Graphene: lattice structure, tight-binding, and all that...

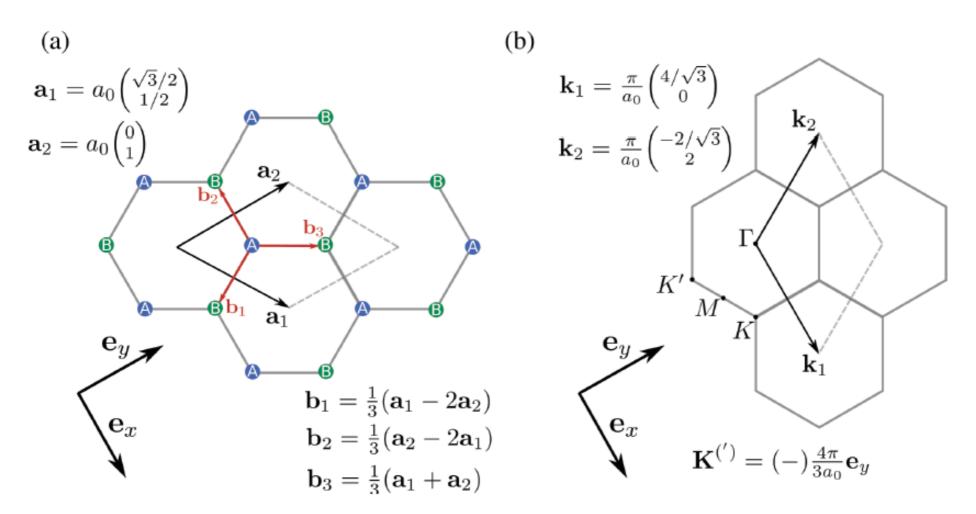

(a)

$$\mathbf{a}_1 = a_0 \begin{pmatrix} \sqrt{3}/2 \\ 1/2 \end{pmatrix}$$

$$\mathbf{a}_2 = a_0 \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\mathbf{b}_1 = \tfrac{1}{3}(\mathbf{a}_1 - 2\mathbf{a}_2)$$

$$\mathbf{b}_2 = \tfrac{1}{3}(\mathbf{a}_2 - 2\mathbf{a}_1)$$

$$\mathbf{b}_3 = \tfrac{1}{3}(\mathbf{a}_1 + \mathbf{a}_2)$$

(b)

$$\mathbf{k}_1 = \tfrac{\pi}{a_0} \begin{pmatrix} 4/\sqrt{3} \\ 0 \end{pmatrix}$$

$$\mathbf{k}_2 = \tfrac{\pi}{a_0} \begin{pmatrix} -2/\sqrt{3} \\ 2 \end{pmatrix}$$

$$\mathbf{K}^{(')} = (-)\tfrac{4\pi}{3a_0}\mathbf{e}_y$$

Figure 2.1.: (a) Honeycomb structure of the graphene lattice. The unit cell, defined by the two lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, contains two atoms, which constitute two equivalent sublattices A and B. Furthermore, the nearest neighbor vectors directed from an A-atom to the nearest B-atoms are depicted. (b) Brillouin zone of graphene defined by the reciprocal lattice vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ containing the high symmetry points Γ, M, K and K'.

the electronic wave function $\Psi(\mathbf{k})$ can be approximated within a tight-binding ansatz as a linear combination of both equivalent sublattices A and B

$$\Psi_{\mathbf{k}}(\mathbf{r}) = c_A(\mathbf{k})\Phi_{A,\mathbf{k}}(\mathbf{r}) + c_B(\mathbf{k})\Phi_{B,\mathbf{k}}(\mathbf{r}), \tag{2.8}$$

where $c_l(\mathbf{k})$ are the tight-binding coefficients and $\Phi_{l,\mathbf{k}}(\mathbf{r})$ is the sublattice wave function with $l = A,B$ [48, 51]. The latter is normalized and periodic on the respective sublattice $\mathbf{R}_l$, reading

$$\Phi_{l,\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_l} e^{i\mathbf{k}\cdot\mathbf{R}_l} \phi(\mathbf{r} - \mathbf{R}_l), \tag{2.9}$$

where N is the number of unit cells in the system and $\phi(\mathbf{r})$ is the atomic $2p_z$ orbital. With this ansatz the Schrödinger equation

$$H\Psi_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}}\Psi_{\mathbf{k}}(\mathbf{r}) \tag{2.10}$$

can be solved analytically.

It remains to determine the matrix elements H_{ij} and S_{ij}, e.g.

$$H_{AB} = \frac{1}{N} \sum_{\mathbf{R}_A, \mathbf{R}_B} e^{i\mathbf{k}(\mathbf{R}_B - \mathbf{R}_A)} \langle \phi(\mathbf{r} - \mathbf{R}_A) | H | \phi(\mathbf{r} - \mathbf{R}_B) \rangle. \qquad (2.14)$$

Due to the localization of the atomic orbital, H_{AB} can be treated within the nearest neighbor approximation[1] [52]. That means for each summand $\mathbf{R}_A$ only the three adjacent B atoms at $\mathbf{R}_{B_i} = \mathbf{R}_A + \mathbf{b}_i$ contribute, where the $\mathbf{b}_i$ with $i = 1,2,3$ are the nearest neighbor vectors, which are shown in Fig. 2.1(a). Note that the opposite case, i.e. fixing the B-sublattice and considering the nearest A-atoms, leads to the same eigenvalues. The three remaining integrals in Eq. (2.14) $\gamma_0 = \langle \phi(\mathbf{r} - \mathbf{R}_A) | H | \phi(\mathbf{r} - \mathbf{R}_{B_i}) \rangle$ are independent on i, since the $2p_z$-orbital depends in the plane only on the distance $\phi(\mathbf{r}_\parallel, z) \equiv \phi(|\mathbf{r}_\parallel|, z)$ [48]. Common values of the integral are in the range between $-2.5\,\text{eV}$ and $-3.0\,\text{eV}$ [48, 53], where throughout this work $-2.84\,\text{eV}$ is applied, which is denoted by γ_0 in the following. Therewith, Eq. (2.14) yields

$$H_{AB} = \gamma_0 e(\mathbf{k}), \qquad (2.15)$$

where

$$e(\mathbf{k}) = \sum_{i=1}^{3} e^{i\mathbf{k}\mathbf{b}_i} \qquad (2.16)$$

is the nearest neighbor sum, which accounts for the graphene lattice symmetry. The other matrix elements can be treated in analogy, where $H_{AA} = \epsilon_0$ is a constant, which is chosen to be $0\,\text{eV}$ to benchmark the energy scale with respect to the intrinsic Fermi level ε_F. The normalization of the sublattice wave function $\Phi_{l,\mathbf{k}}(\mathbf{r})$ directly yields $S_{AA} = 1$. Finally, S_{AB} represents the overlap between neighboring orbitals orbital and is given by $S_{AB} = s_0 e(\mathbf{k})$. The overlap integral $s_0 = \langle \phi(\mathbf{r}) | \phi(\mathbf{r} - \mathbf{b}_1) \rangle$ can be evaluated numerically via the $2p_z$ orbital. Common values of the overlap integral lie between 0.06 and 0.13, depending on the applied effective charge Z^* [48,54]. However, later the overlap integral will be neglected providing a good description in energy regime addressed in this work.

Linear band approximation Close to the Dirac point the tight-binding bandstructure can be linearly approximated. Therefore, the overlap integral s_0 is neglected and the nearest neighbor sum, Eq. (2.16), is expanded up to the first order around the K (or K') point

$$e(\mathbf{k}) \approx e(\mathbf{K}) + [\nabla_\mathbf{k} e(\mathbf{k})]\Big|_{\mathbf{k}=\mathbf{K}} (\mathbf{k} - \mathbf{K}) = -\frac{a_0\sqrt{3}}{2}\left(i\tilde{k}_x + \tilde{k}_y\right), \qquad (2.20)$$

where $\mathbf{K} = \frac{4\pi}{3a_0}\mathbf{e}_y$ and $\tilde{\mathbf{k}} = \mathbf{k} - \mathbf{K}$ is the electron wave vector with respect to the Dirac point [56]. In the following $\tilde{\mathbf{k}}$ is denoted by $\mathbf{k}$, if the respective consideration is restricted to a Dirac valley.