Electronic Structure Trends of Möbius Graphene Nanoribbons from Minimal-Cell Simulations

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Abstract
Investigating topological effects in materials requires often the modeling of material systems as a whole. Such modeling restricts system sizes, and makes it hard to extract systematic trends. Here, we investigate the effect of Möbius topology in the electronic structures of armchair graphene nanoribbons. Using density-functional tight-binding method and minimum-cell simulations through revised periodic boundary conditions, we extract electronic trends merely by changing cells’ symmetry operations and respective quantum number samplings. It turns out that for a minimum cell calculation, once geometric and magnetic contributions are ignored, the effect of the global topology is unexpectedly short-ranged.

Keywords:

1. Introduction

Bulk crystals are conventionally simulated using translational symmetry and periodic boundary conditions. Periodicity means that the electron wave function is symmetric with respect to a certain number of translations along a given dimension of the simulation cell. Since the periodicity occurs for all three dimensions of the cell simultaneously—with all the opposing faces of a parallelepiped inter-twined to come into contact with one another—it cannot represent physical reality; the periodicity is often just a mathematical trick. For some structures, however, the periodicity does represent physical reality, even without the need to consider the limit of infinite system size. Such structures include a ring-like structure due to one-dimensional periodicity, a toroidal structure due to two-dimensional periodicity, and a Möbius ribbon due to one-dimensional roto-translational periodicity.

Möbius ribbon forms upon connecting the ends of a half-twist rectangular strip, so it has only one surface and one edge. Its periodicity is fascinating: one must traverse a distance twice the length of the ribbon to return to the starting point. This periodicity has profound implications on electron wave functions, and it has triggered interest for both experimental and theoretical investigations. Experiments have realized Möbius hydrocarbons and single crystal Möbius strips. Theoretical works have addressed electronic properties of Möbius graphene or other ribbons, as well as classical properties of elastic Möbius ribbons. Unfortunately, first-principles calculations are hard to analyze, making trends and their origins difficult to extract.

Here, we compare Möbius graphene nanoribbons to straight ones by using density-functional tight-binding employing revised periodic boundary conditions. The revised periodic boundary conditions enable the extraction of length- and width-dependent trends that arise from topological effects alone. The approach requires only minimal simulation cells; both topology and length are controlled by parameters external to the cell. We find that the topology has an unexpectedly short-ranged effect in the electronic properties of Möbius graphene nanoribbons.
with realistic aspect ratios. While the changes in topology for real ribbons makes big differences for total energies, geometries, and electronic structures, we find that, when excluding the geometrical effects, the Möbius topology itself has an unexpectedly small effect on ribbons’ properties, especially for realistic aspect ratios.

2. Minimal-cell simulations

To establish the approach of treating the Möbius topology, we briefly present the framework of revised periodic boundary conditions.\[14, 15\]. Let the potential $V(\mathbf{r})$ in a non-interacting Hamiltonian $\hat{H} = -\nabla^2/2 + \hat{V}(\mathbf{r})$ be invariant under the symmetry operation $S^n \equiv S_1^n S_2^n \cdots$, that is,

$$\hat{D}(S^n)V(\mathbf{r}) \equiv V(S^{-n}\mathbf{r}) = V(\mathbf{r}) \quad (1)$$

for a set of commuting symmetry operations $S^n_i$. Energy eigenstates $\psi_{\kappa}(\mathbf{r})$ then satisfy

$$\hat{D}(S^n)\psi_{\kappa}(\mathbf{r}) = e^{-i\kappa \cdot n}\psi_{\kappa}(\mathbf{r}), \quad (2)$$

with the quantum numbers $\kappa = (\kappa_1, \kappa_2, \ldots)$. This framework differs from Bloch’s theorem only in choosing generalized symmetry operations $S^n_i$ over simple translations. The key ingredient is that, by a clever choice of $S^n_i$’s, a minimal simulation cell will suffice to investigate extended structures with custom-made symmetries, periodicities, and even topologies.\[16, 17, 18\]

Figure 1: Periodic boundary conditions of Möbius ribbons. a) Topological Möbius ribbon is effectively a straight ribbon, periodicity being imposed only upon the topology of the wave function. b) The $\pi$-rotation $\mathcal{R}$ (dashed arrow) and roto-translation $\mathcal{RT}$ (solid arrow) performed on a minimal unit cell of a zigzag graphene nanoribbon. By combining $\mathcal{TR}$ and $\mathcal{R}$, we may construct the whole ribbon from the minimal cell. Here the Möbius topology comes through associating the two cells (solid rectangles) that are connected by three operations of $\mathcal{RT}$ (periodic boundary condition $\mathcal{TR}^3 = \mathcal{R}$). c) Illustration of the equivalence of $\mathcal{TR}^3 = \mathcal{R}$ for a finite, real-space Möbius ribbon.

Bearing this framework in mind, consider two symmetry operations, $\mathcal{R}$ for a $\pi$-rotation (half-twist) around the $z$-axis and $\mathcal{T}$ for a translation of $l$ in the $z$-direction. For a Möbius ribbon of length $L = Ml$, the wave function should then satisfy

$$\hat{D}(\mathcal{T}^M)\psi(\mathbf{r}) = \hat{D}(\mathcal{R})\psi(\mathbf{r}), \quad (3)$$

which means that translating a length $L$ along the ribbon equals to a half-twist. We term ribbons modeled this way topological Möbius ribbons, as they include the correct topology, and yet exclude geometric contributions from bending or stretching.\[13, 19\]

To apply the revised periodic boundary conditions to simulate Möbius ribbons in practice, we choose two symmetry operations, rotation $\mathcal{R} = S_1$ and roto-translation $\mathcal{TR} = S_2$. This choice suggests a minimal simulation cell (Fig.1). For ribbons with symmetric edges, $S_1^N = 1$ implies either $\kappa_1 = 0$ (symmetric state) or $\kappa_1 = \pi$ (antisymmetric state). The periodicity along the ribbon is defined by the boundary condition

$$\hat{D}(\mathcal{S}_M^N)\psi_{\kappa}(\mathbf{r}) = \hat{D}(\mathcal{S}_1^N)\psi_{\kappa}(\mathbf{r}), \quad (4)$$

where $N = 0$ or 1 and the ribbon length $L = Ml$. Rearranging the above boundary condition into

$$\hat{D}(\mathcal{T}^M)\psi_{\kappa}(\mathbf{r}) = \hat{D}(\mathcal{R}^{N-M})\psi_{\kappa}(\mathbf{r}), \quad (5)$$

and comparing it with Eq. (3) reveals that even $N - M$ represents a straight ribbon and odd $N - M$ a Möbius ribbon. Juxtaposing this boundary condition with Eq. (2) we get $e^{-iM\kappa_2} = e^{-iN\kappa_1}$, which gives the quantum-number sampling for $\kappa_2$ as

$$\kappa_2 = \frac{N\kappa_1 + 2\pi m}{M}, \quad m = 0, \ldots, M - 1, \quad (6)$$
where $\kappa_1 = 0$ or $\pi$, as mentioned. Thus, both the topology (via $N - M$) and the length (via $M$) can be controlled by controlling the boundary conditions, while keeping the simulation cell the same.

The choice of the symmetry operations could be different as well. Möbius ribbons could be simulated by the symmetry operation $S = TR$ alone, with simulation cell spanning the entire width of the ribbon. This choice, with the boundary condition $(RT)^M = \hat{1}$, leads to straight ribbons for even $M$ and Möbius ribbons for odd $M$. The quantum number sampling is $\kappa = 2\pi m/M \ (m = 0, \ldots, M - 1)$. Unfortunately, this choice cannot be used to simulate Möbius ribbons for lengths $L = Ml$ when $M$ is even.

The idea of a "Möbius boundary condition" has been around for some time. Apart from real, finite Möbius ribbon simulations, Möbius or "twisted" periodic conditions have been used for before, especially using a nearest-neighbour tight-binding picture.\cite{10, 5, 12, 20} Unlike previous works, with the exception of the recent paper by Cüçlü et al.\cite{21}, our minimal-cell setting enables investigating the effect of boundary conditions as a function of length, to extract trends and separate the effect of topology from the geometrical effects.

Calculations were done by density-functional tight-binding code hotbit, which is equipped with a flexible implementation of custom-made symmetries and boundary conditions.\cite{22, 23} The sole implementation needed was the function for the symmetry operation $r' = S_i r$, along with the corresponding boundary conditions. The quantum-numbers ($\kappa$-point) were sampled according to Eq. (6). Structures were optimized using the criterion of $10^{-6}$ eV/Å for the atoms’ maximum forces.

As explained above, we impose the topology only through symmetry operations and boundary conditions. Thus, the ribbon is structurally straight graphene nanoribbon regardless of the topology. In real and finite Möbius ribbons the strains and bendings would constitute considerable energy contributions already with a single half-twist.\cite{24} However, as the purpose of this work is to investigate the effects of the topology alone, the exclusion of the geometrical effects is a sheer advantage.

Finally, we verified the minimum-cell method by comparing the results to corresponding finite Möbius ribbons. We constructed finite Möbius ribbons by removing the geometrical variations from the matrix elements. All the electronic properties of the finite Möbius ribbons and the topological Möbius ribbons were numerically identical. The minimum-cell method was proven valid.

3. Electronic structure trends

We performed calculations for hydrogen-passivated armchair graphene nanoribbons with widths ($W$) up to 4.0 nm, with lengths ($L$) up to 14 nm, and with both topologies (straight and Möbius) for all ribbons. Furthermore, we restricted ourselves to ribbons with symmetric edges (symmetric under $\pi$-rotation) in order to single out the effect of topology for a ribbon of given length. Asymmetric edges would have blurred comparisons between straight and Möbius ribbons due to different number of atoms. This restriction is not a constraint due to the method, but a constraint due to the Möbius topology. Aspect ratios, however, had no restrictions. While the smallest realistic aspect ratios for Möbius ribbons lie around $L/W \gtrsim 4$ \cite{13, 5}, the method enabled investigating the effects of topology for even smaller aspect ratios, for the sheer purpose of trend extraction.

The first observation was that both straight and Möbius armchair graphene nanoribbons share the three known structural families. Classified by $q = \left( \begin{array}{c}
\frac{3}{2}
\end{array} \right)$,
Figure 3: Effect of Möbius topology on energies. a) The number of Clar rings per carbon atom in the ribbon (same curve for both topologies; left scale). The degeneracy of optimal Clar ring arrangements as a function of ribbon width for straight (solid line) and Möbius (dashed line) topologies. b) Energy difference $E_{\text{straight}} - E_{\text{Möbius}}$ for the two topologies as a function of ribbon width. Symbols indicate structural families.

The role of Clar ring arrangements can be illustrated by a look at the energetics (Fig. 3b). For a finite ribbon of given length, width, and topology, the arrangement of Clar rings can be calculated explicitly (two adjacent hexagons are never Clar rings simultaneously; therefore in graphene the number of Clar rings per carbon atom attains its maximum value of 1/6, Fig. 3a). Such explicit calculations show that the number of Clar rings in optimal arrangements do not depend on topology, while the arrangement degeneracies do (Fig. 3a). When the degeneracies are larger, also the energy differences between different topologies are smaller. This relationship is intuitive: when the arrangement of Clar rings is "rigid", structure will be sensitive to the change in topology (compare Figs. 3a and 3b). If, however, the arrangement is not rigid but flexible due to a large degeneracy, it will be insensitive to changes in topology. This is why for the incomplete-Clar family, which has the largest degeneracy for the arrangements, the energy changes the least. Clar structures, on the other hand, have only one arrangement of Clar rings, no degeneracy, and are the most sensitive for changes in topology (Fig. 3b).

Similar arguments are valid also for energy gaps. The gaps of straight ribbons oscillate as a function of width according to the three structural families (Fig. 4). Topology affects the gaps in Clar and Kekulé families, but not in the incomplete-Clar family. In the incomplete-Clar family the smallness of the gap is a reminiscent of the large degeneracy of Clar ring arrangements, representing a “metallic” electronic structure with its delocalized electron wave functions. Large degeneracy in Clar rings hence implies a certain degree of disorder in Clar ring arrangements, which gives a plausible explanation to why incomplete-Clar family is insensitive to changes in topology also with respect to energy gaps.

A complementary point of view for the changes in the energy gaps is to use the symmetry of the bands near the Fermi-level. Consider an eigenstate $\psi$ with the translational symmetry $\hat{D}(T)\psi = e^{-i\varepsilon T}\psi$ and the roto-translational symmetry $\hat{D}(RT)\psi = e^{-i\kappa_{RT}\psi}$. The state $\psi$ can be labeled both by the quantum numbers $\kappa_T$ and by $\kappa_{RT}$. Because
Figure 4: The effect of Möbius topology on energy gaps. a) Band gaps as a function of ribbon width for different lengths and topologies. b) Band structure of straight and Möbius ribbons near Fermi-level. If the wavefunctions are odd, the bands of the straight ribbon (solid line) shift by $\pi$ upon changing the topology to Möbius. Since the $\kappa$-point sampling remains the same (sampled energies with solid spheres), the resulting energy gap changes.

The monotonous decay of the effect from Möbius topology can be seen also in the energy gap (Fig. 5b). The decay is understood easily by inspecting the energy gap in Fig. 4b as the ribbon lengthens. When the length increases—meaning larger $M$ and denser $\kappa$-point sampling—the gap will become independent of the band shifting that is caused by the change in topology. If the bands are symmetric, as they are for the incomplete-Clar family, gaps will remain indepen-
dent of topology altogether.

Finally, these results prove—perhaps for the first time explicitly—that the boundary conditions do not matter after the total energy has been converged with respect to the number of \( k \)-points in the calculation. This is a highly non-trivial observation, as a convergence with respect to the number of \( k \)-points does not automatically mean that topology would become unimportant—topology is, after all, a conserved property whose effect cannot be monitored continuously. Although these results are for one-dimensional ribbons, they give reassurance that the bizarre, unphysical three-dimensional translational-periodic topology would become equally unimportant upon \( k \)-point convergence.

4. Conclusion

The treatment of these topological Möbius ribbons bears certain natural concerns. The first concern, as mentioned earlier, is the absence of strain in the bond lengths. The second concern is the absence of the finiteness of the twisted structure, essential for some of the calculated effects of Möbius ribbons, such as the spectral splitting under weak electric fields. The third concern is the constrained symmetry, the inability for symmetry breaking and for localized electronic states. The fourth concern is the absence of spin. *Ab initio* calculations have shown that Möbius zigzag graphene ribbons are stable ferromagnets. This spontaneous spin-polarization of zigzag graphene nanoribbons was our excuse to exclude them. Armchair ribbons, again, do not have such a spontaneous polarization, and provide more reasonable systems for spin-unpolarized calculations. All the same, the investigation of magnetic properties will require calculations with finite ribbons; unit cell calculations with Möbius boundary conditions could never account for such effects.

However, the above concerns are not detrimental for our goal. The purpose of this work was to investigate the effects of topology *without these other effects*, to investigate the effect of topology alone. We found that the same structural families survive the topological change, and that within each family the effects can be understood in terms of Clar ring arrangements and their rigidity. We found that purely topological effects are unexpectedly short-ranged, which means that the more important effects of Möbius topology will arise from geometrical distortions, finite-size effects, and electron-electron interactions. Our findings also help to understand the ubiquitous phrase regarding “\( k \)-point convergence” which can now be understood to mean convergence not only with respect to the system size, but also with respect to the global, overall topology: a small unit cell with many enough repetitions *soon loses its perception of the global topology*.

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