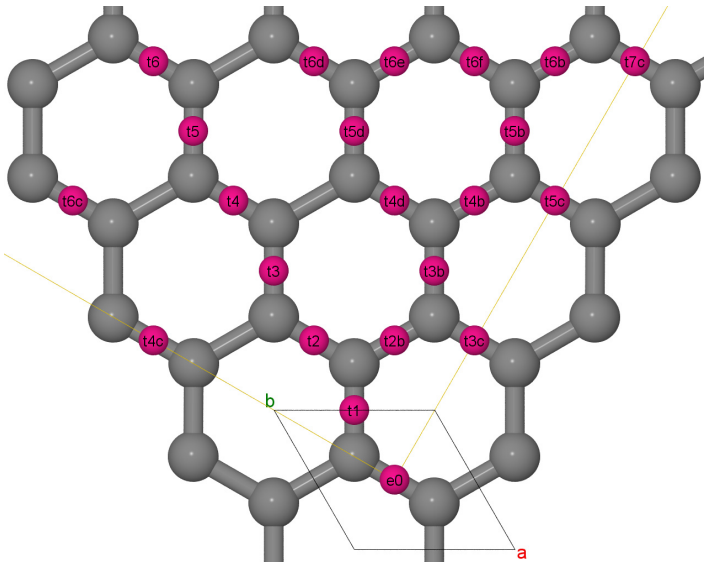

Figure 3: Symmetry unique TB elements of graphene σ-VB.

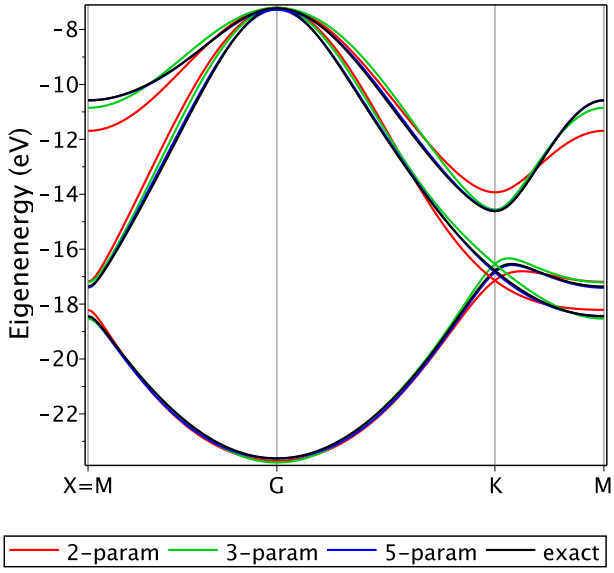

Figure 4: Energy bands of graphene σ-VB for a series of models of increasing accuracy.

§4. TB for graphene σ-VB

The symmetry unique TB elements are shown in Fig. 3. There are 7 high-symmetry energy reference values at 3 k-points: Γ, K and M. At our best, we use 5-parameter model including the onsite energy ε_0 and 5 independent transfer integrals: t_1, t_2, t_{2b}, t_3 and t_{4d}. Other nonzero integrals include $t_{3b} = -t_3/2$, $t_{3c} = t_3/2$, $t_{4c} = t_3/2$, $t_4 = -t_3/3$, $t_5 = t_3/9$, $t_6 = -t_3/27$. This model fits high-symmetry points with 10 meV accuracy. With up to third-order terms, the Hamiltonian is given by

$$H_{11}(k_1,k_2,k_3) = \varepsilon_0 + 2t_2\left(\cos k_1 + \cos k_2\right) + 2t_{3c}\cos k_3, \tag{4.1}$$

$$H_{12} = t_1\left(1+\mathrm{e}^{\mathrm{i}k_2}\right) + t_{2b}\left(\mathrm{e}^{-\mathrm{i}k_1}+\mathrm{e}^{-\mathrm{i}k_3}\right) + t_3\left(\mathrm{e}^{-\mathrm{i}k_2}+\mathrm{e}^{\mathrm{i}2k_2}\right) + t_{3b}\left(\mathrm{e}^{\mathrm{i}k_1}+\mathrm{e}^{\mathrm{i}k_3}+\mathrm{e}^{\mathrm{i}(k_2-k_1)}+\mathrm{e}^{\mathrm{i}(k_2-k_3)}\right), \tag{4.2}$$

$$H_{22}(k_1,k_2,k_3) = H_{11}(k_2,k_3,k_1), \qquad H_{33}(k_1,k_2,k_3) = H_{11}(k_3,k_1,k_2), \tag{4.3}$$

$$H_{23}(k_1,k_2,k_3) = H_{12}(k_2,k_3,k_1), \qquad H_{31}(k_1,k_2,k_3) = H_{12}(k_3,k_1,k_2), \tag{4.4}$$

where $k_3 = -k_1 - k_2$. In high-symmetry points:

$$E_{1,2}(1/3,1/3) = \varepsilon_0 + t_1 - 2t_2 - 2t_{2b} - 2t_3 + 2t_{3b} - t_{3c}, \tag{4.5}$$

$$E_3(1/3,1/3) = \varepsilon_0 - 2t_1 - 2t_2 + 4t_{2b} + 4t_3 - 4t_{3b} - t_{3c}, \tag{4.6}$$

$$E_1(0,0) = \varepsilon_0 + 4t_1 + 4t_2 + 4t_{2b} + 4t_3 + 8t_{3b} + 2t_{3c}, \tag{4.7}$$

$$E_{2,3}(0,0) = \varepsilon_0 - 2t_1 + 4t_2 - 2t_{2b} - 2t_3 - 4t_{3b} + 2t_{3c}, \tag{4.8}$$

$$E_1(1/2,0) = \varepsilon_0 + 2t_1 - 2t_{2b} + 2t_3 - 4t_{3b} - 2t_{3c}, \tag{4.9}$$

$$E_2(1/2,0) = \varepsilon_0 - 4t_2 + 2t_{3c}, \tag{4.10}$$

$$E_3(1/2,0) = \varepsilon_0 - 2t_1 + 2t_{2b} - 2t_3 + 4t_{3b} - 2t_{3c}, \tag{4.11}$$

$$\tag{4.12}$$

In particular, if we fit 5-parameter model to PBE/p2p calculations, we obtain (in eV):

$$\varepsilon_0 = -14.97,\ t_1 = -2.19,\ t_2 = 0.55,\ t_{2b} = -0.52,\ t_3 = -0.14,\ t_{4d} = 0.03, \tag{4.13}$$

giving band structure visually coinciding with the exact one. If we neglect 4-order integrals we come to reasonably accurate 3-parameter model: t_1, t_2, t_3 with $t_{2b} = -t_2$, $t_{3b} = -t_3/2$ and $t_{3c} = t_3/2$. The minimal is the 2-parameter model: t_1 and t_2 with $t_{2b} = -t_2$. Exact TB integrals fade with distance quickly:

$$\varepsilon_0 = -14.965,\ t_1 = -2.162,\ t_2 = 0.555,\ t_{2b} = -0.522, \tag{4.14}$$

$$t_3 = -0.157,\ t_{3b} = 0.072,\ t_{3c} = -0.082,\ t_4 = 0.049,\ t_{4c} = -0.049, \tag{4.15}$$

$$t_{4d} = 0.024,\ t_{5c} = -0.020,\ t_{4b} = -0.010,\ t_6 = 0.008,\ t_{5b} = 0.005,\ t_{6b} = -0.002, \ldots \tag{4.16}$$