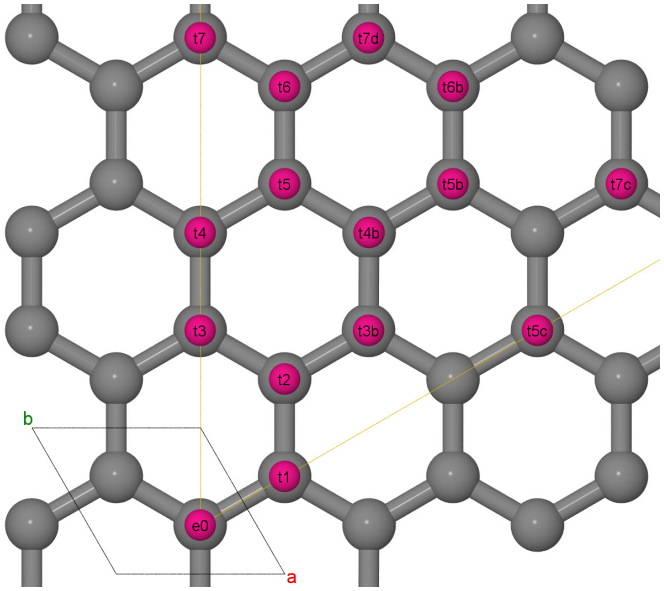

Figure 1: Symmetry unique TB elements of graphene π-system.

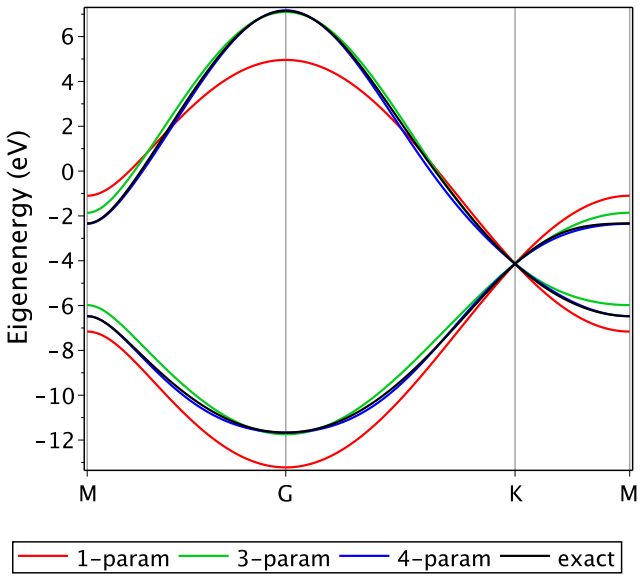

Figure 2: Energy bands of graphene π-system for a series of models of increasing accuracy.

§3. TB for graphene π-system

The symmetry unique TB elements are shown in Fig. 1. Because there are 5 high-symmetry energy reference values at 3 k-points: Γ, K and M, the largest 'fittable' model includes the onsite energy ε_0 and 4 transfer integrals including 3 directly interacting pairs: t_1, t_2, t_3. The 4th integral should be t_4 to balance the accuracy of diagonal and off-diagonal Hamiltonian matrix elements containing even and odd (by chemical distance) transfer integrals respectively. The resulting Hamiltonian is given by

$$H_{11} = H_{22} = \varepsilon_0 + 2t_2\left(\cos k_1 + \cos k_2 + \cos k_3\right) + 2t_4\left(\cos(k_1 - k_2) + \cos(k_2 - k_3) + \cos(k_3 - k_1)\right), \tag{3.1}$$

$$H_{12} = t_1\left(1 + \mathrm{e}^{\mathrm{i}k_1} + \mathrm{e}^{-\mathrm{i}k_2}\right) + t_3\left(\mathrm{e}^{\mathrm{i}(k_1 - k_2)} + \mathrm{e}^{\mathrm{i}k_3} + \mathrm{e}^{-\mathrm{i}k_3}\right) \tag{3.2}$$

where $k_3 = -k_1 - k_2$. Therefore $E_{1,2} = H_{11} \mp |H_{12}|$. In high-symmetry direction $k_1 = k_2 = k$:

$$H_{11} = \varepsilon_0 + 2t_2\left(2\cos k + \cos 2k\right) + 2t_4\left(1 + 2\cos 3k\right), \tag{3.3}$$

$$H_{12} = t_1\left(1 + 2\cos k\right) + t_3\left(1 + 2\cos 2k\right). \tag{3.4}$$

In high-symmetry direction $k_1 = k$, $k_2 = 0$:

$$H_{11} = \varepsilon_0 + 2t_2\left(1 + 2\cos k\right) + 2t_4\left(2\cos k + \cos 2k\right), \tag{3.5}$$

$$H_{12} = t_1\left(2 + \mathrm{e}^{\mathrm{i}k}\right) + t_3\left(2\mathrm{e}^{\mathrm{i}k} + \mathrm{e}^{-\mathrm{i}k}\right). \tag{3.6}$$

In high-symmetry points ($k = \{0, \pi, 2\pi/3\}$):

$$E(1/3, 1/3) = \varepsilon_0 - 3t_2 + 6t_4, \tag{3.7}$$

$$E_{1,2}(0,0) = \varepsilon_0 + 6t_2 + 6t_4 \mp (3t_1 + 3t_3), \tag{3.8}$$

$$E_{1,2}(1/2, 0) = E_{1,2}(1/2, 1/2) = \varepsilon_0 - 2t_2 - 2t_4 \mp (t_1 - 3t_3). \tag{3.9}$$

In particular, if we fit parameters at these high-symmetry points to PBE/p2p calculations, we obtain (in eV):

$$\varepsilon_0 = -3.87,\ t_1 = -2.87,\ t_2 = 0.21,\ t_3 = -0.27,\ t_4 = 0.06, \tag{3.10}$$

giving band structure visually coinciding with the exact one. Although t_4 is small, neglecting it results in large error at M-point. The minimal model (t_1 only) is still qualitatively accurate. Exact TB integrals fade with distance quickly:

$$\varepsilon_0 = -3.778,\ t_1 = -2.887,\ t_2 = 0.218,\ t_3 = -0.239, \tag{3.11}$$

$$t_4 = 0.046,\ t_{5c} = -0.029,\ t_{4b} = -0.015, \tag{3.12}$$

$$t_{3b} = 0.004,\ t_{5b} = 0.004,\ t_6 = 0.003,\ t_{6b} = -0.002,\ t_5 = 0.001, \ldots \tag{3.13}$$