The unprecedented increase of the power conversion efficiency of metal-halide perovskite solar cells has significantly outpaced the understanding of their fundamental properties. One of the biggest puzzles of perovskites has been the exciton binding energy, which has proved to be difficult to determine experimentally. Many contradictory reports can be found in the literature with values of the exciton binding energy from a few meV to a few tens of meV. In this review the results of the last few years of intense investigation of the exciton physic in perovskite materials are summarized. In particular a critical overview of the different experimental approaches used to determine exciton binding energy is provided. The problem of exciton binding energy in the context of the polar nature of perovskite crystals and related polaron effects which have been neglected to date in most of work is discussed. It is shown that polaron effects can reconcile at least some of the experimental observations and controversy present in the literature. Finally, the current status of the exciton fine structure in perovskite materials is summarized. The peculiar carrier–phonon coupling can help to understand the intriguing efficiency of light emission from metal-halide perovskites.

1. Introduction

Organic and inorganic metal halide perovskites have emerged in recent years as revolutionary semiconductor materials for lighting[1,2] and energy harvesting applications.[3–5] The unprecedented success of organic–inorganic lead halide perovskites results from their unique combination of optoelectronic properties. Namely, they exhibit strong broadband absorption[6–8] together with long carrier lifetime and diffusion length,[9,10] which makes them almost ideal materials for energy harvesting. These materials, characterized by ABX₃ structure, seem to defy conventional wisdom concerning semiconductors. Despite their preparation with room temperature wet chemistry (essentially bucket chemistry), which is prone to result in a high concentration of defects, these materials are almost immune to the influence of defects.[11,12] In contrast to conventional semiconductors, their ionic crystal lattice has relatively low energy phonon modes (which cannot be described within the widely used harmonic approximation) and low elastic constant,[13–15] suggesting that perovskites should be considered as crystalline liquids with a dynamic lattice disorder rather than hard semiconductor materials.[16–18] In general this set of properties is not associated with high optoelectronic quality.[19] Remarkably, in perovskites the mixed crystalline/liquid/glassy behavior is inherent and even crucial in explaining their outstanding performance.[17] Therefore, metal-halide perovskite form a most peculiar system with an unexpected and unprecedented synergy of mechanical and optoelectronic properties.[19] Our understanding of the complex properties of metal halide perovskites is still in its infancy with an increasing awareness of the important role played by the lattice softness and vibration.

In this review we focus on excitons in bulk semiconductors, and in particular how the physics of excitons has to be adapted to the specific case of soft perovskites. The simple concept of elementary excitations in semiconductors, known and investigated since decades, needs to be revisited in the context of metal-halide perovskite semiconductors if erroneous conclusions are to be avoided. In particular, a reliable determination of the exciton binding energy is nontrivial, with a significant spread of reported values to be found in the literature. The exact value of the exciton binding energy in metal-halide perovskites is especially relevant for their application as active materials in solar cells. The operation mechanism of a solar cell depends on the fraction of excitons which thermally dissociate into free electrons and holes, giving rise to the required free charge transport. If the fraction is too small an additional heterojunction should be incorporated into the solar cell architecture to force the exciton dissociation. Another interesting subject of ongoing discussion is related to the origin of the exciton fine structure, crucial for efficient light emission and quantum technology. In both of these aspects of exciton physics a significant progress has been made in the last few years, however, our fundamental understanding of excitons in metal-halide perovskite remains far from complete.

The manuscript is organized as follows: i) We start by discussing the reported experimental values of exciton binding energy determined by various experimental techniques, which
are based for the most part on the hydrogen model of the exciton. ii) We then discuss the consequences of going beyond the hydrogen model, in particular we focus on polaron effects and their potential impact on the exciton spectrum in the light of available experimental results. iii) Finally we provide an overview of exciton fine structure in perovskites.

2. Experimental Determination of the Exciton Binding Energy

In a semiconductor, the absorption of a photon with an energy higher or equal to the energy of the bandgap can lead to the formation of a quasiparticle. In Equation (1) the effective mass of the carriers is usually smaller than the free electron mass. Moreover, the carrier interactions are screened by the lattice. Therefore, the effective Rydberg can be understood as a renormalization of the Rydberg constant ($R_0 = 13.6 \text{ eV}$) and

$$R^* = \frac{R_0 \mu}{m_e \varepsilon_{\infty}}$$

with an exciton reduced mass $1/\mu = 1/m_h + 1/m_e$, where $m_{h,e}$ are the effective masses of the hole and electron, respectively, and $\varepsilon_\infty$ is the relative dielectric constant of the crystal, which accounts for the screening of the carriers by the crystal lattice.

In this picture, the exciton binding energy ($R^*$) depends on the effective mass of the carriers and the dielectric constant of the crystal. Much of the controversy related to the exciton binding energy in perovskites arises from the particularly large difference between the static and optical dielectric constants (absent in other intensively investigated systems such as III–V or II–VI semiconductors). In halide perovskites the static $\varepsilon_s = 30$ and high frequency dielectric constant $\varepsilon_\infty = 5$ are very different. It is far from obvious which value should be used in the calculation of Equation (2) and an arbitrary choice of the dielectric constant results in exciton binding energies in the range of 2–50 meV. Many experimental attempts have been made to determine exciton binding energy with widely varying results. A brief review of them is presented below.

2.1. Absorption

The absorption measurements are expected to be the most straightforward and simplest method to determine the exciton binding energy. The absorption spectrum of a direct bandgap semiconductor including hydrogen-like excitonic effects is described by the Eliot formula:

$$\alpha = \left[ A \cdot \Theta(\hbar \omega - E_g) \cdot D_v(h\omega) \right] \frac{\pi x \exp(\pi x)}{\sinh(\pi x)} + A \cdot R \sum_{n=1}^{4\pi} \delta \left( \hbar \omega - E_g + \frac{R^*}{n} \right)$$

where $A$ is a constant related to the transition matrix element, $\hbar \omega$ is photon energy, $D_v$ is the joint density of valence and conduction bands states, $\Theta$ is the Heaviside (step) function, $\delta$ denotes a delta function, $E_g$ is the bandgap, and $x$ is defined as

$$x = \sqrt{R^*(\hbar \omega - E_g)}$$

where $R^*$ is the exciton binding energy. The first term in Equation (3) describes the absorption of continuum states enhanced by the Coulomb interaction (Sommerfeld
The second term describes the discrete excitonic state absorption that lies below the bandgap edge. For an ideal case, when broadening of the transition is negligible, the exciton binding energy can be determined by the energy separation between ground (1s) and excited (2s) state or the energy separation between the 1s and band edge absorption onset as presented in Figure 1a.

In polycrystalline thin perovskite films where the absorption resonances are strongly broadened even at very low temperatures, only the 1s exciton state, merging with a continuum of states, is visible in the absorption spectra. Examples of the absorption spectra for MAPbI₃ thin films are shown in Figure 1b after ref. [24]. The excitonic absorption broadens significantly with increasing temperature. This leads to an excitonic peak which is not well distinguished from the band absorption at room temperature, as shown in Figure 1c after ref. [25]. Therefore, to obtain $R^*$ by fitting the absorption spectra with the Eliot formula, it is usually convoluted with some function which replicates the transition broadening.[26–30] To obtain even better agreement with the experimental data, the nonparabolicity of the band is also often taken in to account.[31,32] However, such an analysis inevitably suffers from the large number of fitting parameters involved, with a large error bar for the extracted exciton binding energy. This is somehow reflected in the very parameters involved, with a large error bar for the extracted exciton binding energy.[26,30,32] In addition, there is a controversy concerning the temperature dependence of the exciton binding energy. Some work report a constant binding energy[26,30,32] in the range $T = 10–300$ K while others show a clear temperature dependence.[8,29] All of these contradictory results raise serious questions concerning the accuracy of the exciton binding energy deduced using the Eliot formula.

Another approach to estimate $R^*$ is based on an investigation of the quenching of the integrated photoluminescence (PL) intensity with the temperature.[15–19] Assuming, that the rate of nonradiative recombination is related solely to the thermally activated exciton dissociation, the PL intensity was fitted using an Arrhenius formula $I(T) = I_0/(1 + A_0 \exp(-R^*/k_BT))$ (see Figure 2a). Values of the exciton binding energy obtained with this method range from 19 to 62 meV for MAPbI₃[35–37] and 84 meV[38] and 98 meV for MAPbBr₃ and MAPbI₃₋ₓClₓ, respectively,[39] significantly higher than those reported from absorption studies. The assumption that a single thermally activated exciton dissociation is the only mechanism responsible for thermal quenching is probably an unacceptable simplification. The overall carrier kinetics in perovskites is relatively complicated and includes mono and bi-molecular processes, as well as Auger recombination.[40–42] In addition, shallow trap states also influences the carrier recombination dynamics,[43,44] and recombination rates of a particular process have each their own temperature dependence.[41]

The exciton transition broadening can be described using

$$\Delta \nu = \Delta \nu_0 + \nu_T \exp(-R^*/k_BT)$$

where $\Delta \nu_0$ is temperature independent broadening and the term $\nu_T \exp(-R^*/k_BT)$ represents a broadening related to the exciton thermal dissociation rate. Based on this approach the exciton binding energy for MAPbI₃₋ₓClₓ was estimated to be $55 \pm 10$ meV. However, a precise experimental determination of the FWHM might be problematic due to the overlap of the exciton and band to band absorption.

### 2.2. Temperature of PL Quenching

Ultrafast THz spectroscopy can be used to estimate the exciton binding energy,[46,47] although it also fails to provide a clear answer. The mobile charge carrier generation efficiency can be described using the Saha–Langmuir equation (mass law for free charges and excitons)

$$\frac{x^2}{1-x} = \frac{1}{n_{tot}} \left(\frac{2\pi nk_BT}{\hbar^2}\right)^{3/2} \exp(-R^*/k_BT)$$

where $x$ is a ratio of excitons to free carriers and $n_{tot}$ is the sum of excitons and free carriers. This method determined an exciton binding energy for MAPbI₃ of 50 meV (at room
temperature assuming a reduced effective mass $\mu = 0.11$).
At the same time, in the same experiment, an absorption at 12 meV (see Figure 2c was attributed to 1s–2p exciton transition giving an exciton binding energy of 17 meV. As the authors of this study pointed out the disagreement between the two results may reside in the assumption of quasi-equilibrium in the use of Equation (6) or in a more complicated energetic structure of the exciton due to the interaction with phonons.

Modulation spectroscopy has the advantage that it provides extremely sharp spectral signature of individual critical points in the density of states. In particular, electroabsorption spectroscopy was employed to determine exciton binding energy and reduced mass. In this technique, the absorption of the material is modulated by an alternating external electric field applied using transparent electrodes. The absorption spectra modulated by an applied electric field have a derivative-like character. Therefore, effects such as optical scattering and background absorption are automatically excluded. Importantly, in this approach, the electric field-induced change in the absorption intensity occurs mainly for the exciton band, which effectively avoids any problems associated with the overlap of the excitonic and band to band transitions (see comparison of absorption and electroabsorption spectra presented in Figure 2b). However, the price to pay is a relatively complex spectrum which has to be modelled. Nevertheless, the reported values of the exciton binding energy are in good agreement with estimations from magneto-optical studies (see next section). At room temperature modulation spectroscopy suggests $R^*$ for MAPbI$_3$ equal to 7.5 meV$^{50}$ and 11.5 meV$^{45}$ while for MAPbBr$_3$ the binding energy was found to be 14 meV$^{45}$ Other work$^{45}$ found values of exciton binding energy for MAPb$_2$Br and MAPbBr$_2$ to be equal to 9 and 13.8 meV, respectively. Modulation spectroscopy also gives reasonable values for the reduced exciton mass of $\mu = 0.12$ for MAPbI$_3$. $^{50}$

### 2.4. Magneto-Optical Investigation

Using magneto-optics, the exciton binding energy can be estimated based on the energy shift of the exciton transition in a magnetic field. In the low magnetic field limit, when the energy related to cyclotron motion of carriers ($\hbar eB/\mu$) is much lower than Coulomb interaction energy $R^*$. Then exciton energy shift can be described by$^{51}$

$$E(B) = E_0 \pm \frac{1}{2} g \mu_B B^2$$

(7)

where $E_0$ is an energy of the exciton ground state, $g$ is the Landé g-factor, $\mu_B$ is the Bohr magneton, and $c_0$ is the diamagnetic coefficient. The latter is described by

$$c_0 = \frac{4\pi^2 e^2 \hbar^4}{\mu^e c^2}$$

(8)
The exciton Bohr radius, reduced mass, and exciton binding energy can be determined from $c_0$ provided the relative dielectric constant $\varepsilon_r$ is known.[52]

\[
\frac{a_B}{a_H} = \left( \frac{\varepsilon_r c_0}{c_H} \right)^{1/3}
\]

(9)

\[
\frac{\mu}{m_0} = \left( \frac{\varepsilon_r c_H}{c_0} \right)^{1/3}
\]

(10)

\[
\frac{R^*}{R_H} = \left( \frac{1}{\varepsilon_r} \right)^{1/3}
\]

(11)

Here $a_B$, $m_0$, $R_H$, and $c_0$ are the Bohr radius, electron mass, binding energy, and diamagnetic coefficient of a hydrogen atom.

This approach was employed in the first magneto-optical attempt to determine the exciton binding energy for MAPbI₃. Hirasawa et al.[53] investigated the magnetoabsorption spectra of the MAPbI₃ in magnetic fields up to 40 T at a temperature of 4.2 K. They measured $c_0 = 2.7 \times 10^{-6}$ eV T⁻². They then used the high frequency dielectric constant $\varepsilon_\infty = 6.5$ to estimate an exciton binding energy of 37 meV, a Bohr radius of 28 Å and a reduced mass of $\mu = 0.12$. A decade later this investigation was extended by Tanaka et al.[52] to 50 T. The new results gave a lower value of $c_0 = 1.35 \times 10^{-6}$ eV T⁻² for MAPbI₃ and $c_0 = 1.28 \times 10^{-6}$ eV T⁻² for MAPbBr₃. Using the dielectric constant of Hirasawa et al. they determined $R^* = 50$ meV, $a_B = 22$ Å, $\mu = 0.15$ for MAPbI₃ and $R^* = 76$ meV, $a_B = 20$ Å, $\mu = 0.13$ for MAPbBr₃.

The investigation of the excitonic absorption shift in high magnetic field has one very important advantage over other methods, namely, the shift is relatively easy to track even if the excitonic transition is strongly broadened making the data analysis more robust. However, there are three main concerns about initial studies of perovskite in magnetic field: i) assumption of low field limit up to 50 T, and ii) the arbitrary choice of the dielectric constant. The use of the high frequency dielectric constant in the calculation of the exciton binding energy is rather controversial as discussed by Lin et al.[54] Analyzing the Tanaka et al. results using the static dielectric constant $\approx 70$ gives an exciton binding energy of 1.7–2.1 meV.[54] Finally, iii) the assumption that the hydrogen model correctly describes excitons in metal-halide perovskites may not be valid[55] or should at least be treated as an approximation (see discussion in the following section).

In recent years the magneto-optical approach has been significantly improved with the use of much higher magnetic fields.[56–61] Using extreme magnetic field ($B \leq 200$ T) it was possible to combine the analysis of the interband free carrier absorption and 1s and 2s exciton absorption (see Figure 3a–d.)

Figure 3. a) Typical low temperature transmission data of FAPbI₃ at different magnetic fields in exciton transition energy range. Red and blue lines correspond to two $\sigma^+$ and $\sigma^-$ light polarization. b) Transmission spectra at given magnetic field divided by 0 field spectra showing energy of Landau levels. c) Fan chart plot of the exciton and Landau levels energy as a function of magnetic field. a–c) Adapted with permission.[57] Copyright 2019, Royal Society of Chemistry.
In high magnetic field, at higher energies than the excitonic features, a series of free carrier transitions from the valence to conduction band are observed. These interband transitions occur between the van Hove singularities of the Landau levels with energies given by

\[ E^L_n = E_g + \left( N + 1/2 \right) \hbar \omega_c + \frac{1}{2} \frac{g_{\text{eff}}}{\mu} eB \]

where \( E_g \) is the bandgap energy, \( N = 1, 2, 3 \ldots \) is the Landau level orbital quantum number, \( \omega_c = eB/\mu \) is the cyclotron frequency, \( B \) is the applied magnetic field, \( e \) is the elementary charge, \( \mu \) is the reduced mass of the exciton, and \( g_{\text{eff}} \) is the effective \( g \)-factor. The variation of the energy of the Landau levels energy versus magnetic field provides a strong constraint on the reduced mass of exciton and bandgap. Moreover, the exciton diamagnetic shift was analyzed using the numerical model of Makado and McGill\[62\] for a hydrogen atom in a magnetic field which is valid for all values of magnetic field (no low field approximation). Importantly the input parameters for this model are only exciton binding energy and reduced mass of exciton therefore, no assumptions concerning the dielectric constant are required which can be determined a posteriori. The high field measurements therefore eliminate two of the three constraints present in the initial magnet-absorption studies. The magnetic field dependence of 1s and 2s exciton states together with Landau level energies were simultaneously fitted on fan chart plot (see Figure 3). In practice the reduce mass is fixed by the free carrier transitions so that the only parameter for the numerical hydrogen model is the exciton binding energy. Under the assumption of constant effective mass of carriers (i.e., when energy of Landau levels exhibit linear dependence vs \( B \)) this allows for robust and reliable determination of exciton binding energy, reduced mass of exciton, bandgap, and effective dielectric constant. However, in the light of last experimental results the assumption of constant effective mass should be treated with caution which is especially visible in case of MAPbI\(_3\) as we discuss in the further part of this work.

In the initial work of Miyata et al.\[56\] the exciton binding energy for MAPbI\(_3\) at 4 K was determined to be 16 meV and reduced mass of exciton \( \mu = 0.104 \). In the same work the authors determined the exciton binding energy in tetragonal phase of MAPbI\(_3\) to be 10–12 meV at 161 K.

This approach was subsequently applied in a series of papers, where the exciton binding energy, effective mass, and dielectric constant were investigated for a variety of metal-halide perovskite compounds and the results are summarized in Figure 4.

In the work\[57\] the binding energy of the excitons (\( R^0 \)) and reduced effective mass \( \mu \) for Cl assisted grown MAPbI\(_3\) as well as MAPbBr\(_3\) and the FA based materials FAPbI\(_3\) and FAPbBr\(_3\) were reported. The values of \( R^0 \) were in the range 14–25 meV for the low temperature phase and decrease considerably at higher temperatures for the tri-iodides. A reduced mass in the range of \( \mu \) of 0.09–0.117 was also reported. The general increase of \( \mu \) with increasing bandgap follows the prediction of a simple 2 band kp model which allows to predict the effective mass for other members of metal-halide perovskite compounds. In refs. [58,59] the exciton properties of single crystal and thin films with different grain size were studied. It was found that the microstructure of MAPbI\(_3\) does not influence the excitonic binding energy disproving the controversial hypothesis from transient absorption studies\[61\] that it is not possible to assign a universal value for the exciton binding energy of lead halide perovskites. This approach allows also for very systematic investigation of effective dielectric screening experienced by the exciton in metal-halide perovskites.

In ref. [60] the authors compared the dielectric constant for cesium-based compounds with the corresponding quantities for the hybrid organic-inorganic perovskites. They found that dielectric constant does not vary significantly for a given lead halide cage, regardless of the organic or inorganic nature of cation. At the same time it decreases with decreasing halide mass, corroborating theoretical predictions that the main contributions to the dielectric permittivity is related to Pb–X stretching modes and Pb–X–Pb rocking modes\[64–67\]. Later these studies were extended to tin-based perovskites\[61\] confirming the general expectation that reducing the mass of the atoms contributing to the vibration mode decreases the screening due to

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**Figure 4.** a) Reduced mass, b) exciton binding energy, and c) effective dielectric constant in hydrogen model as a function of the bandgap. The results for the MAPb\(_{1-x}\)Sn\(_x\)I\(_3\) family (red dots) compared with results from previous work on organolead halides\[57,68\] (blue symbols) and fully inorganic CsPbX\(_3\) compounds\[60\] (orange stars). The dashed parabola in panel (c) is a guide for the eye, suggesting the evolution of the dielectric screening with decreasing mass of vibrating atoms. Adapted with permission.\[61\] Copyright 2019, American Chemical Society.
the increased optical phonon frequency. This studies confirmed the qualitative picture that the dielectric screening properties are mainly determined by the metal halide cage in the low-temperature range, when the motion of the organic cation is frozen.

### 2.5. Discussion

The reported exciton binding energies in various metal-halide perovskite crystals are summarized in Figure 5 as a function of the bandgap. Despite the significant scatter of the $R^*$ values extracted using different methods two general trends are observed. With increasing bandgap the exciton binding energy increases, which is typical also for classic inorganic semiconductors, and can be connected with the increase of the carrier mass when the bandgap opens.\cite{57,61} The second trend is that the exciton binding energies extracted at room temperature are generally smaller than those extracted at cryogenic temperatures. This observation is in agreement with the nowadays accepted dual nature of metal-halide perovskites.\cite{15-19}

At low temperatures they behave like an ordinary semiconductor crystal, however, at higher temperatures a crystal-liquid like behavior appears which is accompanied by a significant increase of the dielectric screening.\cite{69,78} Therefore, a decrease of the exciton binding energy at higher temperatures is expected.\cite{81}

Regarding the accuracy of particular methods to extract the exciton binding energy we are convinced that the magnetooptical studies provide the most accurate upper bound for exciton binding energy in perovskites provided both free carrier and excitonic transitions are observed.\cite{57,61,68} This judgement is supported by the high consistency of the extracted exciton binding energy values. Similarly electroabsorption studies also provide very consistent results at room temperature. Unfortunately, these two method cannot be directly compared because of lack of magneto-optical studies at room temperature, where the excitonic absorption is practically not distinguishable from band to band absorption. Nevertheless, the decreasing exciton binding energy revealed by magneto-optical studies at temperatures just above the phase transition,\cite{57,68} together with electroabsorption\cite{45,50} and some absorption studies\cite{8,29} strongly supports the expectation that the binding energy is reduced to values of order of a few meV at room temperature. Therefore the excellent perovskite device performance can be partially attributed to domination of free carrier species at room temperature. However the precise mechanism leading to exciton binding energy reduction at high temperatures remains elusive.

Some of the theoretical predictions suggest that the exciton binding energy should be constant over cryogenic to room temperature range\cite{73,74} and electron–hole interaction is not affected by thermally activated rotation of organic cations.\cite{73} Therefore further theoretical and experimental efforts are needed to fully reconcile all observation.

In a recent investigation of high optical quality single crystal MAPbI$_3$\cite{39} and MAPbBr$_3$\cite{75,76} the excitonic 1s and 2s states are directly observed in the low temperature reflection spectrum at zero magnetic field. In this case the exciton binding energy can straightforwardly be determined from the 1s–2s splitting ($\Delta_{1s}$) in the hydrogen model ($R^* = 3\Delta_{1s}/4$) giving $R^* = 16$ meV for MAPbI$_3$ and ~14 meV for MAPbBr$_3$. It is interesting to note that despite exciton binding energy for MAPbI$_3$ is higher the Bohr radius ($a_0$) is smaller for MAPbBr$_3$ (4.6 and 3.8 nm, respectively). Since in hydrogen model the oscillator strength scale as $1/a_0^4$ the stronger transition is observed for MAPbBr$_3$ despite lower exciton binding energy. These results provide a benchmark for all studies performed on much lower optical quality thin films. Surprisingly the exciton binding energy and effective mass\cite{76} extracted from single MAPbBr$_3$ crystal studies are different than those obtained in magneto-optical studies of thin films.\cite{57} This observation suggests that some important aspect of exciton physics is missing in the high field magneto-optical data analysis. Importantly the deviation of band dispersion from parabolic cannot explain observed decrease of reduced mass at high fields. Generally the non-parabolic bands lead to the opposite effect.\cite{51} Probably more convincing explanation can be given by inclusion of polaron effects. They enhance the carrier effective mass in the low field (low energy) while at high field limit carrier–lattice interaction decouple resulting in the decrease of carrier effective mass as we discuss in the next section.

### 3. Polaronic Effects

In almost all work that addresses the problem of the exciton binding energy in metal-halide perovskites the polar nature of these materials is simply neglected. In principle, in all polar semiconductors, the electronic and longitudinal optical (LO) phonon states are coupled and their properties should be discussed in terms of polarons, i.e., charge carriers dressed by the local lattice polarization resulting from the Coulomb interaction between the carrier and the ionic lattice. Depending
on the spatial extent of the lattice deformation we can classify polarons according to size. Large polarons are formed by the long range Coulomb interaction between the free carrier and the ionic lattice while small polarons appears due to changes in local bonding. For large polarons the polarization cloud extends over distances much greater than the unit cell. For small polarons the polarization cloud extends over less than a single unit cell. The interaction of carriers with the polarizable lattice can have tremendous impact on the electrical and optical properties of the material, increasing the carrier effective mass,\[^{[77]}\] determining coherent or incoherent carrier transport nature, renormalizing the bandgap,\[^{[78]}\] or even leading to the self-trapping of excitons.\[^{[79]}\]

The concept of electron–phonon coupling and in particular large polaron formation has already been applied to address some of the puzzling aspects of perovskites physics. For example, the formation of large polarons can at least partially explain the low mobility of carriers in perovskites, which is surprising given the low effective mass of the carriers.\[^{[64,80-82]}\] The characteristic slow carrier cooling in perovskites was also attributed to the large polaron formation, along with the phonon glass character which results from the softness of perovskites.\[^{[17,18,83,84]}\] At the same time, in the majority of work addressing the problem of the exciton biding energy, the analysis was restricted to a simple hydrogen model, with only two attempts to take into account polaron effects.\[^{[33,55]}\] While neglecting polaronic effects is appropriate for classical inorganic semiconductors, it is clearly not appropriate for perovskites. Menéndez-Proupin et al.\[^{[55]}\] have shown that the inclusion of polaron effects can significantly modify the exciton spectrum in perovskites. Moreover, some of the controversy resulting from previous studies can be naturally understood in the framework of exciton–polaron picture.

The interaction of carriers with LO phonons is characterized by the dimensionless Fröhlich coupling constant $\alpha$ which is defined as follows

$$\alpha = \frac{e^2}{\hbar} \left[ 1 - \frac{1}{\varepsilon_i - \varepsilon_e} \right] \frac{m_e m_h}{2 E_{\text{LO}}} = \frac{e^2}{\hbar} \alpha \left[ 1 - \frac{1}{\varepsilon_i - \varepsilon_e} \right] \frac{m_e m_h}{2 E_{\text{LO}}} \tag{13}$$

where $e$ is electron charge, $h$ is Planck’s constant, $m_e, m_h$ is the bare effective carrier mass (mass resulting only from band dispersion, neglecting interaction with lattice), and $E_{\text{LO}}$ is the optical phonon energy. The term $(1/\varepsilon_i - 1/\varepsilon_e) = 1/e^\gamma_r$ represents ionic screening of carriers, where $\varepsilon_i$ and $\varepsilon_e$ are optical frequency and static dielectric constants, respectively. Coupling of carriers to the lattice polarization result in an increase of the carrier effective mass which can be approximated in the so called weak coupling regime\[^{[77]}\] by the following expression

$$m^*_{e,h} = m_{e,h} \left( 1 + \frac{\alpha}{\theta} \right) \tag{14}$$

A distinct feature of perovskites is the significant difference between the optical and static dielectric constants which at room temperatures are in the range of $\approx 5$ and above $\approx 30,\[^{[64,69,90,91]}\]$ respectively. In addition, the relative softness\[^{[13,92]}\] of metal-halide perovskite crystals results in low phonon energies compared to traditional semiconductors.\[^{[13,64,93]}\] Both of these result in a much higher Fröhlich coupling constant $\alpha$ than in the case of many inorganic semiconductors. Therefore, a significant increase of the carrier effective masses in perovskites due to polaron effects is expected (see Table 1). Moreover, the polarization cloud around the electron and hole modifies their attractive interaction. Taking all of this into account naturally raises the question to what extent the simple hydrogen model applies to perovskites? The direct inclusion of polaron effects in the exciton calculations is extremely challenging. Fortunately, some relatively simple models for excitons in polar semiconductors have been proposed in the literature, which provide some insight into the correct description of excitons in perovskites.\[^{[94-96]}\] These models take the form of the 3D hydrogen atom problem with a modified potential

$$-\frac{p^2}{2\mu} \phi + V(R)\phi = E\phi \tag{15}$$

where $p$ is the momentum operator, $\mu$ is the reduced mass of bare carriers or polarons, and $E$ is the energy of the eigen states. One of the approximation for the interacting electron–polaron and hole–polaron potential was proposed by Haken\[^{[94]}\]

$$V(R) = \frac{1}{\varepsilon_e} \frac{e^2}{R} - \frac{1}{\varepsilon_i} \frac{e^2}{R} \left( \exp(-R/l_e) + \exp(-R/l_i) \right) \tag{16}$$

where $l_e$ and $l_i$ are the electron and hole polaron radii. They are defined as follows

$$l_{e,i} = \frac{\hbar^2 m_e m_i}{\varepsilon_e \varepsilon_i E_{\text{LO}}} \tag{17}$$

As the Haken potential overestimates the exciton binding energy in polar crystals a phenomenological modification of the Haken potential was proposed by Bajaj\[^{[96]}\]

$$V(R) = \frac{1}{\varepsilon_e} \frac{e^2}{R} \left( \frac{\varepsilon_i}{\varepsilon_e} \right) \left( \frac{1}{\varepsilon_i} \frac{e^2}{R} \right) \left( \exp(-R/l_e) + \exp(-R/l_i) \right) \tag{18}$$

where the $\gamma = 3/5$ parameter was chosen to reproduce experimentally determined values of the exciton binding energy in polar semiconductors. For both approximations the reduced polaron mass $\mu^*$ has to be used in Equation (15). An alternative potential was proposed by Pollmann and Büttner\[^{[95]}\]

$$V(R) = -\frac{1}{\varepsilon_e} \frac{e^2}{R} - \frac{1}{\varepsilon_i} \frac{e^2}{R} \left( \frac{m^*_{e,h}}{\Delta m} \exp(-R/l_e) - \frac{m^*_{e,h}}{\Delta m} \exp(-R/l_i) \right) \tag{19}$$

### Table 1. Fröhlich coupling constants, bare electron effective masses and polaron masses calculated according to Equation (14).

| Material     | $\alpha$ | $m_e$   | $m_h$   |
|--------------|----------|---------|---------|
| GaAs         | 0.068\[^{[33]}\] | 0.067\[^{[33]}\] | 0.068   |
| InAs         | 0.052\[^{[33]}\] | 0.026\[^{[33]}\] | 0.026   |
| CdTe         | 0.29\[^{[33]}\]  | 0.088\[^{[33]}\] | 0.92    |
| MAPbI\(_3\)  | 1.72\[^{[33]}\]  | 0.19\[^{[33]}\]  | 0.26\[^{[33]}\] |
| MAPbBr\(_3\) | 1.69\[^{[33]}\]  | 0.26\[^{[33]}\]  | 0.33\[^{[33]}\] |
| MAPbCl\(_3\) | 2.17\[^{[33]}\]  | 0.39\[^{[33]}\]  | 0.49\[^{[33]}\] |
where $\Delta m = m_h - m_e$ and the bare carrier reduced masses have to be used in Equation (15).

To demonstrate how the properties of the exciton states change when there is a significant difference between the static and optical dielectric constants we solve numerically Equation (15) as a function of $\varepsilon_s$ for the modified potentials. The remaining parameters are fixed and the representative values for MAPbI$_3$, are summarized in Table 2. Figure 6a shows the three potentials calculated for $\varepsilon_{so} = 5$ and $\varepsilon_s = 20$ together with pure Coulomb potential (black lines) for the limiting cases $\varepsilon_{so} = 5$ and $\varepsilon_s = 20$. All of the modified potentials behave in the same manner; at short range they behave as a Coulomb potential with low dielectric screening and at longer distance they mimic a Coulomb potential with enhanced dielectric screening.

Figure 6b shows the energy of the exciton ground state (1s) and first excited state (2s) as a function of the static dielectric constant $\varepsilon_s$. The modified potentials significantly change the energy of the 1s transition with respect to the calculated values for a pure Coulomb potential. When $\varepsilon_s$ is very different from the high frequency dielectric constant the exciton is bound more tightly. This is obviously the result of reduced screening at short distance of the potentials described by Equations (16), (18), and (19). At the same time the energy of the more delocalized 2s state does not change significantly. As a result, under the modified potential the exciton spectrum deviates from hydrogen-like ($E_n \propto 1/n^2$) behavior. Notably, the separation between the 1s and 2s states ($\Delta_{12}$) is larger than $3R^* / 4$. This is shown in Figure 6c where we plot $\Delta_{12} / R^*$ as a function of the static dielectric constant. The 2s state in polar crystals is closer to the continuum of states than expected for a given $R^*$ (always less than 25% of $R^*$). Moreover, in case of enhanced screening the relative oscillator strength between the 1s and 2s states decreases as can be seen in panel (d) of Figure 6.

![Figure 6](image_url)

As pointed by Menéndez-Prupin et al.\textsuperscript{[55]} the decreased oscillator strength of the 2s transition explains why in most studies the 2s state is hardly ever observed (at $B = 0$ T). The decrease of the oscillator strength also explains why there is so large a difference between the 1s and 2s transition intensity observed in MaPbBr$_3$ single crystal reflectance spectrum\textsuperscript{[75,76]} or MAPbI$_3$.\textsuperscript{[59]} Finally, the Pollmann and Büttner or Bajaj potential give very reasonable values of exciton binding energy using the accepted values of the bare effective masses, reported LO phonons energies and $\varepsilon_s$ and $\varepsilon_{so}$ (see Table 2). At low temperatures, the reported static dielectric constant is $\approx 17$\textsuperscript{[98]} which gives exciton binding energy of 12–14 meV ($\varepsilon_s = 5$). This is in reasonable agreement with the estimation from magneto-optical studies\textsuperscript{[56,97]} which were analyzed using the standard hydrogen model giving $E_b = 16$ meV. If we consider the separation between 1s and 2s states in MAPbI$_3$ which is $\approx 12$ meV\textsuperscript{[97]} then according to Pollmann and Büttner or Bajaj model this is 85% of exciton binding energy giving a slightly smaller exciton binding energy of 14 meV (see Figure 6c). At room temperature the static dielectric constant is enhanced and values around 30 or higher have been reported.\textsuperscript{[64,69,90,91]} In such a situation the exciton binding energy according to Pollmann and Büttner or Bajaj model is around 5 meV again in good agreement with some of the reported values.\textsuperscript{[8,29,99]}

Polaron effects can also explain reported discrepancy between reduced carrier mass reported for MAPbBr$_3$ in low\textsuperscript{[76]} and high magnetic field studies\textsuperscript{[77]} (0.185 and 0.12, respectively) which leads to an overestimation of the exciton binding energy of MAPbBr$_3$ in high field studies.\textsuperscript{[57]} In the high field limit the carrier motion is decoupled from the lattice vibration because the cyclotron frequency is larger than the phonon frequencies\textsuperscript{[51]} and lattice distortion cannot follow the fast cyclotron motion of the carriers. Therefore, in the high magnetic field limit the bare carrier mass is probed. In contrast, in the low field limit the carrier mass is enhanced due to the interaction with the lattice.

It has to be noted the solutions of the various exciton models in polar semiconductors, although a rough approximation, nevertheless captures the main features of the exciton absorption spectra in perovskites. Certainly more theoretical efforts are

### Table 2. Parameters used in calculation presented in Figure 6.

| $m_e$ | $m_h$ | $\varepsilon_{so}$ | $\varepsilon_s$ | $E_{10}$ |
|------|------|-------------------|----------------|---------|
| 0.19\textsuperscript{[39]} | 0.22\textsuperscript{[39]} | 5 | 16.5 meV\textsuperscript{[44]} |
required to understand to what extent these models are valid. For example, in perovskites there are multiple optical phonon branches\[^{[13,64,93]}\] and the contribution of each of them should be included.\[^{[80,100]}\] Moreover, the dielectric function exhibits a strong temperature dependence\[^{[69,70]}\] as well as character of the lattice vibration which change from harmonic at low temperatures to anharmonic at room temperature.\[^{[14,15]}\] Additionally, it is questionable if the conclusions drawn from absorption studies which probe exciton state coupled to optical phonon field\[^{[95,101]}\] apply to long lived carriers in perovskites for which additional screening mechanism can be present. The ultrafast THz spectroscopy studies show the finite rise time of photoconductivity\[^{[102,103]}\] which may indicate that the carriers are subject of additional screening in different time scales. Moreover for both organic-inorganic and fully inorganic perovskites an unusual temperature dependence of the PL Stokes shift has been reported.\[^{[16,66]}\] Intriguingly, the Stokes shift increases with increasing temperature, which is in stark contrast to what is generally observed in conventional semiconductors. It has been proposed that this peculiar behavior can be understood on the basis of polar liquid theory.\[^{[16,104]}\] Also a direct coupling of organic cations to charge carriers has been surmised from the change of the PL lifetime after substitution of hydrogen atoms by deuterium in the methylammonium cation.\[^{[105]}\] All of this indicates that in addition to large polaron formation, the long lived excited carriers are subjected to a polar liquid like screening.\[^{[16,18,106]}\] Therefore, a detailed understanding of the carrier screening is required if we are to fully understand exciton physics in perovskite materials.

4. Exciton Fine Structure Splitting

Let us now turn to more subtle aspect of exciton physics in metal-halide perovskites, namely the fine structure of exciton states. While understanding the exciton fine structure might not be crucial for solar cell applications, it nevertheless has a fundamental impact on the emissive properties of perovskite or indeed any semiconductor. In conventional semiconductors, the fine structure of exciton states, has been intensively investigated\[^{[107–118]}\] mainly due to its importance for quantum technology.\[^{[119–122]}\] In perovskites, the physics of the exciton fine structure is the subject of ongoing controversy.

In metal-halide perovskites, the valence and conduction bands derive from cationic Pb orbitals. In contrast to many other semiconductors the valence band is built from s-like orbitals, whereas conduction band is built from p-like orbitals.\[^{[22,89,126–128]}\] Therefore, the spin–orbit coupling affects mainly the conduction band lifting the degeneracy of electron states with total angular momentum \(J_c = 3/2\) (upper band) and \(J_c = 1/2\) (lower band).\[^{[126,129]}\] The band-edge exciton states can be built from one of the s-like valence maximum states with total angular momentum \(J_v = 1/2\) and \(z\) component \(J_{zv} \pm 1/2\) and one of the bottom band electron states \(J_e = 1/2, J_e^z \pm 1/2\). Therefore, the exciton can be in one of four degenerate states: \[^{[123,129–133]}\] \(0^+_0\), \( \pm 1^1\) with zero total angular momentum, \(J_{exc} = 0\), and three states \(Z^+\) with \(J_{exc} = 1\) and \(z\)-components of angular momentum \(J_{zv} = 0\) and \(\pm 1\), respectively. Regardless of the crystal or confinement symmetry, the exchange interaction splits these four degenerate states in to a dark (optically inactive) singlet with \( |0^+_0\rangle\) with \(J_{exc} = 0\) and a bright (optically active) triplet with \(J_{exc} = 1\). In lower symmetry tetragonal and orthorhombic perovskite phases\[^{[134,135]}\] the exchange interaction together with the crystal field lifts the degeneracy of the bright states.\[^{[123,129–133]}\] In the tetragonal phase, the triplet state split into two degenerate \(\pm 1\) states and a \(Z^+\) state, which couple to circularly (electric vector in x̅y plane) and linearly (electric vector along \(z\) direction) polarized light. In orthorhombic phase the degeneracy of exciton states is completely lifted and \(\pm 1\) states split in to \(|X\rangle=\frac{1}{\sqrt{2}}(|V^+\rangle+|V^-\rangle)\), \(|V\rangle=\frac{1}{\sqrt{2}}(|V^+\rangle-|V^-\rangle)\), which couple to the two orthogonal linearly light polarizations. The expected fine structures of excitons in the different crystallographic phases of perovskites are summarized in Figure 7a.

The interest in fine structure of excitonic states in metal-halide perovskites started from optical spectroscopy studies of single perovskite nanocrystals\[^{[123,130,116–141]}\] where at liquid helium temperatures a bright exciton fine structure splitting \(\pm 1\) meV was observed (see Figure 7b). Depending on the particular crystal orientation and structural phase of the nanocrystal, single, double or triple emission lines were observed.\[^{[123,138]}\] Initially, the origin of bright exciton fine structure splitting was attributed to the exchange interaction linked to either the crystal field related to anisotropic nanocrystals shape or the intrinsic reduction of lattice symmetry of tetragonal or orthorhombic phase.\[^{[121,130,132]}\] Very shortly afterward an alternative interpretation of the bright exciton fine structure splitting appeared involving the Rashba effect.\[^{[124,138,141]}\] Becker et al.\[^{[138]}\] argued that the exchange interaction in perovskite nanocrystals is not large enough to explain the observed bright exciton fine structure splitting and an additional mechanism is required. The inclusion of the Rashba effect lead to another very important conclusion, namely that the order of the bright and dark states is reversed in perovskite nanocrystals\[^{[124,138]}\] (see Figure 7c). The authors argued that the bright character of the lowest exciton state immediately explains the high recombination rates and efficiency of PL emission from perovskite nanocrystals. Such a reversed order of the exciton states would be the only known example in both bulk semiconductors materials and nanostructures.\[^{[142]}\]

The Rashba effect\[^{[143]}\] is often invoked in the context of the properties of perovskite crystals\[^{[144–152]}\] and provides an alternative to polaron effects to explain some of their unique properties. However, the Rashba effect requires a lack of inversion symmetry, the microscopic origin of which remains elusive (at least in the low temperature phase). Cation position instabilities\[^{[14]}\] or surface effects\[^{[151]}\] have been invoked to break inversion symmetry. However, despite the detailed arguments provided by Becker et al.\ the hypothesized bright nature of the ground state in perovskite nanocrystals seems to be in striking contrast to many of the PL dynamics studies\[^{[125,153–156]}\] (see Figure 7d). The PL emission from single nanocrystals usually exhibits biexponential decay characteristic of carrier exchange between bright and dark states.\[^{[157–159]}\] The temperature dependent studies together with magnetic field studies consistently suggests that the bright states mix with the lower lying dark states leading to an increasing weight of the long decay component and decreasing weight of the short component with a
simultaneous shortening of long decay component. This behavior was observed for both mixed organic–inorganic and fully inorganic metal-halide perovskite nanocrystals.\cite{125,153–156} Finally, very recently the spectroscopic signature of dark singlet ground state was directly revealed by PL studies in magnetic field on FAPbBr$_3$ nanocrystals.\cite{155} It is also worth to mention recent calculations\cite{130,132,133} showing that the bright exciton fine structure splitting can be qualitatively and quantitatively explained in $k$-$p$ model without invoking a Rashba effect. All of these reports suggest that the Rashba effect plays little role in perovskite crystals, at least for the lowest temperature phase, and the physics of exciton fine structure is similar to that in other semiconductors.

What is somehow peculiar for perovskite nanocrystals is very high photon-emission rate at low temperatures. As discussed in refs.\cite{155,156} this can be attributed to the soft lattice of perovskite crystals which makes the carrier coupling to acoustic phonons via the deformation potential extremely weak. This leads to a suppressed scattering between bright and dark states at low temperatures. The carrier–phonon scattering is dominated by Frölich coupling with longitudinal optical phonons. However, the LO phonon energy is larger than the bright–dark state splitting which implies that a two phonon process is needed for carrier exchange between bright and dark states. As a result the bright-to-dark relaxation rate vanishes at low temperatures.

The suppressing of the bright–dark scattering explains why perovskite nanocrystals remains bright despite the presence of a low-lying dark exciton state.

It is interesting to note that despite the fact that the majority of exciton fine structure investigations were performed on nanocrystals, the splitting of bright exciton states is an intrinsic properties of perovskites related to their low symmetry crystal structure. In many other semiconductors the bright exciton fine structure splitting is usually strongly enhanced by the anisotropic confinement of nanostructures.\cite{112} In perovskite orthorhombic or tetragonal phase the bright exciton fine structure splitting should be present also in bulk crystal.\cite{123} However, the observed variation in the magnitude of bright exciton fine structure splitting in perovskite nanocrystals indicates that it is affected by extrinsic contributions such as quantum confinement. This problem was addressed in ref.\cite{76}. With a detailed analysis of PL and reflectance spectra of MAPbBr$_3$ single crystal the authors observed a splitting of bright exciton state in zero magnetic field $\approx$200 $\mu$eV. In this investigation of a macroscopic single crystal the influence of surface, size, and anisotropic confinement, on the observed bright exciton fine structure splitting can be explicitly excluded, providing information about the intrinsic properties of bulk MAPbBr$_3$. This finding provides an important starting point for the further discussion of the origin of the simultaneous shortening of long decay component. This behavior was observed for both mixed organic–inorganic and fully inorganic metal-halide perovskite nanocrystals.\cite{125,153–156} Finally, very recently the spectroscopic signature of dark singlet ground state was directly revealed by PL studies in magnetic field on FAPbBr$_3$ nanocrystals.\cite{155} It is also worth to mention recent calculations\cite{130,132,133} showing that the bright exciton fine structure splitting can be qualitatively and quantitatively explained in $k$-$p$ model without invoking a Rashba effect. All of these reports suggest that the Rashba effect plays little role in perovskite crystals, at least for the lowest temperature phase, and the physics of exciton fine structure is similar to that in other semiconductors.

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the large bright exciton fine structure splitting observed in perovskite nanocrystals.

5. Conclusions and Outlook

In this article we have reviewed the recent progress in understanding the physics of excitons in metal-halide perovskites. As we have discussed the experimental determination of the exciton binding energy has been a matter of intense debate, with reported literature values for the archetypical perovskite MAPbI$_3$ ranging from 2 to 62 meV. Based on the recent magneto-optical studies we can safely conclude that at low temperatures the exciton binding energy in MAPbI$_3$ and MAPbBr$_3$ are in the range of $\approx$10–15 meV. There exists important experimental and conceptual arguments that the exciton binding energy is reduced to few meV at room temperature due to enhanced screening. Therefore, the excellent perovskite device performance can be at least partially attributed to efficient thermal dissociation of excitons (free carrier generation) at room temperature where $kT \approx 25$ meV.

A fundamental open question concerns the role of polaron effects in the exciton physics. Given the overwhelming experimental evidence for the importance of the Frolich coupling, it is natural question to what extent the simple hydrogen model is correct. The experimental results should be revised/reconsidered in the light of growing awareness of the importance of polaron effects in metal-halide perovskites. As we have discussed in this review the specific carriers–phonons coupling can affect exciton spectrum and also can explain the surprising efficiency of light emission from perovskite crystals without invoking an exotic reversal of the energetic order of the bright and dark states.

Finally, we would like to mention the rapidly emerging plethora of perovskite derivatives, such as 2D perovskites,$^{[160–164]}$ double perovskites,$^{[165–167]}$ or hollow perovskites.$^{[168,169]}$ Metal-halide perovskite derivatives promise to provide a platform to tailor electronic and optical properties by tuning the electron–phonon coupling from the regime of exciton self-trapping$^{[170–174]}$ through pronounced exciton–phonon replicas$^{[175–179]}$ to the very weak coupling.$^{[180]}$ While the variety of possible ways to tune the optical properties of perovskite derivatives is their principal huge advantage, the complexity of their mutual interaction hinders the creation of a development strategy for devices. If we are to fully exploit the enormous potential of perovskites detailed knowledge and understanding of the phonons, excitons, and their mutual interactions is essential. The excitonic properties of these materials are only starting to be explored with many opportunities to explore new physics in the not too distant future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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