



Green functions of graphene: An analytic approach



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ABSTRACT

In this article we derive the lattice Green Functions (GFs) of graphene using a Tight Binding Hamiltonian incorporating both first and second nearest neighbour hoppings and allowing for a non-orthogonal electron wavefunction overlap. It is shown how the resulting GFs can be simplified from a double to a single integral form to aid computation, and that when considering off-diagonal GFs in the high symmetry directions of the lattice this single integral can be approximated very accurately by an algebraic expression. By comparing our results to the conventional first nearest neighbour model commonly found in the literature, it is apparent that the extended model leads to a sizeable change in the electronic structure away from the linear regime. As such, this article serves as a blueprint for researchers who wish to examine quantities where these considerations are important.

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1. Introduction

Green Functions (GFs) are useful tools for describing the electronic structure of materials and various other quantities related to the electronic density of a material, such as the local density of states, inter-impurity interactions and scattering processes. A common strategy is to find a suitable Hamiltonian for the material and then obtain the system GFs computationally. Although the result of such an approach is accurate and it can be computationally expensive and misses the finer mathematical details often masked by numerical intricacies. Hence Green Functions can become more useful when they can be expressed in a simple mathematical form. There has been extensive work done on graphene-based materials and the GFs of these systems throughout the years. In particular, analytic expressions for the GFs of graphene have been derived and used to explain such phenomena as magnetic coupling between impurities [1,7,8] and Friedel Oscillations [14,15]. In those references, the GFs were obtained for a single-orbital tight binding model based on orthogonal states.

In this paper we show how the single-particle lattice Green Functions can be found for graphene using a second nearest neighbour non-orthogonal Tight Binding model. It is common in the literature to find first nearest neighbour approximations, as well as the assumption of an orthogonal basis for the electron wavefunctions [3–9,11]. Work by Reich et al. [12] showed that this approximation is only really valid in the linear regime and that an

improvement can be made by including further interactions. Our motivation is to improve the previous GF results by accounting for the extended electron hoppings and wavefunction overlaps. Extending the model in this way has already shown to be necessary for, among others, the electronic structure of nanoribbons [16], tight-binding modelling of impurities using a self-consistent method [24] and modelling changes in the density of states in the local region around a vacancy in the lattice [25]. Furthermore we will show that previous methods for approximating the off-diagonal GFs via the Stationary Phase Approximation [18] are applicable to this extended case also. These approximations of the off-diagonal GFs improve in accuracy with increasing separations, and as such are perfectly suited for in-depth analysis of long-range phenomena in graphene such as the RKKY interaction [6–8] and Friedel Oscillations [14,15], for energies outside the linear spectrum.

The paper is organised as follows. Firstly there is an introduction to general GF methods, followed by a derivation of the associated lattice GFs for graphene in integral form. Finally, we show how these integrals can be approximated to a high degree of accuracy in the high symmetry directions of the lattice, allowing for a fully analytic expression of the associated GFs.

2. Methodology

2.1. Tight binding Hamiltonian

To apply the techniques of Green Functions to graphene, we must first derive a Hamiltonian to describe the system. This can be

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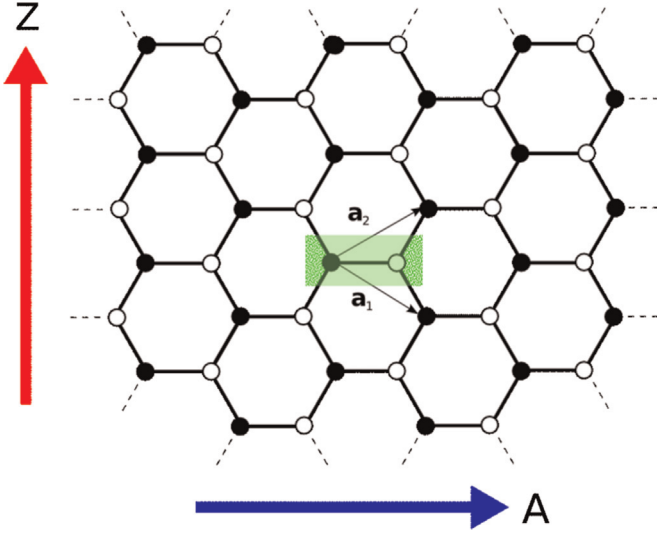


Fig. 1. Schematic of a small part of the graphene lattice showing the primitive lattice vectors $\mathbf{a}_1 = \{(3a/2)\hat{x}, -(\sqrt{3}a/2)\hat{y}\}$ and $\mathbf{a}_2 = \{(3a/2)\hat{x}, (\sqrt{3}a/2)\hat{y}\}$ and the two atom unit cell enclosed by the green transparent box. Using these vectors the location of any unit cell in the lattice is defined as $\mathbf{r} = m\mathbf{a}_1 + n\mathbf{a}_2$ where $m, n \in \mathbb{Z}$. The armchair and zigzag directions are indicated by A and Z respectively and will be used to specify directions for the Green Functions used later in this work. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

done by applying a second nearest-neighbour tight binding model, which assumes that electrons can hop from one atomic site to its first and second nearest neighbours in the lattice. Saito et al. [10] derived the dispersion relation using first nearest neighbour hopping and overlap. In this section we will show, in detail, how a similar approach can be used to obtain the dispersion relation with the inclusion of the second nearest neighbour interactions, and further we identify the eigenvectors of this system. The graphene lattice is composed of two triangular and inter-penetrating sublattices which we will refer to as Black (●) and White (○) and we choose a 2-atom unit cell as shown in Fig. 1. Our assumption means that each atom has three first-nearest neighbours belonging to the opposite sublattice, and six second-nearest neighbours belonging to the same sublattice. The wavefunction overlap is assumed to exist between first-nearest neighbours only.

This system is described by the real-space Hamiltonian

$$\begin{aligned}
 H = & \epsilon_0 \left(\sum_{\mathbf{r}} |\mathbf{r}, \bullet\rangle \langle \mathbf{r}, \bullet| + |\mathbf{r}, \circ\rangle \langle \mathbf{r}, \circ| \right) \\
 & + t \left(\sum_{\mathbf{r}} |\mathbf{r}, \bullet\rangle \langle \mathbf{r}, \circ| + \langle \mathbf{r} - \mathbf{a}_2, \circ| + \langle \mathbf{r} - \mathbf{a}_1, \circ| \right) \\
 & + |\mathbf{r}, \circ\rangle \langle \mathbf{r}, \bullet| + \langle \mathbf{r} + \mathbf{a}_2, \bullet| + \langle \mathbf{r} + \mathbf{a}_1, \bullet| \\
 & + t' \left(\sum_{\mathbf{r}} |\mathbf{r}, \bullet\rangle \langle \mathbf{r} - \mathbf{a}_1, \bullet| + \langle \mathbf{r} - \mathbf{a}_2, \bullet| \right. \\
 & \left. + \langle \mathbf{r} + \mathbf{a}_1 - \mathbf{a}_2, \bullet| + \langle \mathbf{r} + \mathbf{a}_1, \bullet| + \langle \mathbf{r} + \mathbf{a}_2, \bullet| + \langle \mathbf{r} + \mathbf{a}_2 - \mathbf{a}_1, \bullet| \right) \\
 & + |\mathbf{r}, \circ\rangle \langle \mathbf{r} + \mathbf{a}_1, \circ| + \langle \mathbf{r} + \mathbf{a}_2, \circ| + \langle \mathbf{r} + \mathbf{a}_2 - \mathbf{a}_1, \circ| \\
 & \left. + \langle \mathbf{r} - \mathbf{a}_1, \circ| + \langle \mathbf{r} - \mathbf{a}_2, \circ| + \langle \mathbf{r} + \mathbf{a}_1 - \mathbf{a}_2, \circ| \right) \quad (1)
 \end{aligned}$$

where the vector \mathbf{r} is defined as per Fig. 1 and is summed over the entire system to infinity. The parameters t and t' are negative energies denoting the first and second nearest neighbour hopping integrals respectively, and ϵ_0 corresponds to the on-site energy of

each carbon atom.

Accurate values of these parameters can be found through Density Functional Theory, and many examples exist in the literature [12,19]. Numerical calculations throughout this paper will use units of the first nearest neighbour hopping $t = -1$, and using the parameterisation of Reich [12] gives $t' = -0.037$ and $\epsilon_0 = 0.111$. The real-space Hamiltonian can be diagonalised using a Fourier Transform from real- to reciprocal-space

$$|\mathbf{k}, A\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{r}} e^{i\mathbf{k}\cdot\mathbf{r}} |\mathbf{r}, A\rangle,$$

with the inverse transform given by

$$|\mathbf{r}, A\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}} |\mathbf{k}, A\rangle.$$

Here, N is the number of elementary cells. Such a transform results in the equivalent diagonalised Hamiltonian in \mathbf{k} -space given by

$$\hat{H}(\mathbf{k}) = \begin{pmatrix} \epsilon_0 + t'g(\mathbf{k}) & tf(\mathbf{k}) \\ tf^*(\mathbf{k}) & \epsilon_0 + t'g(\mathbf{k}) \end{pmatrix} \quad (2)$$

where $f(\mathbf{k}) = 1 + e^{i\mathbf{k}\cdot\mathbf{a}_1} + e^{i\mathbf{k}\cdot\mathbf{a}_2}$ and $g(\mathbf{k}) = 2(\cos(\mathbf{k}\cdot\mathbf{a}_1) + \cos(\mathbf{k}\cdot\mathbf{a}_2) + \cos(\mathbf{k}\cdot\mathbf{a}_1 + \mathbf{k}\cdot\mathbf{a}_2))$.

2.2. Eigenvalues and eigenvectors of the diagonalised Hamiltonian

The eigenvalues of the Hamiltonian, corresponding to its spectrum, are found through applying the generalised secular equation $\det(\hat{H} - \epsilon\hat{S}) = 0$. The matrix \hat{S} is the wavefunction overlap matrix which can be written explicitly in diagonalised form as

$$\hat{S}(\mathbf{k}) = \begin{pmatrix} 1 & sf(\mathbf{k}) \\ sf^*(\mathbf{k}) & 1 \end{pmatrix}.$$

Here, s is a dimensionless parameter which quantifies the wavefunction overlap of neighbouring p_z orbitals above each carbon site in the graphene lattice. For the purposes of later calculations we will adopt the value of $s=0.1$ from Reich [12]. This non-orthogonality of the wavefunctions is commonly expressed mathematically as

$$\langle \phi_a | \phi_b \rangle = s$$

where a and b are neighbouring lattice sites. The spectral solutions to the secular equation are

$$\epsilon_{\pm} = \frac{\epsilon_0 + t'g \pm t|f|}{1 \pm s|f|}.$$

It is straightforward to identify the eigenvectors of the system via Schrodinger's Equation, $\hat{H}|\Psi\rangle = \epsilon\hat{S}|\Psi\rangle$ where Ψ denotes an eigenstate associated with \hat{H} . Assuming $|\Psi\rangle = \begin{pmatrix} A_1 \\ A_2 \end{pmatrix}$ gives the matrix equation:

$$\begin{pmatrix} \epsilon_0 + t'g & tf \\ tf^* & \epsilon_0 + t'g \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \epsilon_{\pm} \begin{pmatrix} 1 & sf \\ sf^* & 1 \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \end{pmatrix}.$$

Solving this and normalising through the requirement $\langle \Psi_{\pm} | \Psi_{\pm} \rangle = 1$ we find

$$|\Psi_{\pm}\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm e^{i\phi} \end{pmatrix}$$

so

$$|\mathbf{k}, \pm\rangle = \frac{1}{\sqrt{2N}} \sum_{\mathbf{r}} e^{-i\mathbf{k}\cdot\mathbf{r}} (|\mathbf{r}, \bullet\rangle \pm e^{-i\phi} |\mathbf{r}, \circ\rangle).$$

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