ETH
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Solid State Theory
Exercise 5

SS 10
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Carbon nanotubes

Since their discovery in 1991 [S. Iijima, Nature **345**, 56 (1991)] carbon nanotubes have been the object of an intensive research activity. Carbon nanotubes are made by rolling a graphene sheet (a single layer of graphite) into a cylinder. Due to the (hexagonal, cf. Fig. 2) lattice structure of graphene there are several inequivalent ways of rolling up the sheet, depending on the orientation (w.r.t. the lattice) and circumference of the resulting cylinder. In this exercise you will show that whereas graphene is metallic, the geometry change imposed by rolling it up can render the nanotube semiconducting.

Exercise 5.1 Graphene

Compute the low-energy band structure of graphene within a tight-binding description taking only nearest-neighbor hopping into account!

To get started, consider the electronic configuration of C. C has four valence electrons which occupy $2s^2$ and $2p^2$ orbitals. The hexagonal structure of the lattice suggests that three of these valence electrons occupy hybrid sp^2-orbitals to form covalent σ-bonds with their nearest neighbors (bonding angle $2\pi/3$). Due to the large binding energy, there are no low-energy excitations involving these electrons. The remaining electron occupies the p_z orbital that sticks out of the planar lattice forms weaker π-bonds with the neighboring atoms. Based on these considerations, it seems reasonable to focus solely on the electrons in the p_z-orbitals, so that the problem reduces to one electron and one orbital per atom.

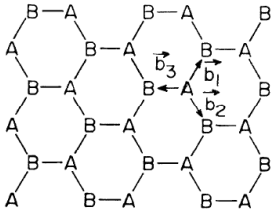

Figure 1:

Hint: Before embarking into the calculation, you may wish to refresh your memory about the unit cell and Brillouin zone for a hexagonal lattice.

To write down the hopping Hamiltonian, divide the lattice into two sublattices A and B as shown in Fig. 1 and introduce fermionic field operators a_i and b_i (i labels the site) on these sublattices. Then argue that the hopping matrix element is the same for all $\vec{b}_i$ ($i = 1, 2, 3$) in Fig. 1 for a given site. Use the Fourier transform,

$$\begin{aligned} a_i &= \frac{1}{\sqrt{N}} \sum_{\vec{k}\in \mathrm{BZ}} \tilde{a}_k e^{i\vec{k}\cdot\vec{R}_{a,i}} \\ b_i &= \frac{1}{\sqrt{N}} \sum_{\vec{k}\in \mathrm{BZ}} \tilde{b}_k e^{i\vec{k}\cdot\vec{R}_{b,i}}, \end{aligned} \tag{1}$$

where N is the number of unit cells and $\vec{R}_{a,i}$ ($\vec{R}_{b,i}$) is the position of the i-th site on sublattice A (B) to obtain a Hamiltonian of the form

$$\mathcal{H} = \sum_{\vec{k}\in \mathrm{BZ}} \left(\tilde{a}^\dagger_{\vec{k}} \tilde{b}^\dagger_{\vec{k}}\right) \begin{pmatrix} h_{aa}(\vec{k}) & h_{ab}(\vec{k}) \\ h_{ba}(\vec{k}) & h_{bb}(\vec{k}) \end{pmatrix} \begin{pmatrix} \tilde{a}_{\vec{k}} \\ \tilde{b}_{\vec{k}} \end{pmatrix}. \tag{2}$$

Plot the band structure and show that the Fermi 'surface' consists of two points by finding the values of $\vec{k}$ for which the energy is zero.

Finally, obtain the low-energy structure by expanding the energy to leading order in small deviations $\vec{k}$ around the Fermi points. The low-energy Hamiltonian can be shown to be equivalent to the celebrated Dirac Hamiltonian for relativistic fermions (in a $(2+1)$-dimensional space-time). Can you see what is 'relativistic' about the dispersion relation?

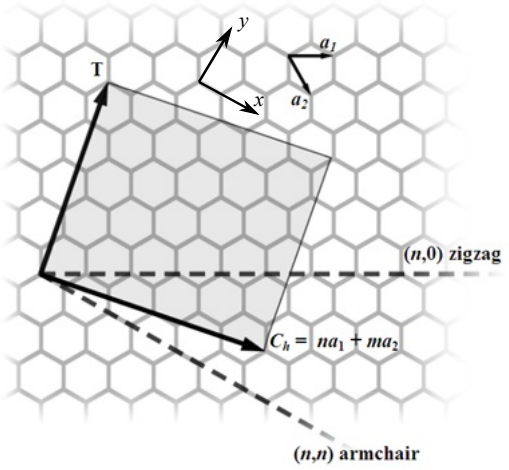

Figure 2: Carbon lattice of graphene. $\{\mathbf{a}_1, \mathbf{a}_2\}$ are the primitive vectors of the unit cell of graphene. $\{\mathbf{C}_h, \mathbf{T}\}$ are the primitive vectors of the nanotube.

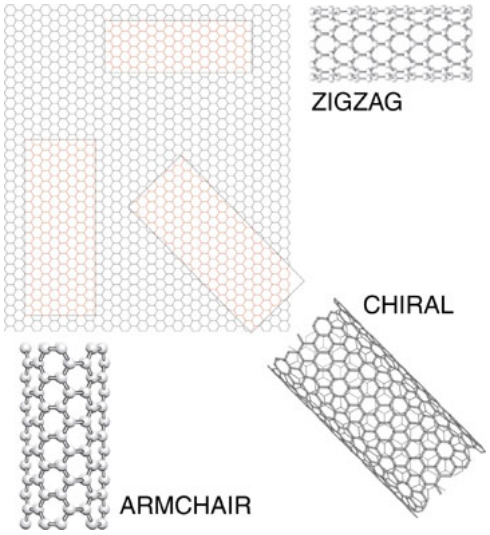

Figure 3: The different geometries of carbon nanotubes: armchair, zigzag and chiral nanotubes.

Exercise 5.2 Carbon nanotubes

The orientation and circumference of a nanotube can be characterized by the so-called chiral vector $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2 \equiv (n, m)$ which joins two atoms that are identified upon rolling up the graphene sheet into a tube (see Fig. 2). Depending on the direction of $\mathbf{C}_h$, we get different geometries: armchair, zigzag and chiral nanotubes (see Fig. 3). The names derive from the pattern observed along the section of the tube. The armchair nanotubes correspond to a chiral vector for which $n = m$. The zigzag nanotubes correspond to $m = 0$. For the chiral nanotubes it is enough to consider $0 \leq |m| \leq n$. The unit cell of a nanotube is spanned by the vectors $\{\mathbf{C}_h, \mathbf{T}\}$, where the translation vector $\mathbf{T} = (t_1\mathbf{a}_1 + t_2\mathbf{a}_2)$ is the vector perpendicular to the chiral vector joining two equivalent lattice sites.

For each of the following chiral vectors $\mathbf{C}_h = (5, 5)$, $(9, 0)$ and $(10, 0)$ find whether the nanotube is metallic or semiconducting.

Hint: Think about the boundary conditions the wavefunction has to satisfy for an infinitely long nanotube. From the unit cell construct the Brillouin zone of the nanotubes. The energy bands are found by evaluating the dispersion relation $E(\mathbf{k})$ (calculated previously for graphene) for all reciprocal vectors $\mathbf{k}$ belonging to the Brillouin zone of the nanotubes.

Exercise 5.3 Specific Heat of a Semiconductor

Calculate the specific heat of a semiconductor under the assumption $k_B T \ll E_g$, where E_g is the band gap. Show that it is given by an ideal gas-like part $(3/2)n(T)k_B$ plus a correction, where $n(T)$ is the number of excitations. Is this correction small or large?
Hint: First, approximate the dispersion of both the conduction and the valence band parabolically, with the two effective masses m_v and m_c. Then, calculate the chemical potential μ from the condition, that the number of electrons in the conduction band $(n_e(T))$ must be equal to the number of holes in the valence band $(n_h(T))$.