

Electronic structure of two-dimensional crystals from *ab initio* theory

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We report on *ab initio* calculations of the two-dimensional systems MoS₂ and NbSe₂, which recently were synthesized. We find that two-dimensional MoS₂ is a semiconductor with a gap which is rather close to that of the three-dimensional analog, and that NbSe₂ is a metal, which is similar to the three-dimensional analog of this compound. We further computed the electronic structure of the two-dimensional hexagonal (graphene-like) lattices of Si and Ge and compared them with the electronic structure of graphene. It is found that the properties related to the Dirac cone do not appear in the case of two-dimensional hexagonal germanium, which is metallic, contrary to two-dimensional hexagonal silicon, also known as silicene, which has an electronic structure very similar to the one of graphene, making them possibly equivalent.

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I. INTRODUCTION

During several years, it was believed that the existence of free-standing two-dimensional (2D) crystals was impossible, because they would ultimately return to a three-dimensional (3D) object.^{1,2} This is because thermal fluctuations should lead to atomic displacements of the same magnitude as the distance between atoms and therefore would make the crystal unstable. Also, it is known experimentally that thin films cannot be synthesized below a certain thickness, because formation of islands or even decomposition is occurring. However, it appeared recently that isolated sheets of graphene could be obtained by mechanical exfoliation of a graphite crystal, which therefore proves the predictions of Refs. 1 and 2 to be questionable.³ This issue was (at least partially) solved when it was shown⁴ that free-standing graphene sheets display spontaneous ripples, and therefore graphene is not perfectly flat. The experimental accomplishment of synthesizing two-dimensional crystals has led to the emergence of a truly different physics since the particular properties of graphene can be considered as a bridge between quantum electrodynamics (QED) and condensed-matter physics.⁵ Indeed, near the *K* point of the Brillouin zone, the one-particle energy dispersion is linear with the momentum, and therefore the corresponding quasiparticles could be described by a Dirac-type Hamiltonian. Then, QED properties can be studied by investigating the electronic structure of graphene.

Later on, it was shown⁶ that the same technique could be used to obtain other compounds, opening the path to the investigation of a large number of two-dimensional crystals. However, it seems that most of the experimental and theoretical efforts in this area are still focusing exclusively on graphene, primarily because of the high quality of samples that could be obtained. In the present paper, we investigate by means of *ab initio* calculations the electronic structure of MoS₂ and NbSe₂, as they have been synthesized experimentally,⁶ as well as hypothetical two-dimensional hexagonal crystals (with a graphene-like structure) made of Si and Ge.

II. COMPUTATIONAL DETAILS

To perform the calculations, we have used density-functional theory (DFT) (Refs. 7 and 8) as implemented in the code VASP (Vienna *ab-initio* simulation package),^{9,10} within the framework of the PAW (projector augmented wave) method.¹¹ The local-density approximation¹² (LDA) as well as the Perdew-Burke-Ernzerhof¹³ variant of the generalized gradient approximation (GGA) were used for the exchange-correlation potential. A cutoff of 500 eV was used for the plane-wave expansion of the wave function to converge the relevant quantities. For Brillouin-zone integrations, a mesh of $40 \times 40 \times 1$ *k* points¹⁴ was used for MoS₂ and NbSe₂, while a mesh of $20 \times 20 \times 3$ was sufficient to describe two-dimensional silicon and germanium.

Concerning the crystal structure MoS₂ and NbSe₂ we used the experimental bulk values since it was noticed in Ref. 6 that 2D crystals in these cases remain very close to their 3D parents. In this case, GGA was used. For the two-dimensional hexagonal crystals made of Si and Ge, we optimized the lattice parameter using either the LDA or the GGA. Moreover, it appeared that the band structure obtained using either LDA or GGA was very similar, so we have chosen to show only results corresponding to LDA. For all studies here, the “*c*” parameter was taken to be large enough to ensure that no interaction remains between layers, making them effectively isolated 2D objects.

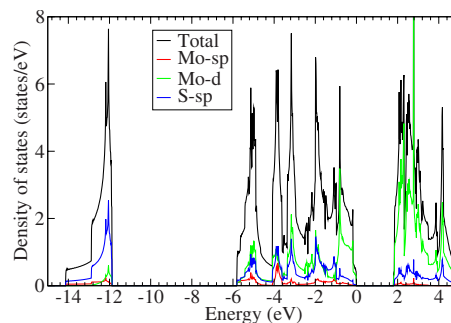


FIG. 1. (Color online) The density of states of two-dimensional MoS₂. The Fermi level is set at 0 eV.

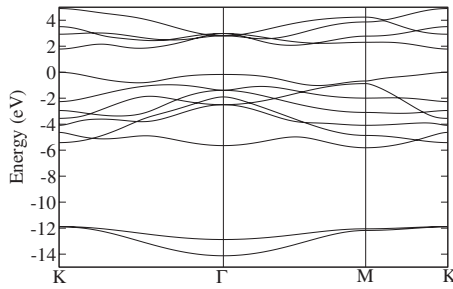


FIG. 2. The band structure of two-dimensional MoS₂. The Fermi level is set at 0 eV.

III. ELECTRONIC STRUCTURE OF TWO-DIMENSIONAL MoS₂ AND NbSe₂

A. MoS₂

There is a big interest in transition-metal dichalcogenides since, due to their layered structure, they have extremely anisotropic properties, and therefore an intercalation process is easy to conduct. In particular, MoS₂ is used in the technology of Li batteries. To investigate purely two-dimensional MoS₂, we have used the bulk lattice parameter ($a=3.16$ Å), as reported in Ref. 15. Since reduced dimensionality can sometimes lead to magnetic behavior in systems which are not magnetic in bulk, we checked the possibility to have a spin-polarized ground state, but it was found that two-dimensional MoS₂ remains in a nonmagnetic state.

Our calculated density of states (DOS) is presented in Fig. 1. As for three-dimensional MoS₂, the two-dimensional variant of this compound is semiconducting: the bands on each side of the band gap are derived mainly from the Mo- d states, which is what a calculation of three-dimensional MoS₂ also shows.¹⁶ Also, a large gap exists in the occupied states, separating the S- s states (between -14 and -12 eV) and the hybridized Mo and S- p states (between -6 and 0 eV).

In Fig. 2, we present the energy bands of two-dimensional MoS₂. We see again a lot of similarities with three-dimensional MoS₂: the bands around the band gap are relatively flat, as expected from the “ d ” character of the electron states at these energies. The band gap, which has a value of 1.78 eV, is direct and occurs at the high-symmetry point K , whereas for three-dimensional MoS₂ the band gap is indirect.¹⁶

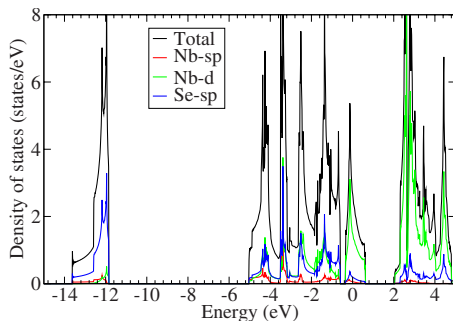


FIG. 3. (Color online) The density of states of two-dimensional NbSe₂. The Fermi level is set at 0 eV.

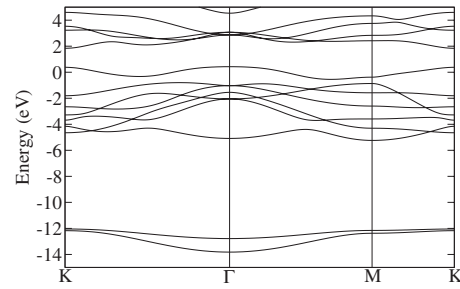


FIG. 4. The band structure of two-dimensional NbSe₂. The Fermi level is set at 0 eV.

B. NbSe₂

As for MoS₂, the NbSe₂ structure is strongly layered, with each Nb layer being sandwiched between two Se layers, where weak van der Waals forces are holding the whole geometry together. NbSe₂ is known to be a prototype to study charge-density waves and is also a superconductor. Here we focus only on the electronic structure of two-dimensional NbSe₂ and a lattice constant of 3.45 Å (Ref. 17) was used to perform the calculation.

As for MoS₂, we have checked the existence of a magnetic solution, since the non-spin-polarized DOS (Fig. 3) is very peaked at the Fermi level, but we found again a non-magnetic ground state. However, contrary to MoS₂, two-dimensional NbSe₂ is metallic, just like the three-dimensional version of this compound. The DOS of two-dimensional NbSe₂ shows a lot of similarities with the one of MoS₂, with a large hybridization between Nb and Se states. In addition, the band state which is pinned at the Fermi level is derived primarily from Nb d orbitals, and this band state becomes separated in energy from all other states (Fig. 4).

IV. ELECTRONIC STRUCTURE OF TWO-DIMENSIONAL SI AND GE

With four “ sp ” electrons in the valence band, silicon and germanium (possibly together with boron nitride) are probably the closest to carbon from a chemical point of view. Therefore, it is of interest to see if in their two-dimensional

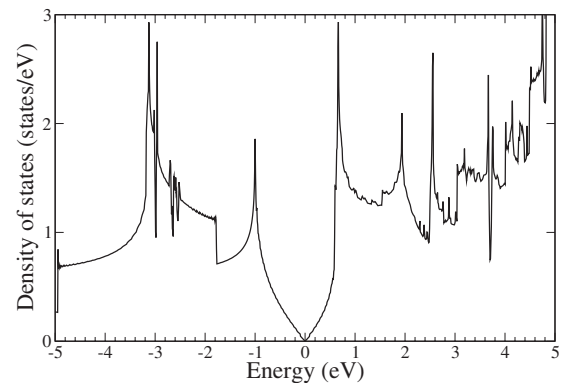


FIG. 5. The density of states of two-dimensional Si. The Fermi level is set at 0 eV.

TABLE I. Lattice parameters of hexagonal Si and Ge computed with either LDA or GGA.

System	LDA (Å)	GGA (Å)
Si	3.860	3.901
Ge	4.034	4.126

form they could present some similarities with graphene, and we have investigated this possibility here.

In Table I, we present our computed lattice parameters (see Sec. II) for hexagonal Si and Ge. As expected, they are larger than the one of graphene (2.46 Å) because of the larger radius of Si and Ge in comparison with C. Also, because of the well-known overbinding of LDA, GGA gives lattice parameters which are larger than the ones given by LDA.

We used these lattice parameters for the calculation of the corresponding densities of states and band structures. As seen in Figs. 5 and 6, two-dimensional silicon shows a lot of similarities with graphene: in particular the gap is also closing at the K point of the Brillouin zone, and the dispersion around this point is linear. In contrast, two-dimensional germanium is quantitatively different from graphene (Figs. 7 and 8): a conduction band is partially filled by electrons around the Γ point and therefore the bands at the K point are shifted up in energy, so that two-dimensional germanium is not a zero-gap material, but rather a poor metal. For three-dimensional germanium, it is known that LDA or GGA gives a non-band-gap behavior, and a more advanced technique such as the GW approximation^{18–20} is required to obtain a band gap. However, our calculations with DFT show that two-dimensional germanium is much more metallic than three-dimensional germanium, and therefore the metallic nature is here much more robust and is likely to be preserved even if a quasiparticle theory (such as the GW approximation) would be used.

V. CONCLUSION

We have studied by means of *ab initio* calculations the electronic structure of two-dimensional MoS_2 and NbSe_2 , as

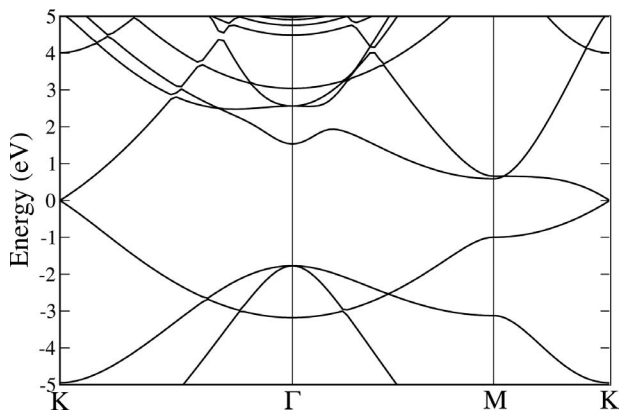


FIG. 6. The band structure of two-dimensional Si. The Fermi level is set at 0 eV.

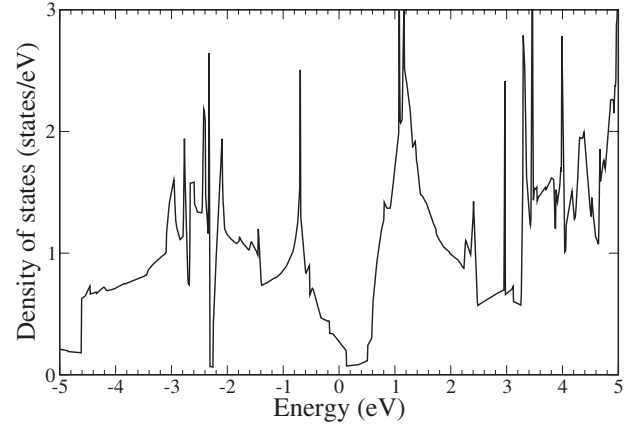


FIG. 7. The density of states of two-dimensional Ge. The Fermi level is set at 0 eV.

well as hypothetical graphene-like structures of Si and Ge. We have found that two-dimensional silicon might from an electronic structure point of view be equivalent to graphene, with a linear dispersion of the electronic structure around the K point. The possible advantage with Si in this regard is that it probably is more easily interfaced with existing electronic devices and technologies. The obvious disadvantage is that sp^2 -bonded Si is much less common than for C, and the synthesis of Si in a graphene-like structure is extremely demanding and is likely to represent a metastable material. The electronic structure of Ge (Figs. 7 and 8) in the graphene structure results in a metallic behavior and the electronic structure of two-dimensional MoS_2 and NbSe_2 is quite similar to that of the three-dimensional counterparts, with MoS_2 being a gapped system with a direct gap and NbSe_2 a metal.

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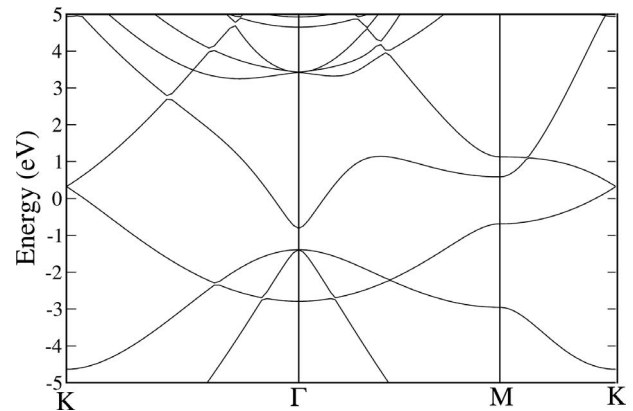


FIG. 8. The band structure of two-dimensional Ge. The Fermi level is set at 0 eV.

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