Appendix C

TRANSFERABLE TIGHT-BINDING MODEL

The transferable tight-binding model proposed by Ho and his collaborator [72, 73] is given here. In the case of the carbon atom, the atomic orbitals to be considered are $2s$, $2p_x$, $2p_y$ and $2p_z$. In this model, the total energy of the system $E_{\rm tot}$ is

$$E_{\rm tot} = E_{\rm bs} + E_{\rm rep}, \tag{C.1}$$

where the $E_{\rm bs}$ is the energy of the electrons that is the summation of the eigenvalues of the occupied states and the $E_{\rm rep}$ is the ionic repulsive energy. The electronic eigenvalues are obtained by solving the tight-binding Hamiltonian $H_{\rm TB}$. This $H_{\rm TB}$ is constructed from the atomic orbital energies ε_s and ε_p, and the two-centre electronic hoppings *i.e.* $h_{ss\sigma}$, $h_{sp\sigma}$, $h_{pp\sigma}$ and $h_{pp\pi}$. To calculate the electronic hoppings, a parametrized function $S(r)$ has been introduced [72, 99]:

$$S(r) = \left(\frac{r_0}{r}\right)^n \exp\left[n\left\{-\left(\frac{r}{r_c}\right)^{n_c} + \left(\frac{r_0}{r_c}\right)^{n_c}\right\}\right], \tag{C.2}$$

where the r_0 is the bond length of the diamond. The electronic hopping is hereby derived as a function of the interatomic distance r, *i.e.*

$$h_\alpha(r) = V_\alpha S(r), \tag{C.3}$$

where α denotes the 4 kinds of the hoppings. The V_α and n, n_c and r_c in Eq. (C.2) are parameters that need to be determined. (See Table C.1.)

On the other hand, the ionic repulsive energy $E_{\rm rep}$ is represented as

$$E_{\rm rep} = \sum_i f\left[\sum_j \phi(r_{ij})\right], \tag{C.4}$$

where the $f(x)$ is a fourth-order polynomial of x:

$$f(x) = \sum_{k=0}^{4} c_k x^k, \tag{C.5}$$

and $\phi(r_{ij})$ is a function of the distance between the atom-i and -j, *i.e.*

$$\phi(r) = \phi_0 \left(\frac{d_0}{r}\right)^m \exp\left[m\left\{-\left(\frac{r}{d_c}\right)^{m_c} + \left(\frac{d_0}{d_c}\right)^{m_c}\right\}\right]. \tag{C.6}$$

The coefficients of the $f(x)$ are:

$$\begin{aligned} c_0 &= -2.590977, \\ c_1 &= 0.527115, \\ c_2 &= -1.789634 \times 10^{-3}, \\ c_3 &= 2.353922 \times 10^{-5}, \\ c_4 &= -1.242511 \times 10^{-7}. \end{aligned}$$

We must also determine the parameters ϕ_0, m, m_c, d_c and d_0 in Eq. (C.6). (See Table C.1.)

Furthermore, the tail of the functions $S(r)$ and $\phi(r)$ are replaced by the third-order polynomials $t_S(r - r_1)$ and $t_\phi(r - d_1)$ in order that the functions $S(r)$ and $\phi(r)$ smoothly go to zero at some cut-off distance r_m. Ho has choosed the cut-off distance both for $S(r)$ and $\phi(r)$ as 2.6 Å [72]. The coefficients of the $t_S(r - r_1)$ and $t_\phi(r - d_1)$ are determined by the conditions that the $S(r)$ ($\phi(r)$) and its first derivative are connected continuously to the $t_S(r - r_1)$ ($t_\phi(r - d_1)$) and its first derivative, respectively, at some match point r_1 (d_1), and that the $t_S(r - r_1)$ ($t_\phi(r - d_1)$) and its first derivative must be zero at r_m. When we write the $t_S(r - r_1)$ and $t_\phi(r - d_1)$ as,

$$t_S(r - r_1) = \sum_{k=0}^{3} A_k (r - r_1)^k, \tag{C.7}$$

$$t_\phi(r - d_1) = \sum_{k=0}^{3} B_k (r - d_1)^k, \tag{C.8}$$

the coefficients A_k and B_k ($k = 0 \sim 3$) are given by,

$$\begin{aligned} A_0 &= S(r_1), \\ A_1 &= S'(r_1), \\ A_2 &= -2\frac{A_1}{\Delta_S} - 3\frac{A_0}{\Delta_S^2}, \\ A_3 &= \frac{A_1}{\Delta_S^2} + 2\frac{A_0}{\Delta_S^3}, \\ B_0 &= \phi(r_1), \\ B_1 &= \phi'(r_1) \\ B_2 &= -2\frac{B_1}{\Delta_\phi} - 3\frac{B_0}{\Delta_\phi^2}, \\ B_3 &= \frac{B_1}{\Delta_\phi^2} + 2\frac{B_0}{\Delta_\phi^3}, \end{aligned}$$

where $\Delta_S \equiv r_m - r_1$ and $\Delta_\phi \equiv r_m - d_1$. The *prime* indicates the derivation with respect to the r.

The parameters given so far are determined in order to reproduce structural properties of several carbon polymorphs obtained from the density functional calculations [72]: The energy-volume

Table C.1: The tight-binding parameters for the interatomic interactions, *i.e.* C–C, C–H and H–H. These parameters determined by Ho *et al.* and Horsfield *et al.* are used for the TTB calculations in this thesis.

Parameter	C–C	C–H	H–H
$V_{ss\sigma}[eV]$	-5.000	-0.441	-6.523
$V_{sp\sigma}[eV]$	4.700		6.811
$V_{pp\sigma}[eV]$	5.500		
$V_{pp\pi}[eV]$	-1.550		
ϕ_0[eV]	8.18555	0.0546	11.4813
r_m[Å]	2.60	1.22	1.85
r_0[Å]	1.5363	2.1393	1.0840
r_c[Å]	2.18	0.7103	1.20011
r_1[Å]	2.45	1.1	1.55
n	2	0.4495	0.5663
n_c	6.5	1.5650	3.1955
d_0[Å]	1.64	2.3010	1.0840
d_c[Å]	2.1052	0.3561	1.5474
d_1[Å]	2.57	1.0600	1.55
m	3.303	1.0200	1.408
m_c	8.6655	0.8458	3.5077

curves are almost identical to those from the density functional calculations for diamond and graphite, and for other polymorphs. The agreement is satisfactory; The calculated elastic constants and phonon frequencies agree with the experimental values within the error of typically 5%. We adopt the functional forms and the parameters determined in the original work [72]: It has been also established that the present model is capable of describing structural properties of fullerenes and liquid and amorphous carbons quantitatively [74, 75, 76, 77, 78, 79].

Horsfield *et al.* have introduced the parameters for carbon-hydrogen and hydrogen-hydrogen interactions (the electronic hoppings and the ionic repulsions) [80]. They have used the functional forms and the parameters for the carbon-carbon interactions proposed by Ho. The parameters for the carbon-hydrogen and hydrogen-hydrogen interactions have been determined in order that the model is capable of describing bond lengths and total energy differences of hydrocarbons, hydrogenated amorphous carbon systems and hydrogen terminated diamond (100) surfaces. The parameters for carbon-hydrogen and hydrogen-hydrogen interactions in this thesis are adopted from the work by Horsfield *et al* [80].

The tight-binding parameters are: $\varepsilon_s = -2.99$ eV and ε_p=3.71 eV for the carbon atom, and $\varepsilon_s = -4.74946$ eV. The other parameters are summarized in Table C.1.