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Quantum valley Hall state in gas molecule-adsorbed bilayer graphene

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ABSTRACT

While a variety of topologically nontrivial insulator phases have been predicted to arise from electron-electron and spin-orbit interactions in bilayer graphene, the trigonal warping of conduction and valence bands leads to a (semi)metallic band structure. An electrostatic potential difference between the two layers due to an external electric field is known to open a bandgap, leading to a topologically nontrivial insulator state. A bandgap may also arise from gas molecules adsorbed on bilayer graphene, implying a topologically nontrivial insulator phase. Here, our density functional theory calculations show that bilayer graphene adsorbing gas molecules is a quantum valley Hall insulator. Thus, adsorption of weak donor (or acceptor) molecules with a large electric dipole moment may be instrumental to realize a topologically nontrivial insulator phase in bilayer graphene even without external electric field.

1. Introduction

Graphene has been one of the most interesting issues in recent years. Charge carriers in monolayer graphene are massless chiral particles with a linear energy dispersion described by a Dirac-like effective Hamiltonian [1]. Bilayer graphene has no bandgap like monolayer graphene but shows a quadratic low-energy dispersion of a massive chiral particle, contrasting to the linear dispersion in monolayer graphene [2]. The bandgap in bilayer graphene can be controlled by an external electric field perpendicular to the layer [3–6], providing a very useful way for graphene field effect devices. In the presence of spin-orbit interaction, monolayer graphene is expected to be a quantum spin Hall (QSH) insulator [7], triggering a great interest in the topologically nontrivial states, although the spin–orbit interaction-induced bandgap is so small that topological effect is not easily confirmed experimentally. Spin-orbit interactions in bilayer graphene are also expected to give rise to a variety of topologically nontrivial insulator phases [8–10].

The quadratic bands in bilayer graphene, touching at low energies and resulting in non-vanishing density of states, have been predicted to be unstable to the electron-electron interactions leading to a broken symmetry state. A number of broken symmetry states, gapped or gapless, have been theoretically suggested in bilayer graphene, including a variety of topologically nontrivial insulator phases [11–14]. Contradicting results, supporting gapped or gapless states, have been reported in experiments or in the theoretical suggestions [15–17]. Renormalization group (RG) studies indicated that the quadratic bands are unstable to arbitrarily weak interactions and that the resulting broken symmetry states are sensitive to microscopic details [12].

In practice, due to the trigonal warping of conduction and valence bands, bilayer graphene has no bandgap, requiring a finite interaction for the broken symmetry states, and the interaction effects can be more pronounced under a perpendicular electric field [2]. Density functional theory (DFT) and tight binding (TB) model calculations showed that, due to the trigonal warping, the band structure of bilayer graphene has no gap in spite of a spin-orbit splitting of about 24 μeV, bandgap opening requiring an electric field perpendicular to the layer [18]. The electric field-induced bandgap in bilayer graphene has been well investigated by DFT and TB studies [3–6,18]. In a phase diagram suggested by the TB models [8–10], bilayer graphene was predicted to be a quantum valley Hall (QVH) insulator for a weak Rashba spin-orbit interaction and, even in the absence of a Rashba spin-orbit interaction, bilayer graphene under an electric field is expected to be a QVH insulator with a valley Chern number $C_v = 4$. The QVH state with $C_v = 4$ supposedly arises from electron-electron interactions according to RG studies [12]. In the presence of exchange field, bilayer graphene was revealed by TB and RG studies to be a quantum anomalous Hall insulator with a (charge) Chern number $C = 4$ [8–10,12,13].

On the other hand, gas molecules adsorbed onto bilayer gaphene were recently shown to open a bandgap arising from charge transfer-induced electrostatic potential difference between

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the layers [19]. Adsorption of gas molecules has long been investigated in single layer graphene, mostly in view of the adsorption configuration and the binding energy [20–29]. The gas molecules are adsorbed onto graphene by the van der Waals interaction acting as dopants. While adsorption of gas molecules onto graphene has been mostly investigated in view of electronic applications, hydrogen storage, and solid-state gas sensors, one can readily expect that the gas molecule-adsorbed bilayer graphene with a bandgap would be a topologically nontrivial insulator.

In this work, we have employed DFT calculations in order to confirm the topological nature of gas molecule-adsorbed bilayer graphene. We have investigated the adsorption of H_2, N_2, CO, and NO_2 gas molecules. Adsorption of H_2 onto graphene has been extensively studied for hydrogen storage [21,22], and H_2 can be easily adsorbed onto a number of materials due to its small size. N_2 is the most abundant gas in air, possibly competing with H_2 in hydrogen storage devices based on graphene [23]. While O_2 is highly reactive and abundant in air, O_2-adsorbed graphene is known to be metallic [25]. CO and NO_2 are well-known pollutants, high sensitivity detection of which has been investigated by using graphene [26–29]. On the other side, H_2 and N_2 are nonmagnetic nonpolar molecules. CO is a nonmagnetic polar molecule, and NO_2 is a paramagnetic polar molecule. By investigating the adsorption of these gas molecules, we can expect to clarify the effects of the electrostatic potential difference and the exchange field on the topological nature of bilayer graphene.

Our DFT calculations show that bilayer graphene with adsorbed gas molecules is a QVH insulator with $C_v = 4$ even without an external electric field when the Fermi level lies in the bandgap. The exchange field effect of paramagnetic NO_2 molecules on bilayer graphene would be negligible. The Fermi levels of N_2- and CO-adsorbed bilayer graphene already lie in the bandgap, requiring no further control of the Fermi level. Adsorption of NO_2, which is a strong acceptor with a large electric dipole, gave the largest bandgap with the Fermi level in the valence band. Thus, adsorption of weak donor (or acceptor) molecules with a large electric dipole, which opens a large bandgap with the Fermi level lying in the gap, appears to be a promising candidate to realize a topologically nontrivial insulator phase in bilayer graphene even without external electric field.

2. Methods

Bernal-stacked bilayer graphene was considered as a two-dimensional system with a lattice constant $a = 2.46$ Å and an interlayer separation $D = 3.35$ Å. The vacuum spacing between the bilayer graphene was set to 24 Å, the gas molecules being adsorbed only on the upper layer of the bilayer graphene. A single gas molecule was modeled in a $2 \times 2 \times 1$ supercell of bilayer graphene. A SIESTA package [30], using a localized linear combination of numerical atomic-orbital basis sets, was employed to locate the adsorbed molecules. The atomic coordinates were optimized by using conjugated gradients method with a maximum force tolerance of 0.01 eV/Å. Norm-conserving scalar-relativistic pseudopotentials and a local density approximation (LDA) of Perdue and Zunger [31] form were used for the exchange-correlation potential. An energy cutoff of 210 Ry and k-points of $16 \times 16 \times 1$ mesh in a Monkhorst-Pack scheme were used. While the van der Waals forces were not included in the LDA functionals, adsorption of gas molecules has been well described by LDA functionals [19,21–28]. Spin-orbit interactions were not considered and spin-unpolarized calculations were used if not specified.

A Quantum Espresso package, using plane waves as the basis set for the wavefunctions, was employed for electronic structure

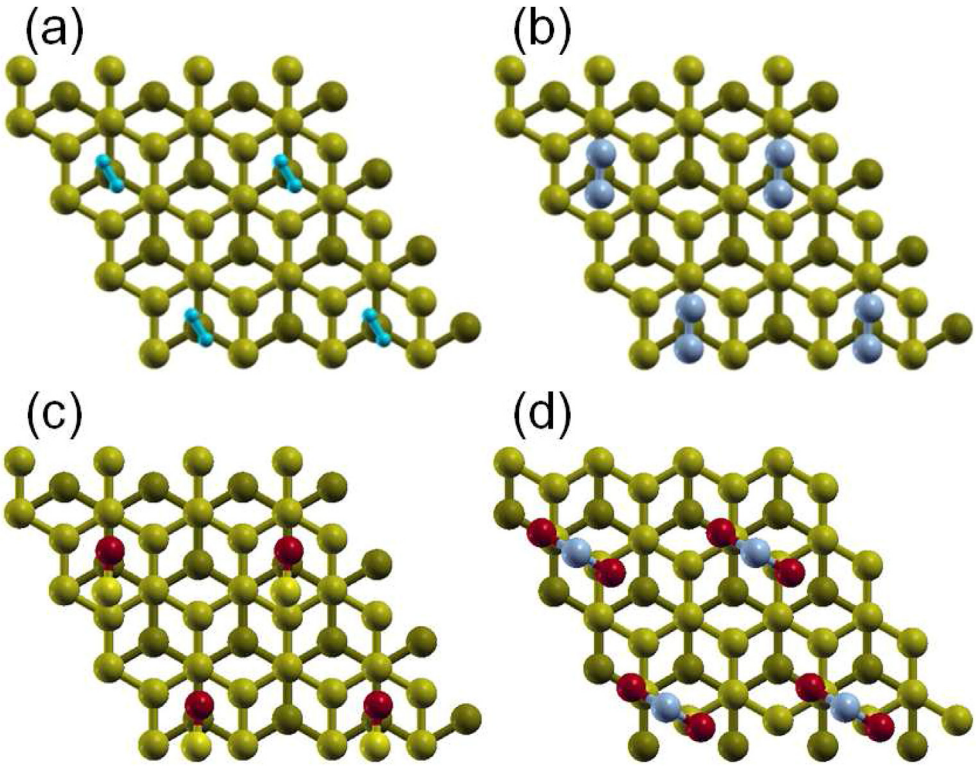

Fig. 1. (Color online) Optimized geometries of gas molecule-adsorbed bilayer graphene for (a) bgH2, (b) bgN2, (c) bgCO, and (d) bgNO2. The cyan, cobalt, and red spheres correspond to hydrogen, nitrogen, and oxygen atoms, respectively. Bright and dark yellow spheres correspond to the carbon atoms in the upper and lower layers, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)