1. INTRODUCTION

As the quest for clean, source-abundant ways for energy harvesting in the 21st century reaches a peak, perovskite materials have played a significant role in the research for solar energy applications, such as photovoltaics and light-emitting diodes (LEDs). An enormous amount of theoretical and experimental work in the last 2 decades has, and continues to, explore the potential of these materials. The majority of the research on perovskites has been concentrated on macrostructured bulk version of these materials. However, in the last years, an increasing amount of research has been carried out on the nanostructures of perovskite materials, in the form of quantum dots (QDs) as well as nanowires and nanorods. The experimental work in the last 2 decades has, and continues to, explore the potential of these materials. The majority of the research on perovskites has been concentrated on macrostructured bulk version of these materials. However, in the last years, an increasing amount of research has been carried out on the nanostructures of perovskite materials, in the form of quantum dots (QDs) as well as nanowires and nanorods. The size of these materials (below 10 nm, and even as small as 2 nm) ensures the occurrence of quantum confinement effects, which enable the materials under study to be used in fields where quantum mechanical properties play a decisive role, such as LED technology and even materials for quantum computers.

A perovskite material has the general formula of ABX₃, where if A is a monovalent cation, then B is usually a divalent cation of dissimilar size, and X is a monovalent anion to achieve charge neutrality. In the case of emerging halide perovskites, X is a halogen such as Cl, Br, or I. The A cation can be inorganic, such as Cs, or organic, such as a methylammonium cation (CH₃NH₃). The basic structure of ABX₃ formula is an octahedron, whereas the final structure of the bulk material can be anything from a high-symmetry cuboid to a low-symmetry monoclinic structure. The family of perovskite materials used in this study consists of MABX₃ and CsBX₃ perovskites with cubic structures, where B is a cation such as Pb, Sn, Ge, Ca, and Sr and X is a halogen such as Cl, Br, and I. These materials have been well studied in the literature and exhibit an abundance of sought-after properties, such as low cost, low difficulty of synthesis, and high carrier mobility.

In addition to the vast amount of literature on bulk perovskites, there is a limited yet rapidly growing number of experimental studies on halide perovskite nanostructures, mainly QDs. Most of these studies regard a few specific materials such as cesium lead (CsPbBr₃) and methylammonium lead perovskites, such as MAPbBr₃ and MAPbI₃. On the other hand, very few theoretical studies on perovskite QDs with first-principles calculations have been conducted so far. Thus, a thorough, ab initio study of a great variety of various-sized QDs of different materials of the MABX₃ formula was in place and could be a basis for future in-depth experimental and theoretical research.

Experimental studies in perovskite QDs share some common features that were used as a guide for our study. Some of these features include the shape of the QDs, which is generally cuboid. Substitution of halide anions (i.e., Br with CI) does not change the cubic structure of the QDs. In order for the structure to be considered a QD, its average size must be below 2 × rₑ, where rₑ is the exciton Bohr radius. The Bohr radii for MAPbBr₃ and MAPbI₃, for instance, are 2 and 2.2 nm, respectively. Generally, the perovskite QDs studied have a diameter below 10 nm, with a general average size of 3 nm, and some of them even less than 1.8 nm. Another shared feature of the studied QDs is that, compared to the corresponding band gap of the bulk material, their highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap is always wider and increases further as the QD size decreases.
exponentially as the QD size increases, converging to the bulk value when the QD size surpasses the $2 \times r_g$ limit. Similarly, the exciton binding energy, which is significantly enhanced in small QDs, is a decreasing function of size. For example, the bulk value of $E_g$ for MAPbBr$_3$ is 65 meV, whereas in the small QD regime, it can be as large as $\sim 300$–$400$ meV.\textsuperscript{9,10,12}

The ability of many of the experimentally studied perovskite QDs to exhibit strong optical absorption and emission in the visible optical regime makes them suitable candidates for optoelectronic applications such as LEDs. In the present study, we focus on the electronic and optical properties of QDs of the halide perovskites having the chemical formula ABX$_3$, where A is either Cs or the methylammonium cation CH$_3$NH$_3$ (widely denoted in the literature with the acronym MA), B is a divalent cation (Ge, Sr, Pb, Ca, or Sr), and X is a halogen atom (Cl, Br, or I). These materials in the form of QDs will exhibit electronic and optical properties which differ substantially from their bulk properties studied before.\textsuperscript{19,20} Note that the halide perovskites with MA are often called hybrid or organometallic halide perovskites in literature. The hybrid halide perovskites with Ge, Sn, and especially Pb are among the most studied perovskites in literature both experimentally and theoretically because of their potential use in photovoltaic applications.\textsuperscript{3}

The article is organized as follows: in Section 2, we present the computational details. In Section 3, we analyze the structure of both the stoichiometric (ST) and nonstoichiometric (NST) QDs studied. In Section 4, the electronic and optical properties of the systems under study are presented, and finally, in Section 5, we summarize our conclusions.

2. OUTLINE OF CALCULATIONS

All calculations were performed in the framework of density functional theory (DFT) using the generalized gradient approximation (GGA) functional of Perdew–Burke–Ernzerhof\textsuperscript{21} (PBE) and its hybrid analogue, to account in a more accurate way for the exchange energy, PBE0.\textsuperscript{22} The initial structures were optimized at the PBE level of theory, which is known to predict accurately the structural properties, but significantly underestimates the band gap. The resulting geometries were then used to calculate the reliable values of the single-particle HOMO–LUMO gap with the help of the PBE0 functional. The optical properties were calculated on top of the PBE0 results, using the time-dependent DFT (TDDFT). In particular, we performed TDDFT calculations in both random-phase approximation and Tamm–Dancoff approximations, while we also employed the simplified TDDFT (sTDDFT) approximation of Grimme,\textsuperscript{23,24} which is most suitable for larger systems where traditional TDDFT becomes prohibitive. It should be clarified that in the context of the present manuscript, we consider as optical gap, the energy of the lowest spin allowed transition regardless of its oscillator strength. This was necessary because all the alkaline earth metal dots exhibit vanishing oscillator strengths. Confusion is avoided by noticing the strength values which are explicitly presented in all absorption spectra plots.

As the aim of the project is to extend to larger nanostructures, we chose a basis set of double zeta quality (namely, the def2-SVP basis sets of the Karlsruhe group\textsuperscript{25,26}), which has been extensively tested to numerous cases and in the same time is small enough to allow for calculations in systems with hundreds of atoms. All calculations were performed with the ORCA suite of programs.\textsuperscript{27,28}

3. ST AND NST-QDs

The construction of NP models can be easily achieved by suitably repeating a fundamental building block along the tree spatial directions. If the building block is the unit cell of the material (i.e., A$_1$B$_1$X$_3$), then the atoms of the resulting structures satisfy the same ratios (i.e., 1/1/3) with the corresponding bulk material. In this context, the NPs derived by repeating this building block two times in each direction are denoted as $2 \times 2 \times 2$, whereas when repeated three times, they are labeled $3 \times 3 \times 3$. The size of the resulting nanocrystals is approximately $\sim 1.0$ and 1.5 nm. This type of QDs (which in the present work are labeled ST), although build upon the same principle as the bulk, exhibits a surface local environment which is structurally very different from the bulk. In particular, the BX$_6$ octahedra, which constitute the backbone of the material, are truncated, exposing either the A or the B cations in three out of six facets of the cuboid QD. This observation led us to an alternative route of QD construction, based on the principle that the BX$_6$ octahedra should not be truncated. Apparently, this leads to violation of the 1/1/3 ratio of the bulk, and consequently, it results in charged NPs (which in the present work are labeled NST). The charge problem can be tackled in two different ways. The first is based on starting with NPs with full surface coverage by A cations and removing a suitable number of them (i.e., create vacancies) in order to achieve neutrality. The second way is based on excluding all the surface cations as it might be argued that they are relatively loosely bound to the BX$_6$ octahedra skeleton and as a result they are easier to desorb. In this case, the excessive charge can be compensated by a suitable surface passivation. In the present manuscript, we have considered only the second type of NST QDs. Their passivation is achieved by pseudohydrogens (in order to maintain neutrality) and the surface A cations are considered desorbed. The size of the resulting $2 \times 2 \times 2$ and $3 \times 3 \times 3$ NST QDs is approximately $\sim 1.2$ and 1.9 nm, respectively. The two distinct types of QDs are graphically presented in Figure 1.

Figure 1. (a) ST CsPbX$_3$ QDs, (b) hydrogen-passivated NST CsPbX$_3$ QDs, and (c) hydrogen-passivated NST MAPbX$_3$ QDs.
The first part of calculations was focused on CsPbX₃ (X = Cl, Br, I) NPs, which consist of a much easier system to study (as compared to MA analogues) and the relevant literature is more abundant. In this way, the theoretical approximations and methodological choices could be rigorously evaluated, offering a useful insight with regard to the study of the more complicated case of MA containing NPs. Moreover, it was a first step toward examining different key morphological characteristics of the QDs such as composition and surface passivation and allowed us to consider explicitly the two aforementioned categories of QDs, avoiding the computational passivation and allowed us to consider explicitly the two characteristics of the QDs such as composition and surface.

As a result, we adopted the solution of passivating pseudohydrogen atoms, with their atomic numbers set to 0.792 and 0.8185 for the 2 × 2 × 2 (24 hydrogen atoms) and 3 × 3 × 3 (54 hydrogen atoms) QDs, respectively. On top of this, an additional geometric constrain was imposed on them. Although their bond lengths were allowed to change on the course of geometric relaxation, the bond angles were kept fixed. This can be rationalized if one considers that in reality, the passivation is achieved by ligands which, in most cases, are long-chain molecules. As a result, the variation of the angles B−X−R is more or less hindered because of steric interactions and the shape of the QDs is stabilized and maintained. This combination of hydrogen passivation and angle freezing somehow imitates the passivating and stabilizing effect that the molecular ligands have on the structure, while in the same time makes the computational cost of the calculations affordable.

Right after the evaluation of the CsPbX₉ (X = Cl, Br, I) results, we turned our focus on the ABX₃ systems with A = CH₃NH₃⁺ obeying the same building principles as above. This time, the B cation was set to B = Sn, Pb, Ge, Ca, Sr, while X = Cl, Br, I. The NST structures have a total of 52 (+24 passivating hydrogens) atoms (size 2 × 2 × 2) and 199 (+54 passivating hydrogens) atoms (size 3 × 3 × 3). The NST NPs consist of 96 and 324 atoms, respectively. It should be emphasized that because of the very flat potential energy surface, which is a consequence of the loose binding of surface CH₃NH₃⁺ cations, the convergence of geometry optimizations is very difficult. For this reason, it was considered necessary to terminate the optimization procedure when the energy reached a very flat and horizontal plateau. Apparently, this practice affects the quality of specific results by introducing some small error bars, which are estimated to be smaller than 0.1 eV. This estimation is consistent with the molecular dynamics (MD) calculations of ref 14 in which the sampling of HOMO−LUMO gap during the MD steps led to this value.

| Table 1. HOMO−LUMO and Optical Gap of CsPbX₃ (X = Cl, Br, I) NPs |
|----------------|----------------|----------------|----------------|----------------|----------------|
| system         | PBE H−L gap (eV) | optical gap (eV) | PBE0 H−L gap (eV) | optical gap (eV) | PBE H−L gap (eV) | optical gap (eV) |
|                |                 |                 |                 |                 |                 |                 |
| ST             |                 |                 |                 |                 |                 |                 |
| X = Cl         | 2.67            | 2.67            | 4.23            | 3.94            | 2.30            | 2.30            |
| X = Br         | 2.56            | 2.56            | 4.09            | 3.70            | 2.13            | 2.13            |
| X = I          | 1.92            | 1.96            | 3.28            | 2.88            | 1.42            | 1.42            |
| NST            |                 |                 |                 |                 |                 |                 |
| X = Cl         | 3.90            | 3.97            | 5.80            | 5.18            | 3.49            | 3.49            |
| X = Br         | 2.78            | 2.80            | 4.66            | 4.05            | 2.51            | 2.51            |
| X = I          | 1.70            | 1.72            | 3.20            | 2.66            | 1.20            | 1.20            |

“Table 1. HOMO−LUMO and Optical Gap of CsPbX₃ (X = Cl, Br, I) NPs”

4. RESULTS AND DISCUSSION

4.1. CsPbX₃ (X = Cl, Br, I) NPs. The comparison of the results between ST and hydrogen-passivated NST CsPbX₃ QDs gives some interesting insight with regard to two interconnected but distinct aspects of the subject. Primarily, it gives evidence on whether the adopted hydrogen passivation scheme is reliable, when the focus is on the size dependence of the HOMO−LUMO and optical gaps of the related materials, and secondarily, it serves as an initial step toward understanding possible deviations from the expected size dependence due to surface manipulation of the QDs.
The first straightforward observation which can be made by a simple inspection of the HOMO−LUMO and optical gap data compiled in Table 1 is related to the performance of the two different functionals. As expected, there is a systematic difference between the PBE and PBE0 values, which can be readily attributed to the well-known tendency of the pure GGA functionals to underestimate the gaps. Moreover, it can be seen that, in almost all cases (considered here), the PBE HOMO−LUMO and optical gaps are practically identical. It is worth noting that this picture is somehow unrealistic as it does not account for the exciton binding energy which is defined as the difference between the single particle and the optical gaps. On the other hand, the PBE0 results appear to be consistent in this respect, predicting exciton binding energies ranging from 210 to 600 meV.

As for the difference between ST and NST QDs, it is evident that the results are strongly dependent on the type of halogen. For X = Cl, the NST NPs exhibit a significantly larger optical gap, while as we go to heavier halogen, the difference gets smaller (or even reversed for X = I). A qualitative interpretation can be obtained with the help of the corresponding density of states (DOS) diagrams presented in Figure 2a,b. On the left panel of these figures, there are comparative DOS plots for the ST and NST NPs. In all cases, the presence of passivants results in a shift of valence states which are close to HOMO, deeper into the valence band. Taking into consideration that these states are mostly halogen-related, it might be inferred that this is the result of a strong X−H bond. The implication of the presence of such strong bonds between the surface halogens and the passivating pseudohydrogens indirectly affects the position of the low-energy conduction band (CB) states. As these CB states are mostly related to the B cation through the antibonding interaction B−X, their shift toward lower energies is indicative of a weaker B−X bonding (which is the consequence of the strong X−H bond). These qualitative arguments are also supported by a Mayer bond order analysis.

As the size of the studied QDs is quite small, comparison with experimental data can be attempted by extrapolating existing experimental data to the current sizes. In particular, if the experimental data of Figure 3b of ref5 (for CsPbBr3) are fitted in a function of the form y = a + b/x^α, the outcome is y = 2.18 + 1.55/x^0.82. For the NST CsPbBr3 dots, application of this formula to sizes relevant to our present calculations (2 × 2 × 2 and 3 × 3 × 3) gives gap values of 3.49 and 3.11 eV, respectively. Similarly, the corresponding values for the ST dots (2 × 2 × 2 and 3 × 3 × 3) are 3.83 and 3.28 eV. These extrapolated values, although rather uncertain, are consistent with the data of ref17 and indicate that the PBE results appear to significantly underestimate the value of the optical gap (in both ST and NST cases). On the contrary, the predictions of the PBE0 calculations, especially for the case of ST QDs, and the aforementioned extrapolated values appear to be in very good agreement ∼0.15 eV. This is strong evidence that the adopted computational methodology is capable of producing reliable results. Moreover, it hints that despite the presence of truncated octahedra, the ST configurations offer a more realistic description of the QDs.

In all CsPbX3 NPs studied, the PBE0 exciton binding energy (which is considered as the difference between the single-particle gap and the optical gap) exhibits a theoretically consistent trend. For the 2 × 2 × 2 ST QDs, the corresponding values are BECsPbCl3 = 290 meV, BECsPbBr3 = 390 meV, and BECsPbI3 = 400 meV and they shift to smaller values as the size of the dots increases. In particular, for the 3 × 3 × 3 QDs, the red shift is as large as 80, 210, and 180 meV, respectively. A similar picture (but with larger values) is also observed for the NST CsPbBr3 dots, application of this formula to sizes relevant to our present calculations (2 × 2 × 2 and 3 × 3 × 3) gives gap values of 3.49 and 3.11 eV, respectively. Similarly, the corresponding values for the ST dots (2 × 2 × 2 and 3 × 3 × 3) are 3.83 and 3.28 eV. These extrapolated values, although rather uncertain, are consistent with the data of ref17 and indicate that the PBE results appear to significantly underestimate the value of the optical gap (in both ST and NST cases). On the contrary, the predictions of the PBE0 calculations, especially for the case of ST QDs, and the aforementioned extrapolated values appear to be in very good agreement ∼0.15 eV. This is strong evidence that the adopted computational methodology is capable of producing reliable results. Moreover, it hints that despite the presence of truncated octahedra, the ST configurations offer a more realistic description of the QDs.

4.2. MABX3 (X = Cl, Br, I) NPs. The case of MABX3 (B = Sn, Pb, Ge, Ca, Sr/X = Cl, Br, I) NPs was a much more challenging task mainly because of the difficulties described in the previous paragraph. Contrary to what happened in cesium-containing dots, the relaxation procedure (especially for ST NPs) leads to significant distortions of the initial geometries, which are more pronounced in the smaller QDs. As expected, the BX6 octahedra, apart from being truncated in three out of six facets of the QD, they also deviate from the ideal symmetric structure. The CH3NH3+ species exhibit a wide range of orientations, which depend heavily on their relative position within the dot. A general trend which (more or less) appears to
be present in all cases is that the surface CH₃NH₃⁺ moieties seem to adopt an orientation with their NH₃ part toward the surface of the cube and the CH₃ group directed outward.

The electronic structure of ST and NST QDs of the most commonly used MAPbX₃ materials is presented with the help of DOS diagrams, in the right panes of Figure 2a,b (for the two different QD sizes). Once again, the presence of pseudohydrogen passivation seems to shift the band edges toward lower energies. The source of this shift appears to be the same as the one described for the case of CsPbX₃ NPs. The related gaps are presented in Tables 2 and 3. Similar diagrams for all the

Table 2. HOMO–LUMO and Optical Gap Values for NST Perovskite QDs

| Material      | 2 × 2 × 2 QD | 3 × 3 × 3 QD |
|---------------|-------------|-------------|
|               | H−L (eV)   | H−L (eV)   | Optical gap (eV) | Optical gap (eV) |
| MAPbCl₁       | 2.77       | 3.87       | 4.39           | 5.42           |
| MAPbBr₁       | 3.38       | 4.17       | 4.86           | 5.77           |
| MAPbI₁        | 4.06       | 4.55       | 5.32           | 6.13           |
| MAPbCl₂       | 4.36       | 4.88       | 5.51           | 6.28           |
| MAPbBr₂       | 4.66       | 5.16       | 5.75           | 6.45           |
| MAPbI₂        | 4.96       | 5.46       | 5.93           | 6.54           |

Table 3. HOMO–LUMO and Optical Gap Values for ST Perovskite QDs

| Material      | 2 × 2 × 2 QD | 3 × 3 × 3 QD |
|---------------|-------------|-------------|
|               | H−L (eV)   | H−L (eV)   | Optical gap (eV) | Optical gap (eV) |
| MAPbCl₁       | 2.77       | 3.87       | 4.39           | 5.42           |
| MAPbBr₁       | 3.38       | 4.17       | 4.86           | 5.77           |
| MAPbI₁        | 4.06       | 4.55       | 5.32           | 6.13           |
| MAPbCl₂       | 4.36       | 4.88       | 5.51           | 6.28           |
| MAPbBr₂       | 4.66       | 5.16       | 5.75           | 6.45           |
| MAPbI₂        | 4.96       | 5.46       | 5.93           | 6.54           |

NPs considered (but only for the 3 × 3 × 3 size) are plotted in Figure 3. The red shift of the band edges is clear in all B = Pb, Sn, Ge QDs and becomes stronger as the halogen type gets heavier. For the case of B = Ca, Sr dots, the picture changes drastically. Although the tendency of the band edges to shift to lower energies as the halogen type gets heavier remains, the ordering with regard to the position of the ST band edges is reversed. The complete picture of the gap variations for both the ST and NST QDs can be conveniently realized with the help of Figure 4, which makes the existing trends apparent (the data are taken from Tables 2 and 3).

The absorption spectra presented in Figure 5 have been calculated in two steps. At first, the lowest few spin allowed transitions are calculated at the PBE0/TDDFT/def2-SVP level of theory giving the reported optical gap. Then, a few hundreds of states are calculated with Grimme’s sTDDFT method. The absorption spectrum is created by introducing a suitable Lorentzian broadening to all excited states, while in the same time, the sTDDFT results are properly shifted so that the lowest transition coincides with the corresponding PBE0/TDDFT/def2-SVP one.

If one attempts to compare with experimental results in a fashion similar to the one adopted for the case of Cs containing NPs (i.e., fit the experimental data and extrapolate to current sizes), several inconsistencies may be observed. For example, it is not uncommon that the reported gaps of similar sizes, but from different studies, do not suit well in a common graph. If, however, we use a single manuscript data (e.g., the experimental results from Zhenfu et al.29) and fit them to the usual formula \( y = a + b/x^2 \), the outcome is \( y = 2.61 + 2.36/x^2 \). If this is extrapolated to current sizes, then for the case of ST \( 3 \times 3 \times 3 \) MAPbBr₃ NPs, one gets the value of \( 3.47 \) eV, whereas for the NST ones, the value is \( 3.14 \) eV. These extrapolated estimations are consistent with both the ST and NST theoretical predictions (3.71 and 3.57 eV). However, the comparison highly favors the case of ST QDs. Moreover, if one focuses on the PL energy differences observed29 in halogen replacement (i.e., Cl → Br → I), they are completely consistent with the present theoretical values which are graphically presented in Figure 4. In particular, the experimental values are \( \Delta E(\text{PL})_{\text{Cl} \rightarrow \text{Br}} = 0.63 \) eV, \( \Delta E(\text{PL})_{\text{Br} \rightarrow \text{I}} = 0.66 \) eV, and \( \Delta E(\text{PL})_{\text{Cl} \rightarrow \text{I}} = 1.29 \) eV, where the current theoretical predictions for the ST QDs are \( \Delta E_{\text{th}}(\text{Cl} \rightarrow \text{Br}) = 0.57 \) eV, \( \Delta E_{\text{th}}(\text{Br} \rightarrow \text{I}) = 0.74 \) eV, and \( \Delta E_{\text{th}}(\text{Cl} \rightarrow \text{I}) = 1.31 \) eV. The corresponding data of the NST NPs exhibit significant deviations from the experimental measurement. At this point, it should be clarified that our theoretical prediction corresponds to absorption energies (not PL). However, it is experimentally verified that the Stokes shift between absorption and emission is quite small (due to direct transitions). As a result, the aforementioned comparison of energy differences might be considered valid. It is worth noting that once again the comparison with experimental data reveals that the ST NPs produce results which are closer to experiments.

For the cases of MAPbX₃ and MASnX₃ NPs, there is a clear trend that the NST QDs have stronger transitions. The MACaX₃ and MASrX₃ QDs exhibit practically vanishing oscillator strengths. At this point, it should be emphasized that in energies well above the optical gap, the height of the peaks is dictated by the DOS rather than the strength of individual transitions. As a means to shed light on this difference, we have plotted the orbital-resolved projected DOS (PDOS) diagrams for two representative NPs along with a graphic representation of their HOMO and LUMO orbitals in Figure 6. The HOMO, HOMO − 1, and so forth states of...
MAPbCl₃ are mainly Cl(p) states while the LUMO, LUMO + 1, and so forth are Pb(p). Additionally, a composition analysis with the help of Multiwf1 code³⁰ revealed that the specific states are quite extended, as is evident in their three-dimensional plots of Figure 6. On the contrary, the corresponding states of the MACaCl₃ QDs are Cl(p) and Ca(s), whereas on the same time, the wave functions exhibit a significant localization on specific atoms (see Figure 6). This completely different picture is reflected on the shape and details of the corresponding absorption spectra. As expected, in all ST QDs, the frontier orbitals are mainly distributed on the surfaces of the cuboids. This allows for property manipulation through appropriate surface treatment.

5. SUMMARY AND CONCLUSIONS

In conclusion, we have performed extensive ground-state DFT and excited-state TDDFT calculations on a large number of ultrasmall perovskite QDs having the chemical formula ABX₃, where A is either Cs or the methylammonium cation CH₃NH₃ (MA), B is a divalent cation (Ge, Sr, Pb, Ca, or Sr), and X is a halogen atom (Cl, Br, or I). For every different material and size examined, two types of dots were considered (ST and pseudohydrogen-passivated NST). In all cases, the single-particle gap, the optical gap, and the absorption spectra were systematically calculated and compared. It is found that the gaps are always a decreasing function of the atomic number of the halogen. The surface passivation by capping the halogen atoms results in a red shift of both the valence and CB edges (HOMO and LUMO orbitals) as compared to unpassivated ST dots for all QDs (although NPs with Ge as a B cation seem to suffer from stability issues). The NPs which contain alkaline earth metals exhibit a different behavior with respect to the ones containing one of the isovalent Ge, Pb, and Sn. The absorption spectra of Pb and Sn containing QDs exhibit strong

Figure 3. Comparative DOS plot of an ST and a NST CH₃NH₃AX₃ (A = Sn, Ge, Ca, Sr and X = Cl, Br, I) cuboid of size 3 × 3 × 3.

Figure 4. Variation of the HOMO–LUMO and optical gaps as a function of the anion atom type of NST QDs. The dotted lines correspond to the optical gap. The gray circle indicates unstable NPs which were completely deformed by the relaxation procedure.
transitions, which are even more enhanced for the case of pseudohydrogen-passivated NST QDs. On the contrary, Ca and Sr NPs exhibit vanishing oscillator strengths, which are related to the nature of their frontier orbitals which appear to be extremely localized. Finally, although the NST QDs with the complete octahedra possess a structural configuration which is more appealing to the eye, the comparison with experimental data reveals that the ST QDs exhibit gaps closer to the experimental ones.

Our study highlights the potential as well as the challenges and issues regarding nanostructured halide perovskite materials and paves the way for future theoretical and experimental work on these materials.

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