

# Computational materials synthesis. I. A tight-binding scheme for hydrocarbons

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A simple quantum mechanical model is presented for hydrocarbons. It is a modified version of the model of Davidson and Pickett [Phys. Rev. B **49**, 11 253 (1994)]. Self-consistency is introduced through the imposition of local charge neutrality, which is appropriate for hydrogen and carbon based systems due to the small amount of charge transfer that takes place. Further, some parameters have been refitted to give the correct *binding energies* as well as forces. The model is found to give excellent agreement with experiment and other calculations for hydrocarbon molecules and the hydrogenated surface of diamond, demonstrating its transferability. [S0163-1829(96)03046-9]

## I. INTRODUCTION

Atomistic computer simulations are being used increasingly as a tool in the study of materials properties. They have been predominantly used in the past to provide detailed atomistic information to help interpret experimental data. However, models are becoming sufficiently accurate, and computers are becoming sufficiently fast that predictions about new materials can now be made with confidence on the basis of atomistic simulations. Clearly, this is an exciting development for materials design: it is a tool that can offer very detailed information under a wide and highly controlled set of external conditions (such as temperature and pressure).

In this and the following two papers, we demonstrate how a simple quantum mechanical model [tight binding (TB)] can be used to simulate the polymerization of small organic molecules, and the synthesis of solid diamondlike carbon from molecular precursors following a procedure that emulates certain experimental procedures<sup>1</sup> (as opposed to the highly artificial theoretical ones frequently used). It is our belief that this marks the beginning of computer synthesis as a useful tool for exploring both the processing conditions and the resulting properties of new materials.

The structure of this paper is as follows. The details of the TB model used for hydrocarbons are given. To demonstrate the accuracy and transferability of the model, cohesive energies, bond lengths, and angles obtained with the model for small hydrocarbon molecules and for the hydrogenated (100) surface of diamond are presented, and shown to agree well with experiment and other calculations.

## II. THE TIGHT-BINDING MODEL FOR HYDROCARBONS

A detailed description of a rigorous formulation of TB theory (the TB bond model) as applied to the calculation of cohesive energies has been worked out by Sutton *et al.*<sup>2</sup> This theory is taken as the basis for the parameters presented here both because of its rigorous nature, and because the form of self-consistency it employs [local charge neutrality (LCN)] is particularly appropriate for hydrogen and carbon based systems, for which little charge transfer takes place in reality. One slight modification that is used here is that the repulsive energy is given by a pair functional rather than a simple pair

potential.<sup>3</sup> Thus the cohesive energy is given by

$$E_{\text{coh}} = 2\text{Tr}\{H_{i\alpha,j\beta}(\rho_{j\beta,i\alpha} - \rho_{j\beta,i\alpha}^0)\} + \sum_i F\left(\sum_{j(\neq i)} \phi(r_{ij})\right), \quad (1)$$

where  $i$  and  $j$  are site indices,  $\alpha$  and  $\beta$  are orbital indices,  $H_{i\alpha,j\beta}$  is the TB Hamiltonian matrix,  $\rho_{j\beta,i\alpha}$  is the density matrix for the condensed system,  $\rho_{j\beta,i\alpha}^0 = \frac{1}{2}N_{i\alpha}^0\delta_{i,j}\delta_{\alpha,\beta}$  is the density matrix for the free atoms,  $F(x)$  is the embedding function for the repulsive energy, and  $\phi(r)$  is the pair repulsive term. LCN is imposed by means of shifts in the on-site energies ( $\varepsilon_{i\alpha} = H_{i\alpha,i\alpha}$ ) of the form  $\varepsilon_{i\alpha} \rightarrow \varepsilon'_{i\alpha} = \varepsilon_{i\alpha} + \Delta\varepsilon_i$ . Note that the shifts depend only on the site, and not on the orbitals (thus all the orbitals on one site shift together). LCN is achieved when the number of electrons on each site equals the number of valence electrons contributed by the atom on that site ( $2\sum_{\alpha}\rho_{i\alpha,i\alpha} = \sum_{\alpha}N_{i\alpha}^0$ ). The intersite elements of the Hamiltonian are given by the product of angular factors, and the Slater-Koster<sup>4</sup> two-center integrals [called *hopping integrals*, and given the symbol  $h_{\alpha}(r)$  from here on]. The angular factors are those tabulated by Slater and Koster,<sup>4</sup> and they are determined by the fundamental transformation laws of the atomic orbitals under rotation.

The TB parameters for the C-C interactions are those of Xu *et al.*<sup>3</sup> The H-H and H-C parameters are based on those given by Davidson and Pickett.<sup>5</sup> None of the H-H parameters is changed, nor are the H-C hopping integrals at the equilibrium bond length for methane. However, the H-C repulsive

TABLE I. The single-site parameters for C and H.  $\varepsilon_s$  and  $\varepsilon_p$  are the  $s$  and  $p$  on-site energies, and  $A_1, A_2, A_3$ , and  $A_4$  are the coefficients for the embedding function.

Parameter	C	H
$\varepsilon_s$	-2.990 eV	-4.74946 eV
$\varepsilon_p$	3.710 eV	
$A_1$	0.572115	0.572115
$A_2$	$-1.789634 \times 10^{-3}$	$-1.789634 \times 10^{-3}$
$A_3$	$2.353922 \times 10^{-5}$	$2.353922 \times 10^{-5}$
$A_4$	$-1.242511 \times 10^{-7}$	$-1.242511 \times 10^{-7}$

TABLE II. The bond parameters. Their definitions are given in Eq. (2).

Parameter	C—C	H—H	H—C
$V_{ss\sigma}$ (eV)	−5.000	−0.441	−6.523
$V_{sp\sigma}$ (eV)	4.700		6.811
$V_{ps\sigma}$ (eV)	−4.700		
$V_{pp\sigma}$ (eV)	5.500		
$V_{pp\pi}$ (eV)	−1.550		
$\phi_0$ (eV)	8.18555	0.0546	11.4813
$r_0$ (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
$r_{\text{cut}}$ (Å)	2.60	1.22	1.85
$n$	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
$d_{\text{cut}}$ (Å)	2.60	1.2200	1.85
$m$	3.303	1.0200	1.408
$m_c$	8.6655	0.8458	3.5077

energy and the scalings with respect to bond length of both the hopping integrals and the repulsive term are refitted to the energy against the bond length curve for methane. The curve was generated from an *ab initio* calculation (Hartree-Fock plus correlation) carried out using the GAMESS(UK) program,<sup>6,7</sup> but with the minimum energy taken from experiment.<sup>8</sup> The correlation was included using second-order perturbation theory (MP2) corrections to the Hartree-Fock result. It should be noted that the zero-point energy has not been subtracted out from the experimental data, but this will have no effect on the curvature of the binding energy curve provided it is harmonic. The parameters take the Goodwin *et al.*<sup>9</sup> form, but with the embedding form for the repulsive energy first given by Xu *et al.*<sup>3</sup> They are defined by the following equations:

$$h_{\alpha}(r) = V_{\alpha} \left( \frac{r_0}{r} \right)^n \exp \left\{ n \left[ - \left( \frac{r}{r_c} \right)^{n_c} + \left( \frac{r_0}{r_c} \right)^{n_c} \right] \right\},$$

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

TABLE III. A comparison of bond lengths found from experiment and calculated from the TB model presented in this paper.

Bond	Calculated length (Å)	Experimental length (Å) <sup>a</sup>
C—C in C <sub>3</sub> H <sub>8</sub>	1.52	1.54
C=C in C <sub>3</sub> H <sub>6</sub>	1.34	1.34
C≡C in C <sub>2</sub> H <sub>2</sub>	1.23	1.20
C—H in CH <sub>4</sub>	1.09	1.09

<sup>a</sup>Reference 10.

TABLE IV. A comparison of cohesive energies for small hydrocarbons found from experiment and calculated from the TB model presented in this paper.

Category	Molecular symbol	Calculated energy (eV)	Experimental energy (eV) <sup>a</sup>
Linear	CH <sub>4</sub>	17.6	17.6
Alkane	C <sub>2</sub> H <sub>6</sub>	30.0	29.7
	C <sub>3</sub> H <sub>8</sub>	42.4	42.0
	C <sub>4</sub> H <sub>10</sub>	54.9	54.3
	C <sub>5</sub> H <sub>12</sub>	67.3	66.5
Alkene	CH <sub>2</sub> =CH <sub>2</sub>	23.6	23.6
	CH <sub>2</sub> =CH—CH <sub>3</sub>	36.1	36.2
	CH <sub>3</sub> —CH=CH—CH <sub>3</sub>	48.6	48.5
	CH <sub>2</sub> =C=CH <sub>2</sub>	29.1	29.6
Alkyne	CH≡CH <sub>2</sub>	16.2	17.1
	CH <sub>3</sub> —C≡C—H	28.8	29.7
Aromatic	C <sub>6</sub> H <sub>6</sub>	57.6	57.5

<sup>a</sup>Reference 8.

$$F^{\text{emb}}(x) = \sum_{i=1}^4 A_i x^i. \quad (2)$$

The on-site energies are given the symbols  $\varepsilon_s$  and  $\varepsilon_p$ . Note that to ensure that good energy conservation is possible in molecular dynamics smooth tails are added to  $\phi(r)$  and the hopping integrals  $h_{\alpha}(r)$ . The tails are joined onto the functions at a radius of  $r_1$  ( $d_1$ ) and are taken to zero at a radius of  $r_{\text{cut}}$  ( $d_{\text{cut}}$ ) for  $h_{\alpha}(r)$  [ $\phi(r)$ ]. The tails [ $t(r)$ ] have the functional form

$$t(r) = B_0 + B_1(r - r_1) + B_2(r - r_1)^2 + B_3(r - r_1)^3, \quad (3)$$

where the coefficients are given by  $B_0 = f(r_1)$ ,  $B_1 = f'(r_1)$ ,  $B_2 = -2(B_1/\Delta) - 3(B_0/\Delta^2)$ ,  $B_3 = (B_1/\Delta^2) + 2(B_0/\Delta^3)$ ,  $\Delta = (r_{\text{cut}} - r_1)$ , and  $f(r)$  is the function to which the tail is being added. The full set of parameters is given in Tables I and II.

As a test of the accuracy of the parameters we looked at the energies, bond lengths, and angles for a number of small hydrocarbons (Tables III and IV), as well as the clean and hydrogenated diamond (100) surface (Tables V and VI). For

TABLE V. A comparison of results from calculations for the (2×1) reconstruction of the clean (100) surface of diamond.  $r_{\text{C—C}}$  is the surface dimer bond length, and  $\Delta d_{ij}$  is the fractional change in the separation between layers  $i$  and  $j$  after relaxation, as compared with the values for the bulk-terminated structure.

	Tight binding (This work)	Tight binding <sup>a</sup>	<i>ab initio</i> <sup>b</sup>
$r_{\text{C—C}}$ (Å)	1.398	1.398	1.40
$\Delta d_{12}$ (%)	−25.4	−24.8	−24
$\Delta d_{23}$ (%)	+7.2	+8.26	+3
$\Delta d_{34}$ (%)	−1.90	−1.15	−0.6

<sup>a</sup>Reference 5.<sup>b</sup>Reference 11.

TABLE VI. A comparison of results from calculations for the monohydride terminated diamond (100) surface.  $\theta_{\text{H-C-}\hat{n}}$  is the angle between the H—C bond, and the normal to the (100) surface.  $r_{\text{C-C}}$  is the surface dimer bond length, and  $\Delta d_{ij}$  is the fractional change in the separation between layers  $i$  and  $j$  after relaxation, as compared with the values for the bulk-terminated structure.

	Tight binding (This work)	Tightbinding <sup>a</sup>	<i>ab initio</i> <sup>b</sup>
$r_{\text{C-C}}$ (Å)	1.616	1.617	1.67
$r_{\text{C-H}}$ (Å)	1.09	1.122	1.17
$\theta_{\text{H-C-}\hat{n}}$	21.8°	20.2°	23.9°
$\Delta d_{12}$ (%)	−8.2	−9.24	−3
$\Delta d_{23}$ (%)	+0.7	+12.71	−0.3

<sup>a</sup>Reference 5.

<sup>b</sup>Reference 11.

the molecules, the bond lengths are in excellent agreement with experiment, and all of the energies agree to within 2%, except for the alkynes for which the errors are about 5%. Further, the model reproduces the 0.3 Å shortening of the C—C single bond in propene as compared with propane.<sup>12,13</sup> The calculations performed for both the clean and hydrogen terminated diamond (100) surface were carried out in exactly the way described in Davidson and Pickett.<sup>5</sup> For both calculations we find very close agreement with both the *ab initio* results and the other TB results. This demonstrates that the parameters are transferable between different environments, and so can be used with confidence.

It should be noted that two other sets of TB parameters for hydrocarbons have been derived: one set by Wang and Mak,<sup>14</sup> and the other by Porezag *et al.*<sup>15</sup> The former differs in three important ways from those presented here: Wang and Mak have subtracted out the zero-point motion energy from the experimental data before fitting their parameters to them; they do not include self-consistency; they have introduced a nonlocal correlation term. The latter differs in having been derived from an *ab initio* formalism, with only minimal fitting, and retains the overlap matrix. Both sets of parameters give good agreement between the calculated and experimental results. This confirms our view that TB is an excellent model for describing bonding in hydrocarbons.

### III. CONCLUSION

We have presented a TB model for cohesion in hydrocarbons, which includes local charge neutrality as an approximation to true self-consistency. It has been shown to be transferable, being able to model the diamond (100) surface (both clean and hydrogenated), and hydrocarbon molecules.

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