FIRST-PRINCIPLES CALCULATION OF ELECTRONIC PROPERTIES OF MONOELEMENT 2D MATERIALS

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I. INTRODUCTION

Atomically thin two-dimensional (2D) materials have made their way to the forefront of several research areas including batteries, electrocatalysis, electronics, and photonics [1]. This development has been prompted by the intriguing and easily tunable properties of atomically thin crystals and is fueled by the constant discovery of new 2D materials and the emergent concepts of lateral [2] and vertical [3] 2D heterostructures, which opens completely new possibilities for designing materials with tailored and superior properties. So far more than fifty compounds have been synthesised or exfoliated as single layers. These include the well-known monoelemental crystals and their ligand functionalised derivatives, transition metal

dichalcogenides, transition metal carbides and -nitrides, group III-V semiconductors and insulators, transition metal halides, post-transition metal chalcogenides and organic-inorganic hybrid perovskites.

In the search for new materials with tailored properties or novel functionalities, first-principles calculations are playing an increasingly important role. The continuous increase in computing power and significant advancements of theoretical methods and numerical algorithms have pushed the field to a point where first-principles calculations are comparable to experiments in terms of accuracy and greatly surpass them in terms of speed and cost. Structural, thermal, and electronic properties, have been a cornerstone of materials science, and in the past decade, the experimental data have been augmented by an explosion of computational data obtained from first-principles calculations. Density functional theory (DFT) methods, when properly conducted, are quite reliable for ground state properties such as structural and thermodynamic properties, they are generally not quantitatively accurate for excited state properties such as electronic band structures and optical absorption spectra.

In this work we did DFT calculations to investigation electronic properties of monoelemental 2D materials previously unknown and potentially synthesisable monolayers.

II. METHODS AND RESULTS

Calculations of the total energy and electronic structure of the materials under study were performed using the VASP software package. For the basis of plane waves, a cutoff energy of 520 eV was taken. To avoid mirror interactions of wave functions with each other arising from the translation of cells in a plane model of 2D systems, periodic plates were separated by a 15 Å-thick vacuum layer along the crystallographic direction c. The nonbonding van der Waals interaction (vdW) between atoms is taken into account when using the semiempirical Green's dispersion correction scheme with Becke and Johnson's corrections (BJ-damping). Integration in the momentum space of the Brillouin zone was carried out using a k-point grid generated by the Monkhorst-Pack scheme with an inverse spatial resolution of $2\pi \times 0.03$ Å^{-1}.

Electronic band structures are calculated along the high symmetry paths of 2D Bravais lattices. The band energies are computed within DFT using two different xc-functionals, namely PBE and HSE06. The electron density is determined self-consistently on a uniform k-point grid of density 10.0/ Å^{-1}. From this density, the PBE band structure is computed non-selfconsistently at 200 k-points distributed along the band path. The band structure is calculated non-selfconsistently using the range-separated hybrid functional HSE06 on top of a PBE calculation with k-point density 12.0/ Å^{-1} and 600 eV plane wave cutoff.

Table 1 shows the results of calculating the electronic properties of monoelement 2D materials using PBE and HSE06 xc-functionals. Band gap, and the type of semiconductor for the compounds under study is indicated. The results obtained may differ from the experimental ones in the direction of underestimating the band gap due to the well-known difficulties arising in the framework of the density functional theory.

Table 1. Electronic properties of monoelement 2D materials

XC-functional	Parameter	Monoelement 2D material								
		C_2	Si_2	Ge_2	Sn_2	Pb_2	P_2	As_2	Sb_2	Bi_2
PBE	Band gat, eV	0.000				–	1.987	1.564	1.485	0.568
	Band character	Semimetallic				Metallic	Indirect			Direct
	Junction type	K - K				–	K - M	G - M	G - M	G - G
HSE06	Band gat, eV	0.000				–	2.753	2.189	1.183	0.977
	Band character	Semimetallic				Metallic	Indirect			Direct
	Junction type	K - K				–	G - M			G - G

The band structures of the studied monoelement 2D materials were obtained and according to which the type of conductivity was established. It was found that C_2, Si_2, Ge_2 and Sn_2 are semimetals with direct transitions. P_2, As_2 and Sb_2 are indirect-gap semiconductors with bandgaps of 2.753, 2.189 and 1.183 eV, respectively. Bi_2 is a direct-gap semiconductor with a band gap of 0.977 eV. Pb_2 is a 2D metal-type material. The Fermi level in this case crosses the conduction bands.

III. CONCLUSIONS

Analysis of band structures indicates the presence of semiconductors and conductors among the studied group of monoelement 2D materials. The results obtained quantitatively and qualitatively characterize the structural, electronic properties of crystal structures based on 2D materials and can be used in the development of methods for calculating the basic electrophysical parameters of promising devices for nanoelectronics and spintronics.

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