

## Bond-order potentials: bridging the electronic to atomistic modelling hierarchies

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Accepted 1 June 2001

### Abstract

Novel analytic bond-order potentials (BOPs) may be derived for atomistic simulations by coarse-graining the electronic structure within the orthogonal two-centre tight-binding (TB) representation. We show that these BOPs allow the concept of single, double, triple and conjugate bonds in carbon systems to be quantified, so that they provide the first ‘classical’ interatomic potentials that handle both structural differentiation and radical formation naturally within their remit. Finally, we indicate that this recently developed BOP formalism allows explicit, analytic expressions for the environmental dependence of the TB bond integrals to be derived, thereby providing a systematic methodology for bridging from the electronic to atomistic modelling hierarchies. © 2002 Elsevier Science B.V. All rights reserved.

The modelling and simulation of materials is a challenging task as it often involves linking the world of the electron theorist to the world of the continuum engineer, thereby spanning at least twelve orders of magnitude in either length or time. This linking is achieved by successively coarse-graining the problem [1]. Firstly, the electronic degrees of freedom may be removed by imagining the atoms to be held together by some sort of glue or interatomic potential, thereby allowing large scale atomistic simulations to be performed on fracture at crack tips, for example

[2]. Secondly, the atoms themselves may be coarse-grained by grouping them together into cells which interact via deterministic or stochastic rules, thereby allowing, for example, the simulation of microstructure evolution during the growth of single crystal turbine blades [3]. Finally, the continuum world may be reached by averaging over the microstructure and describing the material through a set of constitutive relationships [4].

In this paper we outline the derivation of novel analytic bond-order potentials (BOPs) that are obtained directly by bridging the electronic to atomistic modelling hierarchies within a tight-binding (TB) framework. Coulson [5] had shown in 1939 that the *global* description of energy bands with an associated band energy could be broken down into a *local* description of covalent bonds with associated individual bond energies. In

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particular, for the case of a single orbital per site, the bond energy could be written

$$U^{\text{bond}} = \frac{1}{2} \sum_{i \neq j} \sum_j [2\beta(R_{ij})\Theta_{ij}], \quad (1)$$

where  $\beta(R_{ij})$  is the bond integral between a given pair of atoms  $i$  and  $j$ , a distance  $R_{ij}$  apart.  $\Theta_{ij}$  is the bond order, which is one-half the difference between the number of electrons in the bonding state,  $|+\rangle = (|i\rangle + |j\rangle)/\sqrt{2}$ , compared to the antibonding state,  $|-\rangle = (|i\rangle - |j\rangle)/\sqrt{2}$ , namely [6]

$$\Theta_{ij} = \frac{1}{2} (N_{ij}^+ - N_{ij}^-). \quad (2)$$

This can be expressed in terms of the intersite Green's function matrix element  $G_{ij}(\varepsilon)$  as

$$\Theta_{ij} = -\frac{2}{\pi} \text{Im} \int^{\varepsilon_F} G_{ij}(\varepsilon) d\varepsilon, \quad (3)$$

where  $G_{ij}(\varepsilon) = \langle i | (\varepsilon - \hat{H})^{-1} | j \rangle$ .  $\hat{H}$  is the TB Hamiltonian operator,  $\varepsilon_F$  is the Fermi energy, and  $\varepsilon$  is assumed to contain a small imaginary part i.e.  $\varepsilon \equiv \varepsilon + i\eta$ . Thus, the chemists' bond order  $\Theta_{ij}$  of Eq. (2) is none other than twice the physicists' off-diagonal density matrix element  $\rho_{ij}$  which is implicit in Eq. (3).

The derivation of analytic expressions for the  $\sigma$  and  $\pi$  bond orders of sp-valent systems requires an understanding of two basic concepts, namely that of moments and path-counting [7] and that of the Lanczos recursion chain [8]. The TB eigenspectrum at the electronic level is coarse-grained through its moments, namely

$$\mu_p = \frac{1}{\mathcal{N}} \sum_n \varepsilon_n^p, \quad (4)$$

where  $\mathcal{N}$  is the total number of states. A link to interatomic potentials at the atomistic level is provided by the fact that the  $p$ th moment is related to the sum over all self-returning bonding or hopping paths of length  $p$ , as can be proved as follows. Eq. (4) can be re-written as

$$\mu_p = \frac{1}{\mathcal{N}} \sum_n (H^p)_{nn} = \frac{1}{\mathcal{N}} \text{Tr} H^p, \quad (5)$$

since the eigenfunctions  $|n\rangle$  diagonalize the Hamiltonian. Then, since the trace is invariant with respect to the choice of basis functions that are related

by a unitary transformation, we can work instead with the basis of TB atomic orbitals  $|i\rangle$ , so that

$$\begin{aligned} \mu_p &= \frac{1}{\mathcal{N}} \sum_{i_1} (H^p)_{i_1 i_1} \\ &= \frac{1}{\mathcal{N}} \sum_{i_1, i_2, \dots, i_p} H_{i_1 i_2} H_{i_2 i_3} \cdots H_{i_p i_1}. \end{aligned} \quad (6)$$

That is, the  $p$ th moment of an eigenspectrum is given by the sum over all self-returning bonding paths of length  $p$ . Hence, the second moment or mean square width of the spectrum is obtained from self-returning paths of length two, whereas the fourth moment which measures the unimodal versus bimodal behaviour is obtained from self-returning paths of length four [6].

Unfortunately, expansions of functions in terms of their moments are usually very poorly behaved, so that the second basic concept we need is that of the Lanczos recursion chain [8]. As is well documented [9], the *diagonal* element of a Green's function  $G_{00}(\varepsilon) = \langle u_0 | (\varepsilon - \hat{H})^{-1} | u_0 \rangle$ , where  $|u_0\rangle = |i_0\rangle$  say, may be expressed as a continued fraction by using the Lanczos recursion algorithm

$$b_{n+1}|u_{n+1}\rangle = \hat{H}|u_n\rangle - a_n|u_n\rangle - b_n|u_{n-1}\rangle. \quad (7)$$

This transforms the *sparse* TB Hamiltonian with respect to the atomic orbitals  $|i\rangle$  into *tridiagonal* form with respect to the Lanczos basis  $|u_n\rangle$  with corresponding matrix elements  $a_n = \langle u_n | \hat{H} | u_n \rangle$  and  $b_n = \langle u_{n-1} | \hat{H} | u_n \rangle$ . Thus, the original three-dimensional TB problem has been recast as a semi-infinite linear chain with on-site energies  $a_n$  and nearest-neighbour intersite hopping integrals  $b_n$ . The Green's functions with respect to this Lanczos chain can be written down recursively as

$$(\varepsilon - a_n)G_{nm}(\varepsilon) - b_n G_{(n-1)m}(\varepsilon) - b_{n+1} G_{(n+1)m}(\varepsilon) = \delta_{nm}, \quad (8)$$

where

$$G_{00}(\varepsilon) = \frac{1}{\varepsilon - a_0 - \frac{b_1^2}{\varepsilon - a_1 - \frac{b_2^2}{\varepsilon - a_2 - \frac{b_3^2}{\dots}}}}. \quad (9)$$

For a symmetric eigenspectrum, all the on-site energies  $a_n$  vanish and the first two recursion coefficients  $b_n$  take the simple form  $b_1^2 = \mu_2$  and  $b_2^2 =$

$(\mu_4 - \mu_2^2)/\mu_2$ . We see at once, therefore, that the eigenspectrum will be purely bimodal if  $\mu_4 = \mu_2^2$  since then  $b_2 = 0$  in the above continued fraction.

Although the recursion method provides a well-behaved prescription for evaluating the *diagonal* elements of a Green's function matrix, we require the *off-diagonal* elements through Eq. (3). Our bond-order potential theory [10–15] relies on a novel theorem [12] that expresses the off-diagonal Green's function matrix element  $G_{ij}$  as the derivative of a diagonal element.<sup>1</sup> The proof is straight forward. Consider an orbital  $|u_0^\lambda\rangle$  that is an admixture of the two orbitals  $|i\rangle$  and  $|j\rangle$ , namely

$$|u_0^\lambda\rangle = (|i\rangle + e^{i\gamma}|j\rangle)/\sqrt{2}, \quad (10)$$

where  $\lambda = \cos \gamma$ . Then

$$\begin{aligned} G_{00}^\lambda(\varepsilon) &= \langle u_0^\lambda | (\varepsilon - \hat{H})^{-1} | u_0^\lambda \rangle \\ &= \frac{1}{2} [G_{ii}(\varepsilon) + G_{jj}(\varepsilon)] + \lambda G_{ij}(\varepsilon). \end{aligned} \quad (11)$$

Hence, it follows at once that

$$G_{ij}(\varepsilon) = \frac{\partial}{\partial \lambda} G_{00}^\lambda(\varepsilon). \quad (12)$$

This is physically transparent: the intersite Green's function  $G_{ij}$  simply reflects the change in the diagonal Green's function  $G_{00}$  as the phase admixture of the two starting orbitals  $|i\rangle$  and  $|j\rangle$  is altered.

This theorem allows an exact many-atom expansion for the off-diagonal element  $G_{ij}$  to be derived, starting from the continued fraction representation for  $G_{00}^\lambda$  in Eq. (9). For a symmetric eigenspectrum, it takes the form

$$\begin{aligned} G_{ij}(\varepsilon) &= \sum_{n=0}^{\infty} \left( \frac{\partial G_{00}^\lambda}{\partial a_n^\lambda} \frac{\partial a_n^\lambda}{\partial \lambda} \right)_{\lambda=0} \\ &= \sum_{n=0}^{\infty} [G_{0n}^{\lambda=0}(\varepsilon)]^2 \left( \frac{\partial a_n^\lambda}{\partial \lambda} \right)_{\lambda=0}, \end{aligned} \quad (13)$$

where the  $\partial a_n / \partial \lambda$  are related to *interference* terms  $\zeta_{p+1} = (H^p)_{ij}$  that link atoms  $i$  and  $j$  together

through paths of length  $p$  [11]. Very recently the convergence of this expansion has been speeded-up dramatically by constraining the poles of the intersite Green's function  $G_{ij}$  to be the same as those of the average on-site Green's function  $\frac{1}{2}(G_{ii} + G_{jj})$  [14]. This has allowed the derivation of explicit analytic expressions for the  $\sigma$  and  $\pi$  bond orders that accurately reproduce the TB results from direct matrix diagonalization [15].

The  $\sigma$  bond order, for example, can be written

$$\Theta_{ij,\sigma}^{\text{BOP}} = \frac{1}{\sqrt{1 + \frac{2\Phi_{2\sigma} + \delta^2}{\left[1 + \sqrt{(\Phi_{4\sigma} - 2\Phi_{2\sigma}^2 + \Phi_{2\sigma}^j \Phi_{2\sigma}^i) / \Phi_{2\sigma}}\right]^2}}}, \quad (14)$$

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  $i$ , is given by

$$\Phi_{2\sigma}^i = \sum_{k \neq i,j} [g_\sigma^\mu(\theta_{jik})]^2 \hat{\beta}_\sigma^2(R_{ik}), \quad (15)$$

where the greek symbols  $\mu, \nu, \kappa$  refer to the chemical nature of the atomic species at sites  $i, j$  and  $k$ , respectively. Thus, for hydrocarbon systems  $\mu, \nu, \kappa = \text{H}$  for hydrogen, C for carbon.  $\hat{\beta}_\sigma(R_{ik})$  is the normalized  $\sigma$  bond integral  $\beta_\sigma^{\mu\kappa}(R_{ik}) / \beta_\sigma^{\mu\nu}(R_{ij})$ . The angular functions  $g_\sigma^\mu(\theta)$  take the form  $g_\sigma^{\text{H}}(\theta) = 1$  and

$$g_\sigma^{\text{C}}(\theta) = [p_\sigma / (1 + p_\sigma)](p_\sigma^{-1} + \cos \theta), \quad (16)$$

where  $p_\sigma = pp\sigma / |ss\sigma|$ .  $\Phi_{4\sigma}^i$ , the *four-hop* contribution that starts and ends on atom  $i$ , is given by

$$\begin{aligned} \Phi_{4\sigma}^i &= \sum_{k \neq i,j} [g_\sigma^\mu(\theta_{jik})]^2 \hat{\beta}_\sigma^4(R_{ik}) \\ &\quad + \sum_{\substack{k,k' \neq i,j \\ k \neq k'}} g_\sigma^\mu(\theta_{jik}) g_\sigma^\mu(\theta_{kik'}) g_\sigma^\mu(\theta_{k'ij}) \hat{\beta}_\sigma^2(R_{ik}) \hat{\beta}_\sigma^2(R_{ik'}) \\ &\quad + \sum_{\substack{k,k' \neq i,j \\ k \neq k'}} [g_\sigma^\mu(\theta_{jik}) g_\sigma^\kappa(\theta_{ikk'})]^2 \hat{\beta}_\sigma^2(R_{ik}) \hat{\beta}_\sigma^2(R_{kk'}). \end{aligned} \quad (17)$$

The first term corresponds to hopping out and back twice between atom  $i$  and a neighbouring atom  $k$ , i.e.  $i \rightarrow k \rightarrow i \rightarrow k \rightarrow i$ . The second term corresponds to hopping out and back to the first neighbouring atom  $k$  and then to the different neighbouring atom  $k'$  i.e.  $i \rightarrow k \rightarrow i \rightarrow k' \rightarrow i$ . The third term corresponds to hopping out to the

<sup>1</sup> We should note that the use of the recursion method to evaluate  $G_{ij}$  as one-half the difference of the diagonal bonding and antibonding Green's functions, namely  $\frac{1}{2}(G_{++} - G_{--})$ , fails to converge within a computationally manageable set of recursion levels.

neighbouring atoms  $k$  and  $k'$  before hopping back to atom  $i$  i.e.  $i \rightarrow k \rightarrow k' \rightarrow k \rightarrow i$ .  $\hat{\delta}$  in Eq. (14) accounts for the non-negligible sp atomic energy level separation on the C sites and is defined by

$$\hat{\delta}^2 = \frac{1}{2} \left[ (\delta_i^\mu)^2 + (\delta_j^\nu)^2 \right] \left[ 4p_\sigma / (1 + p_\sigma)^2 \right] / \left[ \beta_\sigma^{\mu\nu}(R_{ij}) \right]^2, \quad (18)$$

where  $\delta^H = 0$  and  $\delta^C = (\varepsilon_p^C - \varepsilon_s^C) = 6.7$  eV. An analytic expression for the  $\pi$  bond in terms of neighbouring bond angles and dihedral angles may also be derived [15].

The accuracy of this ‘classical’ interatomic potential is illustrated in Table 1, which compares the BOP predictions for the  $\sigma$  and  $\pi$  C–C bond orders with those obtained by exact TB matrix diagonalization. We will consider the  $\sigma$  bond order first, since the widely used Tersoff potential [16] is analogous to retaining only the second-moment contribution in Eq. (14) so that the bond order varies as  $(1 + \hat{\delta}^2 + 2\Phi_{2\sigma})^{-1/2}$ . Our *predicted* angular function in Eq. (16) mirrors very closely the *empirical* angular function fitted in the Tersoff potential for carbon and silicon [17,18]. However, we see from Table 1 that the predicted values of our Tersoff-type bond order provide an inaccurate measure of the  $\sigma$  bond order within these carbon systems. For example, the value of 0.708 for diamond compared to the TB value of 0.912 would lead to an error of 4.1 eV in the  $\sigma$  bond energy,  $2\beta_\sigma\theta_\sigma$ . These large errors are to be expected because the small differences in binding energy between different non-close-packed structure types are driven by the fourth moment paths of length four that determine the unimodal

versus bimodal *shape* of the electronic eigenspectrum rather than the paths of length two that determine the second moment or mean square *width* of the spectrum [6]. These four-hop contributions appear in the denominator of the quotient in Eq. (14) and lead to BOP values that are in excellent agreement with TB, the error for diamond now only being 0.06 eV/bond.

Including the BOP predictions for the  $\pi$  bond orders, we see from the last column in Table 1 that not only are the single, double and triple carbon–carbon bond orders well reproduced, but also the conjugate bonds in benzene and graphite. In addition, it is clear that this is the first ‘classical’ interatomic potential that handles correctly the formation of radicals within its remit,  $C_2H_5$  remaining essentially a singly bonded system on the abstraction of a H atom from  $C_2H_6$ . Current molecular dynamics simulations using analytic BOP forces are an order of magnitude slower than with Tersoff potentials [19]. However, this is a small price to pay for having a ‘classical’ potential that is sufficiently sophisticated to handle both structural differentiation and radical formation naturally within its framework.

The above derivation of analytic BOPs depends critically on the availability of reliable orthogonal TB parameters. During the past few years it has become recognized that robust schemes require the two-centre orthogonal TB integrals to be environmentally dependent. The Ames group [20,21], in particular, have proposed writing the TB parameters in the form

$$\tilde{\beta}_{ij} = \beta(\kappa R_{ij})(1 - \mathcal{L}_{ij}), \quad (19)$$

Table 1  
C–C bond integrals and bond orders [15]

System	Local coord.	$\beta_\sigma^{CC}$ (eV), $\beta_\pi^{CC}$ (eV)	$\theta_\sigma$ , BOP TB, (Tersoff)	$\theta_{\pi-}$ , BOP TB	$\theta_{\pi+}$ , BOP TB	$\theta_{total}$ , BOP TB
$C_2$	1	17.84, 2.76	0.936, 0.936 (0.936)	1.000, 1.000	1.000, 1.000	2.936, 2.936
$C_2H_2$	2	19.24, 2.98	0.974, 0.986, (0.946)	1.000, 1.000	1.000, 1.000	2.974, 2.986
$C_2H_4$	3	14.89, 2.30	0.955, 0.971, (0.888)	1.000, 1.000	0.194, 0.137	2.149, 2.108
$C_6H_6$	3	13.50, 2.09	0.953, 0.963, (0.850)	0.577, 0.667	0.141, 0.107	1.671, 1.737
$C_{gr}$	3	12.71, 1.97	0.951, 0.957, (0.827)	0.477, 0.528	0.121, 0.094	1.520, 1.579
$C_2H_5$	3.5	10.87, 1.68	0.929, 0.949, (0.784)	0.214, 0.217	0.145, 0.102	1.288, 1.268
$C_2H_6$	4	10.53, 1.63	0.917, 0.936, (0.748)	0.149, 0.105	0.149, 0.105	1.214, 1.146
$C_6H_2$	4	10.02, 1.55	0.913, 0.926, (0.725)	0.141, 0.101	0.134, 0.101	1.188, 1.128
$C_\diamond$	4	10.02, 1.55	0.915, 0.912, (0.708)	0.126, 0.103	0.126, 0.103	1.167, 1.118

where  $\beta(\kappa R_{ij})$  is the usual Slater–Koster two-centre bond integral.  $\mathcal{S}_{ij}$  is a *fitted* empirical screening function that reduces the strength of the bonding between a given pair of atoms  $i$  and  $j$  due to the presence of neighbouring atoms  $k$  in the vicinity of the bond. Very recently we have *derived* the analytic form of this screening function by starting from a non-orthogonal TB representation [22]. We have used BOP theory to find the inverse non-orthogonality matrix,  $(I + O)^{-1}$ , by analogy with our previous derivation of the Green’s function matrix,  $(EI - H)^{-1}$ . Setting  $E = 1$  and  $H = -O$  (where  $I$  and  $O$  are the unit and overlap matrices, respectively) gives *analytic* expressions for the screening function for  $\sigma$ ,  $\pi$  and  $\delta$  bonds that accurately reproduce the behaviour of the bond integrals in the molybdenum disilicides which are predicted numerically by screened LMTO theory [23].

In conclusion, we are hopeful that we now have a methodology for linking systematically between the electronic and atomistic modelling hierarchies. In particular, the numerical results of screened LMTO theory will be used to provide an ab initio density functional data base for fitting the analytic environment-dependent TB parameters. This TB scheme at the electronic level will then be coarse-grained to provide analytic BOPs for performing large-scale simulations at the atomistic level. Immediate areas of application could be the CVD growth of diamond films or the dislocation behaviour of high-temperature intermetallics such as the molybdenum disilicides.

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