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Analytic bond-order potentials beyond Tersoff-Brenner. I. Theory

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Analytic bond-order potentials (BOP's) are derived for the σ and π bond orders by approximating the many-atom expansion for the bond order within the two-center, orthogonal tight-binding (TB) model. The analytic expression, BOP4, is obtained by retaining terms to four levels in the continued fractions for the appropriate Green's functions and describes the σ bonds in the dimer C_2, the tetrahedral methane molecule CH_4 and the trigonal methyl radical CH_3 exactly. A simplified, but accurate, variant, BOP4S, depends only on the two recursion coefficients b_1 and b_2 that characterize the root-mean-square width and the unimodal versus bimodal shape of the σ bond eigenspectrum, respectively. An analytic expression for the π bond order, BOP2M, is obtained by performing matrix recursion to two levels, thereby ensuring that the expression is independent of the choice of coordinate axes, depending only on neighboring bond integrals, bond angles and dihedral angles. A simple analytic expression for the promotion energy is also presented. Advantages of these BOP's over the empirical Tersoff-Brenner potentials are, first, their analytic form is predicted by the theory, second, the σ bond order expression BOP4S includes the very important shape parameter $(b_2/b_1)^2$, and third, the π bond order expression BOP2M describes the breaking of saturated π bonds both on radical formation and under torsion. The following paper examines the accuracy of these BOP's for modeling the energetics of diamond, graphite, and hydrocarbon molecules. [S0163-1829(99)03313-5]

I. INTRODUCTION

The atomistic simulation of many materials processes such as chemical vapor deposition (CVD) growth,[1] etching,[2] or tribological degradation[3] involves breaking and re-making of chemical bonds. Thus, the results of the computer simulations can only be as reliable as the ability of the interatomic potentials to handle bond making and breaking. In the field of drug design and polymer research valence force fields have been highly successful in modeling the weak hydrogen bonds and the electrostatic and Van der Waals interactions that determine the docking energetics of a particular drug[4] or the interchain coupling of a particular polymer.[5] However, in the field of covalently bonded materials that lie at the heart of the semiconductor industry classical interatomic potentials have singularly failed to describe correctly the breaking of the strong covalent bond.[6] This is due to their inability to handle the dangling bonds that are formed during bond rupture and the subsequent rehybridization of the valence electrons.

Somewhat over ten years ago Tersoff[7] proposed an empirical many-body interatomic potential for covalent materials that was based on the quantum-mechanical concept of bond order.[8] Following Abel,[9] he assumed that the total binding energy of the system could be written as a sum over individual bonds, the energy of each bond comprising a repulsive pairwise contribution and an attractive contribution given by the product of the bond order and a pairwise bond integral. The bond order was parametrized in a many-body form to depend on the local atomic environment about the bond so that it was explicitly angularly dependent by involving the nearest-neighbor bond angles. The Tersoff potential has been widely used with reasonable success to model the structural and tribological properties of the group IV elements C, Si, and Ge and their binary systems.[7,10–12] In 1990 Brenner[12] extended the analytic form of the Tersoff potential by introducing two additional *ad hoc* terms H_{ij} and F_{ij} into the bond order between atoms i and j in order to counter the overbinding of radicals and the incorrect treatment of conjugacy in the original Tersoff scheme. The Brenner hydrocarbon potential scored an immediate success with the molecular dynamics prediction of a very important β scission reaction on the (100) diamond surface during CVD diamond growth that allows the reconstructed dimer bond to be broken with the insertion of an adsorbed methylene radical, thereby providing a first step for diamond growth.[13]

However, the Tersoff-Brenner potentials suffer from two important drawbacks. First, their analytic form is empirical with many unknown parameters to be fitted. In addition to the eleven parameters in the usual Tersoff potential for a given elemental system, the Brenner potential introduces a further fourteen H_{ij} parameters and nine F_{ij} parameters for the hydrocarbons. Second, the Tersoff-Brenner potential contains only a single bond-order term whose angular dependence reflects that of a σ bond.[14] The problems associated with the overbinding of radicals and the poor treatment of conjugacy lie in the neglect of an explicit treatment of the π bond.[15]

In this paper (Paper I) we show that the analytic form of the σ and π bond orders can be derived as an approximation to the exact many-atom expansion for the bond order[16,17] within the two-center, orthogonal tight-binding (TB) representation for the electronic structure.[18] The latter TB model has recently been demonstrated to give an excellent description of the energetics of the hydrocarbons.[19] In Sec. II this TB model is presented and the exact many-atom expansion for the bond order outlined. In Sec. III an analytic bond-order potential (BOP) is derived within the so-called four-level approximation that depends explicitly on the Lanczos recursion coefficients $a_1, a_2, a_3, b_1, b_2, b_3$.[20] This provides

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an exact treatment (within the TB model) of the dimer C_2, the tetrahedral molecule CH_4, and the trigonal radical CH_3. In Sec. IV a simplified, but accurate, expression for the σ bond order is obtained by setting the recursion coefficients $b_3=b_1$ and the $a_n=0$. Explicit expressions for b_1 and b_2 are given in terms of nearest-neighbor bond angles and bond integrals. In Sec. V a simplified expression for the π bond order is obtained by performing matrix recursion[21,22] with respect to the π states. The use of matrix rather that scalar recursion guarantees that the expression for the π bond order is independent of the choice of coordinate axes, depending only on the neighboring bond angles, dihedral angles, and renormalized bond integrals. This provides an interatomic potential that correctly describes the formation of radicals, thereby avoiding the endemic problem of overbinding faced by previous potentials such as Tersoff. In Sec. VI a simple analytic expression is derived for the promotion energy which, as expected, is more a property of the *sp*-valent atom in its local environment than a property of a given individual bond. In Sec. VII we conclude.

In the companion paper (Paper II) we show that the simplified expressions for the σ and π bond orders and the promotion energy give a good description of the energetics of diamond, graphite, and hydrocarbon molecules.

II. BOND-ORDER POTENTIALS WITHIN THE TIGHT-BINDING MODEL

A. The tight-binding model

The two-center, orthogonal tight-binding (TB) model[18,23] approximates the total energy of a binary system of *s*-valent atoms (here represented by hydrogen H) and *sp*-valent atoms (here represented by carbon C) as follows:

$$U=U_{rep}+U_{prom}+U_{bond}, \tag{1}$$

where we have assumed that each atom is locally charge neutral (LCN) and nonspin-polarized. Both these constraints may be lifted within the TB model if required.[23,24]

The first term contains the overlap repulsion[25] and may be written in the form[26]

$$U_{rep}=\sum_i F\left[\sum_{j\neq i}\phi^{\mu\nu}(R_{ij})\right], \tag{2}$$

where $F(\varphi)$ is an embedding function[27] and $\phi^{\mu\nu}(R_{ij})$ is the repulsive pairwise potential between a μ atomic species at site *i* and a ν atomic species at site *j*, a distance R_{ij} apart ($\mu,\nu=$H for hydrogen, C for carbon). If the embedding function $F(\varphi)$ is directly proportional to φ, then the repulsive energy U_{rep} is simply pairwise, as is often assumed.[18,28]

The second term is also repulsive and represents the promotion energy of bringing the sp-valent atoms together from infinity. It is given by

$$U_{prom}=\sum_i (E_p^C-E_s^C)(\Delta N_p)_i^C\,\delta_{\mu C}, \tag{3}$$

where $(E_p^C-E_s^C)$ is the splitting between the valence *s* and *p* energy levels on the carbon atom which is assumed to be constant and $(\Delta N_p)_i^C$ is the change in the number of *p* electrons on the carbon atom at site *i* compared to the free atom value. (Note that due to LCN $\Delta N_s+\Delta N_p=0$, so that $\Delta N_s=-\Delta N_p$.) The promotion energy, therefore, tends to zero as the atoms are pulled apart. The Kronecker delta, $\delta_{\mu C}$, ensures that the promotion energy is associated only with the sp-valent atoms, not the *s*-valent atoms.

The third term is the attractive covalent bond energy. It may be written in the form

$$U_{bond}=\frac{1}{2}\sum_{i\neq j}(U_{bond})_{ij}^{\mu\nu}, \tag{4}$$

where the individual bond energies are given by

$$(U_{bond})_{ij}^{\mu\nu}=2\sum_{m,m'}H_{im,jm'}^{\mu\nu}\Theta_{jm',im}^{\nu\mu} \tag{5}$$

in terms of the Hamiltonian and bond-order matrix elements with respect to the valence orbitals $|im\rangle$ and $|jm\rangle$ on sites *i* and *j*, respectively. The prefactor 2 accounts for the spin degeneracy.

Following Slater and Koster[29] the Hamiltonian matrix elements can be expressed directly in terms of the two-center integrals and appropriate direction cosines. We will assume for the C-C bond that the $sp\sigma$ bond integral can be approximated by the geometric mean of $|ss\sigma|$and $pp\sigma$ as this allows the σ bond energy to be described by a single scalar bond order Θ_σ.[30] This approximation is valid to within 12% for Xu *et al.'s* parametrization for carbon.[26] We, therefore, write

$$\left.\begin{matrix} ss\sigma^{CC}\\ pp\sigma^{CC}\\ sp\sigma^{CC}\end{matrix}\right\}=\left.\begin{matrix}-1/(1+p_\sigma)\\ p_\sigma/(1+p_\sigma)\\ \sqrt{p_\sigma}/(1+p_\sigma)\end{matrix}\right\}h_\sigma^{CC}(R) \tag{6}$$

and

$$pp\pi^{CC}=-h_\pi^{CC}(R), \tag{7}$$

where $h_\sigma^{CC}(R)$ and $h_\pi^{CC}(R)$ have been defined above to be positive quantities. In general, the σ and π bond integrals will display different distance dependencies. We see that p_σ gives the ratio of the strength of the $pp\sigma$ bond integral to the $ss\sigma$ bond integral and takes the value of 1.100 for carbon for the particular TB parametrization of Xu *et al.*[26] The C-H bond integrals may be written in the form

$$\left.\begin{matrix} ss\sigma^{CH}\\ sp\sigma^{CH}\end{matrix}\right\}=\left.\begin{matrix}-1/\sqrt{1+p_\sigma}\\ \sqrt{p_\sigma}/\sqrt{1+p_\sigma}\end{matrix}\right\}h_\sigma^{CH}(R), \tag{8}$$

where we have assumed that $(sp\sigma/ss\sigma)^{CH}=(sp\sigma/ss\sigma)^{CC}=\sqrt{p_\sigma}$. This is an excellent approximation for carbon and the hydrocarbons since $(sp\sigma/ss\sigma)^{CH}=1.044$ whereas $\sqrt{p_\sigma}=\sqrt{1.100}=1.048$.[19] Finally, the H-H bond integral is written as

$$ss\sigma^{HH}=-h_\sigma^{HH}(R) \tag{9}$$

so that again $h_\sigma^{HH}(R)$ is a positive quantity. The TB parametrization with the constraints (6) and (8) will be referred to as the *reduced TB model.*

The individual ijth bond energy now takes the transparent form[30]

$$(U_{bond})^{\mu\nu}_{ij} = -2\Theta^{\mu\nu}_{ij,\sigma} h^{\mu\nu}_{\sigma}(R_{ij}) - 2(\Theta^{\mu\nu}_{ij,\pi_x} + \Theta^{\mu\nu}_{ij,\pi_y}) \times h^{\mu\nu}_{\pi}(R_{ij})\,\delta_{\mu C}\delta_{\nu C}, \tag{10}$$

where the bond orders are formally defined to be half the difference between the number of electrons in the bonding state $(1/\sqrt{2})(|i\mu\tau\rangle + |j\nu\tau\rangle)$ and antibonding state $(1/\sqrt{2})(|i\mu\tau\rangle - |j\nu\tau\rangle)$, i.e.,

$$\Theta^{\mu\nu}_{ij,\tau} = \frac{1}{2}(N_+ - N_-)^{\mu\nu}_{ij,\tau}, \tag{11}$$

where $\tau = \sigma, \pi_x$ or π_y. For the case of the C-C bond, the σ states are formed from the particular hybrids

$$\left.\begin{aligned} |i\mathrm{C}\sigma\rangle &= \frac{1}{\sqrt{1+p_\sigma}}[|i\mathrm{C}s\rangle + \sqrt{p_\sigma}|i\mathrm{C}z\rangle \\ |j\mathrm{C}\sigma\rangle &= \frac{1}{\sqrt{1+p_\sigma}}[|j\mathrm{C}s\rangle - \sqrt{p_\sigma}|j\mathrm{C}z\rangle, \end{aligned}\right\} \tag{12}$$

where the z axis runs along the axis of the bond from atom i to atom j. On the other hand, the π states are formed from the valence p_x and p_y orbitals, namely $|i\mathrm{C}\pi_x\rangle \equiv |i\mathrm{C}x\rangle$ and $|j\mathrm{C}\pi_x\rangle \equiv |j\mathrm{C}x\rangle$ and analogously for p_y. The sum of the π_x and π_y bond orders in Eq. (10) must be invariant to the choice of axes x and y.

The definition of the bond order Eq. (11) allows us to quantify the concept of the order of the bond $\Theta^{\mu\nu}_{ij}$ between the μ and ν atomic species on sites i and j, namely

$$\Theta^{\mu\nu}_{ij} = \Theta^{\mu\nu}_{ij,\sigma} + (\Theta^{\mu\nu}_{ij,\pi_x} + \Theta^{\mu\nu}_{ij,\pi_y})\,\delta_{\mu C}\delta_{\nu C}. \tag{13}$$

We will see in the following paper that this correlates with the conventional description of single, double, and triple bonds between carbon atoms. For the case of the H-H and C-H bonds we have only the σ contribution in the Eq. (13). We see at once that the hydrogen molecule has a saturated σ bond with a bond order of unity since from Eq. (11) $\Theta_\sigma = \frac{1}{2}(2-0) = 1$.

B. The bond-order potential expansion

An exact many-atom expansion for the bond order may be derived within the two-center, orthogonal TB model[17,31] by starting from the definition of the bond order in terms of the imaginary part of the intersite Green's function $G_{ij}(E)$, namely

$$\Theta_{ij} = -\frac{2}{\pi}\mathrm{Im}\int^{E_F} G_{ij}(E)\,dE, \tag{14}$$

where $G_{ij}(E) = \langle i|[E-\hat{H}]^{-1}|j\rangle$. $\hat{H}$ is the Hamiltonian operator, E_F is the Fermi energy, and E is assumed to contain a small imaginary part, i.e., $E \equiv E + i\eta$. For simplicity in this and the next section we have dropped the suffices μ and ν which are subsumed into the definition of the states $|i\rangle$ and $|j\rangle$ [see, for example, Eq. (12)]. Equation (14) follows from Eq. (11) since

$$\frac{1}{2}(G_{++} - G_{--}) = G_{ij}, \tag{15}$$

where $|+\rangle$ is the bonding state $(1/\sqrt{2})(|i\rangle + |j\rangle)$ and $|-\rangle$ is the antibonding state $(1/\sqrt{2})(|i\rangle - |j\rangle)$.

The *off-diagonal* Green's-function matrix element G_{ij} may be written as the derivative of the *diagonal* Green's-function matrix element G^{λ}_{00}, where

$$G^{\lambda}_{00}(E) = \langle u^{\lambda}_0|[E-\hat{H}]^{-1}|u^{\lambda}_0\rangle \tag{16}$$

with

$$|u^{\lambda}_0\rangle = \frac{1}{\sqrt{2}}[|i\rangle + \exp(i\psi)|j\rangle], \tag{17}$$

where $\psi = \cos^{-1}\lambda$. It follows by substituting Eq. (17) into Eq. (16) that

$$G^{\lambda}_{00}(E) = \frac{1}{2}[G_{ii}(E) + G_{jj}(E)] + \lambda G_{ij}(E). \tag{18}$$

Hence, we have the exact result that

$$G_{ij}(E) = \frac{\partial}{\partial\lambda}G^{\lambda}_{00}(E). \tag{19}$$

But the diagonal elements of a Green's function may be expressed as a continued fraction by using the Lanczos recursion algorithm.[20,32] In particular,

$$G^{\lambda}_{00}(E) = \cfrac{1}{E - a^{\lambda}_0 - \cfrac{(b^{\lambda}_1)^2}{E - a^{\lambda}_1 - \cfrac{(b^{\lambda}_2)^2}{E - a^{\lambda}_2 - \cfrac{(b^{\lambda}_3)^2}{E - a^{\lambda}_3 - \cdots,}}}} \tag{20}$$

where the recursion coefficients $a^{\lambda}_n, b^{\lambda}_n$ are defined by the Lanczos algorithm

$$b^{\lambda}_{n+1}|u^{\lambda}_{n+1}\rangle = \hat{H}|u^{\lambda}_n\rangle - a^{\lambda}_n|u^{\lambda}_n\rangle - b^{\lambda}_n|u^{\lambda}_{n-1}\rangle \tag{21}$$

with $|u^{\lambda}_0\rangle$ given by Eq. (17). Consequently, $a^{\lambda}_n = \langle u^{\lambda}_n|\hat{H}|u^{\lambda}_n\rangle$ and $b^{\lambda}_n = \langle u^{\lambda}_{n-1}|\hat{H}|u^{\lambda}_n\rangle$ since the Lanczos states $|u^{\lambda}_n\rangle$ are orthonormal.

The recursion coefficients $\{a^{\lambda}_n, b^{\lambda}_n\}$ may be expressed in terms of the moments $\{\mu^{\lambda}_n\}$ of the local density of states associated with the starting Lanczos orbital $|u^{\lambda}_0\rangle$, namely

$$\mu^{\lambda}_n = \int_{-\infty}^{\infty} E^n\left[-\frac{1}{\pi}\mathrm{Im}\,G^{\lambda}_{00}(E)\right]dE = \langle u^{\lambda}_0|\hat{H}^n|u^{\lambda}_0\rangle. \tag{22}$$

Substituting Eq. (17) into Eq. (22) we have

$$\mu^{\lambda}_n = \frac{1}{2}[(\mu_n)_i + (\mu_n)_j] + \lambda(\zeta_{n+1})_{ij}, \tag{23}$$

where $(\mu_n)_i = \langle i|\hat{H}^n|i\rangle$ and $(\mu_n)_j = \langle j|\hat{H}^n|j\rangle$ are the nth moments of the local density of states associated with orbitals $|i\rangle$ and $|j\rangle$, respectively, and $(\zeta_{n+1})_{ij} = \langle i|\hat{H}^n|j\rangle$ is an interference term linking orbitals $|i\rangle$ and $|j\rangle$, as illustrated diagrammatically in Fig. 2 of Ref. 33. The recursion coefficients may then be written in terms of the moments,[32] the lowest four being given explicitly by

$$a_0^\lambda = \mu_1^\lambda \equiv 0, \tag{24}$$

$$(b_1^\lambda)^2 = \mu_2^\lambda, \tag{25}$$

$$a_1^\lambda = \mu_3^\lambda / \mu_2^\lambda, \tag{26}$$

and

$$(b_2^\lambda)^2 = \mu_4^\lambda/\mu_2^\lambda - (\mu_3^\lambda/\mu_2^\lambda)^2 - \mu_2^\lambda. \tag{27}$$

Thus, a_0^λ gives the center of gravity of the local density of states, which we have chosen as the energy zero so that $a_0^\lambda \equiv 0$. b_1^λ and a_1^λ give the root-mean-square width and skewness of the local density of states, respectively. $(b_2^\lambda/b_1^\lambda)^2$ is a measure of the unimodal versus bimodal behavior of the local density of states with the spectrum being said to be bimodal if it takes a value less than unity (see, for example, Sec. 4.5 of Ref. 22).

The intersite Green's function $G_{ij}(E)$ may now be obtained by substituting Eq. (20) into Eq. (19) and writing it in the form

$$G_{ij}(E) = \sum_{n=0}^{\infty} \frac{\partial G_{00}^\lambda}{\partial a_n^\lambda} \frac{\partial a_n^\lambda}{\partial \lambda} + \sum_{n=1}^{\infty} \frac{\partial G_{00}^\lambda}{\partial b_n^\lambda} \frac{\partial b_n^\lambda}{\partial \lambda}. \tag{28}$$

The first factor in each term measures the change in the Green's function $G_{00}^\lambda(E)$ with respect to the change in the recursion coefficients, whereas the second factor gives the change in the recursion coefficients with respect to the change in the phase between the orbitals $|i\rangle$ and $|j\rangle$ in the starting Lanczos orbital $|u_0^\lambda\rangle$. The first factor may be written as the product of the Green's functions $G_{0n}^\lambda(E)$ defined along the semi-infinite recursion chain,[34] namely

$$\frac{\partial G_{00}^\lambda(E)}{\partial a_n} = G_{0n}^\lambda(E) G_{n0}^\lambda(E), \tag{29}$$

$$\frac{\partial G_{00}^\lambda(E)}{\partial b_n} = G_{0n}^\lambda(E) G_{(n-1)0}^\lambda(E) + G_{0(n-1)}^\lambda(E) G_{n0}^\lambda(E) \tag{30}$$

with the semi-infinite chain Green's functions satisfying the recursion relations

$$(E - a_n^\lambda) G_{nm}^\lambda(E) - b_n^\lambda G_{(n-1)m}^\lambda(E) - b_{n+1}^\lambda G_{(n+1)m}^\lambda(E) = \delta_{nm}. \tag{31}$$

The second factor may be written[35] in terms of the interference terms $(\zeta_{n+1})_{ij}$ as

$$\frac{\partial a_n^\lambda}{\partial \lambda} = \sum_{r=1}^{2n+1} \frac{\partial a_n^\lambda}{\partial \mu_r^\lambda} \frac{\partial \mu_r^\lambda}{\partial \lambda} = \sum_{r=1}^{2n+1} \frac{\partial a_n^\lambda}{\partial \mu_r^\lambda} (\zeta_{r+1})_{ij}, \tag{32}$$

$$\frac{\partial b_n^\lambda}{\partial \lambda} = \sum_{r=1}^{2n} \frac{\partial b_n^\lambda}{\partial \mu_r^\lambda} \frac{\partial \mu_r^\lambda}{\partial \lambda} = \sum_{r=1}^{2n} \frac{\partial b_n^\lambda}{\partial \mu_r^\lambda} (\zeta_{r+1})_{ij}, \tag{33}$$

where $\partial \mu_r^\lambda / \partial \lambda = (\zeta_{r+1})_{ij}$ from Eq. (23). It follows that the first three derivatives are given explicitly by[33]

$$\frac{\partial a_0^\lambda}{\partial \lambda} = (\zeta_2)_{ij}, \tag{34}$$

$$\frac{\partial b_1^\lambda}{\partial \lambda} = [1/(4\mu_2^\lambda)^{1/2}] (\zeta_3)_{ij}, \tag{35}$$

$$\frac{\partial a_1^\lambda}{\partial \lambda} = [1/(\mu_2^\lambda)](\zeta_4)_{ij} - [\mu_3^\lambda/(\mu_2^\lambda)^2](\zeta_3)_{ij} - 2(\zeta_2)_{ij}. \tag{36}$$

Finally, the bond order can be written as an exact expansion by substituting Eq. (28) into Eq. (14), namely

$$\Theta_{ij} = -2\left[\sum_{n=0}^{\infty} \chi_{0n,n0}(E_F)\, \delta a_n + \sum_{n=1}^{\infty} 2\chi_{0(n-1),n0}(E_F)\, \delta b_n \right], \tag{37}$$

where $\delta a_n = (\partial a_n^\lambda / \partial \lambda)_{\lambda=0}$ and $\delta b_n = (\partial b_n^\lambda / \partial \lambda)_{\lambda=0}$ is the conventional notation for these derivative terms since in the original linearized version of the theory [see Eqs. (2.26)–(2.30) of Ref. 33] we have

$$\delta a_n = \frac{1}{2}(a_n^{\lambda=1} - a_n^{\lambda=-1}) = \frac{1}{2}\left(\frac{\partial a_n^\lambda}{\partial \lambda}\right)_{\lambda=0} (\delta\lambda = 2) = \left(\frac{\partial a_n^\lambda}{\partial \lambda}\right)_{\lambda=0} \tag{38}$$

and similarly for δb_n. The response functions are defined by

$$\chi_{0m,n0}(E_F) = \frac{1}{\pi} \mathrm{Im} \int^{E_F} G_{0m}(E) G_{n0}(E)\, dE \tag{39}$$

with $G_{0n}(E) \equiv G_{0n}^{\lambda=0}(E)$. The response functions depend on the recursion coefficients $\{a_n, b_n\}$ where $a_n \equiv a_n^{\lambda=0}$, $b_n \equiv b_n^{\lambda=0}$ through the recurrence relation Eq. (31), and the continued fraction Eq. (20), for $G_{00}(E)$. Hence, they depend explicitly on the moments μ_n where from Eq. (23) we have

$$\begin{aligned} \mu_n \equiv \mu_n^{\lambda=0} &= \frac{1}{2}[(\mu_n)_i + (\mu_n)_j] \\ &= \frac{1}{2}[\langle i|\hat{H}|i_1\rangle\langle i_1|\hat{H}|i_2\rangle \cdots \langle i_{n-1}|\hat{H}|i\rangle + \langle j|\hat{H}|j_1\rangle \\ &\quad \times \langle j_1|\hat{H}|j_2\rangle \cdots \langle j_{n-1}|\hat{H}|j\rangle] \end{aligned} \tag{40}$$

where we imply the summation over repeated indices $i_1, i_2, \ldots, j_1, j_2, \ldots$.

We see, therefore, that the nth moment can be written as the sum over all self-returning paths of length n that start from either orbital $|i\rangle$ or $|j\rangle$ that comprises the $i-j$ bond.[36] Thus, expression (37) is referred to as a bond-order potential (BOP) (Ref. 16) because it relates the bond order to explicit hopping paths within the local atomic environment about the bond. This provides the crucial link between the electronic structure (calculated within the TB approximation) and many-body interatomic potentials (calculated from the BOP expansion).

III. AN ANALYTIC BOP TO FOUR LEVELS

The eigenvalues and eigenfunctions of the dimer C_2, the trigonal methyl radical CH_3, and the tetrahedral methane molecule CH_4 may all be found analytically by using the irreducible representations of the appropriate point group to simplify the two-center, orthogonal TB Hamiltonian matrix.[37] Here we shall consider the results for C_2 and CH_4, respectively.

The σ states of the C_2 dimer have even (gerade) and odd (ungerade) symmetry with corresponding eigenvalues[23]

$$E(\sigma_g) = -\frac{1}{2}h_\sigma^{CC} \pm \frac{1}{2}\sqrt{(h_\sigma^{CC})^2 + \delta^2}, \tag{41}$$

$$E(\sigma_u) = +\frac{1}{2}h_\sigma^{CC} \pm \frac{1}{2}\sqrt{(h_\sigma^{CC})^2 + \delta^2}, \tag{42}$$

where $\delta = (E_p^C - E_s^C)$ and we have assumed for algebraic simplicity that $p_\sigma = 1$, a value that is close to that of 1.10 for the carbon system.[26] The energy zero has been chosen so that

$$\mu_1 = \frac{1}{2}[(\mu_1)_i + (\mu_1)_j] = \frac{1}{2}(E_s^C + E_p^C) = 0, \tag{43}$$

where the orbitals $|i\rangle$ and $|j\rangle$ are the carbon hybrids of Eq. (12). It follows from the eigenvectors[38] that the bond order of the carbon-carbon σ bond is given by

$$\Theta_\sigma^{CC} = \frac{1}{\sqrt{1 + (\hat{\delta}^{CC})^2}}, \tag{44}$$

where $\hat{\delta}^{CC} = \delta / h_\sigma^{CC}$. Thus, as expected, we have a perfect, saturated bond with $\Theta_\sigma = 1$ for the idealized case of zero sp splitting, whereas we have zero bond order in the limit $h_\sigma^{CC} \to 0$, corresponding to the atoms being pulled apart towards their free atom ground state s^2p^2 configuration (see, for example, Fig. 3.13 of Ref. 23).

The states of the tetrahedral molecule CH_4 display the A_1 or T_2 symmetry of the tetrahedral point group[37] with corresponding eigenvalues[39]

$$E(A_1) = -\frac{1}{4}\delta \pm \frac{1}{2}\sqrt{8(h_\sigma^{CH})^2 + \left(\Delta + \frac{1}{2}\delta\right)^2}, \tag{45}$$

$$E(T_2) = +\frac{1}{4}\delta \pm \frac{1}{2}\sqrt{\frac{8}{3}(h_\sigma^{CH})^2 + \left(\Delta - \frac{1}{2}\delta\right)^2}, \tag{46}$$

where we have taken $p_\sigma = 1$. $\Delta = E_s^H - \tfrac{1}{2}(E_s^C + E_p^C)$ gives the position of the hydrogen 1s level with respect to the average of the valence s and p energy levels for the carbon atom. The energy zero has been chosen so that

$$\mu_1 = \frac{1}{2}[(\mu_1)_i + (\mu_1)_j] = \frac{1}{2}\left[E_s^H + \frac{1}{2}(E_s^C + E_p^C)\right] = 0, \tag{47}$$

where the orbitals $|i\rangle$ and $|j\rangle$ are the carbon hybrid $|iC\sigma\rangle$ and the hydrogen 1s orbital $|jHs\rangle$, respectively. The present TB model, Eq. (1), requires the hydrogen 1s level to be adjusted self-consistently to guarantee local charge neutrality (LCN). This leads to a quartic equation for $\hat{\Delta}^{CH} = \Delta / h_\sigma^{CH}$ in terms of $\hat{\delta} = \delta / h_\sigma^{CH}$, namely

$$\hat{\Delta}^4 + \frac{26}{3}\left(1 - \frac{2}{52}\hat{\delta}^2\right)\hat{\Delta}^2 - \frac{28}{3}\hat{\delta}\hat{\Delta} + \frac{13}{6}\hat{\delta}^2\left(1 + \frac{3}{104}\hat{\delta}^2\right) = 0, \tag{48}$$

where $\hat{\Delta} \equiv \hat{\Delta}^{CH}$ and $\hat{\delta} \equiv \hat{\delta}^{CH}$. At equilibrium, methane takes a value[19] of $\hat{\delta} = 6.70/9.377 = 0.715$ so that it is an excellent approximation to neglect the fourth-order terms $\hat{\Delta}^4$, $\hat{\delta}^2\hat{\Delta}^2$, and $\hat{\delta}^4$ in Eq. (48). The resultant quadratic equation may be solved to give

$$(\hat{\Delta}^{\mathrm{CH}})_{LCN} = \frac{1}{26}(14 - 3\sqrt{3})\hat{\delta}^{CH}. \tag{49}$$

The bond order of the carbon-hydrogen σ bond may then be written

$$\Theta_\sigma^{CH} = \frac{1}{2\sqrt{2}}\left[\frac{1}{\sqrt{1 + \kappa^2(\hat{\delta}^{CH})^2}} + \frac{\sqrt{3}}{\sqrt{1 + \frac{1}{9}\kappa^2(\hat{\delta}^{CH})^2}}\right], \tag{50}$$

where $\kappa = 3\sqrt{3}(3\sqrt{3} - 1)/(52\sqrt{2}) = 0.296$. The first term inside the square brackets is the contribution to the σ bond order from the occupied nondegenerate bonding orbital A_1, the second term is from the occupied triply degenerate bonding state T_2. We see, therefore, that the carbon-hydrogen bond in methane is nearly saturated as the bond order takes the value 0.957 for $\hat{\delta}^{CH} = 0.715$. This is within 1% of the value 0.966 for the idealized situation of zero energy-level splitting.

These analytic expressions for the bond order, Eqs. (44) and (50), have been derived due to the high symmetry of C_2 and CH_4. The BOP expansion, Eq. (37), on the other hand, has been derived with no assumptions about symmetry and may, therefore, be applied to any atomic configuration of a covalent system. However, if we are to represent the dimer C_2, the trigonal methyl radical CH_3, and the tetrahedral methane molecule CH_4 exactly within the BOP expansion, then the continued fraction must be taken to four levels in Eq. (20) in order to retain the four-level eigenspectrum of Eqs. (41) and (42) and Eqs. (45) and (46), respectively. That is, we approximate

$$G_{00}(E) = \frac{1}{2}[G_{ii}(E) + G_{jj}(E)] \tag{51}$$

by the four-level continued fraction which reduces to

$$G_{00}(E) = \frac{\begin{bmatrix} (E-a_1)(E-a_2)(E-a_3) \\ -b_2^2(E-a_3) - b_3^2(E-a_1) \end{bmatrix}}{\begin{bmatrix} (E-a_0)(E-a_1)(E-a_2)(E-a_3) \\ -(E-a_0)(E-a_1)b_3^2 \\ -(E-a_0)(E-a_3)b_2^2 \\ -(E-a_2)(E-a_3)b_1^2 + b_1^2 b_3^2 \end{bmatrix}}, \tag{52}$$

where the zero of energy has been chosen so that $a_0 = \tfrac{1}{2}[(\mu_1)_i + (\mu_1)_j] = 0$ from Eq. (24).

The poles of this Green's function may be found by reducing the quartic in the denominator to standard form[40] by shifting the energy zero by $\frac{1}{4}(a_0+a_1+a_2+a_3)$ so that the cubic contribution vanishes. We may then write

$$G_{00}(\epsilon)=\frac{\begin{bmatrix}(\epsilon-a_1')(\epsilon-a_2')(\epsilon-a_3')\\ -b_2^2(\epsilon-a_3')-b_3^2(\epsilon-a_1')\end{bmatrix}}{\epsilon^4+p\epsilon^2+q\epsilon+r}, \tag{53}$$

where $\epsilon=E-\frac{1}{4}(a_0+a_1+a_2+a_3)$, $a_n'=a_n-\frac{1}{4}(a_0+a_1+a_2+a_3)$, and the coefficients p, q, and r are given by

$$p=a_0'a_1'+a_2'a_3'+(a_0'+a_1')(a_2'+a_3')-(b_1^2+b_2^2+b_3^2), \tag{54}$$

$$q=-(a_0'+a_1')a_2'a_3'-(a_2'+a_3')a_0'a_1'+b_1^2(a_2'+a_3')+b_2^2(a_0'+a_3')+b_3^2(a_0'+a_1'), \tag{55}$$

$$r=a_0'a_1'a_2'a_3'-b_1^2a_2'a_3'-b_2^2a_0'a_3'-b_3^2a_0'a_1'+b_1^2b_3^2. \tag{56}$$

The poles of $G_{00}(\epsilon)$ are at

$$\epsilon_n=\begin{cases}-\frac{1}{2}\alpha-\frac{1}{2}\sqrt{\alpha^2-4\beta}\\ +\frac{1}{2}\alpha-\frac{1}{2}\sqrt{\alpha^2-4\gamma}\\ +\frac{1}{2}\alpha+\frac{1}{2}\sqrt{\alpha^2-4\gamma}\\ -\frac{1}{2}\alpha+\frac{1}{2}\sqrt{\alpha^2-4\beta}\end{cases}\quad \text{for}\quad n=\begin{cases}1\\2\\3\\4\end{cases}, \tag{57}$$

where α is a nonzero real root of the equation

$$\alpha^6+2p\alpha^4+(p^2-4r)\alpha^2-q^2=0, \tag{58}$$

$$\beta=\frac{1}{2}(p+\alpha^2-q/\alpha) \tag{59}$$

and

$$\gamma=\frac{1}{2}(p+\alpha^2+q/\alpha). \tag{60}$$

We see that $\gamma-\beta=q/\alpha$ is a measure of the asymmetry of the eigenspectrum. For a symmetric eigenspectrum all the odd moments vanish by definition (i.e., $\mu_{2n+1}=0$), so that $a_n'=0$ and $q=0$ from Eq. (55).

We can check the above expression for the poles by considering the dimer and CH_4, respectively. For the dimer with $p_\sigma=1$ the eigenspectrum is symmetric so that $a_n'=0$ for all n. The b_n recursion coefficients may be evaluated from the moments [see, for example, Eqs. (25) and (27)]. We find

$$b_n^2=\begin{cases}h_\sigma^2+\delta^2/4\\ \frac{1}{4}\frac{h_\sigma^2\delta^2}{h_\sigma^2+\delta^2/4}\\ \frac{1}{16}\frac{\delta^4}{h_\sigma^2+\delta^2/4}\end{cases}\quad \text{for}\quad n=\begin{cases}1\\2\\3\end{cases}, \tag{61}$$

where $h_\sigma\equiv h_\sigma^{CC}$. It follows from Eqs. (54)–(56) that $p=-(h_\sigma^2+\frac{1}{2}\delta^2)$, $q=0$, and $r=\frac{1}{16}\delta^4$. Therefore, substituting into Eq. (58) we have $\alpha^2=h_\sigma^2$, and from Eqs. (59) and (60) $\beta=\gamma=-\frac{1}{4}\delta^2$. Hence, the poles in Eq. (57) predict correctly the dimer eigenspectrum in Eqs. (41) and (42).

For methane we have seen that the bond order for the idealized situation of zero energy splitting corresponding to $\delta=0$, $\Delta=0$ agrees to within 1% of the exact TB result. In this idealized case the eigenspectrum is symmetric so that $a_n'=0$ for all n. Again, the b_n recursion coefficients may be evaluated from the moments. We find

$$b_n^2=\begin{cases}7h_\sigma^2/6\\ 5h_\sigma^2/14\\ 8h_\sigma^2/7\end{cases}\quad \text{for}\quad n=\begin{cases}1\\2\\3\end{cases}, \tag{62}$$

where $h_\sigma\equiv h_\sigma^{CH}$. It follows from Eqs. (54)–(56) that $p=-\frac{8}{3}h_\sigma^2$, $q=0$, and $r=\frac{4}{3}h_\sigma^4$. Therefore, substituting into Eq. (58) we have $\alpha^2=\frac{4}{3}(2-\sqrt{3})h_\sigma^2$, and from Eqs. (59) and (60) $\beta=\gamma=-2/\sqrt{3}h_\sigma^2$. The resultant poles predicted by Eq. (57) simplify to $\pm\sqrt{2}h_\sigma$ and $\pm\sqrt{2/3}h_\sigma$ in agreement with the eigenspectrum for CH_4 in Eqs. (45) and (46). [Note that these same four poles would have been obtained by choosing the root $\alpha^2=\frac{4}{3}(2+\sqrt{3})h_\sigma^2$ instead of $\frac{4}{3}(2-\sqrt{3})h_\sigma^2$, but the latter guarantees the desired ordering $\epsilon_1<\epsilon_2<\epsilon_3<\epsilon_4$ in Eq. (57)].

The intersite Green's function $G_{ij}(\epsilon)$ may now be obtained from Eqs. (28)–(30) and Eq. (38) as

$$G_{ij}(\epsilon)=\sum_{n=0}^{3}G_{0n}^2(\epsilon)\delta a_n+2\sum_{n=1}^{3}G_{0(n-1)}(\epsilon)G_{n0}(\epsilon)\delta b_n, \tag{63}$$

where from the recurrence relation, Eq. (31),

$$G_{0n}(\epsilon)=\begin{cases}\frac{b_1[(\epsilon-a_2')(\epsilon-a_3')-b_3^2]}{D(\epsilon)}\\ \frac{b_1b_2(\epsilon-a_3')}{D(\epsilon)}\\ \frac{b_1b_2b_3}{D(\epsilon)}\end{cases}\quad \text{for}\quad n=\begin{cases}1\\2\\3\end{cases}. \tag{64}$$

$D(\epsilon)=\epsilon^4+p\epsilon^2+q\epsilon+r$ is the denominator of $G_{00}(\epsilon)$. Equation (63) may be simplified by requiring that the poles of this four-level intersite Green's function $G_{ij}(\epsilon)$ are the same as those of the four-level Green's function $G_{00}(\epsilon)=\frac{1}{2}[G_{ii}(\epsilon)+G_{jj}(\epsilon)]$. This constraint will be exactly satisfied by those systems which display four-level behavior such as the σ bonds in C_2 and CH_4 which we have considered above. In general, this constraint implies that the numerator in Eq. (63) must factorize as $(A\epsilon^2+B\epsilon+C)D(\epsilon)$. The coefficients A, B, and C may be obtained by equating the coefficients of ϵ^6, ϵ^5, and ϵ^4 in this factorized expression with those of Eq. (63). We find

$$A=\delta a_0, \tag{65}$$

$$B=2(a_0'\delta a_0+b_1\delta b_1), \tag{66}$$

and

$$C = K\delta a_0 - 2b_1(a_1' + 2a_2' + 2a_3')\delta b_1 + b_1^2\delta a_1 \tag{67}$$

with

$$K = [(a_0')^2 + (a_1')^2 + (a_2')^2 + (a_3')^2] + 3(a_1'a_2' + a_2'a_3' + a_3'a_1') + (b_1^2 - b_2^2 - b_3^2), \tag{68}$$

where δa_0, δb_1, and δa_1 are defined by Eqs. (34)–(36) with $\lambda = 0$. Moreover, equating the coefficients of ϵ^3, ϵ^2, ϵ, and ϵ^0 gives δb_2, δa_2, δb_3, and δa_3, respectively, in terms of δa_0, δb_1, and δa_1.

The four-level intersite Green's function, Eq. (63), may thus be written in the form

$$G_{ij}(\epsilon) = \left\{ \frac{\epsilon^2 + 2a_0'\epsilon + K}{D(\epsilon)} \right\} \delta a_0 + \left\{ \frac{2b_1\epsilon - 2b_1(a_1' + 2a_2' + 2a_3')}{D(\epsilon)} \right\} \delta b_1 + \left\{ \frac{b_1^2}{D(\epsilon)} \right\} \delta a_1, \tag{69}$$

where the prefactors in the curly brackets depend on the recursion coefficients defining the continued fraction for $G_{00} = \frac{1}{2}(G_{ii} + G_{jj})$, whereas δa_0, δb_1, and δa_1 also depend on the interference terms linking orbitals $|i\rangle$ and $|j\rangle$. The imaginary part of these prefactors integrated up to the Fermi energy would define the appropriate response functions for the four-level bond-order potential expansion.

However, rather than keeping these terms separate, we group them together and work with the compact form for G_{ij}, namely

$$G_{ij}(\epsilon) = \frac{A\epsilon^2 + B\epsilon + C}{\epsilon^4 + p\epsilon^2 + q\epsilon + r}. \tag{70}$$

This can be written explicitly in terms of the poles ϵ_n and residues w_n as

$$G_{ij}(\epsilon) = \sum_{n=1}^{4} \frac{w_n}{\epsilon - \epsilon_n}, \tag{71}$$

where

$$w_n = \begin{cases} +\dfrac{P}{\alpha} + \dfrac{Q}{\sqrt{\alpha^2 - 4\beta}} \\ -\dfrac{P}{\alpha} + \dfrac{R}{\sqrt{\alpha^2 - 4\gamma}} \\ -\dfrac{P}{\alpha} - \dfrac{R}{\sqrt{\alpha^2 - 4\gamma}} \\ +\dfrac{P}{\alpha} - \dfrac{Q}{\sqrt{\alpha^2 - 4\beta}} \end{cases} \quad \text{for} \quad n = \begin{cases} 1 \\ 2 \\ 3 \\ 4 \end{cases}. \tag{72}$$

The coefficients P, Q, and R are defined by

$$P = \frac{C + \frac{1}{2}[(\gamma - \beta)/\alpha]B - \frac{1}{2}(\gamma + \beta)A}{2(\gamma + \beta) + [(\gamma - \beta)/\alpha]^2}, \tag{73}$$

$$Q = -[1 + (\gamma - \beta)/\alpha^2]P - \frac{1}{2}A + (1/2\alpha)B, \tag{74}$$

and

$$R = -[1 - (\gamma - \beta)/\alpha^2]P - \frac{1}{2}A - (1/2\alpha)B. \tag{75}$$

It follows from Eq. (14) that the bond order is now given simply by the sum of the residues of the poles that are occupied, namely

$$\Theta_{ij}^{(4)} = 2\sum_{n_{occ}} w_n, \tag{76}$$

where the suffix (4) is to remind us that it has been derived within the four-level approximation. We will refer to this bond-order potential expression by the acronym BOP4.

We now consider how BOP4 leads to the analytic expressions Eq. (44) and Eq. (50), for the σ bond order of C_2 and CH_4, respectively. It follows from Eqs. (34)–(36) that $\delta a_0 = -h_\sigma$, $\delta b_1 = 0$, and $\delta a_1 = h_\sigma^3/b_1^2$ where the latter two expressions follow because there are no three- and four-member ring contributions present. Thus, substituting into Eqs. (65)–(68), $A = -h_\sigma$, $B = 0$, and $C = -(b_1^2 - b_2^2 - b_3^2 - h_\sigma^2)h_\sigma$.

For the dimer with b_1^2, b_2^2, and b_3^2 given by Eq. (61) we have that $C = 0$ so that $P = Q = R = \frac{1}{4}h_\sigma$, and

$$w_n = \begin{cases} +\dfrac{1}{4} + \dfrac{1}{4}\dfrac{1}{\sqrt{1 + (\hat{\delta}^{CC})^2}} \\ -\dfrac{1}{4} + \dfrac{1}{4}\dfrac{1}{\sqrt{1 + (\hat{\delta}^{CC})^2}} \end{cases} \quad \text{for} \quad n = \begin{cases} 1 \\ 2 \end{cases}. \tag{77}$$

Thus, for the carbon dimer with both poles ϵ_1 and ϵ_2 occupied, we recover the well-known σ bond-order expression given by Eq. (44). We see that if $\hat{\delta} = 0$, then the contribution for w_2 vanishes, corresponding to a nonbonding σ state. Interestingly, on the other hand, we see that if $\hat{\delta} \neq 0$, then the contribution from w_2 is negative, corresponding to an antibonding state. We will return to this again in Paper II when comparing the nature of the ''*single*'' σ bond in C_2 and C_2H_2, respectively.

For methane with b_1^2, b_2^2, and b_3^2 given by Eq. (62) for the idealized case $\delta = \Delta = 0$, we have that $C = \frac{4}{3}h_\sigma^3$ so that $P = -(1/4\sqrt{3})(2 - \sqrt{3})h_\sigma$ and $Q = R = (1/4\sqrt{3})(2 + \sqrt{3})h_\sigma$. It follows from Eq. (72) that

$$w_n = \begin{cases} \dfrac{1}{8}(\sqrt{2 + \sqrt{3}} - \sqrt{2 - \sqrt{3}}) = \dfrac{1}{4\sqrt{2}} \\ \dfrac{1}{8}(\sqrt{2 + \sqrt{3}} + \sqrt{2 - \sqrt{3}}) = \dfrac{\sqrt{3}}{4\sqrt{2}} \end{cases} \quad \text{for} \quad n = \begin{cases} 1 \\ 2 \end{cases}. \tag{78}$$

Thus, for the methane molecule with both poles ϵ_1 and ϵ_2 occupied, we recover the σ bond order given by Eq. (50) with $\hat{\delta}^{CH}=0$. In Paper II we will see that BOP4 also yields the exact TB bond order for methane under the realistic conditions $\hat{\delta}^{CH}\neq 0$ and $p_\sigma \neq 1$.

IV. SIMPLIFIED EXPRESSION FOR THE σ BOND ORDER

The general expression for BOP4, which we have derived in the previous section, is too complicated for the rapid evaluation of the energies and forces that is required by large-scale molecular-dynamics simulations. Fortunately, however, as we have seen in Eq. (50), the idealized situation with $\delta=\Delta=0$ leads to a bond order for methane in its equilibrium geometry that is within 1% of the correct TB result. This behavior is also exhibited by the other hydrocarbons which we will consider in Paper II. We will, therefore, in this section present a simplified version of BOP4 in which $\delta=\Delta=0$ and $b_3=b_1$. The latter approximation is well satisfied by most hydrocarbons [see Eq. (62) and Table II of Paper II]. We will also assume that there are no odd-membered rings present so that $a_n=a_n'=0$ for all n.

The assumption that all the odd moments vanish leads to a symmetric eigenspectrum in Eq. (57) since $\beta=\gamma$. The eigenvalues are then determined by $\alpha^2=(b_1-b_3)^2+b_2^2$ and $\alpha^2-4\beta=(b_1+b_3)^2+b_2^2$. The corresponding residues in Eq. (72) are determined by $P=\frac{1}{4}h_\sigma+(b_1^2-b_2^2-b_3^2-h_\sigma^2)h_\sigma/(4b_1b_3)$ and $Q=-P+\frac{1}{2}h_\sigma$. The resultant bond order for a half filled eigenspectrum with $E_F=0$ such as for C_2 and CH_4 is then given by

$$\Theta^{(4Z)}_{ij,\sigma}(E_F=0)=\left\{\frac{1+\dfrac{\hat{b}_2^2-(\hat{b}_1^2-1)}{(\hat{b}_1+\hat{b}_3)\hat{b}_3}}{\sqrt{1+\left(\dfrac{\hat{b}_2}{\hat{b}_1+\hat{b}_3}\right)^2}}\right\}\frac{1}{\hat{b}_1}, \qquad (79)$$

where $\hat{b}_n=b_n/h_\sigma$ for $n=1,2,3$. We shall refer to this expression for the bond order, which has been evaluated under the assumption that all the odd moments are *zero,* by the acronym BOP4Z. Finally, taking $b_3=b_1$, we have

$$\Theta^{(4S)}_{ij,\sigma}(E_F=0)=\left\{\frac{1+\dfrac{\hat{b}_2^2-(\hat{b}_1^2-1)}{2\hat{b}_1^2}}{\sqrt{1+\dfrac{\hat{b}_2^2}{4\hat{b}_1^2}}}\right\}\frac{1}{\hat{b}_1}, \qquad (80)$$

where the superscript $4S$ is to remind us that the bond order has been evaluated within the four-level approximation under the *simplifying* assumption that $b_3=b_1$ in addition to all the odd moments vanishing (i.e., $\delta=\Delta=0$ and $\zeta_{2n+1}^{ring}=0$). The error is made in going from Eq. (79) to Eq. (80) by assuming $b_3=b_1$ is small for most hydrocarbons. For CH_4 we have $\Theta^{(4S)}=0.9651$ compared to $\Theta^{(4Z)}=(1+\sqrt{3})/(2\sqrt{2})=0.9659$, so that the error is only 0.1%.

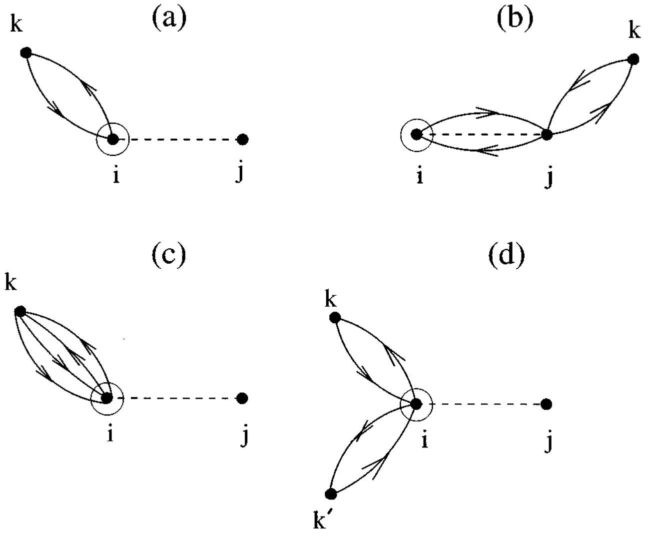

FIG. 1. Hopping paths of length 2 (a) and length 4 (b), (c), (d) that contribute to the recursion coefficients b_1 and b_2, respectively, for the bond $i-j$. There is an equivalent set of three- and four-body diagrams for paths originating from atom j rather than atom i.

The recursion coefficients b_1 and b_2 may be written explicitly in terms of the hopping paths of length two and length four within the local atomic environment about the bond, as illustrated in Fig. 1. It follows[30,40,41] from Eqs. (25) and (40) that for the σ bond

$$\hat{b}_1^2=1+\frac{1}{2}\sum_{k\neq i,j}\{[g_\sigma^\mu(\theta_{jik})]^2[\hat{h}_\sigma^{\mu\kappa}(R_{ik})]^2+(i\leftrightarrow j)\}, \qquad (81)$$

where the renormalized bond integrals are defined by $\hat{h}_\sigma^{\mu\kappa}(R_{ik})=h_\sigma^{\mu\kappa}(R_{ik})/h_\sigma^{\mu\nu}(R_{ij})$ and $(i\leftrightarrow j)$ implies an additional contribution obtained by interchanging i and j in the preceding term (or terms). The angular functions $g_\sigma^\mu(\theta)$ are given by

$$g_\sigma^C(\theta)=[p_\sigma/(1+p_\sigma)](p_\sigma^{-1}+\cos\theta) \qquad (82)$$

and

$$g_\sigma^H(\theta)=1. \qquad (83)$$

For simplicity $g_\sigma^C(\theta)$ has been derived under the assumption that $[h_\pi^{CC}(R)/h_\sigma^{CC}(R)]^2\ll 1$ which is a very good approximation for the carbon system.[26]

Moreover, it follows from Eqs. (27) and (40) that

$$\begin{aligned}\hat{b}_1^2\hat{b}_2^2=&(\hat{b}_1^2-1)-(\hat{b}_1^2-1)^2\\&+\frac{1}{2}\sum_{k\neq i,j}\{[g_\sigma^\mu(\theta_{jik})]^2[\hat{h}_\sigma^{\mu\kappa}(R_{ik})]^4+(i\leftrightarrow j)\}\\&+\frac{1}{2}\sum_{\substack{k,k'\neq i,j\\ k\neq k'}}\{[g_\sigma^\mu(\theta_{jik})g_\sigma^\mu(\theta_{kik'})g_\sigma^\mu(\theta_{k'ij})]\\&\times[\hat{h}_\sigma^{\mu\kappa}(R_{ik})]^2[\hat{h}_\sigma^{\mu\kappa'}(R_{ik'})]^2+(i\leftrightarrow j)\}.\end{aligned} \qquad (84)$$

The first term $(\hat{b}_1^2-1)$ on the right-hand side of Eq. (84) represents the four-path contribution arising from hopping from $|i\rangle$ (or orbital $|j\rangle$) through $|j\rangle$ (or $|i\rangle$) and then out to the neighbors and back as illustrated in Fig. 1(b). The second term, $-(\hat{b}_1-1)^2$, is a small correction factor that remains after subtracting μ_2^2 from μ_4 in Eq. (27). The third term on the right-hand side of Eq. (84) corresponds to the self-retracing paths of length four between orbital $|i\rangle$ (or orbital $|j\rangle$) and a neighboring atom k that is illustrated in Fig. 1(c). The fourth term on the right-hand side corresponds to the paths of length four between orbital $|i\rangle$ (or orbital $|j\rangle$) and the nearest-neighbor atoms k and k' as illustrated in Fig. 1(d). Again the angular function has been approximated by assuming $[h_\pi/h_\sigma]^2 \ll 1$. We have evaluated $\hat{b}_2$ in Eq. (84) by retaining only the hopping paths within the first nearest-neighbor shell of atoms about the bond. The contribution from the four-hop term from first- to second-nearest-neighbor shell and back is negligible for the σ bond. We are also assuming no four-member ring contributions. These have been given explicitly elsewhere.[41]

We can check these expressions for $\hat{b}_1$ and $\hat{b}_2$ by evaluating them for CH_4 under the assumption that $p_\sigma = 1$. Then, since for the tetrahedral bond $\cos\theta = -1/3$, we have from Eqs. (81) and (84) that

$$\hat{b}_1^2 = 1 + \frac{1}{2}\times 3\times\frac{1}{9} = \frac{7}{6} \tag{85}$$

and

$$\hat{b}_1^2\hat{b}_2^2 = \frac{1}{6} - \left(\frac{1}{6}\right)^2 + \frac{1}{2}\times 3\times\frac{1}{9} + \frac{1}{2}\times 3\times 2\times\frac{1}{27} = \frac{5}{12} \tag{86}$$

which agrees with our earlier values in Eq. (62) We shall compare the predictions of this simplified bond-order expression $\Theta^{(4S)}$ with the exact TB results for diamond, graphite, and the hydrocarbons in Paper II. It will be referred to by the acronym BOP4S.

Finally, we comment on the analytic form of BOP4S. The factor $1/\hat{b}_1$ outside the curly brackets in Eq. (80) with $\hat{b}_1$ given by Eq. (81) is very similar to Tersoff's[7] empirical expression for the bond order, as has been stressed previously.[14] It arises from embedding the bond in its local atomic environment and determining the energy scale of the bonding through the square root of the corresponding second moment μ_2. However, as has been stressed by Nishitani *et al.*,[42] this second moment approximation does not differentiate between the binding energies of different elemental structure types with the same dimensionality if the reasonable assumption is made that the pairwise repulsive potential falls off with the distance as the square of the bond integral. This follows because the two-level approximation for the bond order of symmetric structures such as graphite, diamond, or simple cubic takes the form

$$\Theta^{(2S)}_{ij,\sigma} = 1/\hat{b}_1 = [(1+p_\sigma)/(1+p_\sigma^2/d)^{1/2}]/z^{1/2}, \tag{87}$$

where d is the dimensionality of the lattice and z is the local coordination within a first-nearest-neighbor model. Thus, since each atom has z bonds, the bond energy *per atom* is proportional to $z^{1/2}$ which results in the equilibrium binding energy being independent of the coordination z (for a given dimensionality d). This is illustrated by the left-hand panel in Fig. 2 where we see that the three-dimensional structures diamond, simple cubic, and face-centered cubic have identical binding energies.

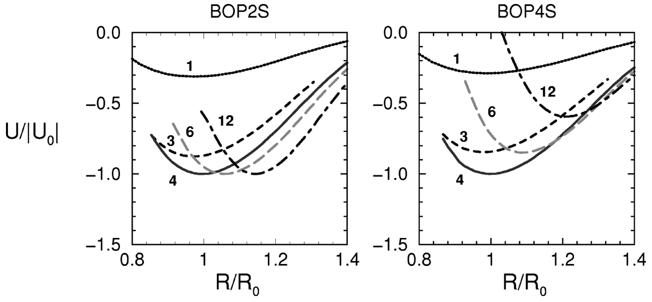

FIG. 2. Model binding energy curves within the simplified two-level approximation BOP2S (left-hand panel) and the simplified four-level approximation BOP4S (right-hand panel) for the dimer $(z=1)$, graphite $(z=3)$, diamond $(z=4)$, simple cubic $(z=6)$, and fcc $(z=12)$. The repulsive energy is assumed to be pairwise with the potential falling off with the distance as the square of the bond integral. The π bond energy and the promotion energy contributions are neglected. Note that BOP2S gives no structural differentiation between the three-dimensional structures diamond, simple cubic, and fcc.

This failure to differentiate between structure types within the second moment approximation is not unexpected since $\mu_2^{1/2}$ fixes the *energy scale* but not the *shape* of the eigenspectrum. The latter is determined by the higher moments, in particular, μ_4 which reflects the unimodal versus bimodal behavior.[23] The fourth moment has been shown to control the structural trends within the periodic table of the sp-valent elements.[43] However, evaluating the bond order to the third level by taking $b_3=0$ would lead to an unphysical nonbonding state for the hydrocarbons at the Fermi energy. Our symmetric four-level approximation, on the other hand, has an energy gap given by

$$E_{gap}=E_{homo}-E_{lumo}=\sqrt{(b_1+b_3)^2+b_2^2}-\sqrt{(b_1-b_3)^2+b_2^2}. \tag{88}$$

This leads to the additional factor inside the curly brackets for the bond order in Eq. (79) for the symmetric four-level approximation BOP4Z or in Eq. (80) for the simplified BOP4S expression when $b_3=b_1$. This inclusion of the fourth moment in BOP4S now ensures structural differentiation as is illustrated by the right-hand panel in Fig. 2. We will find in Paper II that it also causes an increase in the σ bond order by up to 5% for the hydrocarbons.

V. SIMPLIFIED EXPRESSION FOR THE π BOND ORDER

The Tersoff-Brenner potential[7,12] does not include an explicit π bond contribution. This causes radicals to be overbound. For example, within the Tersoff formalism the C-C bond in the radical C_2H_5 will behave approximately as the average of the C-C bonds in C_2H_4 and C_2H_6. This implies that the C-C bond in the ethyl radical C_2H_5 is being treated as a bond with strength midway between that of a single bond (as in ethane C_2H_6) and a double bond (as in ethylene C_2H_4). In practice, the π bond is broken in going from C_2H_4 to C_2H_5 so that the C-C bond in the radical is essentially a single bond rather than a double bond.

The π bond contribution in Eq. (10) must be invariant to the choice of the x and y coordinate axes, once the z coordinate has been fixed along the bond axis R_{ij}. In order to guarantee this within an approximate scheme, we must use the matrix rather than scalar form of the Lanczos algorithm,[21,22] namely

$$|u_{n+1})B_{n+1}=\hat{H}|u_n)-|u_n)A_n-|u_{n-1})B_n^+, \tag{89}$$

where A_n and B_n are matrices analogous to the scalar recursion coefficients a_n and b_n in Eq. (21). The Lanczos states $|u_n)$ are obtained recursively by acting with the Hamiltonian operator $\hat{H}$ on the starting state

$$|u_0)=(|\pi_x\rangle,|\pi_y\rangle), \tag{90}$$

where

$$|\pi_x\rangle=\frac{1}{\sqrt{2}}(|ix\rangle+\sqrt{-1}|jx\rangle) \tag{91}$$

and

$$|\pi_y\rangle=\frac{1}{\sqrt{2}}(|iy\rangle+\sqrt{-1}|jy\rangle) \tag{92}$$

by generalizing for the π bond the scalar starting orbital $|u_0^{\lambda=0}\rangle$ in Eq. (17).

The diagonal block of the Green's function $G_{00}(E)$ may be written

$$G_{00}(E)=\begin{bmatrix} EI-A_0- \\ -B_1^+[EI-A_1-B_2^+[\cdots]^{-1}B_2]^{-1}B_1\end{bmatrix}^{-1}, \tag{93}$$

where I is the 2×2 unit matrix. We now derive the simplest approximation for the π bond by setting $A_n=0$ (an excellent approximation for the π bond if the energy zero is chosen as E_p^C) and $B_{n\neq 1}=0$, so that

$$G_{00}(E)=\left[EI-\frac{1}{E}B_1^+B_1\right]^{-1}, \tag{94}$$

where

$$B_1^+B_1=(u_0|\hat{H}^2|u_0)=\begin{pmatrix} b_{xx}^2 & b_{xy}^2 \\ b_{yx}^2 & b_{yy}^2\end{pmatrix} \tag{95}$$

with $b_{xx}^2=\langle\pi_x|\hat{H}^2|\pi_x\rangle$, $b_{yy}^2=\langle\pi_y|\hat{H}^2|\pi_y\rangle$, $b_{xy}^2=b_{yx}^2=\langle\pi_x|\hat{H}^2|\pi_y\rangle$. It follows that

$$G_{00}(E)=\left\{\frac{E}{(E^2-b_{xx}^2)(E^2-b_{yy}^2)-b_{xy}^4}\right\}\times\begin{pmatrix} E^2-b_{yy}^2 & b_{xy}^2 \\ b_{yx}^2 & E^2-b_{xx}^2\end{pmatrix}. \tag{96}$$

The poles of this Green's function are solutions of a simple quartic equation, namely

$$E_{1,2,3,4}=\pm b_\pm = \pm\sqrt{\frac{1}{2}(b_{xx}^2+b_{yy}^2)\pm\sqrt{\frac{1}{4}(b_{xx}^2-b_{yy}^2)^2+b_{xy}^4}}. \tag{97}$$

As expected, these poles are invariant to the choice of the x and y coordinate axes. This can be seen by writing the Hamiltonian matrix elements in terms of the appropriate bond integrals and directional cosines[29] and substituting into Eq. (97). We find after manipulating the algebra that

$$\frac{1}{2}(\hat{b}_{xx}^2+\hat{b}_{yy}^2)=1+\frac{1}{4}\sum_{k\neq i,j}\left\{\sin^2\theta_{jik}\frac{p_\sigma}{1+p_\sigma}[\hat{h}_\sigma^{C\kappa}(R_{ik})]^2 +(1+\cos^2\theta_{jik})[\hat{h}_\pi^{CC}(R_{ik})]^2\delta_{\kappa C}+(i\leftrightarrow j)\right\} \tag{98}$$

and

$$\frac{1}{4}(\hat{b}_{xx}^2-\hat{b}_{yy}^2)^2+\hat{b}_{xy}^4=\frac{1}{16}\sum_{k,k'\neq i,j}\{\sin^2\theta_{jik}\sin^2\theta_{jik'}\hat{\beta}_{ik}^2\hat{\beta}_{ik'}^2 +\sin^2\theta_{jik}\sin^2\theta_{ijk'}\hat{\beta}_{ik}^2\hat{\beta}_{jk'}^2+(i\leftrightarrow j)\} \times\cos 2(\phi_k-\phi_{k'}), \tag{99}$$

where

$$\hat{\beta}_{ik}^2=\frac{p_\sigma}{1+p_\sigma}[\hat{h}_\sigma^{C\kappa}(R_{ik})]^2-[\hat{h}_\pi^{CC}(R_{ik})]^2\delta_{\kappa C} \tag{100}$$

and $\hat{b}_{xx}$, $\hat{b}_{yy}$, $\hat{b}_{xy}$, $\hat{h}_\sigma^{C\kappa}$, and $\hat{h}_\pi^{CC}$ are the quantities b_{xx}, b_{yy}, b_{xy}, $h_\sigma^{C\kappa}$, and h_π^{CC} normalized by $h_\pi^{CC}(R_{ij})$. Thus the poles $\pm b_\pm$ in Eq. (97) depend only on the bond integrals, bond angles θ_{ijk} and θ_{jik}, and dihedral angles $(\phi_k-\phi_{k'})$, so that they are independent of the choice of the x and y coordinate axes. It follows from Eq. (87) that the π bond order for $E_F=0$ can be written

$$\Theta_{ij,\pi}^{(2M)}(E_F=0)=\Theta_{ij,\pi_-}^{(2M)}(E_F=0)+\Theta_{ij,\pi_+}^{(2M)}(E_F=0) =\frac{1}{\hat{b}_-}+\frac{1}{\hat{b}_+}, \tag{101}$$

where π_- and π_+ refer to the π bond orders along the two principal axes. We shall refer to this expression for the π bond order, where $\hat{b}_+$ and $\hat{b}_-$ are given by Eqs. (97)–(100), by the acronym BOP2M since we have derived it by using *matrix* recursion to two levels.

This analytic BOP2M expression for the π bond order handles correctly the changing order of the bond in going from $C_2H_2\rightarrow C_2H_4\rightarrow C_2H_5\rightarrow C_2H_6$. Taking the ideal trigonal and tetrahedral bond angles for C_2H_4 and C_2H_6 rather than the experimental values of 121.3° and 111.2°, respectively, and assuming C_2H_5 also takes these ideal bond angles, we have for the case $p_\sigma=1$ that

$$\Theta_{ij,\pi}^{(2M)}=\begin{cases} 1 + 1 & \text{for } C_2H_2 \\ 1 + \dfrac{1}{\sqrt{1+\frac{3}{4}\hat{h}_\sigma^2}} & \text{for } C_2H_4 \\ \dfrac{1}{\sqrt{1+\frac{1}{3}\hat{h}_\sigma^2}} + \dfrac{1}{\sqrt{1+\frac{17}{24}\hat{h}_\sigma^2}} & \text{for } C_2H_5 \\ \dfrac{1}{\sqrt{1+\frac{2}{3}\hat{h}_\sigma^2}} + \dfrac{1}{\sqrt{1+\frac{2}{3}\hat{h}_\sigma^2}} & \text{for } C_2H_6 \end{cases} \tag{102}$$

where $\hat{h}_\sigma = h_\sigma^{CH}(R_{ik})/h_\pi^{CC}(R_{ij})$. In order to examine the changing behavior of the π bond within this hydrocarbon sequence we now assume that the C-C and C-H bond lengths do not alter so that $\hat{h}_\sigma$ is constant. Taking the typical value of $\hat{h}_\sigma = 6$,[19] we have that the π bond order decreases from $2.000 \rightarrow 1.189 \rightarrow 0.471 \rightarrow 0.400$ on going from $C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_5 \rightarrow C_2H_6$.

Thus, we see that BOP2M predicts correctly the saturated double π bond behavior in C_2H_2 and the saturated single π bond behavior in C_2H_4. Moreover, it follows from Eq. (102) that the conventional saturated π bond in C_2H_4 that corresponds to $1/\hat{b}_- = 1.000$ is effectively broken on going to C_2H_5 and C_2H_6, since $1/\hat{b}_-$ takes the reduced values of 0.277 and 0.200, respectively, for $\hat{h}_\sigma = 6$. We find, therefore, that the total π bond order in the radical C_2H_5 is only 10% that of C_2H_4 but 90% that of C_2H_6. The Tersoff potential,[7] on the other hand, would have predicted 50% C_2H_4, 50% C_2H_6 which gives rise to the inherent problems associated with overbinding of radicals.[12]

BOP2M also leads to a rotational barrier in ethylene due to the saturated π bond again being effectively broken under rotation. It follows from Eqs. (97)–(99) that rotation through a dihedral angle of 90° leads to the reduced bond order

$$\Theta_{ij,\pi}^{(2M)}\left(\Delta\phi = \frac{\pi}{2}\right) = \frac{1}{\sqrt{1+\frac{3}{8}\hat{h}_\sigma^2}} + \frac{1}{\sqrt{1+\frac{3}{8}\hat{h}_\sigma^2}} \tag{103}$$

compared to that of C_2H_4 with $\Delta\phi = 0$ in Eq. (102). This corresponds to an energy barrier of

$$\Delta U_\pi = -2h_\pi^{CC}(R_{ij})\Delta\Theta_{ij,\pi}^{(2M)} \tag{104}$$

which takes the value of 3.1 eV for $\hat{h}_\sigma = 6$ eV and $\hat{h}_\pi = 2.3$ eV.[26] This energy barrier falls between the *ab initio* values of 2.1 eV and 4.7 eV for relaxed[44] and unrelaxed[45] configurations during twisting. Interestingly, BOP2M predicts no rotational barrier for ethane C_2H_6. This is consistent with a detailed Hartree-Fock analysis that deduced zero barrier height for zero charge transfer.[45]

BOP2M is similar to that of BOP4S in that both require the solution of a quartic equation to determine the poles of the appropriate Green's functions. However, BOP2M is less accurate than BOP4S since it only satisfies up to the second moment exactly. Fortunately, however, we will see in Paper II that the absolute errors in the π bond energy are usually not much greater than those in the σ bond energy because the π bond integral is smaller than the σ bond integral.

VI. SIMPLIFIED EXPRESSION FOR THE PROMOTION ENERGY

The promotion energy is a term that is not considered explicitly in the Tersoff-Brenner potentials.[7,12] It arises from the fact that in carbon the s^2p^2 configuration of the free-atom ground state must be promoted to a configuration closer to that of sp^3 in order to achieve the optimum binding energy. In the simplest version of valence bond theory exactly one p electron would be promoted in order to create the sp, sp^2, or sp^3 hybrids for the σ bonds in linear, trigonal, or tetrahedral coordinations and the corresponding p^2, p^1, or p^0 orbitals for the π bonds. In practice, within molecular orbital or TB theory, there is a competition between maximizing the magnitude of the bond integral by choosing the preferred hybrid and minimizing the cost of the promotion energy, so that ΔN_p is usually less than one (see Sec. 3.7 of Ref. 22).

The promotion energy is a property of the carbon atom in its environment rather than a property of the individual bond. In fact, within the simplest version of valence bond theory, the promotion energy *per C atom* is independent of whether we have two-fold, three-fold, or four-fold coordination since $\Delta N_p = 1$ in all these cases. In practice, the promotion energy does depend on the local environment. This environment dependence could be displayed explicitly by deriving an expression for ΔN_s (and hence ΔN_p) by taking the appropriate Green's function, $G_{C_s,C_s}(E)$, to four levels as in Eq. (20). Unfortunately, however, the resultant expression would be too time consuming to evaluate within large-scale molecular dynamics simulations. In this section, therefore, we present a simple analytic expression for the promotion energy that we will demonstrate in Paper II reproduces the TB promotion energies of most hydrocarbon molecules in their ground state.

The promotion energy of the trigonal CH_3 radical and the tetragonal CH_4 molecule can be found analytically by using group theory to simplify the TB Hamiltonian matrix.[37] We find that

$$\Delta N_s = -\left[1 - \frac{\frac{1}{2}\Delta\hat{E}_{ss}^{CH}}{\sqrt{1+\frac{1}{4}(\Delta\hat{E}_{ss}^{CH})^2}}\right], \tag{105}$$

where

$$\Delta\hat{E}_{ss}^{CH} = (E_s^H - E_s^C)/\sqrt{z(ss\sigma^{CH})^2} \tag{106}$$

with the local coordination z taking the values 3 and 4 for CH_3 and CH_4, respectively. Therefore, not unexpectedly, ΔN_s depends on the energy difference between the C and H s levels, $E_s^H - E_s^C$, normalized by the root-mean-square width of the resultant eigenspectrum determined by the $ss\sigma^{CH}$ bonding integral. The latter factor varies as $z^{1/2}$.

However, this coordination dependence that enters $\Delta\hat{E}_{ss}^{CH}$ through the root-mean-square width in the denominator is countered by a not too dissimilar coordination dependence of the energy difference $(E_s^H - E_s^C)$ in the numerator. This is found to increase with increasing coordination in order to maintain local charge neutrality (LCN). We shall, therefore, assume that after LCN $\Delta\hat{E}_{ss}^{CH}$ is explicitly coordination independent and takes the value displayed by CH_4, namely

$$(\Delta\hat{E}_{ss}^{CH})_{LCN} = \frac{1}{2}\sqrt{1+p_\sigma}\,\frac{(27-3\sqrt{3p_\sigma})\,\hat{\delta}^{CH}}{(27-p_\sigma)}, \tag{107}$$

where, as before, $\hat{\delta}^{CH} = \delta/h_\sigma^{CH}$. Finally, substituting Eq. (107) into Eq. (105), the promotion energy per C atom can be written as

$$U_{prom} = \delta[1-\kappa\hat{\delta}/\sqrt{1+\kappa^2\hat{\delta}^2}\,], \tag{108}$$

where

$$\kappa = \frac{1}{4}\sqrt{1+p_\sigma}(27-3\sqrt{3p_\sigma})/(27-p_\sigma). \tag{109}$$

For $p_\sigma = 1$ this reduces to the expression for κ in Eq. (50). This simple analytic expression for the promotion energy is assumed to be valid for a carbon atom in any environment. This is achieved by defining the normalized energy difference $\hat{\delta}$ by $\hat{\delta} = \delta/\langle h_\sigma\rangle$ where the average σ bond integral is given by

$$\langle h_\sigma\rangle = \sqrt{\frac{1}{z}\sum_{k\neq i}[h_\sigma^{C\kappa}(R_{ik})]^2}, \tag{110}$$

where z is the local coordination of the carbon atom at site i (see, for example, Eq. (14) of Ref. 12). We see, therefore, from Eqs. (108) and (110) that the promotion energy tends to zero as the atoms are pulled apart to infinity.

In Paper II we will show that Eq. (108) reproduces the promotion energy of most hydrocarbon molecules in their ground states and even predicts accurately the promotion energy of a carbon atom in a purely carbon environment such as trigonal graphite or tetrahedral diamond. However, in order to handle transverse vibrational models, Eq. (108) will probably need to be generalized to include changes of bond angle about the ground state since Eq. (108) is dependent solely on the bond length. This will require the additional information contained in the fourth moment of the local density of states of the carbon atom rather than just the second moment that enters Eq. (106). This will be considered elsewhere.

VII. CONCLUSIONS

In this paper we have derived analytic expressions for the σ and π bond orders by approximating the many-atom expansion for the bond order within the TB model. In particular, by retaining terms to four-levels in the continued fractions for the appropriate Green's functions, we have obtained an expression, BOP4, that describes exactly the σ bonds in the dimer C_2, the trigonal methyl radical CH_3, and the tetrahedral methane molecule CH_4. A simplified, but accurate variant of this expression, BOP4S, depends only on the two recursion coefficients b_1 and b_2 that characterize the root-mean-square width and the unimodal versus bimodal shape of the σ bond eigenspectrum, respectively. The coefficients themselves may be written explicitly in terms of three- and four-body contributions involving the σ bond integrals $h_\sigma(R)$ and simple angular functions $g_\sigma(\theta)$ where R and θ are the bond lengths and bond angles, respectively. We have also obtained an analytic expression for the π bond order, BOP2M, by performing matrix recursion to two levels. The use of matrix rather than scalar recursion guarantees that the BOP2M is independent of the choice of the x and y coordinate axes, depending only on the neighboring bond angles, dihedral angles, and renormalized bond integrals. In addition, a simple analytic expression for the promotion energy is presented that has the required feature that it tends to zero as the atoms are pulled apart to infinity.

These analytic BOP's have four main advantages over the empirical Tersoff-Brenner potentials. First, their analytic form is *predicted* by the theory, thereby providing insight into the origin of each term and reducing the number of fitting parameters. Second, the σ bond-order expression BOP4S includes explicitly the shape parameter $(b_2/b_1)^2$ that is essential for understanding structural trends within molecules[46] and solids.[43] Third, the π bond-order expression BOP2M describes the breaking of saturated π bonds on radical formation, thereby avoiding the endemic overbinding of radicals of previous interatomic potentials. Fourth, BOP2M also describes the breaking of the saturated π bond in the ethylene molecule C_2H_4 under torsion, thereby avoiding the necessity of including an *ad hoc* torsional stiffness contribution.

In the following paper we examine the accuracy of these analytic BOP's for modeling the energetics of diamond, graphite, and hydrocarbon molecules that would be relevant for the atomistic simulation of CVD diamond growth, for example.

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