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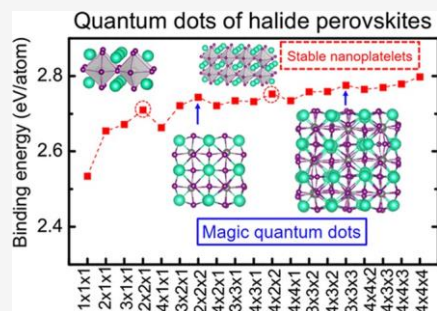
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Atomic Structure, Stoichiometry, and Electronic Properties of CsPbI₃ Quantum Dots Using *Ab Initio* Calculations

Anu Bala* and Vijay Kumar*

ABSTRACT: *Ab initio* calculations on atomic structures of charge-balanced CsPbI₃ quantum dots (QDs) up to a size of ~2.5 nm show that cubic structures such as 2 × 2 × 2 and 3 × 3 × 3 are magic and should be more abundant than others in this size range. Also, 2 × 2 × 1 and 4 × 2 × 2 nanoplatelets have locally high stability. These results are in good agreement with experiments where the formation of cubic QDs or magic clusters as well as platelets has been reported. We find that it costs the least to detach Cs atoms from the surfaces of QDs. We used this as a strategy to find the stoichiometries of charge-balanced QDs and their lowest-energy structures. The electronic properties have been calculated with both the PBE form of generalized gradient approximation and the HSE06 hybrid exchange-correlation functional in density functional theory and by including effects of spin-orbit coupling. The calculated density of states shows quantum confinement with a local maximum in the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap for magic QDs and p orbitals of I (Pb) contributing near the HOMO (LUMO) as in the bulk. We hope that similar results will hold for other perovskite QDs in this family and further help in understanding the structures and properties of ligand-capped magic clusters/QDs, their assemblies, and QDs of other perovskites to explore new magic clusters of potential future materials for developing advanced perovskite semiconductor technologies.



INTRODUCTION

Semiconductor nanocrystals or nanoparticles having sizes typically of the order of a few nm, also known as quantum dots (QDs), have attracted great interest in the past three decades due to quantum confinement (QC), which gives rise to size-, shape-, and composition-dependent electronic and optical properties.^{1,2} There have been great efforts to produce QDs and understand their properties and commercial applications. Their growing importance led to a Nobel Prize in 2023. QDs of traditional semiconductors such as group IV elements and III–V, II–VI, IV–VI, and I–III–VI₂ compounds have been synthesized routinely.^{3–5} This has led to the finding⁶ of magic clusters or small QDs of such semiconductors with well-defined stoichiometries and bright emissions. In recent years, the discovery of a new class of halide perovskite direct band gap semiconductors with excellent optical properties has opened new possibilities for making QDs of these novel perovskites and their many applications. Accordingly, their study has attracted great interest and spurred intense research that has shown halide perovskite QDs to have outstanding optoelectronic properties different from the bulk due to QC, such as near-unity photoluminescence (PL) quantum yield,^{5,7,8} tunable PL maxima (400–800 nm) via both the halide composition engineering and QC effect, narrow emission line widths,⁹ and multiple exciton generation.^{10,11} These compelling features of halide perovskite QDs have led to applications ranging from solar energy harvesting¹² to next-generation lighting and display,¹³ X-ray detection,¹⁴ and medical imaging technologies.¹⁵ Moreover, an

enhancement in the stability of the cubic CsPbI₃ QDs at room temperature has also been observed compared to their bulk black phase, which is unstable at operating temperature and under moisture.¹⁶ The increased phase stability of cubic QDs can be a ray of hope in overcoming the grand challenge related to the stability of halide perovskites. The demonstration of these novel properties in halide QDs has opened new opportunities in designing low-cost photovoltaic and optoelectronic devices due to the ease of formation of these materials.

Perovskite QDs can be categorized as (1) all inorganic and (2) hybrid organometallic. Examples of all inorganic QDs are those made of halide perovskites such as CsPbX₃ (X = I, Br, Cl) that are known to have overall higher stability than the hybrid organometallic halide perovskite QDs of the type APbX₃ (here A belongs to an organic entity such as MA: CH₃NH₂ or FA: CH(NH₂)₂; X = I, Br, Cl).¹⁷ The size of the QDs can be controlled by controlling parameters like solution temperature, precursor ratio, and/or ligand concentration. Increasing the ligand concentration generally leads to smaller QDs and the formation of magic clusters.¹⁸ Monodispersed CsPbX₃ QDs

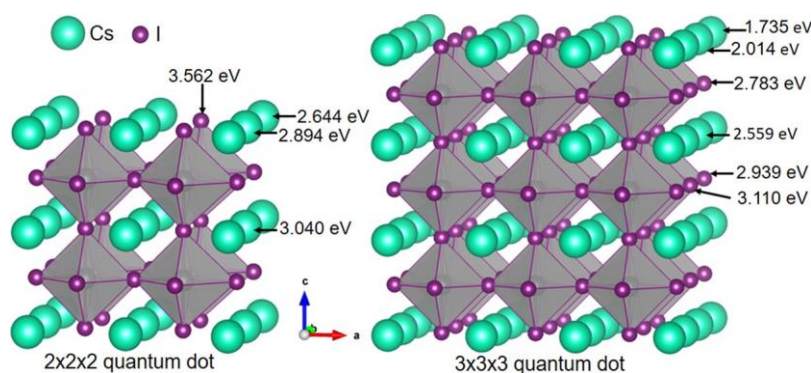


Figure 1. Schematic diagram shows the energy cost of removing various surface Cs (green balls) and I (violet balls) atoms (indicated by arrows) from relaxed $2 \times 2 \times 2$ and $3 \times 3 \times 3$ cubic fragments (QDs) extracted from bulk cubic CsPbI_3 . The Pb atoms are represented with slightly visible balls inside the octahedra. The structures were again relaxed after the atom was removed.

have been synthesized via the hot injection method by Protesescu's group.⁵ Further advancements have been made in synthesizing CsPbBr_3 QDs of less than 5 nm size with a homogeneous size distribution.^{19,20} For photovoltaics, colloidal CsPbI_3 QD solar cells were demonstrated with a power conversion efficiency (PCE) exceeding 10% and also used in many applications described above.^{12–16,21–23} Therefore, perovskite nanocrystals/QDs can provide a new platform for developing photovoltaics and optoelectronics with a tailored highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap and advanced device architecture, such as tandem, flexible, and more stable solar cells and other optoelectronic devices. However, despite significant successes in fabricating highly emissive CsPbX_3 ($X = \text{I}, \text{Br}, \text{Cl}$) QDs and magic clusters following different reaction protocols,^{5,24–28} a fundamental understanding of their atomic

structure and accurate stoichiometry still remains elusive.^{29–33} This is paramount for a proper understanding and tuning of their

electronic and optical properties.^{34,35} Further, it is highly

important to explore their preferred sizes and shapes because clusters or nanoparticles of some elements³⁶ and compound semiconductors³⁷ show magic behavior with much higher abundances than clusters of their neighboring sizes. This unique property is related to the high stability of clusters with a certain number of atoms and compositions. For clusters of free electron-like metals, this is related to the filling of electronic shells, and in many cases, they also have atomic closed shells. Magic clusters of semiconductors generally have symmetric closed atomic shells of specific sizes such as the Cd_5Se_5 and Cd_6Se_6 clusters embedded in a $\text{Cd}_{28}\text{Se}_{28}$ cage for $\text{Cd}_{33}\text{Se}_{33}$ and $\text{Cd}_{34}\text{Se}_{34}$ ultrastable magic nanoparticles,⁶ respectively, and stoichiometry with a high HOMO–LUMO gap and sharp PL lines. On the other hand, QDs with a distribution of sizes generally have broader emissions. Therefore, the goal of the present work is to understand the nanoclusters of halide perovskites at the atomic scale along with exploring their magic structures/sizes. This work also highlights the energetics and shines light on a suitable exchange–correlation functional for calculating the electronic properties of halide perovskite QDs. An understanding of these systems at the atomic level can help with further advancements in this fast-developing field.

■ COMPUTATIONAL DETAILS

The calculations have been performed using a plane wave

(VASP).³⁹ The exchange–correlation functional is treated within generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE).⁴⁰ We used 15 Å vacuum in all three directions so that the interactions between the nearest neighbor QDs due to periodic boundary conditions are negligible. The structural optimization and total energy calculations of QDs have been performed using the Γ -point only due to the large size of the supercell. The ionic positions were relaxed until the absolute value of each component of the force on each ion became less than 0.01 eV/Å. The spin–orbit coupling (SOC) which is important for heavy elements like Pb and I is also included to obtain the correct ground-state energy of the QDs and to understand its effect on the electronic properties. We also performed calculations using the HSE06 hybrid functional to check the effect on the HOMO–LUMO gap.

High-resolution synchrotron X-ray measurements show the

average crystal structure of CsPbX_3 ($X = \text{I}, \text{Br}, \text{and Cl}$)

nanocrystals to be cubic at room temperature. Further high-

method with projector augmented wave³⁸ pseudopotentials as implemented in the Vienna *Ab initio* Simulation Package

resolution transmission electron microscopy also confirmed the cubic phase of nanocrystals of CsPbBr₃.⁴² A similar crystal structure has also been observed for QDs of MAPbBr₃ using X-ray diffraction.⁴³ Therefore, in the present work, we have considered the cubic structure of CsPbI₃ QDs as a representative of inorganic halide perovskite QDs. We started with the smallest $1 \times 1 \times 1$ structure and moved up to a $4 \times 4 \times 4$ cubic QD, considering intermediate platelet- and nanowire-shaped structures of the $n \times m \times l$ type with n , m , and l as integers. In the case of QDs, the surface-to-volume ratio is very high. Therefore, the type of surface on QDs such as either PbI₂ or CsI can play a crucial role in determining their properties. It has been found that surface termination with CsI is energetically more favorable for iodide perovskites than with PbI₂.^{44,45} Accordingly, in this study, we have preferred QD surfaces with CsI termination.

We believe that our present results regarding the atomic and electronic structures of the inorganic QDs would also be broadly applicable to QDs with ligands. This trust is based on our earlier work^{46,47} on layered halide perovskites where we have studied in detail the role of spacer cations (ligands) on the atomic structure as well as on the electronic and optical properties. As a test case, we further performed calculations (details in the [Supporting Information](#)) considering a $1 \times 1 \times 1$ QD of MA₄PbI₆ (MA: CH₃NH₃). Our results confirm weak effects of ligands on the electronic properties while providing better stability to the structure. Thus, our results for inorganic QDs can be extended to understand the atomic and electronic properties of hybrid halide perovskite QDs also.

RESULTS AND DISCUSSION

Atomic Structure and Stoichiometry of Neutral Quantum Dots of CsPbI₃. The bonding in halide perovskites is predominantly ionic. Therefore, it is important to construct charge-balanced structures. The Pb atom in these perovskites behaves as a divalent atom. Therefore, the options for constructing charge-neutral QDs are either to adjust (1) the number of Cs atoms or (2) the number of I atoms on the surface of the cubic QDs. We compared the cost of removing different Cs and I atoms from different regions of the cubic QD surface by considering $2 \times 2 \times 2$ and $3 \times 3 \times 3$ fragments extracted from a cubic bulk CsPbI₃. The fragments were relaxed after removal of a Cs or I atom from different surface sites. Figure 1 shows that it requires the least energy of ~ 2.644 and 1.735 eV to remove a corner Cs atom from $2 \times 2 \times 2$ and $3 \times 3 \times 3$ bulk fragments, respectively. The energy cost increases to 2.894 and 2.014 eV for removing a Cs atom nearest neighbor to a corner Cs atom in $2 \times 2 \times 2$ and $3 \times 3 \times 3$ QDs, respectively. Further, the cost of removing Cs atoms from the central part of the surface becomes 3.040 and 2.559 eV for $2 \times 2 \times 2$ and $3 \times 3 \times 3$ structures, respectively. However, all these energy costs are lower than the cost for removing a corner I atom from a $2 \times 2 \times 2$ and $3 \times 3 \times 3$ QD as can be seen from Figure 1. For this reason, in the present work, we considered removing various surface Cs atoms only for the purpose of balancing the charge. It should be noted that we find the overall trend of the energy cost to remove Cs to be

similar for all of the sizes of QDs, but the value decreases with the increase in the size of the QD (Figure 1).

Considering the cost of removing various Cs and I surface atoms as discussed above, we did not change the octahedra of I₆ around each Pb in PbI₆ in all of the structures for the different QDs. This way, we studied many configurations by fully relaxing the ionic positions and shapes for each neutral QD from $1 \times 1 \times 1$ to $2 \times 2 \times 2$ to $3 \times 3 \times 3$ to $4 \times 4 \times 4$ including $2 \times 1 \times 1$, $3 \times 1 \times 1$, and $4 \times 1 \times 1$ nanowire-like structures as well as $2 \times 2 \times 1$, $3 \times 3 \times 1$, $4 \times 4 \times 1$, ... platelet-like structures. Some of the studied configurations for $2 \times 2 \times 1$ and $2 \times 2 \times 2$ QDs are shown in the Supporting Information. The energetically most favorable configurations for all the considered QDs and their stoichiometries are depicted in Figures 2 and 3 in the order of an increasing number of atoms.

The smallest charge-balanced QD obtained from the $1 \times 1 \times 1$ fragment has the stoichiometry, Cs₄PbI₆, and it consists of a PbI₆ octahedron surrounded by four Cs atoms. In this structure, Pb-I bond lengths (~ 3.317 Å) and I-I distances (~ 4.705 Å) are longer than the values (3.189 and 4.510 Å, respectively), for bulk CsPbI₃ (Table 1). On the other hand, Pb-Cs (4.347 Å) and Cs-I (3.639 Å) distances are shorter than in the bulk. This shows strong effects of the surface and stoichiometry acting on QDs. The Cs₄PbI₆ QD has a tetrahedral shape as shown in Figure 2. Experimentally, small nanoclusters of Cs₄PbI₆ have been observed to be nearly spherical in shape.^{48–50} In the case of an energetically favorable configuration of the $2 \times 2 \times 2$ QD, seven Cs corner atoms were removed to maintain the charge balance, while for a $3 \times 3 \times 3$ QD, six Cs atoms were taken out, resulting in Cs₂₀Pb₈I₃₆ and Cs₅₄Pb₂₇I₁₀₈ stoichiometries, respectively.

The nearest neighbor distances between different atoms for the lowest-energy isomers of charge-balanced QDs obtained from $1 \times 1 \times 1$, $2 \times 2 \times 2$, $3 \times 3 \times 3$, and $4 \times 4 \times 4$ fragments are given in Table 1. It is noticed that the surface Pb-I bond lengths for $2 \times 2 \times 2$ and $3 \times 3 \times 3$ QDs are shorter by ~ 0.04 – 0.08 Å or

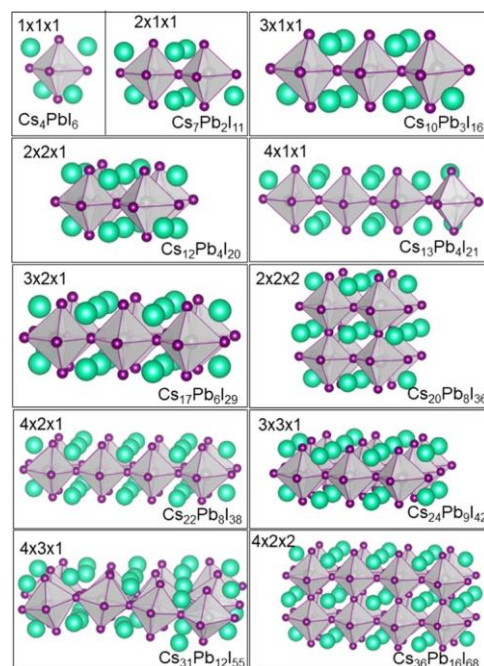


Figure 2. Optimized atomic structures and stoichiometries of the energetically most favorable configurations for neutral QDs of different sizes up to 120 atoms. Refer to Figure 1 for the color code of atoms. Partially visible Pb atoms are at the centers of the octahedra.

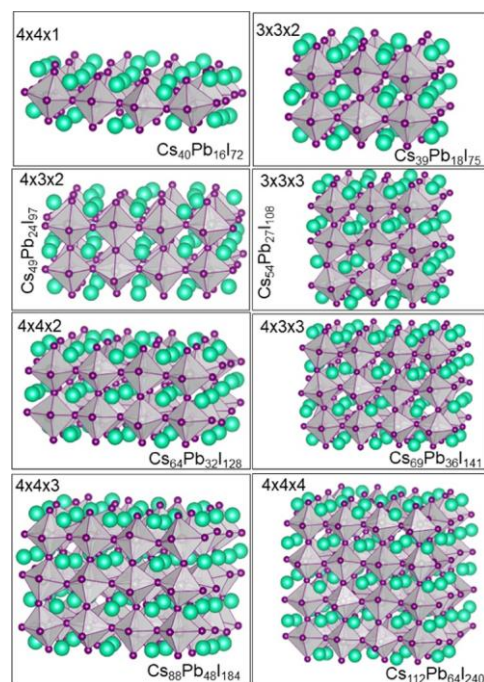


Figure 3. Optimized atomic structures and stoichiometries of the energetically most favorable configurations for neutral QDs of different sizes in continuation to Figure 2. Refer to Figure 1 for the color code of atoms. Partially visible Pb atoms are at the center of the octahedra.

nearly equal to the bulk value (Table 1). The contraction increases significantly for Pb-Cs and Cs-I bonds by ~ 1 and 0.8 Å, respectively, compared with the corresponding bulk values. Most of the contracted bonds which include Pb-I, Pb-Cs, and Cs-I lie on the surface as shown in Figure S3 in the Supporting Information. We also found that the shorter I-I bonds

Table 1. Nearest Neighbor Distances (Å) between Atoms in the Lowest-Energy Isomers of Cs_4PbI_6 , $\text{Cs}_{20}\text{Pb}_8\text{I}_{36}$, $\text{Cs}_{54}\text{Pb}_{27}\text{I}_{108}$, and $\text{Cs}_{112}\text{Pb}_{64}\text{I}_{240}$ QDs, along with Bulk CsPbI_3

bond ^a	Cs_4PbI_6 ($1 \times 1 \times 1$)	$\text{Cs}_{20}\text{Pb}_8\text{I}_{36}$ ($2 \times 2 \times 2$)	$\text{Cs}_{54}\text{Pb}_{27}\text{I}_{108}$ ($3 \times 3 \times 3$)	$\text{Cs}_{112}\text{Pb}_{64}\text{I}_{240}$ ($4 \times 4 \times 4$)	CsPbI_3 (bulk)
Pb-I	3.317	~3.141–3.190	~3.101–3.184	3.075–3.130	3.189
I-I	4.705	~4.142–4.195	~4.147–4.300	4.140–4.300	4.510
Pb-Cs	4.347	~4.510–4.604	~4.500–4.650	4.497–4.651	5.524
Cs-I	3.639	~3.649–3.691	~3.735–3.861	3.707–3.811	4.510

^aI-I bonds are found to be shorter in various parts of a QD, while the rest of the mentioned bonds are contracted at the surface as shown in Figure S3.

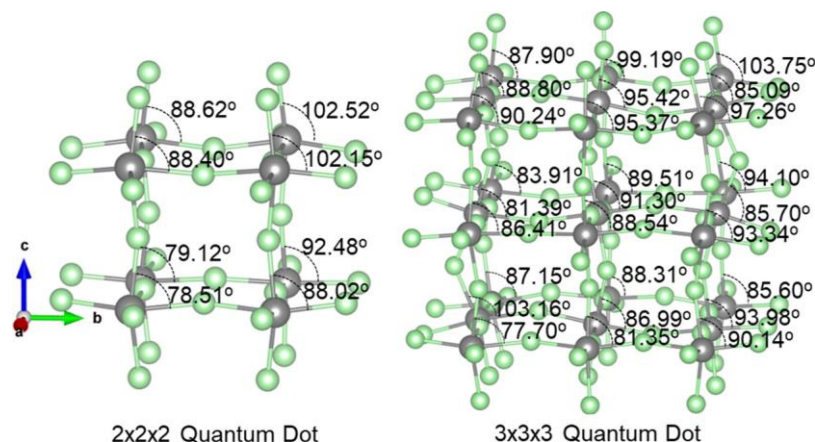


Figure 4. Distortions in octahedral symmetry are shown by demonstrating values of $\angle \text{IPbI}$. Notably, octahedra are symmetric in bulk cubic CsPbI_3 with all $\angle \text{IPbI} = 90^\circ$.

compared with the bulk value lie in various parts of the QDs (Figure S3). As the bonding in these perovskite QDs has a strong ionic character along with covalent behavior and the Pb-I as well as Cs-I bond lengths are much shorter than the values for Pb-Cs and I-I, we envisage that the shortening of the surface Pb-I and Cs-I bonds signifies strengthening of these bonds, which may in turn increase the bond dissociation energy. Thus, stronger bond character as compared to the bulk as well as attachment of ligands may lead to better phase stability in QDs, which has already been experimentally verified.^{16,51–53} Further, our results show that the octahedra are not symmetric as in a cubic bulk phase and distortions in the QDs are visible (Figure 4) in terms of rotation of octahedra. The variation in the value of $\angle \text{IPbI}$ is found to be between 78.51° and 102.52° for the $2 \times 2 \times 2$ QD, and it increases to 77.70° – 103.75° for $3 \times 3 \times 3$ QDs (Figure 4) besides changes in the bond distances (Table 1). These findings also agree well with experimental observations on cubic halide perovskite QDs.⁵⁴

Magic QDs and Their Electronic Properties. Magic QDs (also referred in the literature as magic clusters due to the small size) of halide perovskites have been produced in experiments.⁵⁵ These perovskite magic clusters are attractive in fundamental research and device applications compared to QDs due to their highly uniform size, high stability, narrow optical bandwidth, and bluer absorption and emission bands.^{56,57} In particular, magic clusters can be used as building blocks for creating larger nanostructures. However, one major challenge in the study of magic clusters is to determine their structure and stoichiometry. Due to the ultrasmall size and instability of halide perovskites in polar solvents, experimentally, it is hard to determine the structure of these magic clusters. Therefore, in our present study, we calculated binding energies of different QDs with respect to free atoms, and these are plotted in Figure 5 along with their HOMO–LUMO gaps, to explore charge-neutral magic clusters

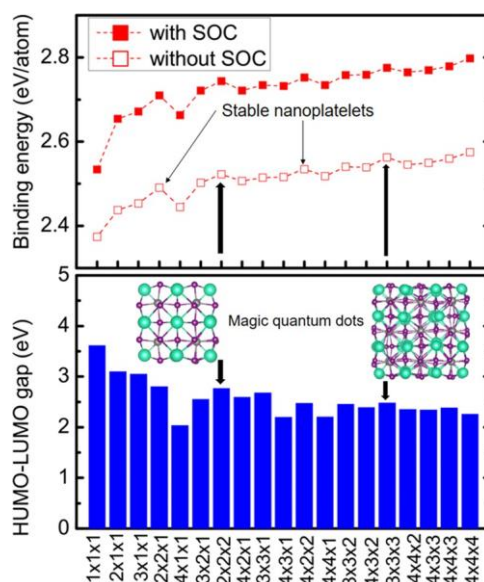


Figure 5. Binding energy and HOMO–LUMO gap for the energetically most favorable configurations of the considered QDs. The atomic structures of the magic QDs are shown in the inset. Here, thick arrows indicate the local maximum in the binding energy of the magic QDs and in the HOMO–LUMO gap, which are unique features of magic quantum dots.

of lead iodide perovskite. We have given results of the binding energy with PBE and with the inclusion of SOC. It is seen that SOC lowers the energy and therefore increases the binding energy in all cases. As a whole, the binding energy approaches the value of bulk cohesive energy (2.565 eV/atom within PBE) as the size of the QD increases. An interesting observation is that the binding energy shows a local maximum for the charge-

balanced cubic $2 \times 2 \times 2$, $3 \times 3 \times 3$, and $4 \times 4 \times 4$ QDs. Our results therefore suggest high possibility of finding cubic QDs, which agrees well with the experimental findings where QDs having cubic shapes have been found mostly.^{5,41} Figure 5 also shows that $2 \times 2 \times 1$ and $4 \times 2 \times 2$ platelet-like structures have a local maximum in the binding energy, indicating their stable nature, but all the nanowire-like structures are found to be the least stable. There are many experimental reports, which support our finding of stable nanoplatelet structures for halide perovskites.^{58–60}

The HOMO–LUMO gap is very important for optoelectronic applications. In bulk lead halide perovskites, it has been well explored that the PBE exchange–correlation functional works quite well in predicting the band gap close to the experimental value.⁶¹ This is due to the incidental cancellation of the increase in the band gap value by using the HSE06 exchange–correlation functional and a decrease in the band gap when SOC is incorporated to treat the heavy elements Pb and I in lead halide perovskites. While this has been tested well in the bulk, it is also desirable to check the same for the state-of-the-art halide perovskite QDs. Therefore, the HOMO–LUMO gap value for the tetrahedral QD obtained from the $1 \times 1 \times 1$ fragment has been calculated using PBE, PBE + SOC, and HSE06 exchange–correlation functionals. Similar studies were done on $2 \times 2 \times 2$ and $3 \times 3 \times 3$ QDs. It can be seen from Figure 6 that inclusion of

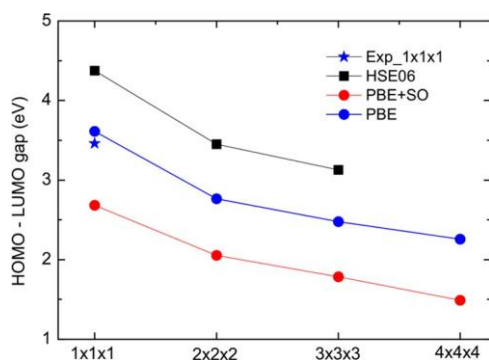


Figure 6. Comparison of the HOMO–LUMO gap values for the magic QDs using PBE, PBE+SOC, and HSE06. The available experimental value [ref 53] for the $1 \times 1 \times 1$ QD is also given for comparison. The HOMO–LUMO gap using the HSE06 exchange and correlation functional for the $4 \times 4 \times 4$ QD was not calculated due to its large size, but the behavior is expected to be similar to other cases.

SOC in PBE decreases the HOMO–LUMO gap value by nearly 0.7 eV, while HSE06 increases the HOMO–LUMO gap by nearly 0.67 eV. These values are slightly higher for the $1 \times 1 \times 1$ QD. The calculated large HOMO–LUMO gap (3.611 eV) using PBE for the $1 \times 1 \times 1$ QD agrees very well with the reported experimental value where Cs_4PbI_6 powders were found colorless with the band gap in the UV region, i.e., 3.38 eV.⁶² The strong effect of QC can be seen through the change in the HOMO–LUMO gap value for this smallest size QD, which is quite large compared with the bulk value (1.44 eV).

Further, the calculations of the HOMO–LUMO gap with different exchange–correlation functionals for $1 \times 1 \times 1$ bromide halide perovskite QDs, Cs_2PbBr_6 , and a comparison with the available experimental value in the literature show that our calculated value using PBE (3.841 eV) is in good agreement with the experimental value, which lies in the range of 3.95–4 eV.^{48,63} Hence, our values using PBE are a reasonable estimate of the HOMO–LUMO gap for the QDs of lead halide perovskites like

the bulk. Therefore, we calculated the HOMO–LUMO gap for different sizes of QDs using PBE and these are shown in Figure 5. Notably, the HOMO–LUMO gap for $2 \times 2 \times 2$ and $3 \times 3 \times 3$ QDs is blue-shifted compared with the bulk in addition to showing higher values with respect to the nearest neighbor structures (Figure 5). It has been noticed that the HOMO–LUMO gap for the $2 \times 2 \times 2$ magic QD increases by ~ 0.214 and 0.171 eV as compared to $3 \times 2 \times 1$ and $4 \times 2 \times 1$ QDs, respectively. Similar behavior is observed for $3 \times 3 \times 3$ magic QDs where the HOMO–LUMO gap increases by ~ 0.1 eV compared to the values for the nearest neighbor structures. These features agree with the experimental observations where magic clusters showed higher stability and a blue shift in the PL spectrum. Thus, $2 \times 2 \times 2$ and $3 \times 3 \times 3$ QDs clearly showed magic behavior. The formation of magic clusters/QDs is dominant in the small size range (less than ~ 2 nm),⁶⁴ and it slowly decreases for larger sizes such as $4 \times 4 \times 4$ QDs. The HOMO–LUMO gap decreases with the increase in the size of the QDs ($2 \times 2 \times 2$ to $3 \times 3 \times 3$ to $4 \times 4 \times 4$) due to the reduction in QC. The effect of size and QC can be seen from the shortening of bonds connecting Pb and I ions, which enhances the overlap between the p orbitals of each I ion and s and p orbitals of some Pb ions. This increased orbital overlap leads to a larger hybridization resulting in a marked decrease in the HOMO–LUMO gap from a $1 \times 1 \times 1$ single $[\text{PbI}_6]^{4-}$ cluster (3.611 eV) case in which the Pb–I bond lengths in fact increase to a $4 \times 4 \times 4$ magic cluster (2.257 eV). The large variation in the HOMO–LUMO gap as the size of the QDs is changed offers excellent possibilities of tailoring them for optoelectronic applications. As in the bulk where the band gap can be tuned with composition engineering, in nanocrystals of metal halide and organometallic halide perovskites, size engineering offers an additional very useful way for tuning the HOMO–LUMO gap. Experimentally, UV-visible absorbance peaks for mostly cubic CsPbI_3 nanocrystals are observed at around 470 nm or 2.637 eV.⁶⁵ We find that the experimentally observed HOMO–LUMO gap value for the nanoclusters of CsPbI_3 lies close to the value (2.475 eV) for a $3 \times 3 \times 3$ QD having the size of 17.57 Å, which is ~ 7 Å smaller than a $4 \times 4 \times 4$ QD (23.86 Å).

The total and projected density of states (DOS) for the magic QDs of halide perovskites along with the $1 \times 1 \times 1$ QD is shown in Figure 7. The isolated $[\text{PbI}_6]^{4-}$ octahedron in the $1 \times 1 \times 1$ Cs_4PbI_6 QD compared to the halide-coupled octahedra in larger cubic magic QDs causes the DOS of Cs_4PbI_6 to essentially behave like that of a single molecule. This behavior of the DOS shows that the Cs_4PbI_6 QD has the strongest confinement of charge carriers, and it is insulating in nature, which agrees with experiments performed on NCs of Cs_4PbI_6 .⁶⁶ However, with the increase in the size of QDs i.e., for $2 \times 2 \times 2$, $3 \times 3 \times 3$, and $4 \times 4 \times 4$ magic clusters, the orbital overlap increases, resulting in widening of the bandwidths as shown in the total DOS plot in Figure 7. The projected DOS plots show that the HOMO arises primarily from the p orbitals of I atoms, with a small contribution from the Pb 6s orbitals. This is very similar to the bulk behavior.⁶¹ The LUMO and the states near it are formed predominantly from the Pb 6p orbitals with some contribution from the antibonding 5s and 5p orbitals of iodine as one can see in the case of magic QDs.⁶⁷ This results in mostly p like high DOS contribution from Pb. Notably, the energy states arising from the Cs^+ ions do not couple directly to the HOMO and LUMO. Thus, the HOMO is localized primarily on I ions, while the LUMO is localized on Pb ions.

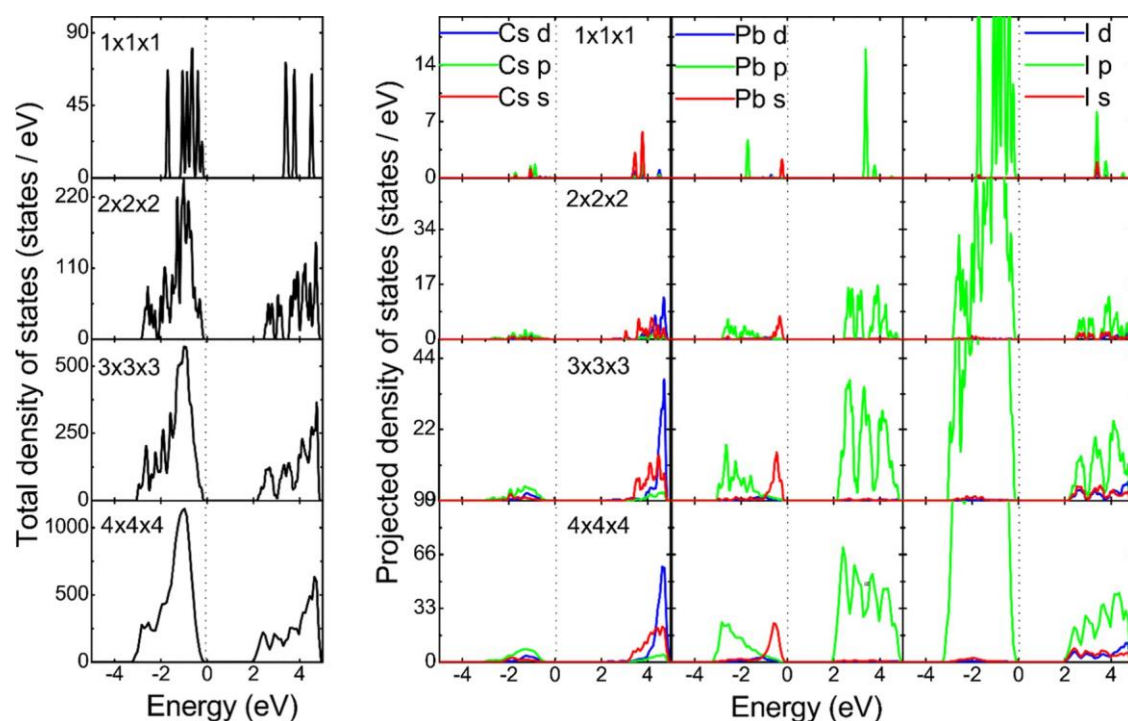


Figure 7. Total (left panel) and projected (right panels) density of states (states/eV) for the $1 \times 1 \times 1$, $2 \times 2 \times 2$, $3 \times 3 \times 3$, and $4 \times 4 \times 4$ magic QDs. The HOMO is taken to be at 0 eV.

CONCLUSIONS

We have studied QDs of CsPbI_3 inorganic halide perovskite with sizes ranging from $1 \times 1 \times 1$ to $2 \times 2 \times 2$ to $3 \times 3 \times 3$ to $4 \times 4 \times 4$ including intermediate platelet and nanowire structures. The stoichiometries for charge-balanced QDs and their lowest-energy structures were obtained in different cases. Our results suggest that it costs the least to remove Cs atoms from the surface rather than to remove I atoms to achieve charge balance in QDs. The overall trend of energy cost is similar for all sizes of QDs, but the value decreases with an increase in size. The calculated binding energy values show local maxima for $2 \times 2 \times 2$, $3 \times 3 \times 3$, and $4 \times 4 \times 4$ QDs, suggesting their higher stability as compared to neighboring sizes, which agrees with the experimental findings. Also, platelets such as $2 \times 2 \times 1$ and $4 \times 4 \times 2$ show higher stability than QDs of other neighboring sizes and they should be abundant in experiments. These results also agree with experimental findings of platelets, but nanowires are the least stable. There is contraction in Pb–I, Pb–Cs, and Cs–I bonds at the surface except for a $1 \times 1 \times 1$ QD for which Pb–I and I–I bonds show an expansion compared with the bulk. On the other hand, there is contraction of various I–I bonds in the QDs. As the bonding in these QDs has significant ionic character and Cs–I and Pb–I bonds are shorter than Pb–Cs and Cs–Cs bonds, such variations in the bond lengths can play an important role in the phase stability of the cubic QDs as compared to the bulk. Also, the PbI_6 octahedra are rotated and are not the same as in a cubic bulk structure. These results again agree with the experimental findings. Further, as in bulk lead halide perovskites, we find that the PBE exchange–correlation functional works quite well for QDs in predicting the HOMO–LUMO gap close to the experimental value. The HOMO–LUMO gap decreases with increasing size of the QDs ($2 \times 2 \times 2$, $3 \times 3 \times 3$, and $4 \times 4 \times 4$) due to the reduction in QC. The density of electronic states shows that Cs_4PbI_6 QDs have the strongest confinement of charge carriers due to an isolated octahedron, and with the

increase in the size of QDs, i.e., for $2 \times 2 \times 2$, $3 \times 3 \times 3$, and $4 \times 4 \times 4$ magic QDs, the orbital overlap increases, resulting in the widening of the bandwidths. The states near the HOMO have predominantly the *p* character of I, while near the LUMO, there lie the *p* states of Pb very similar to the bulk behavior. We hope that our conclusions would be applicable to QDs of other perovskite materials in this family and help in further understanding of the properties of halide perovskite QDs and their applications in future optoelectronic devices such as lasing, light-emitting diodes, photovoltaics, and photon detection.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.4c02142>.

Explanation for considering inorganic halide perovskite QDs and different isomers for $2 \times 2 \times 1$ and $2 \times 2 \times 2$ QDs with their binding energies and selected nearest neighbor distances for $2 \times 2 \times 2$ and $3 \times 3 \times 3$ QDs (PDF)

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Notes

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