



MSN 514 - Computational Methods for Material Science and Complex Systems

Homework 03

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I. INTRODUCTION

Graphene nanoribbons (GNRs) are interesting materials for nanoelectronics because their electronic properties change depending on their width. In particular, armchair graphene nanoribbons (AGNRs) show a pattern in their band gaps: according to a simple tight-binding (TB) model, ribbons with widths following $N_a \equiv 3p + 2$ should be metallic. However, more advanced calculations using density-functional theory (DFT) show that a small energy gap actually forms due to edge effects¹. In this report, we use a TB approach with modified edge hopping to calculate the band structures of AGNRs with $N_a = 12, 13$, and 14 and compare our results with those from DFT.

A. Schrödinger Equation and Hamiltonian Operators

Our analysis starts from the time-independent Schrödinger equation:

$$\hat{H} \psi = E \psi, \quad (1)$$

where \hat{H} is the Hamiltonian operator, ψ is the wavefunction, and E is the energy eigenvalue.

In the tight-binding (TB) approximation we assume that electrons are localized around atomic sites. The Hamiltonian is then written as

$$\hat{H} = \sum_i \epsilon_i c_i^\dagger c_i + \sum_{\langle i,j \rangle} t_{ij} c_i^\dagger c_j, \quad (2)$$

where ϵ_i are the on-site energies (set to zero in our work) and t_{ij} are the hopping parameters between nearest-neighbor sites. For pristine graphene, a typical value is $t = 2.70$ eV.

The wavefunction is expanded in a basis of localized atomic orbitals:

$$\psi(\mathbf{r}) = \sum_i c_i \phi_i(\mathbf{r}), \quad (3)$$

where $\phi_i(\mathbf{r})$ is the π orbital on the i th carbon atom and c_i are the expansion coefficients. For periodic systems, Bloch's theorem implies that these coefficients take the form $c_i \propto e^{ikna}$, where a is the lattice constant and n labels the unit cell.

For a time-independent Hamiltonian the full time-dependent solution is simply

$$\psi(\mathbf{r}, t) = \sum_n c_n \phi_n(\mathbf{r}) e^{-iE_n t/\hbar}, \quad (4)$$

so that each eigenstate evolves only by a phase factor. This property is why the eigenstates are called stationary (or time-invariant).

While some numerical methods consider the collapse of the wavefunction when a measurement is made, our focus here is on solving the eigenvalue problem [Eq. (1)] to obtain the stationary states of the system.

1. Molecular Orbitals and the SSH Model

The molecular orbital picture describes the electronic states as linear combinations of atomic orbitals:

$$\Psi(\mathbf{r}) = \sum_n c_n \phi_n(\mathbf{r}). \quad (5)$$

In the Su–Schrieffer–Heeger (SSH) model², which was originally developed for polyacetylene, a one-dimensional dimerized chain is considered. The Hamiltonian is written as

$$H(k) = \begin{pmatrix} 0 & t_1 + t_2 e^{-ika} \\ t_1 + t_2 e^{ika} & 0 \end{pmatrix}, \quad (6)$$

yielding the dispersion relation

$$E(k) = \pm \sqrt{t_1^2 + t_2^2 + 2t_1 t_2 \cos(ka)}. \quad (7)$$

This model elegantly demonstrates how dimerization opens a gap. For GNRs, a similar philosophy applies; however, the geometry is extended to a two-leg ladder structure to capture the two-dimensional nature of the ribbon.

B. Graphene Nanoribbon Problem

In Ref.¹, Fig. 2(c) displays DFT-calculated band structures for AGNRs with 12, 13, and 14 dimer lines. In our study, we adopt a TB model with:

- $t = 2.70$ eV for hopping between nearest-neighbor carbon atoms in the bulk.
- An enhanced edge hopping $t' = 3.024$ eV for the edge atoms.
- Zero on-site energies and neglect of C–H hopping.

The ribbon is modeled as a two-leg ladder with $2N_a$ sites (each dimer contributes two sites). Periodic boundary conditions along the ribbon direction (with Bloch phase factors $e^{\pm ik}$) yield a k -dependent Hamiltonian, whose diagonalization gives the energy bands $E(k)$.

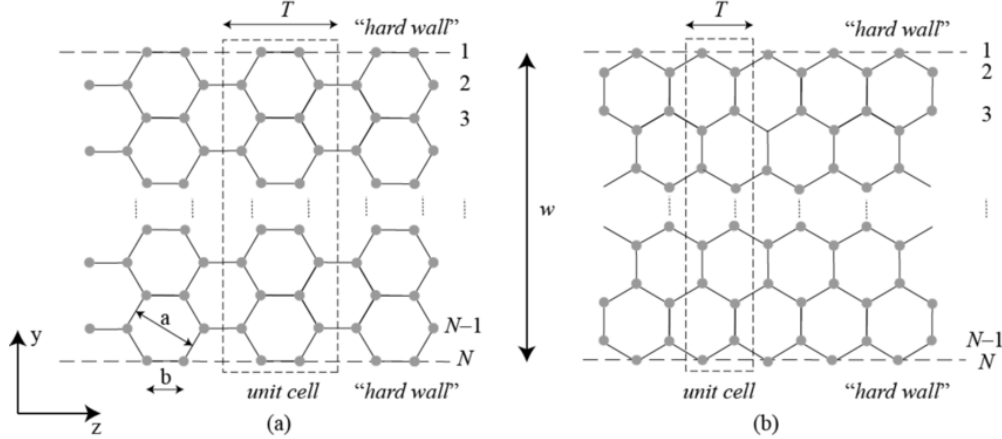


FIG. 1. Schematic representations of graphene nanoribbon edge geometries: (Left) Armchair, (Right) Zigzag.

II. RESULTS

A. Band Structure Calculation

We have implemented the TB model in Python. For a given ribbon width N_a (12, 13, or 14), the k -dependent Hamiltonian is constructed by incorporating:

- Horizontal (intra-leg) hopping between adjacent dimer lines, with periodic boundary conditions.
- Vertical (inter-leg) hopping within each dimer, modified at the edges.

A band-tracking algorithm is applied to follow each eigenvalue continuously as a function of k (sampled densely with 1000 points over $[0, \pi]$) so that the resulting band curves are smooth.

Figure 2 shows the smooth band structures obtained when the edge effect is included.

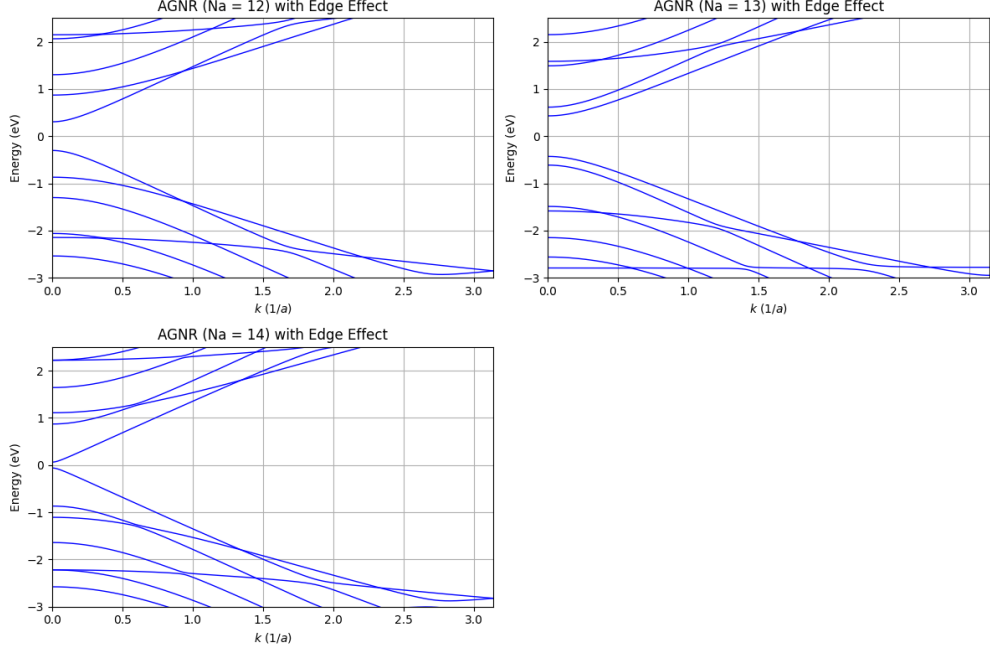


FIG. 2. Tight-binding band structures for AGNRs with $N_a = 12, 13, 14$ computed over $k \in [0, \pi]$, using the modified edge hopping $t' = 3.024 \text{ eV}$.

B. Edge Effect Comparison

For further insight, we also computed the band structures with uniform hopping ($t' = t$) so that edge effects are neglected. Figure 3 compares the two cases. Notably, for the $3p + 2$ family the increased edge hopping opens a finite gap. To quantify this, we compute the L_2 norm of the difference between the two sets of eigenvalues:

$$\Delta E_{L_2}(k) = \|E_{\text{edge}}(k) - E_{\text{no-edge}}(k)\|_2. \quad (8)$$

Figure 4 presents this norm as a function of k , showing that the maximum differences occur near the Brillouin zone boundary.

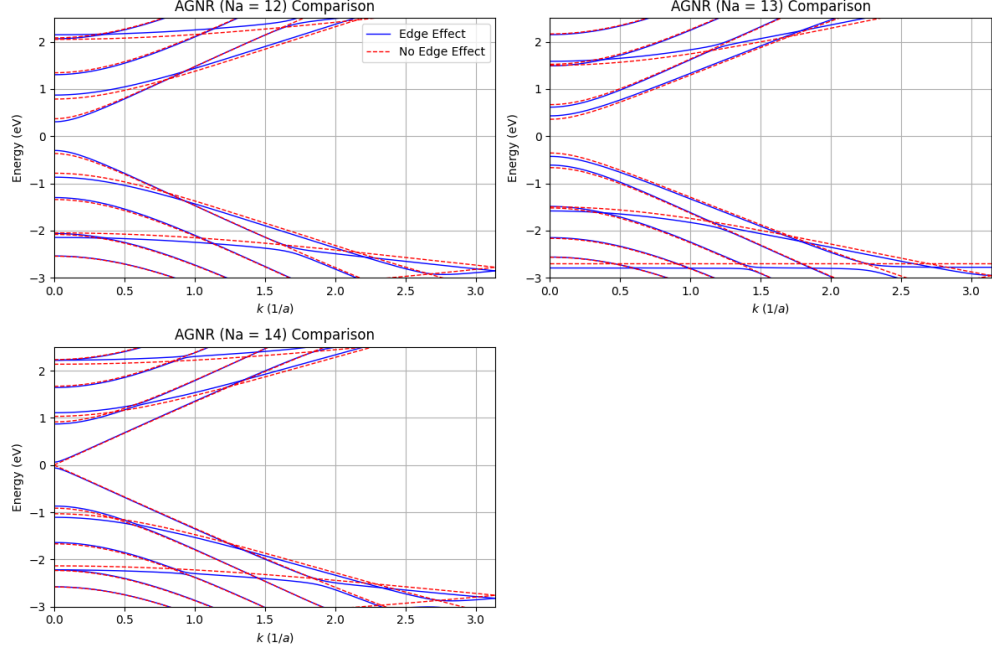


FIG. 3. Comparison of band structures: blue solid lines (edge effect) versus red dashed lines (no edge effect) for $N_a = 12, 13, 14$.

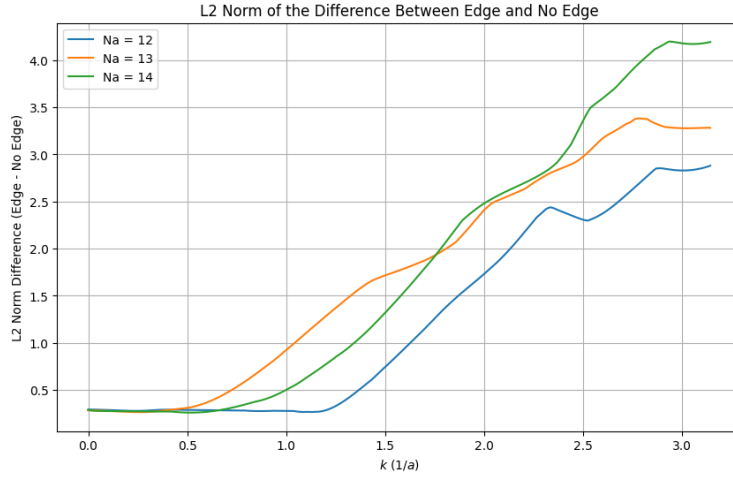


FIG. 4. L_2 norm of the difference between edge-effect and no-edge-effect band energies as a function of k for different ribbon widths.

C. Discussion of Results

The TB Hamiltonian is derived from the Schrödinger equation [Eq. (1)] by expressing the electronic states as linear combinations of atomic orbitals and incorporating periodic

boundary conditions. Our formulation, which extends the SSH model (see Eqs. (6) and (7)), is generalized to a two-leg ladder that captures the geometry of AGNRs. In our model, the inter-leg (vertical) hopping is modified at the edges ($t' = 3.024\text{ eV}$), which is crucial to reproduce the family behavior observed in DFT calculations¹.

Our numerical results show that the inclusion of edge effects opens a finite gap in ribbons that would be metallic under a uniform TB model (i.e., those with $N_a \equiv 3p + 2$). The band-tracking algorithm ensures that each eigenvalue is continuously followed across k , resulting in smooth curves. The L_2 norm analysis further quantifies the importance of the edge correction.

III. CONCLUSION

In this report, we have developed a detailed tight-binding model for armchair graphene nanoribbons, starting from the time-independent Schrödinger equation and using operator methods to construct the Hamiltonian. Our derivation, inspired by the SSH model, illustrates how molecular orbitals arise from a linear combination of atomic orbitals and how a modified interatomic hopping at the edges can open a bandgap.

We applied this model to compute the band structures for AGNRs with $N_a = 12, 13, 14$, using a dense k -point sampling and a band-tracking algorithm to ensure smooth curves. Our results reproduce key features observed in DFT calculations¹, especially the finite gap opening in the $3p + 2$ family due to enhanced edge hopping. The computed L_2 norm differences further highlight the significance of the edge modifications.

Overall, the study demonstrates that a relatively simple TB model—augmented by an appropriate treatment of edge effects—can capture the essential physics of graphene nanoribbons, bridging the gap between basic theoretical models and more complex *ab initio* approaches.

¹ Y.-W. Son, M. L. Cohen, and S. G. Louie, “Energy Gaps in Graphene Nanoribbons,” *Phys. Rev. Lett.* **97**, 216803 (2006).

² W. P. Su, J. R. Schrieffer, and A. J. Heeger, “Solitons in Polyacetylene,” *Phys. Rev. Lett.* **42**, 1698 (1979).

- ³ K. Nakada, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, “Edge state in graphene ribbons: Nanometer size effect and edge shape dependence,” *Phys. Rev. B* **54**, 17954 (1996).