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

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Abstract

We report on ab-initio calculations of the two-dimensional systems MoS\textsubscript{2} and NbSe\textsubscript{2}, which recently were synthesized. We find that two-dimensional MoS\textsubscript{2} is a semiconductor with a gap which is rather close to that of the three dimensional analogue, and that NbSe\textsubscript{2} is a metal, which is similar to the three dimensional analogue of this compound. We further computed the electronic structure of the two-dimensional hexagonal (graphene like) lattices of Si and Ge, and compare 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, 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 crystals was impossible, because they would be unstable and ultimately return to a three dimensional object\textsuperscript{1,2}. 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 Ref.\textsuperscript{1,2} to be inaccurate\textsuperscript{3}. The experimental accomplishment of synthesizing two-dimensional crystals has lead to the emergence of a truly new physics, since the particular properties of graphene can be considered as a bridge between quantum electrodynamics (QED) and condensed matter physics\textsuperscript{4}. Indeed, near the $K$ point of the Brillouin zone (BZ), the one-particle energy dispersion is linear with the momentum, and therefore the corresponding quasiparticles could be described by a Dirac-like Hamiltonian. Then, QED properties can be studied by investigating the electronic structure of graphene.

Later on, it was shown\textsuperscript{5} 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 MoS\textsubscript{2} and NbSe\textsubscript{2}, as they have been synthesized experimentally\textsuperscript{5}, 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)\textsuperscript{6,7} as implemented in the code VASP (Vienna Ab-initio simulation package)\textsuperscript{8,9}, within the framework of the PAW (projector augmented waves) method\textsuperscript{10}. The Local Density Approximation\textsuperscript{11} (LDA) as well as the Perdew Burke Ernzerhof\textsuperscript{12} variant of the generalized gradient approximation (GGA) were used for the exchange-correlation potential. A cut-off 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 $40 \times 40 \times 1$ $k$-points\textsuperscript{13} was used for MoS\textsubscript{2} and NbSe\textsubscript{2}, while a mesh of $20 \times 20 \times 3$ was sufficient to describe two-dimensional silicon and
Concerning the crystal structure MoS$_2$ and NbSe$_2$ we used the experimental bulk values since it was noticed in Ref. 5 that 2D crystals in these cases remains 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 were 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.

III. THE ELECTRONIC STRUCTURE OF TWO-DIMENSIONAL MoS$_2$ AND NbSe$_2$

A. MoS$_2$

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, MoS$_2$ is used in the technology of Li batteries. To investigate purely two-dimensional MoS$_2$, we have used the bulk lattice parameter ($a = 3.16$ Å), as reported in Ref 14. Since reduced dimensionality can sometimes leads 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 MoS$_2$ remains in a non-magnetic state.

Our calculated DOS is presented in Fig 1. As for three-dimensional MoS$_2$, 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 MoS$_2$ also shows. 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 MoS$_2$. We see again a lot of similarities with three dimensional MoS$_2$: 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
FIG. 1: The density of states of two-dimensional MoS$_2$. The Fermi level is put at zero eV.

FIG. 2: The band structure of two-dimensional MoS$_2$. The Fermi level is put at zero eV.

point $K$, whereas for three dimensional MoS$_2$ the band gap is indirect$^{15}$.

B. **NbSe$_2$**

As for MoS$_2$, the NbSe$_2$ 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. NbSe$_2$ is known to be a prototype to study charge density waves (CDW), and is also a superconductor. Here we focus only on the electronic structure of two-dimensional NbSe$_2$ and a lattice constant of 3.45 Å$^{15}$ was used to perform the calculation.

![Graph](image)

**FIG. 3:** The density of states of two-dimensional NbSe$_2$. The Fermi level is put at zero eV.

As for MoS$_2$, 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 MoS$_2$, two dimensional NbSe$_2$ is metallic, just like the three dimensional version of this compound. The DOS of two-dimensional NbSe$_2$ shows a lot of similarities with the one of MoS$_2$, 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 Nd d-orbitals, and this band state becomes separated in energy from all other states (Fig. 4).

**IV. THE ELECTRONIC STRUCTURE OF TWO-DIMENSIONAL SI AND GE**

With four 'sp' electrons in the valence band, silicon and germanium (possibly together with BN) are probably the closest to carbon from a chemical point of view. Therefore, it is of interest to see if in their two-dimensional form they could present some similarities with graphene, and we have investigated this possibility here.

In Table II we present our computed lattice parameters (see computational section) 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: 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/GGA gives a non band-gap behavior, and a more advanced technique like the GW approximation\textsuperscript{17,18,19} is required to obtain a

| System | LDA  | GGA  |
|--------|------|------|
| Si     | 3.860 Å | 3.901 Å |
| Ge     | 4.034 Å | 4.126 Å |

TABLE I: Lattice parameters of hexagonal Si and Ge computed with either LDA or GGA.
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 (like 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 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 meta-stable material. The electronic structure of Ge 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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