Electronic structure of monolayer graphene

Graphene seminar 25/04/13

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Literature

M. I. Katsnelson: Graphene (Cambridge University Press)

ArXiv:1205.4849
Crystal lattice of monolayer graphene

Hexagonal lattice of carbon atoms

Two atoms in the unit cell:

More realistic view
Electronic structure from DFT calculations


Electronic structure from DFT calculations

Crossing of \( \pi \) bands at the K point of the Brillouin zone

Dispersion is linear in Wavenumber close to the K point

Band dispersion from Angle Resolved Photoelectron Spectroscopy (ARPES)

**Tight-binding model: general theory**

It is assumed that the system has translational invariance => we consider an infinite graphene sheet

In general, there are $n$ atomic orbitals in the unit cell

We can form $n$ Bloch functions

$$
\Phi_j(k, r) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} e^{ik \cdot R_{j,i}} \phi_j(r - R_{j,i})
$$

An electronic function is a linear combination of these Bloch functions

$$
\Psi_j(k, r) = \sum_{l=1}^{n} c_{j,l}(k) \Phi_l(k, r)
$$
Tight-binding model: general theory

The energy of the jth band:

\[ E_j(k) = \frac{\langle \Psi_j | \mathcal{H} | \Psi_j \rangle}{\langle \Psi_j | \Psi_j \rangle}, \]

Substituting the expansion

\[ E_j(k) = \frac{\sum_{i,l}^n c_{ji}^* c_{jl} \langle \Phi_i | \mathcal{H} | \Phi_l \rangle}{\sum_{i,l}^n c_{ji}^* c_{jl} \langle \Phi_i | \Phi_l \rangle} = \frac{\sum_{i,l}^n \mathcal{H}_{il} c_{ji}^* c_{jl}}{\sum_{i,l}^n \mathcal{S}_{il} c_{ji}^* c_{jl}} \]

\[ \mathcal{H}_{il} = \langle \Phi_i | \mathcal{H} | \Phi_l \rangle \]

\[ \mathcal{S}_{il} = \langle \Phi_i | \Phi_l \rangle \]
**Tight-binding model: general theory**

Minimizing the energy with respect to the coefficients:

\[ c_{jm}^* \rightarrow \frac{\partial E_j}{\partial c_{jm}^*} = 0 \]

\[
\sum_{l=1}^{n} H_{ml} c_{jl} = E_j \sum_{l=1}^{n} S_{ml} c_{jl}
\]

For the special case of two orbitals per unit cell:

\[
\begin{pmatrix}
H_{11} & H_{12} \\
H_{21} & H_{22}
\end{pmatrix}
\begin{pmatrix}
c_{j1} \\
c_{j2}
\end{pmatrix}
= E_j
\begin{pmatrix}
S_{11} & S_{12} \\
S_{21} & S_{22}
\end{pmatrix}
\begin{pmatrix}
c_{j1} \\
c_{j2}
\end{pmatrix}
\]

In short:

\[ H\psi_j = E_j S\psi_j \]

Eigenenergies:

\[ \det (H - E_j S) = 0 \]
Tight-binding model: graphene

There are \( n=2 \) orbitals in the unit cell.

**Diagonal matrix elements**

\[
H_{AA} = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} e^{i \mathbf{k} \cdot (\mathbf{R}_{A,j} - \mathbf{R}_{A,i})} \langle \phi_{A} (\mathbf{r} - \mathbf{R}_{A,i}) | \mathcal{H} | \phi_{A} (\mathbf{r} - \mathbf{R}_{A,j}) \rangle
\]

\( \mathbf{k} = (k_x, k_y) \)

**Assumption:** dominant contribution comes from \( i=j \), others can be neglected

\[
H_{AA} \approx \frac{1}{N} \sum_{i=1}^{N} \langle \phi_{A} (\mathbf{r} - \mathbf{R}_{A,i}) | \mathcal{H} | \phi_{A} (\mathbf{r} - \mathbf{R}_{A,i}) \rangle
\]

\( \langle \phi_{A} | \mathcal{H} | \phi_{A} \rangle \) Within the summation this expectation value is the same for every value of \( i \)

\[
H_{AA} \approx \frac{1}{N} \sum_{i=1}^{N} \epsilon_{2p} = \epsilon_{2p}
\]
**Tight-binding model: graphene**

Carbon atoms on sublattice B are chemically identical to atoms on sublattice A:

\[
H_{BB} = H_{AA} \approx \epsilon_{2p}
\]

**Overlap integrals:** assuming again that same site contribution dominate (nearest neighbours are B atoms)

\[
S_{AA} \approx \frac{1}{N} \sum_{i=1}^{N} \langle \phi_A (r - R_{A,i}) | \phi_A (r - R_{A,i}) \rangle = 1
\]
**Tight-binding model: graphene**

Off-diagonal matrix elements

\[ H_{AB} = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} e^{ik \cdot (R_{B,j} - R_{A,i})} \langle \phi_A (r - R_{A,i}) | \mathcal{H} | \phi_B (r - R_{B,j}) \rangle \]

Assumption: dominant contribution comes from nearest-neighbors, other contributions can be neglected. Looking at, e.g., A type atoms, there are 3 nearest-neighbor B atoms

\[ H_{AB} \approx \frac{1}{N} \sum_{i=1}^{N} \sum_{l=1}^{3} e^{ik \cdot (R_{B,l} - R_{A,i})} \langle \phi_A (r - R_{A,i}) | \mathcal{H} | \phi_B (r - R_{B,l}) \rangle \]

The index “l” depends on the index “i”
Tight-binding model: graphene

Off-diagonal matrix elements

\[ H_{AB} = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} e^{i\mathbf{k} \cdot (\mathbf{R}_{B,j} - \mathbf{R}_{A,i})} \langle \phi_A (\mathbf{r} - \mathbf{R}_{A,i}) | \mathcal{H} | \phi_B (\mathbf{r} - \mathbf{R}_{B,j}) \rangle \]

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The index “l” depends on the index “i”
Tight-binding model: graphene

The matrix element between nearest-neighbor A and B atoms has the same value for each neighboring pair:

\[
\gamma_0 = - \langle \phi_A (r - R_A, i) | \mathcal{H} | \phi_B (r - R_B, i) \rangle
\]

Note, at this step we have made use of the fact that the atomic orbitals \( \phi_j \) are actually \( p_z \) orbitals, hence have a rotational symmetry.
Footnote: general method to obtain tight-binding Hamiltonians

General method: Slater-Koster parametrization of hopping integrals
For recent introduction see, e.g., Sergej Konschuh PhD thesis

Slater-Koster parametrization is still useful, especially in connection with first principles methods and group theory.
Recent examples: Bilayer MoS2, arXiv:1304.4831

Spin-orbit coupling in trilayer graphene:
Tight-binding model : graphene

The matrix element between nearest-neighbor A and B atoms has the same value for each neighboring pair:

$$\gamma_0 = -\langle \phi_A (r - R_{A,i}) | \mathcal{H} | \phi_B (r - R_{B,l}) \rangle$$

Note, at this step we have made use of the fact that the atomic orbitals $\phi_j$ are actually $p_z$ orbitals, hence have a rotational symmetry

Therefore

$$H_{AB} \approx -\frac{\gamma_0}{N} \sum_{i=1}^{N} \sum_{l=1}^{3} e^{ik \cdot \delta_i} \equiv -\gamma_0 f(k)$$

$$f(k) = \sum_{l=1}^{3} e^{ik \cdot \delta_l}$$

$$\delta_l = R_{B,l} - R_{A,i}$$

Position of atom B relative to atom A
**Tight-binding model : graphene**

\[ \delta_1 = \left( 0, \frac{a}{\sqrt{3}} \right) \quad \delta_2 = \left( \frac{a}{2}, -\frac{a}{2\sqrt{3}} \right) \]

\[ \delta_3 = \left( -\frac{a}{2}, -\frac{a}{2\sqrt{3}} \right) \]

\[ f(\mathbf{k}) = e^{ik_y a/\sqrt{3}} + 2e^{-ik_y a/2\sqrt{3}} \cos \left( k_x a/2 \right) \]
Tight-binding model: graphene

Finally

\[ \delta_1 = \left( 0, \frac{a}{\sqrt{3}} \right) \quad \delta_2 = \left( \frac{a}{2}, -\frac{a}{2\sqrt{3}} \right) \]
\[ \delta_3 = \left( -\frac{a}{2}, -\frac{a}{2\sqrt{3}} \right) \]

\[ f(k) = e^{ik_ya/\sqrt{3}} + 2e^{-ik_ya/2\sqrt{3}} \cos(k_xa/2) \]

Finally

\[ H_{AB} \approx -\gamma_0 f(k) \quad H_{BA} \approx -\gamma_0 f^*(k) \]

In a similar fashion:

\[ S_{AB} = s_0 f(k) \]
Tight-binding model : graphene

In summary:

\[ H_1 = \begin{pmatrix} \epsilon_{2p} & -\gamma_0 f(k) \\ -\gamma_0 f^*(k) & \epsilon_{2p} \end{pmatrix} \]

\[ S_1 = \begin{pmatrix} 1 & s_0 f(k) \\ s_0 f^*(k) & 1 \end{pmatrix} \]

The corresponding eigenenergies:

\[
\det \begin{pmatrix} \epsilon_{2p} - E & -\left(\gamma_0 + E s_0\right) f(k) \\ -\left(\gamma_0 + E s_0\right) f^*(k) & \epsilon_{2p} - E \end{pmatrix} = 0
\]

From


\[ \gamma_0 = 3.033 \text{ eV} \quad \epsilon_{2p} = 0 \quad \text{Choice of the origin of the energy axis} \]

\[ s_0 = 0.129 \quad \text{Such parameters can be obtained from DFT or experiments} \]
Tight-binding model: graphene

\[ E_{\pm} = \frac{\epsilon_2 p \pm \gamma_0 |f(k)|}{1 \mp s_0 |f(k)|} \]
Low-energy physics, Dirac-like Hamiltonian

Fermi energy lies at $E=0$

Only two $K$ points are inequivalent, the others are connected by reciprocal vector, or see the original Brillouin zone

$$K_\xi = \xi \left( \frac{4\pi}{3a}, 0 \right)$$

$K_-, K_+$ points often called "valleys"

$$E_\pm = \frac{\epsilon_{2p} \pm \gamma_0 |f(k)|}{1 \mp \gamma_0 |f(k)|}$$

$$f(K_\xi) = e^0 + e^{i\xi2\pi/3} + e^{-i\xi2\pi/3} = 0$$

Gaples band structure
**Low-energy physics, Dirac-like Hamiltonian**

Introducing the momentum measured from the K point(s)

\[ \mathbf{p} = \hbar \mathbf{k} - \hbar \mathbf{K}_\xi \]

and expanding \( f(k) \) up to first order in \( p \)

\[ f(k) \approx -\frac{\sqrt{3}a}{2\hbar} (\xi p_x - ip_y) \]

and we obtain the famous 2D massless Dirac Hamiltonian of graphene

\[ H_{1,\xi} = \nu \begin{pmatrix} 0 & \xi p_x - ip_y \\ \xi p_x + ip_y & 0 \end{pmatrix} \quad \nu = \frac{\sqrt{3}a\gamma_0}{(2\hbar)} \]
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and we obtain the famous 2D massless Dirac Hamiltonian of graphene

\[ H_{1,\xi} = v \begin{pmatrix} 0 & \xi p_x - ip_y \\ \xi p_x + ip_y & 0 \end{pmatrix} \]

\[ v = \sqrt{3}a\gamma_0/(2\hbar) \]

The actual value of the velocity \( v \) is \( 10^6 \) m/s \( \approx c/300 \)
Low-energy physics, Dirac-like Hamiltonian

\[ H_{1,\xi} = \nu \begin{pmatrix} 0 & \xi p_x - ip_y \\ \xi p_x + ip_y & 0 \end{pmatrix} \]

If we now consider \( H_1 \) to be an effective Hamiltonian and solve the corresponding Schrödinger equation:

\[ E_{\pm} = \pm \nu p \]

\[ \psi_{\pm} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm \xi e^{i\xi \varphi} \end{pmatrix} e^{i \mathbf{p} \cdot \mathbf{r} / \hbar} \]

\[ \mathbf{p} = (p_x, p_y) = p (\cos \varphi, \sin \varphi) \]

What about the overlap matrix \( S \)?

\[ E_{\pm} = \frac{c_{2p} \pm \gamma_0 |f(\mathbf{k})|}{1 \mp s_0 |f(\mathbf{k})|} \]

Finite overlap contributes with \( \sim p^2 \) terms
Low-energy physics, Dirac-like Hamiltonian

\[ H_{1, \xi} = v \begin{pmatrix} 0 & \xi p_x - i p_y \\ \xi p_x + i p_y & 0 \end{pmatrix} \]

If we now consider \( H_1 \) to be an effective Hamiltonian and solve the corresponding Schrödinger equation:

\[ \psi_\pm = \frac{1}{\sqrt{2}} \left( \begin{pmatrix} 1 \\ \pm \xi e^{i \xi \varphi} \end{pmatrix} \right) e^{i p \cdot r / \hbar} \]

\[ p = (p_x, p_y) = p (\cos \varphi, \sin \varphi) \]

What about the overlap matrix \( S \)?

\[ E_\pm = \frac{\varepsilon_2 p \pm \gamma_0 |f(k)|}{1 \mp s_0 |f(k)|} \quad \text{Finite overlap contributes with } \sim p^2 \text{ terms} \]
**Low-energy physics, Dirac-like Hamiltonian**

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\[ E_{\pm} = \pm vp \]

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What about the overlap matrix \( S \)?

\[ E_{\pm} = \frac{\varepsilon_{2p} \pm \gamma_0 |f(k)|}{1 \pm s_0 |f(k)|} \quad \text{Finite overlap contributes with } \sim p^2 \text{ terms} \]

Higher order terms in momentum in \( E(p) \) are negligible for energies \( \leq 1 \) eV
Pseudospin and chirality

The eigenstates have two components, reminiscent of spin $\frac{1}{2}$

$$\psi_{\pm} = \frac{1}{\sqrt{2}} \left( \begin{array}{c} 1 \\ \pm \xi e^{i\xi \varphi} \end{array} \right) e^{ip \cdot r/\hbar}$$

Looking back to the original definitions, the two components correspond to the relative amplitude of the Bloch function on the A and B sublattice.

This degree of freedom is called pseudospin.

If the wavefunction was finite only on A sublattice $\rightarrow (1,0)^T = |\uparrow\rangle$

on B sublattice $\rightarrow (0,1)^T = |\downarrow\rangle$

In graphene, the density is usually shared equally between A and B sublattice.

Some substrates can break this symmetry, though
Pseudospin and chirality

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$$\psi_{\pm} = \frac{1}{\sqrt{2}} \left( \pm \xi e^{i\xi \varphi} \right) e^{ip \cdot r/\hbar}$$

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Some substrates can break this symmetry, though

**Note the index $\xi$:** in addition to pseudospin, there is another degree of freedom: valley

The valleys are usually not coupled, except in the case of atomic scale scatterers and certain boundaries $\Rightarrow$ two independent Hamiltonians
**Pseudospin and chirality**

The particles described by the Dirac Hamiltonian of monolayer graphene have yet another property: they are **chiral**

This means that the orientation of pseudospin depends on the direction of the electronic momentum $\mathbf{p}$

To see this more clearly, let's write the effective Hamiltonian as

$$H_{1,\xi} = v \left( \xi \sigma_x p_x + \sigma_y p_y \right)$$

and define a pseudospin vector as $\mathbf{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$

and a unit vector as $\hat{n}_1 = (\xi \cos \varphi, \sin \varphi, 0)$
**Pseudospin and chirality**

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and define a pseudospin vector as

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\]

and a unit vector as

\[
\mathbf{\hat{n}}_1 = (\xi \cos \varphi, \sin \varphi, 0)
\]

Then

\[
H_{1,\xi} = vp \mathbf{\sigma} \cdot \mathbf{\hat{n}}_1
\]

therefore \( \sigma \) is linked to the direction of \( n_1 \)
**Pseudospin and chirality**

In other words, the eigenstates of the effective Hamiltonian are also eigenstates of the chiral operator \( \mathbf{\sigma} \cdot \hat{n}_1 \)

\[
\mathbf{\sigma} \cdot \hat{n}_1 \psi_\pm = \pm \psi_\pm
\]

Another way to express this is to calculate with respect to \( \psi_\pm \).

\[
\langle \mathbf{\sigma} \rangle_{e/h} = \pm (\xi \cos \varphi, \sin \varphi, 0)
\]

In valley \( K_+ \)
Pseudospin and chirality

Important consequence of the chirality of particles: the probability to scatter into a direction characterized by the angle $\varphi$ ($\varphi=0$ corresponds to forward Scattering) is proportional to

$$w(\varphi) = |\langle \psi_\pm(\varphi) | \psi_\pm(0) \rangle|^2$$

For monolayer graphene

$$w(\varphi) = \cos^2(\varphi/2)$$

No backscattering!