## Theoretische Festkörperphysik – Herbstsemester 2010 **Exercise series 3**

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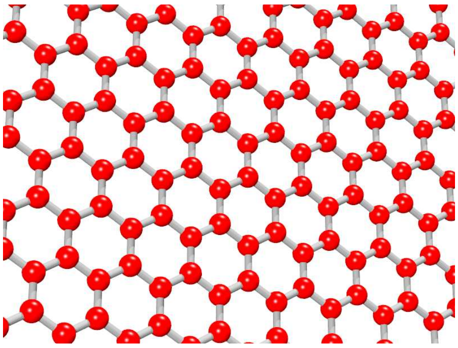
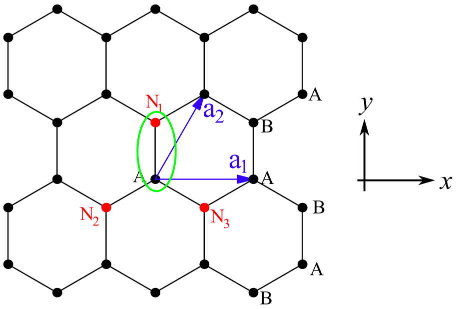
Two-dimensional tight-binding model for graphene

**Motivation.** Graphene is one of the hot topics in current research. It is often speculated that it will be the basis material for future electronics applications because of its remarkable properties (truly 2D, very strong, ...). In this and the next exercises, we aim at a basic understanding of this material. Luckily, graphene is simple enough to gain considerable insight with straightforward models.

Most important for a theoretical understanding of graphene is its underlying crystal structure - the so-called honeycomb lattice of carbon atoms.





Our strategy is as follows: A central concept in solid-state physics is the hopping of electrons between orbitals of nearby atoms. For instance, a hopping integral between an orbital of an atom at the origin with a wave function $\psi_\alpha(\mathbf{r})$ and an orbital of an atom at $\mathbf{R}$ with a wave function $\psi_\beta(\mathbf{r}-\mathbf{R})$ is

$$t_{\alpha\beta}(\mathbf{R}) = \int \mathrm{d}^3r\, \psi^*_\alpha(\mathbf{r}) \left[-\frac{\hbar^2\nabla^2}{2m} + V(\mathbf{r})\right] \psi_\beta(\mathbf{r}-\mathbf{R}) \tag{1}$$

Due to the simple crystal structure, the form of this hopping integral can be calculated directly from the symmetry of the orbital wave functions and it turns out that only one band - the so-called $\pi$-band - is important for the electronic properties of graphene. This band is derived only from the p$_z$-orbitals of the carbon atoms.

**Exercise 1: The relevant part of the Hamiltonian (4 points).** We first need to find out which part of the Hamiltonian is relevant.

1. Find out how many electrons are owned by an isolated carbon atom. What is the configuration of the atomic shells?
2. The s-orbital of the first shell has a very low energy. Thus, the two electrons in these this orbital are strongly bound to the carbon site and we can neglect their hopping to neighboring sites (what does this mean for the radial wave function of this orbital?).

   It is most convenient to choose the local basis of the second shell as the 2s,2p$_x$,2p$_y$,2p$_z$ wave functions. What is the form of the wave functions of these orbitals?
3. Consider two carbon atoms in the xy-plane. Show that an electron in the p$_z$ orbital of one atom can *only* hop to the p$_z$ orbital of the other atom. No explicit calculations are required here. The symmetry properties (e.g. $V(x,y,z) = V(x,y,-z)$) of the Hamiltonian and the wave functions are sufficient to show this. *Hint:* You should use cartesian coordinates!
4. The general tight-binding Hamiltonian of graphene in real space is

   $$H = \sum_{i,j,\alpha,\beta} t_{\alpha\beta}(\mathbf{R}_i - \mathbf{R}_j) c^\dagger_{i,\alpha} c_{j,\beta}, \qquad \alpha,\beta \in \{s, p_x, p_y, p_z\} \tag{2}$$

   where $\mathbf{R}_i$ are the positions of the carbon atoms. Under what conditions is it suffient to respect only the p$_z$-orbitals and neglect all other orbitals (atomic positions, hoppings, energy)? Write down the real space $\pi$-band Hamiltonian which respects only nearest-neighbor hopping.

*Hint:* The nearest neighbor real space Hamiltonian of the $\pi$-band should read like

$$H_\pi = t \sum_{\langle i,j \rangle} c^\dagger_{i,p_z} c_{j,p_z} \tag{3}$$

where $t = t_{\pi\pi}(\mathbf{R}_{NN})$ with a vector $\mathbf{R}_{NN}$ connecting nearest neighbors. $\langle i, j \rangle$ is a sum over nearest neighbors.

**Exercise 2: The $\pi$-band in k-space (4 points).** The lattice vectors of the graphene lattice are $\mathbf{a}_1 = a_0[\sqrt{3}, 0, 0]$, $\mathbf{a}_2 = a_0 \left[\frac{\sqrt{3}}{2}, \frac{3}{2}, 0\right]$ (see Figure). Furthermore, graphene is a bipartite lattice. This means that it has two atoms in the unit-cell (green circle in the Figure). The A atoms are at the origin of the unit cell and the B atoms are at $\mathbf{d}_1 = [0, a_0, 0]$. $a_0 \simeq 1.4$Å is the distance of the carbon atoms. The position vector is $\mathbf{R}_{n_1,n_2,s} = n_1\mathbf{a}_2 + n_2\mathbf{a}_2 + s\mathbf{d}_1$ where $s = 0, 1$ stands for an A or B site, respectively.

1. Transform the electron operators in the $\pi$-band Hamiltonian (3) to k-space:

   $$d_{k_1,k_2,s} = N^{-\frac{1}{2}} \sum_{n_1,n_2} e^{-i(k_1 n_1 + k_2 n_2)} c_{n_1,n_2,s,p_z} \tag{4}$$

   $N = N_{\mathbf{a}_1} N_{\mathbf{a}_2}$ is the total number of unit cells and $N_{\mathbf{a}_i}$ is the number of unit cells in $\mathbf{a}_i$-direction.

2. $k_1, k_2$ are *not* k-space coordinates w.r.t. an orthogonal basis. We want to resolve this issue by translating $(k_1, k_2)$ to $(k_x, k_y)$. To do this, calculate the reciprocal vectors $\mathbf{b}_i$, defined by $\mathbf{b}_i^\dagger \mathbf{a}_i = \delta_{ij}$ and find $k_x, k_y$ as functions of $k_1, k_2$. Give one possible Brillouin zone.

3. Write the Hamiltonian in form of a pseudo-spin Hamiltonian where A (B) sites correspond to spin-up (spin-down) and calculate the eigenvalues of the Hamiltonian as a function of $k_x$ and $k_y$.

4. Usually, the $\sigma$-band which we have neglected contributes exactly three electrons per lattice site. How much of the $\pi$-band is then filled if the system has no excess charges? What is the “Fermi-surface“ of graphene?
   *Hint:* There are two interesting points in the Brillouin zone.

5. Near the Fermi energy, the Hamiltonian may be expanded to linear order in $k$. In many respects, this approximation yields extremely accurate results. Assume that this expansion reads

   $$H_\pi \simeq \hbar v_F \sum_{\mathbf{k},s,s'} d^\dagger_{\mathbf{k},s} \left[k_x \sigma^x + k_y \sigma^y\right]_{ss'} d_{\mathbf{k},s}, \tag{5}$$

   where $\sigma^{x,y}$ are the Pauli matrices. What is the spectrum of this Hamiltonian? Find the unitary transformation which diagonalizes this approximate Hamiltonian.
   *Hint:* Think about pseudo-spin rotations!

**Exercise 3: Density of states (2 points).** In Exercise 2 we have found that, in contrast to usual Schrödinger particles, the elementary excitations in graphene have a linear dispersion. This has many interesting consequences. For instance, the density of states is rather unusual for a two-dimensional electron system.

The density of states (without spin degeneracy) of a two-dimensional system is defined by

$$n(E) = A^{-1} \sum_{\mathbf{k}} \delta(E - \epsilon(\mathbf{k})) \simeq \int_{BZ} \frac{\mathrm{d}^2 k}{(2\pi)^2} \, \delta(E - \epsilon(\mathbf{k})) \tag{6}$$

where $A$ is the area of the system.

1. Calculate the density of states of a usual 2DEG with dispersion $\epsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m}$ (Schrödinger particles).

2. Calculate the density of states of graphene.