



# Lithium halide monolayer sheets: First-principles many-body calculations



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## ABSTRACT

The geometric, electronic and optical properties of two-dimensional lithium halide (LiF, LiCl, LiBr) monolayers are systematically explored by using ab initio density functional theory, the HSE06 functional, the GWA method and Bethe–Salpeter equation calculations. The stabilities of these structures have been further evaluated by cohesive energy, phonon spectra, mechanical stability analysis and ab initio molecular dynamics. The structural results exhibit that the buckled configurations of these monolayer systems are stable; therefore, it is possible to synthesize these structures in experiments. The electronic properties were analyzed by HSE06 functional and quasi-particle many-body perturbation theory (MBPT) via GW approach. It is found that all these nanostructures are indirect band gap insulators. The HSE06 and  $G_0W_0$  gave remarkably larger band gaps than the PBE functional. The optical properties and excitonic effects of these materials are investigated in independent-particle, independent-quasiparticle and including excitonic effects (BSE). The formation of first exciton peaks at 8.48, 7.7, and 6.92 eV with large binding energy of 2.92, 2.13 and 1.70 eV was observed for LiF, LiCl and LiBr monolayers, respectively. The strong Coulomb interaction between electrons and holes in these compounds leads to the large binding energy and small exciton Bohr radius. The interesting stability, electronic and optical properties of these monolayers are potentially useful for future electronic and optoelectronic device design such as VUV transmitter and X-ray monochromator plates.

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## 1. Introduction

Over the past few years there has been increasing interest in studying two-dimensional (2D) monolayer systems, mainly because of their extraordinary electronic, magnetic, mechanical and optical properties (e.g., graphene, SiC, BN, ZnO, ZnS, BeO, Mo<sub>2</sub>C and GaN monolayers) [1–13]. The 2D nanostructured materials have shown unique physicochemical properties, which are quite different from those of the corresponding bulk crystals with potential applications in energy storage and conversion technologies. Alkali halide materials known as ionic compounds are of special interest because of their stability and photoluminescence efficiency at room temperature [14]. Their bulk crystals generally crystallize in both B1 (NaCl-type) and B2 (CsCl-type) structures and their large electronic band gap place their useful transmission limit near 8–12 eV, further into the ultraviolet region than any other known materials [15]. LiF, LiCl and LiBr have been

investigated in bulk phase theoretically and experimentally [15–17]. These materials can be considered as ideal candidates for numerous pits [18] because of the presence of color centers and can be used for optical applications such as optical waveguides [19] microcavities [20] and molecular laser sources [21]. Due to these powerful applications, a number of studies have been devoted to exploring new possible structural phases for alkali halide materials. For example, theoretical studies have previously predicted their phase transition [22]. Furthermore, the existence of the alkali halide nanostructures were investigated experimentally [23] and theoretically [14,24]. Although the structural, electronic and optical properties of alkali halides monolayers have been recently studied [25], to the best of our knowledge, information about their properties is rather scarce. For example in all theoretical studies, stability of these monolayer nanostructures has not been investigated carefully. Moreover, the electronic and optical properties of alkali halide nanostructures have been investigated using the density functional theory (DFT) [26] and the random phase approximation (RPA) [27] which are not sufficient to yield results in quantitative agreement with experiments

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because these methods do not take many-body effects into account. It is known that The HSE06 functional, the many-body GW approximation and Bethe-Salpeter equation approach (BSE) develop the electronic and optical properties of the semiconductors and insulators [28,29], in contrast to the DFT and RPA.

In this paper we investigate the structural, stabilities, the band gap and the role of excitons on optical properties of 2D alkali halides monolayers. Systematic studies of electronic properties, such as electronic band structures and density of states, using various approaches (PBE, HSE06 and three levels of GWA) on these materials are reported. The optical spectra of the studied materials were modeled using the  $GW_0$  plus BSE approach, which includes both electron–electron (e–e) and electron–hole (e–h) correlation effects. To our knowledge, no experimental data exist about the structural geometry, band gaps and the optical properties of these monolayer systems. Hence, we compare our results with previous theoretical results of Li halides monolayers.

The paper is organized as follows: In next section, the details of the computational methods employed to compute the structural, electronic and optical properties are presented. Section 3.1 covers the geometry and stability results related to cohesive energy, phonon dispersion, mechanical properties and dynamical stability of these nanostructures. In Section 3.2 the electronic properties of the 2D Li halides monolayers using PBE, HSE06,  $G_0W_0$ ,  $GW_0$ , and GW levels are presented. In Section 3.3, optical properties, evaluated from BSE on top of GWA, are described and the role of excitonic effects is discussed. In the last section we summarize our studies and present the conclusions.

## 2. Computational details

In the present work, the ground state electronic properties are computed using the DFT methods implemented in the Vienna ab initio simulation package (Vasp) [30]. The DFT calculations are within the frame work of generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof (PBE) [31] for the exchange correlation potential and the ion–electron interaction is treated using the projector augmented wave (PAW) [32] method. Electronic wave functions have been expanded using a plane-wave basis set with a cut-off energy of 450 eV. Due to underestimating experimental band gap values in PBE functional, we also used the screened hybrid functional HSE06 [33] and quasi-particle many-body perturbation theory (MBPT) via GW approximation [34] to evaluate the electronic properties of these materials.

For the Brillouin zone integration, a  $14 \times 14 \times 1$   $\Gamma$  centered Monkhorst-Pack [35]  $k$ -point mesh is used to ensure converged structural and electronic results within PBE and HSE06. In all cases a unit-cell with a vacuum region of 30 Å in the direction normal to the sheet plane has been used. Geometry optimization and mechanical properties of these systems were performed by a conjugate gradient method with termination criteria of  $10^{-5}$  eV and 0.001 eV/Å for the energy and the forces, respectively. The phonon calculations in this paper were performed by Phonopy package [36]. In the  $G_0W_0$  approximation, the quasi-particle energies were obtained as a first-order correction to the corresponding Kohn–Sham single-particle energies.

$$E_{nk}^{QP,1} = \text{Re} \left[ \left\langle \varphi_{nk} \left| T + V_{n-e} + V_H + \sum_{XC} (G, W; E_{nk}) \right| \varphi_{nk} \right\rangle \right] \quad (1)$$

Here,  $G$  (Green's function) and  $W$  (screened Coulomb interaction) in the self-energy operator  $\Sigma$  are calculated using the DFT energies and wave functions [27,34,37]. The updated QP energy  $E_{nk}^{QP,i+1}$  for  $GW_0$  and GW levels is then obtained by linearization of Eq. (1) as follows [28]

$$E_{nk}^{QP,i+1} = E_{nk}^{QP,i} + Z_{nk} \text{Re} \left[ \left\langle \varphi_{nk} \left| T + V_{n-e} + V_H + \sum_{XC} (G, W; E_{nk}^{QP,i}) \right| \varphi_{nk} \right\rangle - E_{nk}^{QP,i} \right] \quad (2)$$

The iterative process is generally carried out until self-consistency is reached. To obtain excellent converged results, we used four iterations in our calculations. The GWA calculations were performed with a  $k$ -sampling grid of  $22 \times 22 \times 1$ , a cutoff energy of 350 eV, 200 empty conduction bands and 200 frequency grid points. The convergence for all these parameters have been obtained in the same method as we explained in our previous work [2]. Finally, the optical absorption spectra including e–h interaction were calculated via the Bethe–Salpeter equation (BSE) [38]

$$(E_{ck}^{QP} - E_{vk}^{QP}) A_{cvk}^S + \sum_{c'v'k'} \langle cvk | K^{e-h} | c'v'k' \rangle A_{c',v',k}^S = \Omega^S A_{cvk}^S \quad (6)$$

where  $E_{vk}^{QP}$  and  $E_{ck}^{QP}$  represent the QP eigenvalues of valence and conduction bands,  $K^{e-h}$  is the electron–hole coupling kernel,  $A_{cvk}^S$  donates the exciton wavefunction and  $\Omega^S$  is the energy of the given excitation, respectively. In BSE calculations we consider 6 valence and 32 conduction bands with a  $k$ -sampling grid of  $40 \times 40 \times 1$  for all cases.

## 3. Results and discussion

### 3.1. Stability and structural properties

In order to find stable configurations of 2D lithium halides monolayers energetically, we have optimized buckled and planar configurations of these nanostructures. The geometry optimization results predicted cubic structures for these ionic monolayers which are in excellent agreements with previous calculations for alkali halide nanotubes and nanosheets [14,25]. The top- and side-view of buckled and planar Li halides monolayers are schematically shown in Fig. 1. The optimized parameters, i.e. lattice constant, bond length, thickness, angle between each three close atoms and cohesive energy for both configurations are presented in Table 1. The optimized lattice constants of buckled LiF, LiCl and LiBr monolayers within PBE are 3.77, 4.34 and 4.52 Å, respectively. The corresponding values within HSE06 for the same structures are 3.74, 4.30 and 4.48 Å. It is found that the lattice parameter for buckled configuration of LiF monolayer (3.77 Å) is slightly larger than planer one (3.75 Å). In contrast, LiCl and LiBr lattice parameters in buckled configuration are significantly smaller than those in planer structure. Hence the thickness of buckled LiCl and LiBr monolayers is greater than LiF monolayer. Compared to F, Cl and Br have larger atomic radii. Consequently,  $\pi$  bonds in LiCl and LiBr formed by coupling of adjacent  $p_z$  orbitals are much weaker than those in LiF due to the longer interatomic distance. To examine the energetic stability of the 2D Li halides nanostructures, the cohesive energy per atom has been calculated as defined by Ref. [39] Table 2

$$E_{coh} = \left( \sum_i E_i - E_t \right) / n \quad (7)$$

where  $E_t$ ,  $E_i$  and  $n$  denote the total energy per cell, the energy of the  $i$ -th isolated atom and the total number of atoms per cell. The results exhibit that the cohesive energy for buckled and planar configurations is positive and cohesive energy of buckled configurations is greater than those of planar structures, hence buckled configurations of these structures are energetically more favorable than planar ones. The positive cohesive energy for these systems cannot determine whether the free-standing state of these structures would exist in practice. To this end, the phonon dispersion

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