Engineering Quantum Spin Hall Effect in Graphene Nanoribbons via Edge Functionalization

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Kane and Mele predicted that in presence of spin-orbit interaction graphene realizes the quantum spin Hall state. However, exceptionally weak intrinsic spin-orbit splitting in graphene ($\approx 10^{-5} \text{eV}$) inhibits experimental observation of this topological insulating phase. To circumvent this problem, we propose a novel approach towards controlling spin-orbit interactions in graphene by means of covalent functionalization of graphene edges with functional groups containing heavy elements. Proof-of-concept first-principles calculations show that very strong spin-orbit coupling can be induced in realistic models of narrow graphene nanoribbons with tellurium-terminated edges. We demonstrate that electronic bands with strong Rashba splitting as well as the quantum spin Hall state spanning broad energy ranges can be realized in such systems. Our work thus opens up new horizons towards engineering topological electronic phases in nanostructures based on graphene and other materials by means of locally introduced spin-orbit interactions.

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In their pioneering paper, Kane and Mele showed that in the presence of spin-orbit coupling graphene becomes a two-dimensional $Z_2$ topological insulator or, in other words, realizes the quantum spin Hall (QSH) state [1]. This topologically non-trivial insulating phase is characterized by the presence of spin-filtered edge states protected from elastic back-scattering and localization by time-reversal symmetry. While the prediction of Kane and Mele contributed tremendously to the development of the emerging field of topological insulators [2–4], no QSH effect in graphene has been observed experimentally. The reason being that the exceptionally weak intrinsic spin-orbit coupling in graphene results in a band gap of the order of only $10^{-5} \text{eV}$, according to recent theoretical predictions [5–7].

Subsequent efforts have focused on circumventing the problem of weak intrinsic spin-orbit coupling in graphene. One proposed approach for enhancing spin-orbit interactions is based on the effect of adatoms on the electronic structure of graphene [8–9]. More recently, several groups have demonstrated theoretically by depositing the adatoms of heavy elements with large magnitudes of atomic spin-orbit splitting it is possible to increase the spin-orbit gap up to tens meV [10–13]. However, realizing such this strategy in practice will inevitably face the challenge of uniform deposition since adatoms are mobile citecha08,yaz10b and tend to form aggregates due to attractive interactions. Moreover, large metal adatoms coverages required for enhancing spin-orbit coupling in graphene result in strong doping [11,14,15] while covalently bonded species such as hydrogen adatoms give rise to undesired resonant states [16,17].

In this paper, we propose an alternative approach for engineering spin-orbit interactions in graphene based on covalent chemical functionalization of the edges. The edges of graphene nanostructures provide a natural interface for coupling heavy-element functional groups to the $\pi$-electron states of graphene. By using a modification of the Kane-Mele model we show that through introducing spin-orbit interaction locally, only at the edges, it is possible to realize the QSH state in narrow graphene nanoribbons. We then focus our attention on realistic models of tellurium (Te) terminated graphene nanoribbons which can be produced using current methods of synthetic chemistry. Our first-principles calculations show that very strong spin-orbit coupling can be induced in narrow Te-terminated graphene nanoribbons. In particular, we discuss in detail two configurations that exhibit the presence of a parabolic band with strong Rashba splitting and the robust QSH state spanning a broad energy range, respectively.

The band structure of graphene nanoribbons can be described accurately using the one-orbital nearest-neighbor tight-binding model. Following Kane and Mele, it is possible to include the intrinsic spin-orbit coupling by adding a second-nearest-neighbor complex term with sign dependent on the spin of electron and the hopping direction $\mathbf{1}$. The resulting Hamiltonian reads

\begin{equation}
\mathcal{H} = -t \sum_{\langle i,j \rangle,\sigma} c_{i\sigma}^\dagger c_{j\sigma} + i\lambda_{\text{so}} \sum_{\langle\langle i,j \rangle\rangle,\sigma} \nu_{ij} c_{i\sigma}^\dagger \sigma_z c_{j\sigma},
\end{equation}

where $\langle i, j \rangle$ and $\langle\langle i, j \rangle\rangle$ indicate the pairs of first and second nearest neighbors [Fig. 1a], respectively, and $\sigma$ is the spin index. Parameter $t \approx 2.7 \text{eV}$ is the tight-binding hopping energy [18] while $\lambda_{\text{so}}$ defines the strength of spin-orbit coupling. $\nu_{ij} = \pm 1$ is the site-dependent Haldane factor given by $\nu_{ij} = (\mathbf{d}_{ik} \times \mathbf{d}_{jk})/(|\mathbf{d}_{ik} \times \mathbf{d}_{jk}|)$ with $\mathbf{d}_{ik}$ and $\mathbf{d}_{jk}$ being the vectors connecting second nearest neighbors $i$ and $j$ with their common neighbor $k$. $\sigma_z$ is the corresponding Pauli matrix describing the spin of the electron.

The introduction of the spin-orbit term opens a band gap $\Delta_{\text{so}} = 6\sqrt{3}\lambda_{\text{so}}$ at the Dirac points of otherwise semimetallic graphene making it a two-dimensional $Z_2$ topological insulator. When one-dimensional nanostructures of graphene are considered, spin-orbit coupling lifts the degeneracy of zero-energy edge states [20,22] resulting in a crossing of linear dispersion bands as illustrated in Fig. 1b for the case of a narrow graphene strip (nanoribbon). At this band crossing the electronic states of opposite spins are localized at the opposite edges of the nanoribbon while time-reversal symmetry is...
preserved. In other words, the nanoribbon is in the QSH state.

Let us now consider a situation in which spin-orbit interaction are introduced only at the edges due to, for instance, the presence of heavy-element functional groups terminating the edges due to finite size effects and the fact that low-energy states are strongly localized at the edges. One can expect that such local spin-orbit coupling will have a significant effect on the behavior of the system.

We would now like to discuss the possible competing role of electron-electron interactions in graphene systems with locally induced spin-orbit interactions. For the purpose of our discussion we introduce into our Hamiltonian the Hubbard term of the form

$$\mathcal{H} = U \sum_i n_{i\uparrow} n_{i\downarrow},$$

where $n_{i\sigma} = \frac{1}{2} (\psi_{i\sigma}^\dagger \psi_{i\sigma} + \psi_{i\sigma} \psi_{i\sigma}^\dagger)$ is the spin-resolved electron density on site $i$ and $U > 0$ defines the magnitude of the on-site Coulomb repulsion. For practical reasons, we evaluate this term using the mean-field approximation

$$\mathcal{H}_{\text{mf}} = U \sum_i (n_{i\uparrow} \langle n_{i\downarrow} \rangle + n_{i\downarrow} \langle n_{i\uparrow} \rangle - \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle).$$

In the absence of spin-orbit coupling the introduction of electron-electron interactions results in a magnetically ordered state characterized by ferromagnetic correlations along...
FIG. 2: (Color online) Magnitude of the QSH marker $M_{ik}$ as a function of energy $E$ and spin-orbit coupling strength $\lambda_{so}$ for a zigzag nanoribbon in the Kane-Mele model with (a) a full spin-orbit coupling term and (b) spin-orbit interactions introduced only at the edges. The dashed lines in (a) indicate the bulk spin-orbit gap $\Delta_{so}$. The dotted lines delimit the regions of existence of electronic phases driven by electron-electron interactions. (c) Schematic drawing of the evolution of edge-state band dispersion upon increasing $\lambda_{so}$ in the presence of electron-electron interactions.

In order to provide a proof of concept of the presented model we performed a detailed first-principles investigation of realistic models of graphene nanoribbons with edges terminated by functional groups containing heavy elements. Our first-principles calculations were performed within the density functional theory framework employing the local density approximation (LDA) as implemented in the QUANTUM-ESPRESSO package [32]. Spin-orbit effects were accounted for using fully relativistic pseudopotentials acting on valence electron wavefunctions represented in the two-component spinor form [33]. A plane-wave cutoff of 30 Ry was used for the wave-functions. Atomic positions were fully relaxed. Below, we focus on two representative examples involving tellurium (Te), a heavy element with large atomic spin-orbit splitting [29] and chemical properties very similar to that of isoelectronic sulfur for which synthetic organic chemistry is well established. The atomic configurations of the proposed model systems are motivated by the recent advances in producing atomically-precise graphene nanoribbons as discussed below. The first configuration represents a 1-nm-wide armchair graphene nanoribbon with edge termination composed of very stable tellurophene fragments. Such narrow armchair nanoribbons can be produced with atomic precision using the recently developed chemical self-assembly route [34]. Fairly complex nanostructures based on thiophene units (the sulfur analogue of tellurophene) can be synthesized using standard organic chemistry methods (for examples, see Ref. [35]). The second configuration is a zigzag graphene nanoribbon with a larger Te coverage density at the edges. The sulphur analogues of such nanostructures have been produced recently by fusing sulfur-rich precursor molecules inside a carbon nanotube matrix through heating or electron beam irradiation [36, 37]. In order to account for the experimentally observed out-of-plane deformation resulting from steric repulsion of Te atoms at the edge we consider a supercell model composed of 6 unit cells.

Figure 3 shows the band structure of Te-terminated armchair nanoribbon [Fig. 3]. The parabolic valence and conduction bands with extrema at $k = 0$ and the presence of a direct band gap of 0.42 eV are typical for $\pi$-symmetry states subjected to quantum confinement in armchair graphene nanoribbons [20]. However, we note the presence of an additional band at $\approx 0.5$ eV above the conduction band maximum which displays a clear Rashba-type splitting ($\alpha_R = 0.014$ eV Å) and a large magnitude of $M_{ik}$. Analysis of the spatial distribution of the Rashba-split states [Fig. 3] for the momentum and the energy indicated by label A in Fig. 3 shows that they are formed by the hybridization of edge C and Te orbitals. These electronic states are spin degenerate but localized at the opposite edges (that is, spin-filtered); the spin is oriented along the $y$ direction. Strictly speaking, such a system is not in the QSH regime, but this example proves that the edge functionalization of graphene nanoribbons can result in strong spin-orbit driven effects, in particular, the emergence of spin-filtered edge states.

We will now discuss the second model characterized by a...
significantly larger coverage density of Te atoms on the edges. In this case, hybridization of graphene $\pi$-states with Te orbitals strongly modifies the band-structure features that are typical for zigzag graphene nanoribbons passivated by “neutral” functional groups such as hydrogen atoms. However, we note the dominance of low-dispersion bands close to the Fermi level ($E = 0$) remnant of the edge-state flat band in H-terminated graphene nanoribbons. As in the previous model, the ground state configuration of the Te-terminated zigzag nanoribbons shows no magnetic ordering, hence time-reversal symmetry is preserved. The spatial orientation of the spin is also along the $y$ direction. Importantly, the electronic bands at low energies form a number of crossings at the Kramer’s degeneracy points $k = 0$ and $k = \pi/a$ characterized by large magnitudes of $M_{ik}$. One such crossing, even though characterized by a band gap opening of 47 meV, is situated at the Fermi level of the charge-neutral graphene nanoribbon [Fig. 3e]. We ascribe the gap opening to the hybridization between the edge states localized at the opposite edge of the nanoribbon analogous to the band gaps observed in thin films of bulk topological insulators [38–40]. Importantly, there are not other bands present in the energy range $-0.32 \, \text{eV} < E < 0.26 \, \text{eV}$. The corresponding states are spin-filtered and the system in the QSH regime in this energy range. The relevant electronic states are mostly Te-derived as shown in Fig. 3f.

To summarize, we proposed a new method for engineering spin-orbit interactions in graphene by means of the covalent chemical functionalization of the edges. First-principles calculations performed on realistic models of tellurium-terminated graphene nanoribbons demonstrate the efficiency of our approach and the possibility of realizing the quantum spin Hall state spanning broad energy ranges. Our work thus opens up new perspectives for controlling spin-orbit interactions as well as the practical realization of novel topological electronic phases in graphene nanostructures by means of bottom-up chemical routes.

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