# Bounded Analytic Bond-Order Potentials for $\sigma$ and $\pi$ Bonds

D. G. Pettifor and I. I. Oleinik
*Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, United Kingdom*

(Received 10 December 1999)

Novel analytic bond-order potentials (BOP's) are derived for the $\sigma$ and $\pi$ bonds of $sp$-valent systems that are correctly bounded from above by unity. We show that these BOP's allow the concept of single, double, triple, and conjugate bonds in carbon systems to be quantified, the average error compared to accurate tight-binding predictions being only 1% for the $\sigma$ bonds and 15% for the $\pi$ bonds. Although molecular dynamics simulations are an order of magnitude slower than with standard Tersoff potentials, these new BOP's provide the first "classical" interatomic potentials that handle both structural differentiation and radical formation naturally within its framework.

PACS numbers: 61.50.Lt, 34.20.Cf, 71.15.Fv

The development of interatomic potentials that can handle the making and breaking of covalent bonds is key to the successful large-scale atomistic simulation of processes such as the growth of films [1] or tribological degradation [2]. Until now, the most widely used potentials in this area have been those of the Tersoff [3]–Brenner [4]-type in which the energy of the individual bonds comprises a repulsive pairwise contribution and an attractive contribution given by the product of the bond order and a pairwise bond integral. The bond order is parametrized in a many-body form to depend on the local atomic environment through the nearest-neighbor bond angles and bond distances. Despite numerous successful applications of Tersoff-Brenner potentials [5], they suffer from two serious drawbacks. First, they do not guarantee correct structural differentiation. For example, they fail to distinguish between different competing structures of the $\Sigma 13\{510\}$ symmetric tilt boundary in silicon and diamond, even though *ab initio* and tight-binding (TB) calculations find a large 50% variation in the energies [6]. Second, they do not treat the $\pi$ bond correctly, the Tersoff-Brenner potential containing only a single bond-order term whose angular dependence reflects that of a $\sigma$ bond [7]. This neglect of a separate $\pi$ bond contribution leads to problems with the overbinding of radicals and a poor treatment of conjugacy [4].

In a recent paper [8] we showed that it was possible to overcome these deficiencies by deriving explicit analytic expressions for the $\sigma$ and $\pi$ bond orders by approximating an exact many-atom expansion for the bond order [9,10] within the two-center, orthogonal TB representation of the electronic structure [11]. Interestingly, the first term in the many-atom expansion for the $\sigma$ bond is similar to that written down intuitively by Tersoff [3]. This term, resulting from a correct description of the second moment or mean square width of the electronic structure $\mu_2$, is unable to differentiate between different three-dimensional structure types [12]. This requires information about the *shape* of the density of states, not just its root mean square *width* $b_1 = \mu_2^{1/2}$. In particular, the fourth moment $\mu_4$ reflects the unimodal versus bimodal character of the eigenspectrum through the shape parameter $(b_2/b_1)^2 = \mu_4/\mu_2^2 - 1$ [13] and when included in the analytic bond-order potential (BOP) provides structural differentiation (see Fig. 2 of Ref. [8]). The sixth moment $\mu_6$ (or, equivalently, the third Lanczos recursion coefficient $b_3$) is required for an exact treatment within the TB approximation of four-level $\sigma$-bonded systems such as the dimer $C_2$ or the tetrahedral methane molecule $CH_4$ [14]. However, since the evaluation of the sixth moment is time consuming, as it requires the counting of all self-returning hopping or bonding paths of length six, we suggested in Ref. [8] to approximate $b_3$ by $b_1$ in order to perform large-scale atomistic simulations.

Unfortunately, this approximation has been found to lead to unphysical instabilities during molecular dynamics simulations [15] which can be traced back to the $\sigma$ bond order becoming larger than unity. This is in direct violation of the original definition of the bond order $\Theta$ as one-half the difference between the number of electrons in the bonding state compared to the antibonding state, so that the bond order must always be bounded by unity, i.e., $\Theta \le 1$. In this Letter we will show that we can derive a bounded analytic expression for the bond order by making use of the constraint that the poles of the intersite Green's function $G_{ij}$ are the same as those of the average on-site Green's function $\frac{1}{2}(G_{ii} + G_{jj})$. This constraint allows us to find an expression for $b_3$ in terms of $b_1$ and $b_2$ that is exact for four-level systems and leads to the bond order being bounded by unity in general.

The bond order $\Theta_{ij}$ may be defined [9] in terms of the imaginary part of the *off-diagonal* Green's function matrix element $G_{ij}(\epsilon)$ through

$$\Theta_{ij} = -\frac{2}{\pi} \operatorname{Im} \int^{\epsilon_F} G_{ij}(\epsilon)\, d\epsilon\,, \qquad (1)$$

where $G_{ij}(\epsilon) = \langle i|(\epsilon - \hat{H})^{-1}|j\rangle$. $\hat{H}$ is the TB Hamiltonian operator, $\epsilon_F$ is the Fermi energy, and $\epsilon$ is assumed to contain a small imaginary part, i.e., $\epsilon \equiv \epsilon + i\eta$. Using BOP theory to four levels in the Lanczos recursion chain allows the off-diagonal Green's function to be written [8]

$$G_{ij}(\epsilon) = \sum_{n=0}^{3} G_{0n}^2 \delta a_n \,, \tag{2}$$

where in the absence of four-membered rings [16] $\delta a_0 = h_\sigma$, $b_1^2 \delta a_1 = -h_\sigma^3$, and

$$b_1^2 b_2^2 \delta a_2 = 2 b_2^2 h_\sigma^3 - b_1^4 h_\sigma + h_\sigma^5 + \Delta\mu_2^i \Delta\mu_2^j \,, \tag{3}$$

with $h_\sigma$ being the $\sigma$ bond integral and $\Delta\mu_2^k = (\mu_2^k - h_\sigma^2)$ for $k = i, j$ [17]. $G_{0n}(\epsilon)$ are the Green's functions defined along the Lanczos chain, namely, $\langle u_0 | (\epsilon - \hat{H})^{-1} | u_n \rangle$, where the starting Lanczos orbital $|u_0\rangle = (1/\sqrt{2})(|i\rangle + \sqrt{-1}|j\rangle)$. It follows that

$$\begin{aligned} G_{00}(\epsilon) &= \frac{1}{2}[G_{ii}(\epsilon) + G_{jj}(\epsilon)] \\ &= \epsilon(\epsilon^2 - b_2^2 - b_3^2)/D(\epsilon) \,, \end{aligned} \tag{4}$$

where the denominator results from taking the usual continued fraction for the *diagonal* element [18] to four levels and is given by $D(\epsilon) = \epsilon^4 - (b_1^2 + b_2^2 + b_3^2)\epsilon^2 + b_1^2 b_3^2$. The other Lanczos Green's functions $G_{0n}(\epsilon)$ are defined recursively and may be written in the form $P_n(\epsilon)/D(\epsilon)$, where $P_n(\epsilon) = b_1^2(\epsilon^2 - b_3^2)$, $b_1 b_2 \epsilon$, and $b_1 b_2 b_3$ for $n = 1$, 2, and 3, respectively.

We now impose the constraint [8] that the poles of the four-term expansion, Eq. (2), for the off-diagonal Green's function $G_{ij}$ are the same as those of the four-level continued fraction, Eq. (4), for the diagonal Green's function $G_{00} = \frac{1}{2}(G_{ii} + G_{jj})$. This constraint is, of course, exactly satisfied, in general, if all the nonvanishing terms in the continued fraction, Eq. (4), and series, Eq. (2), had been retained. It implies that the numerator of $G_{ij}$ must be factorizable in terms of the denominator $D(\epsilon)$, so that

$$G_{ij}(\epsilon) = \frac{(A\epsilon^2 + C)D(\epsilon)}{[D(\epsilon)]^2} = \frac{A\epsilon^2 + C}{D(\epsilon)} \,. \tag{5}$$

Equating powers of $\epsilon^6$ and $\epsilon^4$ in the numerator of Eq. (2) with that in the first equation above, we find that $A = \delta a_0$ and $C = (b_1^2 - b_2^2 - b_3^2)\delta a_0 + b_1^2 \delta a_1$. Substituting Eq. (5) into Eq. (1), we recover the result of Eq. (79) of Ref. [8] for the bond order of a half-filled eigenspectrum, namely,

$$\Theta_{ij,\sigma}^{(4Z)} = \left\{ \frac{1 + [\hat{b}_2^2 - (\hat{b}_1^2 - 1)]/(\hat{b}_1 + \hat{b}_3)\hat{b}_3}{\sqrt{1 + \hat{b}_2^2/(\hat{b}_1 + \hat{b}_3)^2}} \right\} \frac{1}{\hat{b}_1} \,, \tag{6}$$

where $\hat{b}_n = b_n/h_\sigma$ for $n = 1, 2, 3$. The label 4$Z$ refers to the approximation of four levels with zero odd moments.

This analytic expression for the bond order is well behaved if the exact values of $\hat{b}_1$, $\hat{b}_2$, and $\hat{b}_3$ are evaluated [14]. However, as we have already mentioned, it can exceed the upper bound of unity if we approximate $\hat{b}_3$ by $\hat{b}_1$ in order to provide a usable interatomic potential for molecular dynamics (MD) simulations. Fortunately, we now show that this serious flaw can be remedied by using the constraint of identical poles to determine $b_3$ in terms of $b_1$ and $b_2$. Equating terms with power $\epsilon^2$ in the numerator of Eq. (2) with those in Eq. (5) we find the new constraint equation

$$b_1^2 b_2^2 \delta a_2 = b_1^2 (b_3^2 - b_1^2)\delta a_0 + (b_3^2 - b_1^2 - b_2^2) b_1^2 \delta a_1 \,. \tag{7}$$

It, thus, follows immediately from Eqs. (3) and (7) that

$$\hat{b}_3^2 = [(\hat{b}_2^2 - \hat{b}_1^2 + 1) + \Delta\hat{\mu}_2^i \Delta\hat{\mu}_2^j]/(\hat{b}_1^2 - 1) \,. \tag{8}$$

This expression for $\hat{b}_3$ is exact for the symmetric, four-level dimer and methane systems.

Substituting Eq. (8) into (6) and using the expressions in Ref. [8] for $\hat{b}_1$ and $\hat{b}_2$ in terms of the self-returning hopping paths of length two and four which are illustrated in Fig. 1, we find [19]

$$\Theta_{ij,\sigma}^{\mathrm{BOP}} = \frac{1}{\sqrt{1 + \dfrac{2\Phi_{2\sigma} + \hat{\delta}^2}{[1 + \sqrt{(\Phi_{4\sigma} - 2\Phi_{2\sigma}^2 + \Phi_{2\sigma}^i \Phi_{2\sigma}^j)/\Phi_{2\sigma}}]^2}}} \,, \tag{9}$$

where $\Phi_{n\sigma} = \frac{1}{2}(\Phi_{n\sigma}^i + \Phi_{n\sigma}^j)$. $\Phi_{2\sigma}^i$, the two-hop contribution that starts and ends on atom $i$, can be written

$$\Phi_{2\sigma}^i = \sum_{k \neq i,j} [g_\sigma^\mu(\theta_{jik})]^2 \hat{h}_\sigma^2(R_{ik}) \,, \tag{10}$$

where the Greek symbols $\mu$, $\nu$, and $\kappa$ refer to the nature of the atomic species at sites $i$, $j$, and $k$ respectively ($\mu$, $\nu$, $\kappa$ = H for hydrogen, C for carbon). $\hat{h}_\sigma(R_{ik})$ is the normalized bond integral $h_\sigma^{\mu\kappa}(R_{ik})/h_\sigma^{\mu\nu}(R_{ij})$. The angular functions $g_\sigma^\mu(\theta)$ are given by $g_\sigma^{\mathrm{H}}(\theta) = 1$ and $g_\sigma^{\mathrm{C}}(\theta) = [p_\sigma/(1 + p_\sigma)](p_\sigma^{-1} + \cos\theta)$, where $p_\sigma = pp\sigma/|ss\sigma|$. $\Phi_{4\sigma}^i$, the four-hop contribution that starts and ends on atom $i$, can be written

$$\begin{aligned} \Phi_{4\sigma}^i = {} & \sum_{k \neq i,j} [g_\sigma^\mu(\theta_{jik})]^2 \hat{h}_\sigma^4(R_{ik}) + \sum_{\substack{k,k' \neq i,j \\ k \neq k'}} g_\sigma^\mu(\theta_{jik}) g_\sigma^\mu(\theta_{kik'}) g_\sigma^\mu(\theta_{k'ij}) \hat{h}_\sigma^2(R_{ik}) \hat{h}_\sigma^2(R_{ik'}) \\ & + \sum_{\substack{k,k' \neq i,j \\ k \neq k'}} [g_\sigma^\mu(\theta_{jik}) g_\sigma^\kappa(\theta_{ikk'})]^2 \hat{h}_\sigma^2(R_{ik}) \hat{h}_\sigma^2(R_{kk'}) \,. \end{aligned} \tag{11}$$

$\hat{\delta}$ accounts for the non-negligible $sp$ atomic energy level separation on the C sites and is defined by $\hat{\delta}^2 = \frac{1}{2}[(\delta_i^\mu)^2 + (\delta_i^\nu)^2][4p_\sigma/(1 + p_\sigma)^2]/[h_\sigma^{\mu\nu}(R_{ij})]^2$ with $\delta^{\mathrm{H}} = 0$ and $\delta^{\mathrm{C}} = (\epsilon_p^{\mathrm{C}} - \epsilon_s^{\mathrm{C}}) = 6.7$ eV [20]. It is clear that Eq. (9) reduces to the correct results of $1/\sqrt{1 + \hat{\delta}^2}$ for the isolated dimer and $(1 + \sqrt{3})/2\sqrt{2}$ for methane with $\epsilon_p^{\mathrm{C}} = \epsilon_s^{\mathrm{C}} = \epsilon_s^{\mathrm{H}}$ for the case $p_\sigma = 1$ [8].

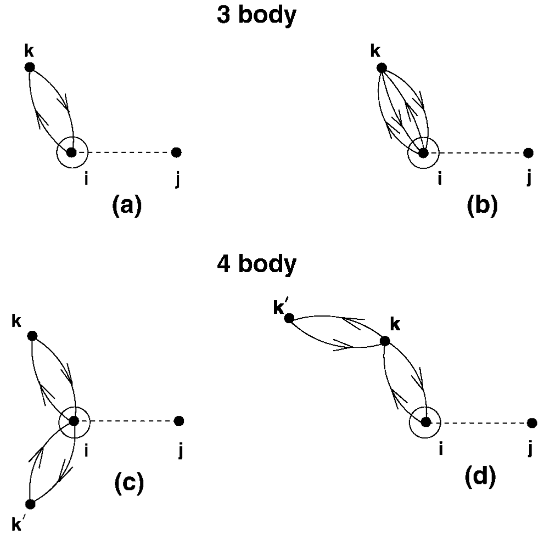

FIG. 1. Self-returning hopping paths of length 2 [(a)] and length 4 [(b), (c), (d)] that contribute to the potential functions $\Phi^{i}_{2\sigma}$ and $\Phi^{i}_{4\sigma}$, respectively. The atoms included in these paths are determined by the range of the TB bond integrals which usually cut off smoothly beyond the nearest neighbor distance.

Equation (9) is the key result of this Letter. We see that this analytic expression for the $\sigma$ bond order is automatically bounded by unity as the numerator of the quotient is non-negative and the denominator is a square. This removes the deficiency of the previous approximation derived by taking $b_3 = b_1$. We have labeled expression (9) by the acronym BOP as it is a true analytic interatomic potential that is explicitly dependent on local bond angles and bond distances.

The concept of a constraint equation may also be applied to our earlier derivation of the $\pi$ bond order [8]. In this case the matrix form of the Lanczos algorithm [22,23] must be used in order that the $p_x$ and $p_y$ orbitals are treated on an equal footing at all levels of approximation. This results in $2 \times 2$ matrices $B_n$ for the Lanczos recursion coefficients rather than the scalar coefficients $b_n$ that enter the continued fraction in Eq. (2). Taking the matrix continued fraction to two levels results in a quartic equation with two uncoupled sets of poles $\pm b_{1+}$ and $\pm b_{1-}$. Having information only about $\hat{b}_1$, constraining the poles of $G_{ij}$ to equal these of $\frac{1}{2}(G_{ii} + G_{jj})$ provides a constrained value for $\hat{b}_2 = \sqrt{\hat{b}_1^2 - 1}$ within the three-level approximation. This results in a bond-order $1/\sqrt{\hat{b}_1^2 + \hat{b}_2^2} = 1/\sqrt{1 + 2(\hat{b}_1^2 - 1)}$.

The analytic expression for the $\pi$ bond order then takes the form

$$\Theta^{\mathrm{BOP}}_{ij,\pi} = \frac{1}{\sqrt{1 + \Phi_{2\pi} + \Phi_{4\pi}^{1/2}}} + \frac{1}{\sqrt{1 + \Phi_{2\pi} - \Phi_{4\pi}^{1/2}}}, \tag{12}$$

where the two-hop contribution,

$$\Phi_{2\pi} = \frac{1}{2}\sum_{k \neq i,j}\{\sin^2\theta_{jik}[p_\sigma/(1 + p_\sigma)][\hat{h}^{\mathrm{C}\kappa}_{\sigma}(R_{ik})]^2 + (1 + \cos^2\theta_{jik})[\hat{h}^{\mathrm{CC}}_{\pi}(R_{ik})]^2\delta_{\kappa\mathrm{C}} + (i \leftrightarrow j)\},$$

and the four-hop contribution,

$$\Phi_{4\pi} = \frac{1}{4}\sum_{k,k' \neq i,j}\{\sin^2\theta_{jik}\sin^2\theta_{jik'}\hat{\beta}^2_{ik}\hat{\beta}^2_{ik'} + \sin^2\theta_{jik}\sin^2\theta_{ijk'}\hat{\beta}^2_{ik}\hat{\beta}^2_{ik'} + (i \leftrightarrow j)\}\cos 2(\phi_k - \phi_{k'}),$$

with

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

The capped bond integrals have been normalized by the $\pi$ bond integral $h^{\mathrm{CC}}_{\pi}(R_{ij})$ and $(i \leftrightarrow j)$ implies an additional contribution obtained by interchanging $i$ and $j$ in the preceding terms.

Table I illustrates the accuracy of our analytic expressions for the $\sigma$ and $\pi$ bond orders by comparing their predicted values with those of the exact TB results [21] for the C-C bond in elemental carbon systems and the hydrocarbons. Let us consider the $\sigma$ bond order first. The Tersoff potential [3] is equivalent to retaining only the second moment two-hop contribution in Fig. 1 so that from Eq. (9) the bond order varies as $(1 + \hat{\delta}^2 + 2\Phi_{2\sigma})^{-1/2}$. The predicted angular function, $g_\sigma(\theta)$, that appears in $\Phi_{2\sigma}$ in Eq. (10) mirrors very closely the empirical angular function fitted in the Tersoff potential for C and Si [7,14]. However, we see that the predicted values of our Tersoff-type bond order, which are given in parentheses in Table I, provide an inaccurate measure of the $\sigma$ bond order within these carbon systems. The value of 0.708 for diamond, for example, compared to the TB value of 0.912 would lead to an error in the $\sigma$ bond energy, $2h_\sigma\Theta_\sigma$, of 4.1 eV. These large errors are not unexpected because it is well known [13] that the small differences in binding energy between different non-close-packed structure types are driven by the fourth moment paths of length 4 in Fig. 1 that determine the unimodal versus bimodal *shape* of the electronic eigenspectrum rather than the paths of length 2 that determine the second moment or mean square *width* of the spectrum. These four-hop contributions appear in the denominator of the quotient in Eq. (9) and lead to BOP values that are in excellent agreement with TB, the average error over all the systems considered in Table I being 1.2%. The corresponding error for the $\sigma$ bond energy in diamond is now only 0.06 eV/bond.

The analytic expression (12) for the $\pi$ bond order, on the other hand, predicts correctly not only the doubly saturated $\pi$ bond in $C_2$ and $C_2H_2$ but also the singly saturated $\pi$ bond in $C_2H_4$. Moreover, it predicts values for the conjugate bond orders in graphite and benzene that are within 16% of the exact TB values of 0.528 and 0.667, respectively. It does less well for the unsaturated $\pi$ bond

TABLE I. C-C bond integrals [14] and bond orders.

| System | Local Coord. | $h_\sigma^{CC}$ (eV)<br>$h_\pi^{CC}$ (eV) | $\Theta_\sigma$ BOP TB (Tersoff) | $\Theta_{\pi_-}$ BOP TB | $\Theta_{\pi_+}$ BOP TB | $\Theta_{\rm total}$ BOP TB |
|---|---|---|---|---|---|---|
| $C_2$ | 1 | 17.84 | 0.936 | 1.000 | 1.000 | 2.936 |
| | | 2.76 | 0.936 | 1.000 | 1.000 | 2.936 |
| | | | (0.936) | | | |
| $C_2H_2$ | 2 | 19.24 | 0.974 | 1.000 | 1.000 | 2.974 |
| | | 2.98 | 0.986 | 1.000 | 1.000 | 2.986 |
| | | | (0.946) | | | |
| $C_2H_4$ | 3 | 14.89 | 0.955 | 1.000 | 0.194 | 2.149 |
| | | 2.30 | 0.971 | 1.000 | 0.137 | 2.108 |
| | | | (0.888) | | | |
| $C_6H_6$ | 3 | 13.50 | 0.953 | 0.577 | 0.141 | 1.671 |
| | | 2.09 | 0.963 | 0.667 | 0.107 | 1.737 |
| | | | (0.850) | | | |
| $C_{gr}$ | 3 | 12.71 | 0.951 | 0.477 | 0.121 | 1.520 |
| | | 1.97 | 0.957 | 0.528 | 0.094 | 1.579 |
| | | | (0.827) | | | |
| $C_2H_5$ | 3.5 | 10.87 | 0.929 | 0.214 | 0.145 | 1.288 |
| | | 1.68 | 0.949 | 0.217 | 0.102 | 1.268 |
| | | | (0.784) | | | |
| $C_2H_6$ | 4 | 10.53 | 0.917 | 0.149 | 0.149 | 1.214 |
| | | 1.63 | 0.936 | 0.105 | 0.105 | 1.146 |
| | | | (0.748) | | | |
| $C_6H_{12}$ | 4 | 10.02 | 0.913 | 0.141 | 0.134 | 1.188 |
| | | 1.55 | 0.926 | 0.101 | 0.101 | 1.128 |
| | | | (0.725) | | | |
| $C_\diamond$ | 4 | 10.02 | 0.915 | 0.126 | 0.126 | 1.167 |
| | | 1.55 | 0.912 | 0.103 | 0.103 | 1.118 |
| | | | (0.708) | | | |

contributions where the error in diamond, for example, is 23%. Fortunately, however, because the $\pi$ bond integral is much smaller than the $\sigma$ bond integral ($h_\pi/h_\sigma = 0.155$ [20]) this would lead to an error in the diamond $\pi$ bond energy, $2h_\pi(\Theta_{\pi_-} + \Theta_{\pi_+})$, of only 0.14 eV/bond. The average error in the total $\pi$ bond order over all the systems in Table I is 15% which corresponds to an average error of 0.6 eV/bond. These errors would be significantly reduced by refitting the BOPs directly to experiment and the *ab initio* data base.

In conclusion, therefore, the analytic BOP expressions for the $\sigma$ and $\pi$ bond orders quantify the ubiquitous concept of single, double, triple, and conjugate bonds. Moreover, it is clear from the last column in Table I that they provide the first "classical" interatomic potential that handles correctly the formation of radicals, $C_2H_5$ remaining essentially a singly bonded system on the abstraction of a H atom from $C_2H_6$. Current MD simulations using analytic BOP forces are an order of magnitude slower than with Tersoff potentials [15,24]. However, this is a small price to pay for having an interatomic potential that is sufficiently sophisticated to handle both structural differentiation and radical formation within its framework.

We thank Detlef Conrad for first bringing to our attention the instabilities associated with our earlier approximation of $b_3 = b_1$. D. G. P. thanks Vasek Vitek and the Department of Materials Science and Engineering at the University of Pennsylvania for their hospitality during the summer of 1999 when this work was initiated with financial support from DOE (BES) and Oak Ridge National Laboratories. I. I. O. thanks DARPA for the financial support under Contract No. N00014-97-1-G015.

[1] See the recent review, G. H. Gilmer, H. C. Huang, and C. Roland, Comput. Mater. Sci. **12**, 354 (1998).

[2] See, e.g., J. A. Harrison and S. S. Perry, MRS Bull. **23**, 27 (1998).

[3] J. Tersoff, Phys. Rev. Lett. **56**, 632 (1986).

[4] D. W. Brenner, Phys. Rev. B **42**, 9458 (1990).

[5] See, e.g., A. Omeltchenko, J. Yu, R. K. Kalia, and P. Vashishta, Phys. Rev. Lett. **78**, 2148 (1998).

[6] J. R. Morris *et al.,* Phys. Rev. B **58**, 11 241 (1998).

[7] P. A. Alinaghian, P. Gumbsch, A. J. Skinner, and D. G. Pettifor, J. Phys. Condens. Matter **5**, 5795 (1993).

[8] D. G. Pettifor and I. I. Oleinik, Phys. Rev. B **59**, 8487 (1999).

[9] D. G. Pettifor, Phys. Rev. Lett. **63**, 2480 (1989).

[10] M. Aoki and D. G. Pettifor, in *Physics of Transition Metals,* edited by P. M. Oppeneer *et al.* (World Scientific, Singapore, 1993), p. 299.

[11] Analytic environment-dependent $\sigma$ and $\pi$ bond integrals may be derived within the two-center orthogonal TB representation by inverting the nonorthogonal matrix using BOP theory [D. Nguyen-Mahn, D. G. Pettifor, and V. Vitek (to be published)].

[12] S. R. Nishitani *et al.,* Philos. Mag. Lett. **69**, 177 (1994).

[13] D. G. Pettifor, *Bonding and Structure of Molecules and Solids* (Clarendon Press, Oxford, 1995).

[14] I. I. Oleinik and D. G. Pettifor, Phys. Rev. B **59**, 8500 (1999).

[15] D. Conrad (private communication).

[16] Four-membered ring terms can be included within the present BOP formalism, their analytic behavior having been given explicitly by D. G. Pettifor and M. Aoki, in *Structural and Phase Stability of Alloys,* edited by J. L. Moran-Lopez *et al.* (Plenum, New York, 1992), p. 119.

[17] The six-member ring term will vary as $[g_\sigma(\theta)]^6$ which is of the order $4^{-6}$ and has been neglected in Eq. (3).

[18] R. Haydock, Solid State Phys. **35**, 216 (1980).

[19] Second order contributions $\Phi_{2\sigma}^i \Phi_{2\sigma}^j$ in both numerator and denominator of the quotient in Eq. (9) have been neglected as well as cross terms between $\hat{\delta}$ and $\hat{h}_\sigma$.

[20] C. H. Xu *et al.,* J. Phys. Condens. Matter **4**, 6047 (1992).

[21] "Exact TB values" implies that the reduced TB model of Refs. [8] and [14] has been solved exactly.

[22] R. Jones and M. W. Lewis, Philos. Mag. B **49**, 95 (1984).

[23] J. Inoue and Y. Ohta, J. Phys. C **20**, 1947 (1987).

[24] But analytic BOP is still 2 orders of magnitude faster than using order $N$ TB methods.