

The Electronic Properties Of Graphene: Theoretical Modelling of Doping

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What is Graphene?

- ▶ Formed from Carbon atoms in a hexagonal lattice.
- ▶ First 2D crystal observed experimentally - Geim and Novoselov 2004.
- ▶ Produced by the micromechanical exfoliation of graphite:
 1. Use sticky tape to repeatedly peel off thin layers of carbon.
 2. Dissolve the sticky tape in solution.
 3. Transfer layers to a Silicon Dioxide substrate.
 4. Use an optical microscope to observe interference from Graphene samples.



Figure: A diagram of the basic structure of Graphene. (Taken from <http://www.chem1.com/acad/webtext/states/states.html>)

Possible applications of Graphene

- ▶ Possible uses in high frequency transistors
 - ▶ But Graphene Field Effect Transistors show low on-off ratio - “off” state still has relatively high conduction compared to “on” state
 - ▶ Large energy wastage
 - ▶ Need band gap
 - ▶ Can be engineered through doping - the addition of Hydrogen to produce “graphane” or fluorine to produce fluorinated graphene.

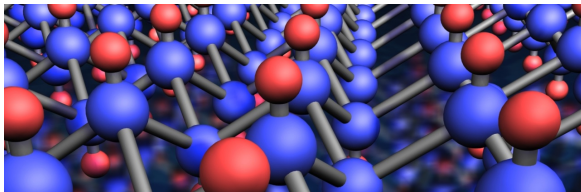


Figure: An artist's impression of graphane, Carbon atoms in blue, Hydrogen atoms in red. Taken from

<http://www.physorg.com/news152545648.html>

The Aim of our project

- ▶ Computationally model the effect of defects in graphene
- ▶ Relevant for Hydrogenated and Fluorinated graphene
- ▶ Basic methodology:
 1. Compute the Hamiltonian to obtain the density of states and eigenvectors for the system - using the Tight Binding Model
 2. Use this to calculate the transmission coefficients - considering the transmission at a potential barrier
 3. Use these to calculate the conductance of the modelled sample - using the Landauer formula
- ▶ Will also later model the effect of magnetic fields to investigate the Quantum Hall Effect in graphene (not included in this talk)

Crystal Lattice structure - Real Lattice

- ▶ Carbon atoms in a hexagonal lattice
- ▶ Two unique sublattices labelled A and B.
- ▶ Lattice vectors: $\mathbf{a}_{1,2} = \frac{3a}{2} \hat{\mathbf{i}} \pm \frac{\sqrt{3}a}{2} \hat{\mathbf{j}}$
- ▶ Lattice constant: $a \approx 2.461\text{\AA}$

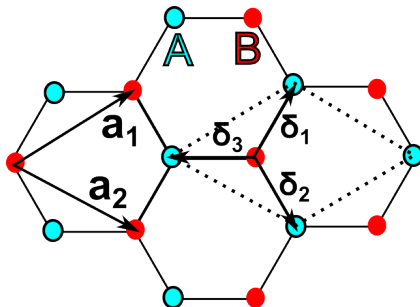


Figure: A diagram of the real space lattice of graphene.

The Tight Binding Model - Calculating the Hamiltonian

- ▶ Assume electrons reside on lattice sites only
- ▶ Assume that electrons can only hop to nearest neighbours (can include higher nearest neighbour interactions)
- ▶ So electrons can only move from sublattice A points to sublattice B points and vice versa.
- ▶ In the Hamiltonian matrix, H_{ij} is the energy cost for hopping from position i to position j .

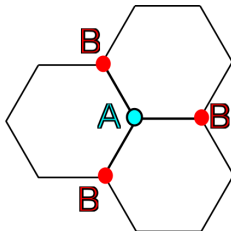


Figure: A diagram showing hopping possibilities from a Carbon atom in the lattice.

The Tight Binding Model (continued)

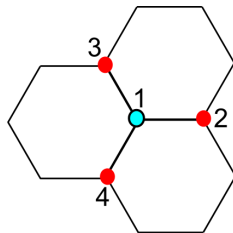


Figure: Labelling the sites 1-4.

- ▶ With a nearest-neighbour hopping energy t ($t \approx 2.8\text{eV}$), the Hamiltonian is:

$$\hat{H} = \begin{pmatrix} E_0 & -t & -t & -t \\ -t & E_1 & 0 & 0 \\ -t & 0 & E_2 & 0 \\ -t & 0 & 0 & E_3 \end{pmatrix} \quad (1)$$

The Tight Binding Model (continued)

- By considering the lattice geometry, and the sum of the wavefunctions across both sublattices, the following expression is obtained for the Time Independent Schrödinger Equation:

$$E\psi = \begin{pmatrix} 0 & -\tilde{t}(k) \\ -\tilde{t}^*(k) & 0 \end{pmatrix} \psi \quad (2)$$

where

$$t(\tilde{k}) = t \left(e^{ik_x a} + e^{\frac{-ik_x a}{2}} 2 \cos \left(\frac{k_y \sqrt{3} a}{2} \right) \right) \quad (3)$$

- Taking the eigenvalues of the matrix yields:

$$E = \pm |\tilde{t}(k)| \quad (4)$$

Dirac Points on band structure

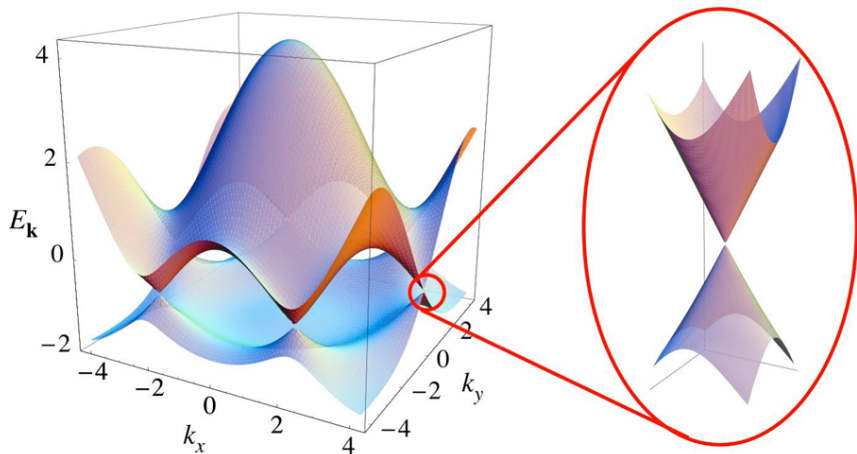


Figure: A diagram of the band structure of graphene. The Dirac points are where the bands converge. Taken from <http://nextbigfuture.com/2011/04/nrl-researchers-take-step-toward.html>

Dirac Points

- ▶ Points in reciprocal space where $|\tilde{t}(k)| = 0$.
- ▶ These lie on the vertices of the first Brillouin Zone in reciprocal space.
- ▶ The unique Dirac points are K and K'.

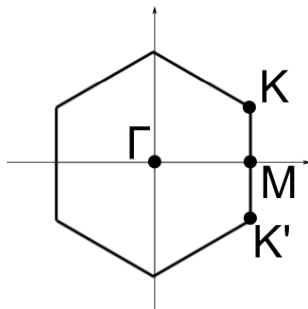


Figure: A diagram of the first Brillouin zone of graphene in reciprocal space.

Dispersion near the Dirac points

- ▶ Near the Dirac points the Hamiltonian reduces to:

$$\hat{H} = \hbar v \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} \quad (5)$$

- ▶ Taking the eigenvalues of this yields:

$$E = \pm \hbar v k \quad (6)$$

- ▶ This is a linear dispersion relation, and means that the quasiparticles are massless fermions near the Dirac points - they act as relativistic particles with a constant velocity $v \approx 10^6 \text{ m s}^{-1}$
- ▶ Note that since the Dirac points are points in *reciprocal* space, this relation applies for electron transport through-out the graphene sample as energy is always small compared to peak energy ($t \approx 2.8 \text{ eV}$ corresponds to $\sim 30,000 \text{ K}$).

Showing the effective mass is zero at the Dirac points

- ▶ At the Dirac points we obtained the dispersion relation:

$$E = \hbar v k \quad (7)$$

- ▶ From Special Relativity we know:

$$E = \sqrt{p^2 c^2 + m^2 c^4} \quad (8)$$

- ▶ So the dispersion relation is just the $m \rightarrow 0$ case of this.

$$\therefore E = \sqrt{p^2 c^2} = pc = \hbar kc \quad (9)$$

- ▶ Constant velocity is $v \approx 10^6 \text{ m s}^{-1}$ instead of c ($\sim 3 \times 10^8 \text{ m s}^{-1}$).
- ▶ So effective mass is zero and relativistic effects much more apparent.

Dispersion near the Dirac points

- This means that near the Dirac points, the dispersion follows “Dirac cones”:

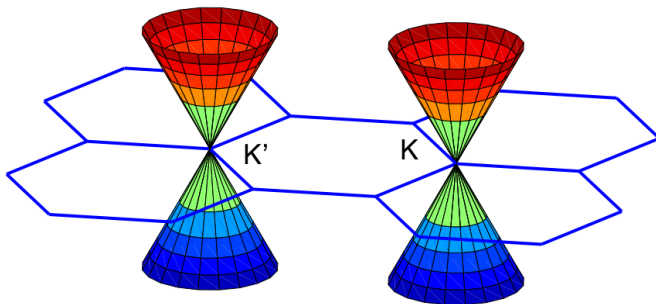


Figure: A diagram showing Dirac Cones at the Dirac points in reciprocal space. Taken from: <http://www.mpi-pks-dresden.mpg.de/mpi-doc/CondensedMatter//content/QuantHall.shtml>

Klein Paradox

- ▶ The Klein Paradox results as a consequence of the massless Dirac fermion quasiparticles, and their linear dispersion.
- ▶ Unintuitive result that transmission probability increases with the height of the potential barrier, and tends to 1 as the potential tends to infinity.
- ▶ This means that the quasiparticles cannot be localised.
- ▶ We should observe this effect when calculating transmission coefficients.

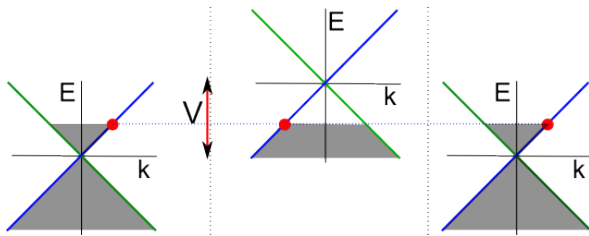


Figure: A diagram showing the principle of how the transmission occurs by shifting the quasiparticle to the lower cone.

The Landauer Formula - calculating the conductance

- ▶ By considering the electrons that are able to move across a potential and the density of states of graphene near the Dirac points, the following equation is obtained for the net conductance:

$$G \approx \frac{e^2}{\pi \hbar} \sum_i T_i \quad (10)$$

where the sum is taken across all channels (taking in to account the possibility for varying transmission amplitudes)

- ▶ So per channel the conductivity is:

$$\sigma \approx \frac{e^2}{\pi \hbar} \quad (11)$$

- ▶ Note that this means there is a minimum conductivity even in ideal, undoped Graphene, where there should be no scattering and no net current carriers!

The Missing Pi Problem

- ▶ But experimental results show the minimum conductivity to be an order of π larger:

$$\sigma_{\text{experimental}} \approx \frac{e^2}{h} \quad (12)$$

- ▶ This is known as the “Missing Pi(e) Problem”
- ▶ Problem still unsolved
- ▶ But 2007 report by Miao *et al.* in Science **317** 3150, reported that the experimental value approached the theoretical value for specific shapes - small, wide graphene rectangles were closer to theory.

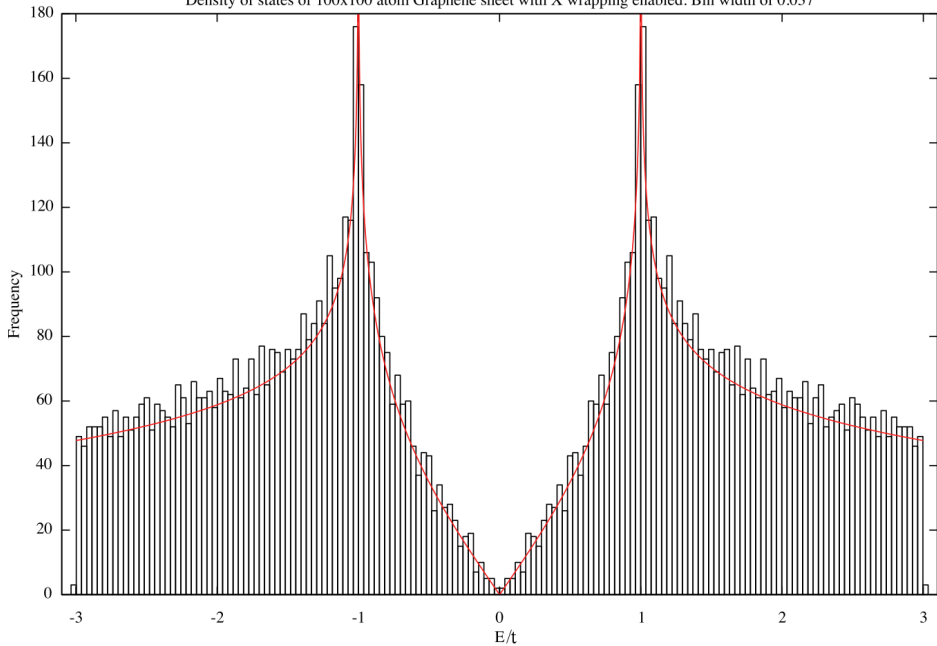
Summary: The interesting theory of Graphene

- ▶ Exhibits high crystal quality - electrons can thousands of interatomic distances without scattering.
- ▶ Massless Dirac fermions near Dirac points - show relativistic effects in ordinary conditions!
- ▶ Klein Paradox - Particles tunnel through a potential barrier with a transmission coefficient which tends to 1 as the potential tends to infinity.
- ▶ Universal minimum conductivity:
 - ▶ Finite conductivity in undoped graphene at Dirac points (where there are no net charge carriers) even at low T (when there is no scattering)
 - ▶ Conductivity without charge carriers!
 - ▶ Normally materials would transition to insulators at low T
 - ▶ But in Graphene there is a suppression of localisation
- ▶ Missing π problem - observed minimum conductivity is a multiple of π greater than predicted by theory

Preliminary Work

- ▶ We have already started work on the project
- ▶ Program written in C
- ▶ Produce Hamiltonian eigenvectors and eigenvalues
- ▶ Produce density of states
- ▶ Already have data for the density of states plotted with a fit from an analytical approach by Dr. Shytov
- ▶ Resolution of histogram limited by the size of the modelled sample

Density of states of 100x100 atom Graphene sheet with X wrapping enabled. Bin width of 0.037



Conclusion - What is to be done?

- ▶ Add method to normalise the density of states per unit area
- ▶ Add method for modelling defects
 - ▶ For vacancies this means setting the energy to occupy a point to a very large number
- ▶ Add methods to obtain transmission coefficients and conductance
- ▶ Will later consider magnetic field effects
- ▶ Some computational challenges due to the size of the considered samples
 - ▶ High memory usage if all zeros are stored as double precision floats too
- ▶ The Hamiltonian is sparse and so we will attempt to use sparse matrix methods

Any questions?

- ▶ Thank you for your time!
- ▶ Thanks to my supervisor Dr. Shytov for his help and discussions.
- ▶ Thanks to my colleagues Chris Beckerleg and Will Smith for their continuing work.
- ▶ Presentation produced using \LaTeX and Beamer.

Supplementary slides

Why is the “impossible” possible?

- ▶ From the Mermin-Wagner theorem, thermal fluctuations would make 2D structures unstable at any finite temperature.
- ▶ This was confirmed as the melting temperature of thin films rapidly decreased with decreasing temperature¹.
- ▶ In graphene, the gentle 3D warping (~10nm) provides stability by minimising thermal vibrations.

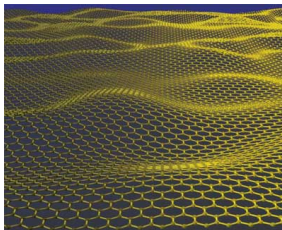



Figure: An artist's impression of corrugated Graphene: Jannik Meyer. (Taken from <http://www.nanowerk.com/>)

¹See Geim & Novoselov, The rise of graphene, *Nat. Mat.* **6**, 183 (2007). 

Why is localisation suppressed?

- ▶ The suppression of localisation is a result of the relativistic effects on the quasiparticles.
- ▶ The quasiparticles cannot be localised due to the Zitterbewegung (jittery motion) effect.
- ▶ The Klein effect also means that the quasiparticles are transmitted through potential barriers with a probability ≈ 1 .
- ▶ This also contributes to the suppression of localisation.

Translation to “brick wall” model for computation

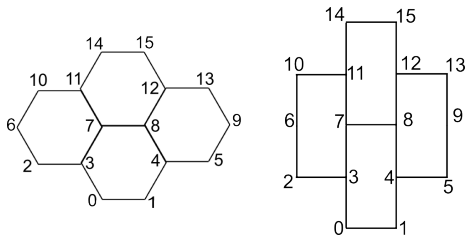


Figure: Diagram showing the principle of the translation.

- ▶ We translate to the “brick-wall” model when considering the bonds.
- ▶ So all bonds are straight horizontal or vertical - no $\sqrt{3}$ factors.
- ▶ But we must reconsider these when normalising the density of states per unit area and other considerations.

The Tight Binding Approximation derivation

- ▶ The Time Independent Schrödinger Equation (TISE) states:

$$E\psi = \hat{H}\psi \quad (13)$$

- ▶ From Bloch theory we know:

$$\psi_A = \tilde{\psi}_A e^{i(\mathbf{k} \cdot \mathbf{r})}, \quad \psi_B = \tilde{\psi}_B e^{i(\mathbf{k} \cdot \mathbf{r})} \quad (14)$$

- ▶ So from point 1, the TISE becomes:

$$E\tilde{\psi}_A = - \sum_{i,j} H_{ij} \psi_j = H_{12}\psi_2 + H_{13}\psi_3 + H_{14}\psi_4 = -t(\psi_2 + \psi_3 + \psi_4) \quad (15)$$

- ▶ But recall that:

$$\mathbf{k} \cdot \mathbf{r} = k_x x + k_y y \quad (16)$$

The Tight Binding Approximation derivation (2)

- So by considering the geometry of the lattice points, assuming \mathbf{r} has its origin at point 1, the TISE becomes:

$$E\tilde{\psi}_A = -t \left(\tilde{\psi}_B \left(e^{ik_x a} + e^{\frac{-ik_x a}{2} + \frac{iky a \sqrt{3}}{2}} + e^{\frac{-ik_x a}{2} - \frac{iky a \sqrt{3}}{2}} \right) \right) \quad (17)$$

- Which can be written as:

$$E\tilde{\psi}_A = -t(k)\tilde{\psi}_B \quad (18)$$

- Combining this with an equation for a point on sublattice B (repeating the same steps), one obtains:

$$E\psi = \begin{pmatrix} 0 & -\tilde{t}(k) \\ -\tilde{t}^*(k) & 0 \end{pmatrix} \psi \quad (19)$$

Derivation of Hamiltonian near Dirac points

- ▶ From previous derivation:

$$\begin{aligned} |\tilde{t}(k)| &= t \left| e^{ik_x a} + e^{\frac{-ik_x a}{2} + \frac{iky a \sqrt{3}}{2}} + e^{\frac{-ik_x a}{2} - \frac{iky a \sqrt{3}}{2}} \right| \\ &= t \left| e^{ik_x a} + e^{\frac{-ik_x a}{2}} 2 \cos \left(\frac{k_y \sqrt{3} a}{2} \right) \right| = 0 \end{aligned}$$

Near K and K'.

- ▶ Dividing by $e^{ik_x a}$:

$$|\tilde{t}(k)| = t \left| 1 + e^{\frac{-ik_x a}{2}} 2 \cos \left(\frac{k_y \sqrt{3} a}{2} \right) \right| \quad (20)$$

- ▶ Using Taylor approximation near K:

$$\tilde{t}(K + \delta k) \approx \tilde{t}(K) + \delta k_x \frac{\partial \tilde{t}(k)}{\partial k_x} + \delta k_y \frac{\partial \tilde{t}(k)}{\partial k_y} \quad (21)$$

Derivation of Hamiltonian near Dirac points (2)

- ▶ Calculating the differentials:

$$\begin{aligned}\tilde{t}(K + \delta k) \approx \tilde{t}(K) &+ \delta k_x \left(\frac{-3ai}{2} e^{\frac{-ik_x 3a}{2}} \cdot 2 \cos \left(\frac{k_y \sqrt{3}a}{2} \right) \right) t \\ &+ \delta k_y \left(-\sqrt{3}a \sin \left(\frac{k_y a \sqrt{3}}{2} \right) e^{\frac{-ik_x 3a}{2}} \right) t\end{aligned}$$

- ▶ Substituting for K: $\left(0, \frac{4\pi}{3\sqrt{3}a}\right)$

$$\tilde{t}(K + \delta k) \approx 0 + \delta k_x \left(\frac{3ait}{2} \right) + \delta k_y \left(\frac{-3at}{2} \right) \quad (22)$$

- ▶ So the Hamiltonian can be written:

$$H_K(k) = \frac{3at}{2} \begin{pmatrix} 0 & k_y - ik_x \\ k_y + ik_x & 0 \end{pmatrix} \quad (23)$$

Derivation of Hamiltonian near Dirac points (3)

- Can write this in terms of Pauli matrices σ :

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad (24)$$

- But must swap k_x and k_y to make this simple (rotating the k vector):

$$k_x \rightarrow k_y, \quad k_y \rightarrow -k_x \quad (25)$$

- So the Hamiltonian at K becomes:

$$H_K(k) = \frac{3at}{2} \begin{pmatrix} 0 & -k_x - ik_y \\ -k_x + ik_y & 0 \end{pmatrix} \quad (26)$$

- Which can be written as:

$$H_K(k) = -\frac{3at}{2} (\vec{\sigma}^* \cdot \vec{k}) \quad (27)$$

Derivation of Hamiltonian near Dirac points (4)

- ▶ Similarly for K' : $\left(0, \frac{-4\pi}{3\sqrt{3}a}\right)$

$$H_{K'}(k) = \frac{3at}{2} (\vec{\sigma} \cdot \vec{k}) \quad (28)$$

- ▶ Taking the eigenvalues of $H_K(k)$:

$$\begin{vmatrix} E & \frac{3at}{2} (-k_x - ik_y) \\ \frac{3at}{2} (-k_x + ik_y) & E \end{vmatrix} = 0 \quad (29)$$

$$\therefore E^2 - \left(\frac{3at}{2}\right)^2 (k_x^2 - ik_x k_y + ik_x k_y + k_y^2) \quad (30)$$

$$\therefore E^2 - \left(\frac{3at}{2}\right)^2 k^2 = 0 \quad \therefore E = \pm \frac{3at}{2} k \quad (31)$$

- ▶ Linear dispersion - can be written as $E = v\hbar k$