Band Structure Calculation of Graphene Nanoribbons (GNRs) with and without Si Impurity: Theory and Tight-Binding Hamiltonian

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Introduction

Graphene is a two-dimensional (2D) material consisting of carbon atoms arranged in a honeycomb (hexagonal) lattice. Its low-energy electronic properties are dominated by the p_z orbitals, which form the π and π^* bands. The tight-binding (TB) model, especially with nearest-neighbor hopping, provides an accurate yet computationally simple way to study the band structure of graphene and its derivatives such as graphene nanoribbons (GNRs) and doped GNRs.

1 Tight-Binding Model for Graphene

The TB wavefunction in graphene is constructed as a linear combination of p_z orbitals centered on sublattices A and B:

$$\Psi(\mathbf{k}, \mathbf{r}) = c_A(\mathbf{k})\tilde{p}_z^A(\mathbf{k}, \mathbf{r}) + c_B(\mathbf{k})\tilde{p}_z^B(\mathbf{k}, \mathbf{r}), \tag{1}$$

where $\tilde{p}_z^{A,B}$ are Bloch sums of atomic orbitals.

The Hamiltonian reduces to a 2×2 matrix in the basis of A and B sublattices:

$$H(\mathbf{k}) = \begin{pmatrix} 0 & -t\,\alpha(\mathbf{k}) \\ -t\,\alpha^*(\mathbf{k}) & 0 \end{pmatrix} \tag{2}$$

where t is the nearest-neighbor hopping parameter ($t \approx 2.7$ eV in pristine graphene) and

$$\alpha(\mathbf{k}) = 1 + e^{-i\mathbf{k}\cdot\mathbf{a}_1} + e^{-i\mathbf{k}\cdot\mathbf{a}_2} \tag{3}$$

with $\mathbf{a}_1$ and $\mathbf{a}_2$ the primitive lattice vectors.

The energy bands are then given by:

$$E_{\pm}(\mathbf{k}) = \pm t\,|\alpha(\mathbf{k})| \tag{4}$$

For GNRs, the quantization along the transverse direction results in a set of discrete subbands.

2 Tight-Binding Hamiltonian for Zigzag GNRs (ZGNR)

For a ZGNR of width N (number of dimer lines across the width), the Hamiltonian can be written in site basis as an $M \times M$ matrix (with $M = 2N$, for two atoms per dimer). For nearest-neighbor TB:

$$H = \begin{pmatrix} E_1 & t_{1,2} & 0 & \cdots & 0 \\ t_{2,1} & E_2 & t_{2,3} & \cdots & 0 \\ 0 & t_{3,2} & E_3 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & t_{M-1,M} \\ 0 & 0 & 0 & t_{M,M-1} & E_M \end{pmatrix}$$

where E_i is the onsite energy of site i, and $t_{i,j}$ the hopping term, which may depend on whether a Si atom is present.

For periodic (1D) ribbons, Bloch phase factors $e^{\pm ik_x a}$ are introduced at the cell boundaries.

3 Pure (Pristine) Zigzag GNR

- **Onsite energies:** $E_i = 0$ (for all carbon sites)
- **Hopping:** $t_{i,j} = t$ (all nearest neighbors)
- **Matrix form (example for $M = 12$):**

$$H_{\text{pure}} = \begin{pmatrix} 0 & a & 0 & \cdots & 0 \\ b & 0 & -t & \cdots & 0 \\ 0 & -t & 0 & b & \cdots \\ 0 & 0 & a & 0 & -t \\ \vdots & \vdots & \vdots & -t & \ddots \end{pmatrix}$$

with

$$a = -t + (-t)e^{-ik_x a_0}, \quad b = -t + (-t)e^{ik_x a_0}$$

where a_0 is the C–C bond length (1.42 Å).

4 Si-Doped (Impure) Zigzag GNR

- **Onsite energies:** $E_i = 0$ for carbon sites, E_{Si} for the Si impurity site.
- **Hopping:** t for C–C bonds, t_{Si} for C–Si or Si–C bonds.
- **Matrix form (example for $M = 12$, Si at site 3):**

$$H_{\text{Si}} = \begin{pmatrix} 0 & a & 0 & \cdots & 0 \\ b & 0 & -t_{Si} & \cdots & 0 \\ 0 & -t_{Si} & E_{Si} & c & \cdots \\ 0 & 0 & d & 0 & -t \\ \vdots & \vdots & \vdots & -t & \ddots \end{pmatrix}$$

with

$$c = -t_{Si} + (-t_{Si})e^{-ik_x a_0}, \quad d = -t_{Si} + (-t_{Si})e^{ik_x a_0}$$

where E_{Si} is the onsite energy for Si, and t_{Si} the Si-related hopping.

5 Band Structure Calculation

For each k_x in the 1D Brillouin zone, the Hamiltonian $H(k_x)$ is constructed as above. The eigenvalues $E_n(k_x)$ are obtained by solving

$$H(k_x)\boldsymbol{C}_n = E_n(k_x)\boldsymbol{C}_n \tag{5}$$

where n is the band index.

The resulting eigenvalues for all k_x are plotted to obtain the band structure. The presence of Si changes E_{Si} and t_{Si}, leading to impurity states and possible bandgap modifications.

6 Parameter Values (from Literature)

Typical values (see *S.M.-M. Dubois et al., EPJB 2009* and *Ervasti et al., arXiv:1509.00084*):

- $t \approx 2.7$ eV (C–C)
- $E_{Si} \approx 0.1$–0.2 eV (see DFT for details)
- $t_{Si} \approx 1.1$–1.3 eV
- $a_0 = 1.42$ Å

7 Summary

The tight-binding approach, when adapted for GNRs and extended to impurity cases, enables direct simulation of the effects of Si impurities on the band structure. The relevant Hamiltonian matrices can be constructed as above for numerical diagonalization at each k-point.

References

1. S.M.-M. Dubois, Z. Zanolli, X. Declerck, J.-C. Charlier, Eur. Phys. J. B (2009), `https://doi.org/10.1140/epjb/e2009-00327-8`
2. Mikko M. Ervasti, Zheyong Fan, Andreas Uppstu, Arkady Krasheninnikov, Ari Harju, arXiv:1509.00084
3. H. S. Şen, M.S. thesis, Bilkent University (2008).