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

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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.

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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 function $\mu_s/\mu_s^2 - 1$ [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., $\Theta \leq 1$. 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

$$ \Theta_{ij} = -\frac{2}{\pi} \text{Im} \int_{-\epsilon_{F}}^{\epsilon_{F}} G_{ij}(\epsilon) d\epsilon , \quad (1) $$

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]
where the denominator results from taking the usual continued fraction for the diagonal element [18] to four levels and is given by $D(e) = e^4 - (b_1^2 + b_2^2 + b_3^2)e^2 + b_1^2b_2^2$. The other Lanczos Green’s functions $G_{0n}(e)$ are defined recursively and may be written in the form $P_n(e)/D(e)$, where $P_n(e) = b_1^2(e^2 - b_2^2)$, $b_1b_2e$, and $b_1b_2b_3$ for $n = 1, 2, 3$, 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 $G_{0i} = 1/2(G_{ii} + G_{ji})$. This constraint is, of course, 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 $D(e)$, so that

$$G_{ij}(e) = \frac{(Ae^2 + C)D(e)}{[D(e)]^2} = \frac{Ae^2 + C}{D(e)}.$$ (5)

Equating powers of $e^6$ and $e^4$ 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 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 $e^2$ in the numerator of Eq. (2) with those in Eq. (5) we find the new constraint equation

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

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

$$b_3^2 = [(b_1^2 - b_1^2 + 1) + \Delta \mu_2^2 \Delta \mu_2^2]/(b_1^2 - 1).$$ (8)

This expression for $b_3$ is exact for the symmetric, four-level dimer and methane systems.

Substituting Eq. (8) into (6) and using the expressions in Ref. [8] for $b_1$ and $b_2$ in terms of the self-returning hopping paths of length two and four which are illustrated in Fig. 1, we find [19]

$$\Theta_{ij,\sigma}^{(4Z)} = \frac{1}{\left[1 + \sqrt{(\Phi_{2\sigma} - 2\Phi_{2\sigma} + \Phi_{2\sigma}^4)/\Phi_{2\sigma}^2}\right]},$$ (9)

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

$$\Phi_{2\sigma}^i = \sum_{k \neq i,j} [g_{2\sigma}^{\mu\nu}(\theta_{ijk})]^2 h_{2\sigma}(R_{ik}) + \sum_{k \neq i,j} g_{2\sigma}^{\mu\nu}(\theta_{ikj})g_{2\sigma}^{\mu\nu}(\theta_{jik})h_{2\sigma}(R_{ki})h_{2\sigma}(R_{ik}).$$ (10)

$\delta$ accounts for the non-negligible $sp$ atomic energy level separation on the C sites and is defined by $\delta^2 = 4\delta^2/[4\delta^2 + \delta^2]/[b_{2\sigma}^0(R_{ij})]^2$ with $\delta^2 = 0$ and $\delta^2 = (\epsilon_f^C - \epsilon_f^C) = 6.7 eV$ [20]. It is clear that Eq. (9) reduces to the correct results of $1/\sqrt{1 + \delta^2}$ for the isolated dimer and $(1 + \sqrt{3})/2\sqrt{2}$ for methane with $\epsilon_f^p = \epsilon_f^C = \epsilon_f^H$ for the case $p_\sigma = 1$ [8].
In this case the matrix form of the Lanczos algorithm provides a constrained value for the bond order. This results in the matrix continued fraction to two levels results in a quartic equation with two uncoupled sets of poles. Having information only about $b_3 = b_1$, 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 bond order [8]. In this case the matrix form of the Lanczos algorithm [22,23] must be used in order that the $p_1$ and $p_2$ orbitals are treated on an equal footing at all levels of approximation. This results in a $2 \times 2$ 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 $b_1$, constraining the poles of $G_{ij}$ to equal these of $\frac{1}{2}(G_{ii} + G_{jj})$ provides a constrained value for $\tilde{b}_2 = \sqrt{\tilde{b}_1^2 - 1}$ within the three-level approximation. This results in a bond-order

$$1/\sqrt{\tilde{b}_1^2 + \tilde{b}_2^2} = 1/\sqrt{1 + 2(\tilde{b}_1^2 - 1)}.$$  

The analytic expression for the bond order then takes the form

$$\Theta_{ij,\pi} = \frac{1}{\sqrt{1 + \Phi_{2\pi} + \Phi_{4\pi}^{1/2}}} + \frac{1}{\sqrt{1 + \Phi_{2\pi} - \Phi_{4\pi}^{1/2}},}$$  

where the two-hop contribution,

$$\Phi_{2\pi} = \frac{1}{2} \sum_{k,i,j} (\sin^2 \theta_{jik}[p_{\sigma}(1 + p_{\sigma})][\tilde{h}_{i\sigma}^{CC}(R_{ik})]^2$$

$$+ (1 + \cos^2 \theta_{jik})[\tilde{h}_{i\pi}^{CC}(R_{ik})]^2 \delta_{\pi C}$$

$$+ (i \leftrightarrow j)],$$  

and the four-hop contribution,

$$\Phi_{4\pi} = \frac{1}{4} \sum_{k,k',i,j} (\sin^2 \theta_{jik} \sin^2 \theta_{jik} \tilde{b}_{ik}^2 \tilde{b}_{ik'}^2$$

$$+ \sin^2 \theta_{jik} \sin^2 \theta_{jik} \tilde{b}_{ik}^2 \tilde{b}_{ik'}^2$$

$$+ (i \leftrightarrow j) \cos(\phi_k - \phi_{k'})],$$  

with

$$\tilde{b}_{ik}^2 = [p_{\sigma}(1 + p_{\sigma})][\tilde{h}_{i\sigma}^{CC}(R_{ik})]^2 - [\tilde{h}_{i\pi}^{CC}(R_{ik})]^2 \delta_{\pi C} - \tilde{\gamma}_{ik}^2.$$  

The capped bond integrals have been normalized by the bond integral $h_{ij}^{CC}(R_{ij})$ and $\tilde{g}_{ij}$ 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 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 bond energy, $2h_{ij}\Theta_{ij}$, 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 eigen-spectrum 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 bond energy in diamond is now only 0.06 eV/bond.

The analytic expression (12) for the bond order, on the other hand, predicts correctly not only the doubly saturated bond in C$_2$ and C$_2$H$_2$ but also the singly saturated bond in C$_2$H$_4$. 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 bond...
is clear from the last column in Table I that they remain essentially a singly bonded system on the abstraction of a H atom from C$_2$H$_6$. 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 $b_1 = b_1$. 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.

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**Table I.** C-C bond integrals [14] and bond orders.

<table>
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<tr>
<th>System</th>
<th>Local Coord.</th>
<th>$\Theta^\text{CC}$ (eV)</th>
<th>$\Theta^\text{CC}$ (eV)</th>
<th>$\Theta_{\sigma}$ BOP</th>
<th>$\theta_{\pi}$ BOP</th>
<th>$\Theta_{\pi}$ BOP</th>
<th>$\Theta_{\sigma\pi}$ BOP</th>
<th>$\theta_{\text{total}}$ BOP</th>
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<tr>
<td>C$_2$</td>
<td>1</td>
<td>17.84</td>
<td>9.36</td>
<td>1.00</td>
<td>1.00</td>
<td>2.936</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.76</td>
<td>9.36</td>
<td>1.00</td>
<td>1.00</td>
<td>2.936</td>
<td></td>
<td></td>
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<tr>
<td>C$_2$H$_2$</td>
<td>2</td>
<td>19.24</td>
<td>9.74</td>
<td>1.00</td>
<td>1.00</td>
<td>2.974</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.98</td>
<td>9.86</td>
<td>1.00</td>
<td>1.00</td>
<td>2.986</td>
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<tr>
<td>C$_2$H$_4$</td>
<td>3</td>
<td>14.89</td>
<td>9.55</td>
<td>1.00</td>
<td>0.194</td>
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<tr>
<td></td>
<td></td>
<td>2.30</td>
<td>9.71</td>
<td>1.00</td>
<td>0.137</td>
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<td>13.50</td>
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<td></td>
<td></td>
<td>2.09</td>
<td>0.963</td>
<td>0.667</td>
<td>0.107</td>
<td>1.737</td>
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<tr>
<td>C$_{gr}$</td>
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<td>0.477</td>
<td>0.121</td>
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<td></td>
<td></td>
<td>1.97</td>
<td>0.957</td>
<td>0.528</td>
<td>0.094</td>
<td>1.579</td>
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<td>C$_2$H$_5$</td>
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<td>0.214</td>
<td>0.145</td>
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<td>1.68</td>
<td>0.949</td>
<td>0.217</td>
<td>0.102</td>
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<td>C$_2$H$_6$</td>
<td>4</td>
<td>10.53</td>
<td>0.917</td>
<td>0.149</td>
<td>0.149</td>
<td>1.214</td>
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<td></td>
<td></td>
<td>1.63</td>
<td>0.936</td>
<td>0.105</td>
<td>0.105</td>
<td>1.146</td>
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<tr>
<td>C$<em>8$H$</em>{12}$</td>
<td>4</td>
<td>10.02</td>
<td>0.913</td>
<td>0.141</td>
<td>0.134</td>
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<td></td>
<td></td>
<td>1.55</td>
<td>0.926</td>
<td>0.101</td>
<td>0.101</td>
<td>1.128</td>
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<tr>
<td>C$_\circ$</td>
<td>4</td>
<td>10.02</td>
<td>0.915</td>
<td>0.126</td>
<td>0.126</td>
<td>1.167</td>
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<tr>
<td></td>
<td></td>
<td>1.55</td>
<td>0.912</td>
<td>0.103</td>
<td>0.103</td>
<td>1.118</td>
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</tbody>
</table>

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[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. Pettitorn, and V. Vitek (to be published)].


[16] Four-membered ring terms can be included within the present BOP formalism, their analytic behavior having been given explicitly by D.G. Pettitorn 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 $[g_s(\theta)]^6$ which is of the order $4^{-6}$ and has been neglected in Eq. (3).


[19] Second order contributions $\Phi^\sigma_{\nu\sigma}$ and $\Phi^\sigma_{\pi\sigma}$ in both numerator and denominator of the quotient in Eq. (9) have been neglected as well as cross terms between $\delta$ and $h_{\sigma}$.


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


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