the experiments.$^{1-3}$
Therefore, this observation reinforces our approach to accurately determine the fundamental gap (GW bandgap). Hence, we have generalized our approach for the HIOPs perovskite, now it will be interesting to discern its applicability for the inorganic perovskite.

Figure S4: Imaginary part of dielectric function of FAPbI$_3$ calculated using single shot GW and BSE, where several $\epsilon_{xc}$ functional are used as a starting point ($i$): (a) PBE (b) PBE+SOC (c) HSE06 ($\alpha=25\%$) (d) HSE06+SOC ($\alpha=25\%$) (e) HSE06+SOC ($\alpha=53\%$).

For CsPbI$_3$ perovskite, we have obtained bandgap or optical peak at 1.50 eV using PBE functional. Unlike, HIOPs perovskites, there is no accidental matching of the PBE bandgap with the experimental value 1.73 eV.\textsuperscript{4,5} However, the bandgap can be overestimated using GW@PBE, but this results in peak value obtained at 2.07 eV, thus, not in agreement with the experiment (see Fig S5(a)). The BSE peak is obtained at 1.84 eV. Inclusion of SOC shifts the peak position at low energy value (see Fig S5(b)). The role of hybrid functional with and without SOC to be used as a starting point for the GW calculation can be seen explicitly in Fig S5(c) and (d), with default $\alpha=25\%$. GW@HSE06 ($\alpha=25\%$) and GW@HSE06+SOC
(α=25%) give peak position at 2.43 eV and 1.37 eV, respectively. These values are no longer close to the experimental data.

![Optical spectra of CsPbI₃](image)

Figure S5: Optical spectra of CsPbI₃ calculated using single shot GW and BSE, where several ϵₓc functional are used as a starting point (i): (a) PBE (b) PBE+SOC (c) HSE06 (α = 25%) (d) HSE06+SOC (α = 25%) (e) HSE06+SOC (α = 53%).

Therefore, we have tuned α = 53% in HSE06+SOC calculations, that results in peak position at 1.69 eV. Then performing GW@HSE06+SOC (α=53%) leads to optical peak at 1.73 eV, which results in excellent agreement with the experiment (see Fig S5(e)). Hence, we can conclude that, this method is sophisticated enough to predict accurate GW bandgap as well as correct optical peak position for all types of perovskites without going for computationally demanding high k-grid sampling.
V. Comparison between model-BSE (mBSE) and BSE approach

We have used a local model dielectric function $\varepsilon^{-1}_\infty$ in the BSE calculations, in order to converge the exciton binding energies on dense k-point grids. This model allows us to calculate the experimental features of the optical spectra. The parameter $\varepsilon^{-1}_\infty$ comes from DFPT calculations on a shifted high k-point grid (8×8×8 or 11×11×11). The screening length parameter ($\lambda$) are fitted to match the diagonal ($G = G'$) part of dielectric function from the GW calculations on the shifted 4×4×4 k-point grid. This approximation works very well, particularly, in the low energy part as shown in Fig S6. Here, we have shown only for FAPbI$_3$ perovskite. However, we have checked that this approach is applicable for all systems (MAPbI$_3$, CsPbI$_3$). The imaginary part of the dielectric function calculated with BSE@GW@PBE, including SOC, matches with the one, which is calculated with the model BSE (mBSE) method, where input is PBE+SOC. Therefore, the excitonic features (i.e first peak) information are always retained by mBSE approach. Note that both the calculations are carried out using a 4×4×4 k-point grid with a same starting point. It is worth to note that mBSE approach can predict the optical spectra for a dense high k-grid along with a very affordable computational cost. However, convergence of BSE calculations with such high k-grid is next to impossible, because of its huge computational cost.
From Fig S7, we observe that valence band is primarily composed of I atom, whereas conduction band is mainly contributed by Pb atom for MAPbI$_3$, FAPbI$_3$ and CsPbI$_3$, respectively. Note that, the contribution of the organic cation (MA, FA) and the inorganic cation (Cs) is in deep inside the valence and conduction band. In short, cations do not play any role at the valence band and conduction band edges.
Figure S7: PDOS shows contribution of each atom.

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