

Bond order potential for molecular dynamics simulation: Relaxation of semiconductor nanostructures

K. Scheerschmidt and V. Kuhlmann

Molecular dynamics (MD) simulations have been performed to study atomic processes related to the reordering at interfaces and the relaxation of nanostructures [1]. The bond order potential (BOP) based on the tight binding (TB) model is used to enhance the MD, as it preserves the essential quantum mechanical nature of atomic bonding, yet abandons the electronic degree of freedom. TB and *ab initio* methods require complete diagonalizations of the Hamiltonian, which scale as $\mathcal{O}(N^3)$ and restrict MD to a few thousand atoms. The analytic BOP, however, achieves $\mathcal{O}(N)$ scaling by diagonalizing the orthogonal TB-Hamiltonian approximately and is recognized as a fast and accurate model for atomic interaction [2, 3]. It allows to explore the dynamics of systems on macroscopic time and length scales on the atomic level that are beyond the realm of *ab initio* calculations. The approximations to develop analytic BOP potentials from DFT may be summarized by the following steps: construct the TB matrix elements by Slater-Koster two-centre integrals including s- and p- orbitals, transform the matrix to the bond representation, replace the diagonalization by Lanczos recursion, obtain the momenta from the continued fraction representation of the Green function up to order n for an analytic BOP $_n$ potential. The total cohesive potential energy U_{coh} has three contributions: pair repulsion, promotion energy U_{prom} , and bond energy as excess of the band energy over the individual atomic interactions $U_{bond} = 2\sum_{i\alpha,j\beta}\Theta_{j\beta,i\alpha}H_{i\alpha,j\beta}$. In the BOP representation [3] the matrix elements $H_{i\alpha,j\beta}$ are replaced by the Slater-Koster two-center integrals h_{ij} and the Goodwin-Skinner-Pettifor distance scaling function. The bond order $\Theta_{i\sigma,j\sigma}$ is equivalent to the electron density for which a concise analytical expression $\left[1 + \frac{N^2(\Phi_{2\sigma}^i + \Phi_{2\sigma}^j) + \Phi_{2\sigma}^i \Phi_{2\sigma}^j (2N + \Delta\Phi_{4\sigma})}{(N + \Delta\Phi_{4\sigma})^2}\right]^{-1/2}$ can be given that employs the normal-

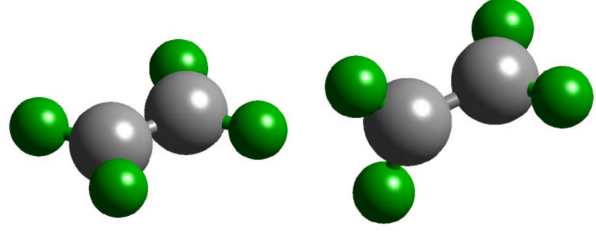


Fig. 1: Planar and rotated ethylene structure C_2H_4 as used for testing the BOP4+, cf. table 1

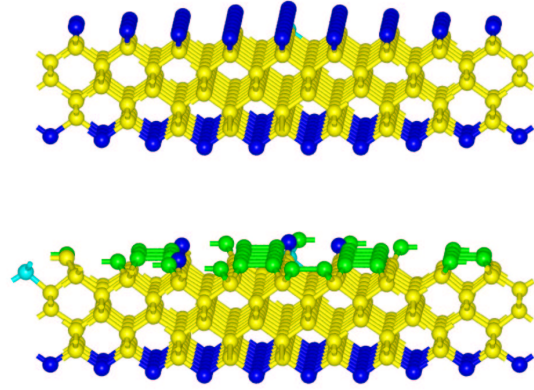


Fig. 2: Spontaneous Si-(100) surface dimerization and $\sigma - \pi$ bond exchange with the BOP4+ after 1ns annealing with 600K maximum temperature

ized second and fourth moment ($\Phi_{2\sigma}, \Phi_{4\sigma}$) of the local density of electronic states and $\Delta\Phi_{4\sigma} = (\Phi_{4\sigma}^i + \Phi_{4\sigma}^j - \Phi_{2\sigma}^{i2} - \Phi_{2\sigma}^{j2}) / (\Phi_{2\sigma}^i + \Phi_{2\sigma}^j)$, $N^2 = \Delta\Phi_{4\sigma} + \Phi_{2\sigma}^i \Phi_{2\sigma}^j$. The contribution $\Phi_{4\sigma}$ to the 4th moment was given in terms of the matrix-elements of the tight binding Hamiltonian,

$$\sum_{k(i) \neq j} \hat{h}_{ik}^4 g_{jik}^2, \quad \sum_{\substack{k(i) \neq j \\ k'(k) \neq i, j}} \hat{h}_{ik}^2 \hat{h}_{kk'}^2 g_{jik}^2 g_{ikk'}^2, \\ \sum'_{k(i), k'(i) \neq j} \hat{h}_{ik}^2 \hat{h}_{ik'}^2 g_{jik} g_{kik'} g_{jik'}.$$

with the cosine of the bond angle C_{jik} , the angular function $g_{ijk} = (1 + \hat{p}_i C_{jik}) / (1 + \hat{p}_i)$, reduced TB-parameters $\hat{p}_i = h_{pp\sigma} / h_{ss\sigma}$, and normalized hopping integrals $\hat{h}_{ik} = h_{ik} / h_{ij}$ etc.

	Θ_{σ}^{CC}	Θ_{σ}^{CH}	$U_{prom}[eV]$	$U_{coh}[eV]$
a	1.000	1.000	11.640	-17.420
	0.986	0.993	11.180	-17.090
	0.986	0.993	11.757	-16.316
b	0.988	0.987	11.070	-25.990
	0.967	0.977	10.690	-25.020
	0.972	0.972	10.838	-23.681
c	0.988	0.987	11.070	-23.580
	0.967	0.977	10.690	-22.580
	0.972	0.959	10.882	-20.342

Tab. 1: Comparison of different contributions to the enhanced bond order potential BOP4+ (middle rows) with the original BOP4 (upper rows) and numerical TB (lower rows) using hydrocarbons: a) C_2H_2 , b) planar C_2H_4 , c) rotated C_2H_4

The resulting semi-empirical many body potential is transferable to describe phases and configurations not included in the parameter fit, a feature not found in other empirical potentials. Moreover, transferability extends to different kinds of materials, where only the parameters need to be refitted. In the implementation of the enhanced BOP4+ a number of angular terms are included that are related to certain π bonds between neighboring atoms and contribute up to 40%, but were ignored previously. With the angle of torsion $\mathcal{C}_{ij,kk'}$ and the abbreviations $\mathcal{Z} = \mathcal{C}_{ij,kk'} + \mathcal{C}_{jik} \mathcal{C}_{ikk'}$ and $\xi = \hat{\pi}_i \hat{p}_k / (1 + \hat{p}_i)$ one yields the new contribution to the 4-th momentum:

$$\sum_{\substack{k(i) \neq j \\ k'(k) \neq i, j}} \hat{h}_{ik}^2 \hat{h}_{kk'}^2 \mathcal{Z} \xi \left(\frac{\mathcal{Z} \xi}{(1 + \hat{p}_k)^2} + \frac{2g_{jik} g_{ikk'}}{1 + \hat{p}_k} \right).$$

Similarly on-site contributions to $\Phi_{4\sigma}$ proportional to the energy splitting δ_i are included $\sum \hat{h}_{ik}^2 \left\{ \tilde{g}_{jik}^2 (2\hat{\delta}_i^2 + \hat{\delta}_k^2) + \hat{p}_i \hat{\delta}_i^2 \frac{(1 - \mathcal{C}_{jik})^2}{(1 + \hat{p}_i)^2} \right\} + \hat{\delta}_i^4$.

Different terms of the extended BOP4+, given by the contributions above, are listed in tables 1, 2 for hydrocarbons and carbon structures, resp. The comparison with the conventional BOP4 (upper rows) and exact TB calculations (lower rows) demonstrates the excellent enhancement of the bond orders in BOP4+ (besides the empirical U_{prom}). The improved

	Θ_{σ}	$U_{prom}[eV]$	$U_{coh}[eV]$
diamond	0.921	5.376	-8.513
	0.904	5.355	-7.780
	0.912	5.356	-7.250
graphite	0.975	5.648	-8.809
	0.959	5.880	-8.214
	0.957	5.631	-7.395
C_5^{dia}	0.972	4.668	-1.785
	0.932	3.326	-2.493
	0.890	2.15	-3.000
C_4^{dia}	0.979	4.890	-1.913
	0.935	3.339	-2.439
	0.907	2.282	-3.475
C_3^{dia}	0.988	5.133	-1.557
	0.936	5.013	-1.709
	0.917	2.309	-3.773
dimer	1.000	5.946	-1.913
	0.936	4.980	-1.740
	0.936	4.352	-2.549

Tab. 2: Comparison of different contributions to the enhanced bond order potential BOP4+ (middle rows) with the original BOP4 (upper rows) and numerical TB (lower rows) calculations using carbon crystals and clusters

BOP4+ allows nanoscopic structure calculations including electronic properties as shown, e.g., in the bond rearrangements of Figure 2 in spontaneous surface dimerization.

References

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