Excitons and their Fine Structure in Lead Halide Perovskite Nanocrystals from Atomistic GW/BSE Calculations

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Abstract

Atomistically detailed computational studies of nanocrystals, such as those derived from the promising lead-halide perovskites, are challenging due to the large number of atoms and lack of symmetries to exploit. Here, focusing on methylammonium lead iodide nanocrystals, we combine a real-space tight binding model with the GW approximation to the self-energy and obtain exciton wavefunctions and absorption spectra via solutions of the associated Bethe-Salpeter equation. We find that the size dependence of carrier confinement, dielectric contrast, electron-hole exchange, and exciton binding energies has a strong impact on the lowest excitation energy, which can be tuned by almost 1 eV over the diameter range of 2–6 nm. Our calculated excitation energies are about 0.2 eV higher than experimentally measured photoluminescence, and they display the same qualitative size dependence. Focusing on the fine structure of the band-edge excitons, we find that the lowest-lying exciton is spectroscopically dark and about 20–30 meV lower in energy than the higher-lying triplet of bright states, whose degeneracy is slightly broken by crystal field effects.

Introduction

Lead-halide perovskite nanocrystals (LHP NCs), with formula APbX₃ where A is a monovalent cation and X is a halide anion, exhibit remarkable electronic and optical properties,¹–³ suggesting promising applications in optoelectronics,⁴–⁶ photonics,⁷,⁸ spintronics,⁹ and photovoltaics.¹⁰ Compared to bulk LHPs, LHP NCs display anomalously short radiative lifetimes and concomitant high photoluminescence quantum yields, the origin of which is still under debate.¹¹–¹³ These interesting optical properties and their temperature dependence have focused attention on the exciton fine structure, i.e., the energy ordering and character of the band-edge excitons.¹⁴–¹⁹ For example, the lowest-energy exciton of Cs-LHP NCs has been suggested to be a bright (emissive) state with total angular momentum \( J = 1 \), which could explain the high photoluminescence quantum yield.¹⁴–¹⁶ This property would be in stark contrast with the case of conventional organic and inorganic semiconductors, where the lowest-energy exciton is a dark (non-emissive) state. Other works have suggested that this conventional behavior persists in the LHP NCs (i.e., the lowest-energy exciton is a dark state with total angular momentum \( J = 0 \)) but that exciton relaxation by phonons is suppressed at low temperatures, yielding long lifetimes for the bright exciton in both NCs¹⁷–¹⁹ and 2D LHPs.⁷ The properties of the band-edge excitons—whose energy separations are very small, of the order of 1–10 meV—are influenced by quantum confinement, electron-hole attraction and exchange,¹⁴–¹⁶,¹⁹ dielectric environment,¹¹ and lattice structure (including the bulk and surface Rashba effects),²²–²⁵ making precise theoretical predictions an incredible challenge. This complexity has led to the development of exciton models based on effective-mass or \( k \cdot p \) Hamiltonians, pioneered especially by Efros and co-workers,¹⁴–¹⁶ among others.²⁶–²⁸ Atomistic simulation, although desirable, is frustrated by the sizes of even the smallest experimentally accessible NCs, which can have hundreds or thousands of atoms. Although atomistic force-fields or density functional theory can be applied to study the ground-state and structural properties of systems of this size,²⁷–³⁰ accurate excited-state theories are more expensive and generally inaccessible in a fully \( ab \ initio \) setting.

Here, we overcome this challenge and construct an atomistic orbital-dependent tight-binding model parametrized by first-principles density functional theory (DFT) calculations, after which we use a model dielectric function to apply self-energy corrections via the GW approximation³¹–³³ and calculate the energies and properties of excitons via the Bethe-Salpeter equation.³⁴–³⁶ The computational approach is similar to previous work by two of us on the properties of layered quasi-two-dimensional LHPs.³⁷ As a specific example, we study methylammonium lead iodide (MAPbI₃) NCs, calculating the exciton binding energies, absorption spectra, and band-edge fine structure. Within the approximations of our approach, we find that the lowest-energy exciton is always a dark state.

We study MAPbI₃ for several reasons, although our approach is general and could be applied to any LHP NC. First, this LHP is one of the most studied in its bulk form, especially for photovoltaics, partly due to its strong absorption at low energies that facilitates sensitization.³⁸,³⁹ Moreover, bulk MAPbI₃ crystals have low lasing thresholds⁴⁰ and are generally more stable than Cs-based ones.⁴¹ For these reasons, the atomic and electronic structure of bulk MAPbI₃ has been extensively studied using DFT,⁴²,⁴³ and the GW approximation,⁴⁴–⁴⁷ providing important points of comparison. These valuable properties have motivated experimental studies of MAPbX₃ NCs with high photoluminescence quantum yields and controllable size, leading to tunable band gaps.⁴⁸–⁵¹ Such MAPbX₃ NCs have been realized by colloidal synthesis⁴⁸–⁵¹ and templated growth inside porous oxide films,⁵²–⁵⁵ providing experimental results to which we can directly compare.
Computational Methods

The parameters of our orbital-dependent tight-binding model are determined from a DFT calculation of bulk MAPbI\textsubscript{3}, which first requires the determination of the crystal structure. (To our knowledge, the crystal structure of LHP NCs is still poorly understood, but the crystal structure of MAPbI\textsubscript{3} NCs is likely tetragonal.\textsuperscript{1} However, this assumption may be incorrect due to surface effects and/or metastability.) From experiments, it is known that the bulk MAPbI\textsubscript{3} exists in an orthorhombic phase below about 160 K, a tetragonal phase between 160 K and 330 K, and a cubic phase above 330 K.\textsuperscript{56} The computational prediction of crystal structures in finite temperature phases is nontrivial because of anharmonic effects. In Ref. 43, it was shown that using zero-temperature DFT for the geometry optimization of the tetragonal and cubic phases yields a large inversion symmetry breaking via distortion of the PbI framework, leading to a large bulk Rashba effect. However, these crystal structures disagree with second harmonic generation rotational anisotropy experiments. Therefore, with interest in room-temperature behavior, we reuse the structure proposed in Ref. 43, which was generated by fixing the PbI framework of the tetragonal phase and relaxing only the MA cations, whose orientations yield a small but nonzero Rashba effect. This crystal structure is shown in Fig. 1(a).

With our MA-relaxed crystal structure of bulk MAPbI\textsubscript{3}, we perform a DFT calculation including spin-orbit coupling, using Quantum Espresso\textsuperscript{57} with the PBE exchange-correlation functional,\textsuperscript{58} relativistic PAW pseudopotentials, a kinetic energy cutoff of 60 Ry, and a 6 × 6 × 6 k-point mesh. Using wannier90,\textsuperscript{59} the DFT solution is used to construct maximally localized Wannier functions (MLWFs) \( \phi_{\mu}(r) \), corresponding to 1s and 5p orbitals and Pb 6s and 6p orbitals, as well as their tight-binding Hamiltonian matrix elements \( h_{\mu \rho} \) and dipole matrix elements \( r_{\mu \rho} \), \( e \in \{x, y, z\} \). Greek indices \( \mu, \nu, \kappa, \lambda \) will be used throughout to indicate MLWF atomic orbitals, including spin. These real-space tight-binding parameters are then used to build a mean-field Hamiltonian \( \mathbf{h}^{\text{NC}} \) of the aperiodic NCs. Our NC surfaces are terminated with halide atoms, in agreement with experimental observations,\textsuperscript{49} with exposed facets that are qualitatively equivalent to the (100) surface of a cubic perovskite. We use the same tight-binding parameters for all atoms, even those near the surface of the NCs, which can be understood as an approximate passivation that does not require microscopic specification. However, the details of surface passivation are important for controlling trap states and associated non-radiative recombination.\textsuperscript{29,51,53} Similarly, relaxation of the atoms at the surface, which we neglect here, would modify these matrix elements and the resulting electronic structure.\textsuperscript{25,28}

With this tight-binding Hamiltonian matrix in the basis of MLWFs \( \phi_{\mu}(r) \), we calculate the molecular orbitals \( C_{\mu \rho} \) and orbital energies \( \varepsilon_\mu \), \( \mathbf{h}^{\text{NC}} \mathbf{C} = \mathbf{C} \varepsilon \). To the orbital energies, we add two self-energy corrections in the spirit of the many-body GW approximation (at the level of approximation made throughout this work, we do not distinguish degrees of self-consistency in the self-energy, but our calculations are all performed in the one-shot \( G_0 \mathbf{W}_0 \) approximation as described here). The first correction is a rigid shift of the conduction and valence band energies by \( \pm \Delta \) to correct the bulk band gap to the previously calculated value of 1.67 eV.\textsuperscript{44} Our DFT and GW band structures of bulk tetragonal MAPbI\textsubscript{3} are shown in Fig. 1, which can be seen to contain a small but nonzero Rashba splitting at the band edges. As is well-known,\textsuperscript{44,47} the GW correction to the band gap of LHPs is sizable—about 1.5 eV in our case. Our second self-energy correction within the GW approximation uses a model dielectric function and a static screening approximation to account for dielectric constrain at the NC interface.\textsuperscript{60,61} In the style of a GoW calculation.\textsuperscript{62} Combining these two corrections, we calculate the GW quasiparticle energies of all conduction (c) and valence (v) bands,

\[
E_c = \varepsilon_c + \Delta_c/2 + \sum_{\mu} |C_{\mu \rho}|^2 \delta \Sigma(r_{\rho})
\]

\[
E_v = \varepsilon_v - \Delta_v/2 - \sum_{\mu} |C_{\mu \rho}|^2 \delta \Sigma(r_{\rho})
\]

where \( r_{\rho} \) is the position of the atom to which the MLWF \( \phi_{\rho}(r) \) belongs.

\[
\delta \Sigma(r_{\rho}) = \frac{1}{2} \lim_{r_{12} \to r_{\rho}} \left[ W(r_{12}) - \frac{1}{\varepsilon_0 |r_1 - r_2|} \right] \tag{2}
\]

and \( W(r_{12}) \) is the classical Coulomb interaction energy between two charges in the NC at \( r_1, r_2 \).\textsuperscript{66} We use the analytical Coulomb energy of charges in a dielectric cuboid with side lengths \( L_x, L_y, L_z \).\textsuperscript{63}

\[
W(r_{12}) = \sum_{i, j, k = -\infty}^{\infty} \frac{[(\varepsilon_0 - \varepsilon_{env})/(\varepsilon_0 + \varepsilon_{env})]^{6[|r_1 - r_2|]}}{\varepsilon_0 |r_1 - r_2|} \tag{3a}
\]

\[
r_{12}^{\Delta} \equiv [(−1)^x x_2 + iL_x, (−1)^y y_2 + jL_y, (−1)^z z_2 + kL_z]. \tag{3b}
\]

With the surface termination described above, For a NC made of \( n^3 \) octahedra, we use \( L_x = L_y = n \times (6.4 \text{ Å}) + 2 \times (1.5 \text{ Å}) \) and \( L_z = n \times (6.4 \text{ Å}) + 2 \times (1.5 \text{ Å}) \), where 6.4 Å and 6.5 Å correspond to the diagonals of the tetragonal octahedra and we have added an additional dielectric buffer region of 1.5 Å on all sides. Throughout this work, we use the bulk MAPbI\textsubscript{3} perovskite high-frequency dielectric constant \( \varepsilon_0 = 6.1 \) and an environmental dielectric constant of \( \varepsilon_{env} = 2.1 \), representative of a generic low-dielectric environment, such as organic ligands.\textsuperscript{2,3,64} For large NCs with small exciton binding energies that are on the order of optical phonon fre-
To evaluate the optical and excitonic properties, we calculate the exciton wavefunction as a solution to the Bethe-Salpeter equation (BSE) in the Tamm-Dancoff approximation,

$$|\Psi_N^N\rangle = \sum_{cv} A_{cv}^N \hat{a}_v^\dagger \hat{a}_c |0\rangle$$ (4a)

$$E_N A_{cv}^N = (E_c - E_v) A_{cv}^N + \sum_{cv'} \left[ (cv|V|v'c') - (cc'|W|v') \right] A_{cv'}^N,$$ (4b)

where $V$ and $W$ indicate the bare and screened Coulomb interactions and we use $|11|22\rangle$ notation for two-electron integrals. For all results in the next section, we included 200 valence bands and 200 conduction bands in the BSE calculation. In approximate theories of Wannier-type excitons, the exchange interaction is commonly neglected on the basis of its short range, but as it is critical in the determination of the exciton line structure,\(^{35}\) we include it here. The bare exchange integral is approximated as

$$(cv|V|v'c') = \sum_{\mu\kappa} C_{\mu c}^* C_{\mu c'} C_{\kappa v} C_{\kappa v'} V_{\mu\kappa} + \sum_{\mu\kappa\nu\kappa'} \left( C_{\mu c}^* C_{\nu c} C_{\kappa c'} C_{\kappa v'} W_{\mu\kappa\nu\kappa'} \right)$$ (5)

where $V_{\mu\kappa} = W(r_{\mu} - r_{\kappa})$ if $\mu$ and $\kappa$ are not on the same atom and $V_{\mu\kappa} = \langle \mu\kappa|\kappa\mu \rangle$ otherwise (i.e., the Coulomb interaction is un-screened at the intra-atomic length scale). The intra-atomic repulsion integrals $\langle \mu\kappa|\kappa\mu \rangle$ and $\langle \mu\kappa|\mu\kappa \rangle$ for Pb and I $s$ and $p$ orbitals are calculated using P$\alpha$SCF\(^{66,67}\) with the def2-TZVP basis set.\(^{68}\)

From the BSE exciton eigenvalues $A_{cv}^N$, we calculate the polarized absorption spectrum and its average

$$I_\nu(\omega) \propto \sum_{N} \left| \sum_{cv} r_{cv}^N A_{cv}^N \right|^2 \delta(\hbar\omega - E_N)$$ (7a)

$$I(\omega) = \sum_{\nu(x,y,z)} I_\nu(\omega).$$ (7b)

Because of our nonperturbative inclusion of spin-orbit coupling, the molecular orbitals have mixed spin character, i.e., $m_j$ is not a good quantum number. Therefore, the total spin $S$ is not a good quantum number for the exciton wavefunctions and they cannot be separated into spin singlets ($S = 0$) and triplets ($S = 1$) with familiar dipole selection rules. Rather, the spectral intensity of the excited states is determined by the lattice symmetry in combination with the spin and orbital character of the molecular orbitals participating in the dominant transitions. This feature is one of the primary origins of the complex fine structure of low-lying excitons in lead-halide perovskites.

**Results and Discussion**

We have performed calculations on halide-terminated, cube-shaped NCs containing $n^3$ octahedra, with $n = 3–10$, corresponding to a NC edge length $L \approx 1.9–6.2$ nm; our largest NCs include almost 4300 Pb and I atoms. Assuming a bulk exciton reduced mass of about $\mu = 0.14^{70–73}$ and dielectric constant $\epsilon_r = 6.1$, a hydrogenic calculation predicts a bulk exciton binding energy $\approx 13.6$ eV and a Bohr radius of $a_0 = \epsilon_r \mu \times (0.053 \text{ nm}) = 3.2$ nm, suggesting that the NCs that we study are in the strong to moderate confinement limits. (This estimated exciton binding energy is 2–3 times larger than the most recent experimental measurements;\(^{69,74}\) see discussion in Conclusions.)

Calculated absorption spectra are shown in Fig. 2, averaged over $x$, $y$, and $z$ polarizations. With increasing size, the spectra become more structured and the absorption onset energy is reduced due to the quantum confinement effect. The first excitation energy is indicated by a filled circle and corresponds to a state that is spectroscopically dark (see further discussion below), in agreement with previous studies on CsPbBr$_3$ NCs.\(^{17–19,52}\) The GW band gap is indicated by vertical dashed lines. For small NCs, the exciton binding energy is large, about 1 eV for $L = 2.5$ nm ($n = 4$). For the largest NCs we study, the exciton binding energy drops to about 0.3 eV for $L = 6.2$ nm ($n = 10$).

We now investigate the character of the lowest-lying excitons and the associated fine structure. We first review the basic picture of exciton fine structure in LHPs.\(^{14–16,72}\) The valence band is primarily composed of Pb 6$s$ and 15$p$ atomic orbitals (with overall s-like symmetry) and is doubly degenerate with $m_j = \pm 1/2$. The conduction band is strongly split by spin-orbit coupling, and the low-energy band is primarily composed of Pb 6$p_{3/2}$ atomic orbitals and is doubly degenerate with $m_j = \pm 1/2$. This minimal picture suggests three triplet excitons with $J = 1$ and one singlet exciton with $J = 0$, all approximately corresponding to an intra-atomic Pb 6$s$→6$p$ transition. Basic spectroscopic selection rules suggest that the singlet is dark and the triplet is bright. Excitons arising from the higher-energy conduction band with Pb 6$p_{1/2}$ character are at least 1 eV higher in energy, due to the large spin-orbit coupling.

For a cubic crystal structure, the bright triplet manifold is degenerate and is higher in energy than the dark singlet exciton $|D\rangle$ due to the electron-hole exchange interaction. For a tetragonal crystal structure, which we use here, the bright triplet degeneracy is broken into a doublet of excitons $|X\rangle$, $|Y\rangle$ with polarized absorption along $x$ and $y$ and a singlet exciton $|Z\rangle$ with polarized absorption along $z$, and their energetic order depends on the crystal field splitting. Note
that the polarization axes are aligned parallel to the NC faces, and not along the axes of the tetragonal unit cell shown in Fig. 1(a).

Our BSE calculations enable direct access to atomistic details of the band-edge exciton wavefunctions beyond this simplified picture. As an example, in Fig. 3, we consider a NC with $n = 7$ ($L = 4.4$ nm). In Fig. 3(a), we plot the wavefunctions of the lowest four excitons,

$$\Psi^\text{v}(r; \vec{r}_h) = \sum_{cv} A^v_{c}\phi_c(r)\phi^\text{v}_v(\vec{r}_h)$$

where $\phi_c(r)$ are molecular orbitals, $A^v_{c}$ is the BSE eigenvector, and we fix the position of the hole $\vec{r}_h$ to the center of the NC. In Fig. 3(b), we show the absorption spectrum with the energy of each transition labeled. Clearly, the lowest energy state is the dark state $|D\rangle$ and the higher energy states are the three bright states $|X\rangle, |Y\rangle, |Z\rangle$, which are labeled according to their polarized absorption spectra. We find the $X/Y$ energy degeneracy to be slightly broken along with a weak violation of the polarization selected rules, which we attribute to the randomly oriented MA cations that lower the crystal symmetry. For this relatively small NC, we see a bright-dark splitting of about 30 meV and an intertriplet splitting of about 3–10 meV.

Extending this analysis to NCs of other sizes, we find that the energy ordering is unchanged and that the lowest energy exciton is a dark state, at least up to $L = 6.2$ nm, as shown in Fig. 4(a). In Fig. 4(b), we plot the bright-dark splitting of the three bright states as a function of the size of the NC. We fit the splitting data to the form $E_c(L) = E_c^\infty + c_1/L + c_2/L^2 + c_3/L^3$, consistent with the binding energy expression in the strong confinement regime. Fitting to our data, we find a nonzero bright-dark splitting of $E_c^\infty = 4$ meV (for $X/Y$) and 22 meV (for $Z$) in the $L \to \infty$ limit. The large and positive splitting between $Z$ and $D$ reflects a relatively weak Rashba effect that is insufficient to invert the ordering. We conclude that, within the approximations made here, our simulations predict that the lowest exciton is dark for any sized NC.

Within the GW/BSE approximation, the exciton energies are determined by three factors: the DFT/GW band energies (which reflect the local lattice structure, the carrier confinement, and the dielectric contrast), the electron-hole Coulomb energy (roughly the exciton binding energy), and the electron-hole exchange energy. The latter two quantities are plotted as function of $L$ in Figs. 4(c),(d). As expected, we see that the dark exciton has a vanishing exchange energy and the bright excitons have exchange energies between 40 meV (for small NCs) and 10 meV (for larger NCs). The exciton binding energies due to the screened Coulomb interaction are large and vary from 1.5 eV to 0.3 eV over the same size range. Interestingly, the dark exciton has a slightly larger Coulomb interaction than the bright excitons, a feature which further increases the bright-dark splitting. In fact, for the NC sizes considered here, we find that the differences in the Coulomb term contribute to the bright-dark splitting to the same order of magnitude as the exchange energy.

Finally, we note that the affordable approach taken here allows us to study NCs that are large enough to be compared directly to experimental results on MAPbI$_3$ NCs with $L > 3$ nm, which are indicated in Fig. 4(a). Experimental values come from photoluminescence data of NCs synthesized in the pores of a patterned SiO$_2$ film. We see that our results overestimate the experimental transition energies by about 0.2 eV. This level of accuracy is typical even for fully ab initio GW/BSE calculations and is thus acceptable here, given the additional approximations that were made. Some fraction of this discrepancy may also be attributable to a Stokes shift between absorption and photoluminescence or other exciton-phonon interactions.
Conclusions

To summarize, we have performed atomistic GW/BSE calculations of the electronic and optical properties of realistically sized MAPbI₃ nanocrystals, using parameters determined from ab initio calculations. Within the approximations of our approach, we find large exciton binding energies of over 0.3 eV and that the exciton fine structure is consistent with a spectroscopically dark lowest-lying exciton. The reasonable agreement between our predicted excitation energies and experimentally measured photoluminescence energies supports our methods and findings.

Two approximations in our work are significant and should be revisited for future improvements. The first is the treatment of the atomic structure: geometry relaxation may yield a crystal structure that is different from the bulk tetragonal structure used here. Moreover, the atomic details of the NC surface, including its passivation and reconstruction, might qualitatively change our results, especially for small NCs. The second related approximation is the neglect of electron-phonon coupling. Bulk LHPs are relatively soft and anharmonic materials and strong electron-phonon interactions have been implicated in their electronic properties. Recent calculations have suggested the importance of lattice screening in determining the exciton properties of LHPs. For example, the authors of Ref. find that the typical BSE exciton binding energy of CsPbX₃ is overestimated with respect to experiment by about a factor of three, and that incorporation of phonon screening partially improves the agreement. Given the already high cost of ab initio GW/BSE calculations, we believe that the approximate approach presented here can serve as a basis for future studies of atomic structure, surface reconstruction, electron-phonon coupling, temperature-dependent optical properties, and external dopants.

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