Analytic bond-order potentials for modeling the growth of semiconductor films

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Funding: DARPA
The Problem

Conclusion: Simple EMPIRICAL potential will not suffice!

Ga

GaAs

As

Mn

α-Fe

Materials Modelling Laboratory

OxfordMaterials
Solution: Coarse Graining from DFT to TB to BOP

Bridge the gap between electronic and atomistic hierarchies to DERIVE analytic many-body potentials

Electronic
- Tight Binding Approximation
- σ and π bond integrals
- Effective one-electron Model
- Density functional theory
- Many-body Quantum Theory

Atomistic
- Monte Carlo
- Introduce lattice
- Molecular Dynamics
- Calculate forces
- Bond-Order Potentials

Coarse grain and link electronic structure to atom-centered moments and bond-centered interference paths
Outline

Introduction

- multiscale materials modelling
- importance of reliable interatomic potentials
- need to bridge gap from electronic to atomistic modelling hierarchies

Coarse graining I

From Density Functional Theory to Tight Binding
- unscreened TB parameters from DFT dimer eigenspectrum
- unscreened repulsive energy from DFT dimer binding energy
- screened TB parameters from DFT bulk eigenspectrum

Coarse graining II

From Tight Binding to Bond-Order Potentials
- exact many-atom expansion for bond order
- analytic BOP
- band filling dependence within BOP
- application: growth of Si and GaAs

Conclusions
Coarse Graining I: from DFT to TB

\[ U = U_{bond} + U_{prom} + U_{rep} + U_{ionic} + U_{mag} \]

where for sp-valent systems

\[ U_{bond} = \frac{1}{2} \sum_{i \neq j} 2\left[ \beta_{\sigma}^{ij} \Theta_{\sigma}^{ij} + \beta_{\pi}^{ij} \Theta_{\pi}^{ij} \right] \]

spin degeneracy \( \sigma \) and \( \pi \) bond integrals

with the Bond Order

\[ \Theta = \frac{1}{2} \left( N_{bond} - N_{anti-bond} \right) \]

Example: \( H_2 \)

\( \Theta = \frac{1}{2} (2 - 0) = 1 \)

(saturated \( \sigma \) bond)

But what is nature of TB parameters and repulsive energy?
Unscreened TB parameters from DFT
Eigenspectrum for Dimers

DFT (Dmol) Si\textsubscript{2} spectrum

$\delta = E_p - E_s$

$\delta_0$

$\beta_\sigma$

$\beta_{exp,\sigma}$

$\beta = (1 - \exp(-\mu(\frac{R}{R_{inf}})^n)) \beta_{exp}$

$\beta_{exp} = a_0 \exp(-\lambda(\frac{R}{R_{inf}}))$

Unscreened repulsive Energy from DFT
Binding Energy for Dimers

\[ U_{rep} = U^{(DFT)} - U^{(TB)}_{prom} - U^{(TB)}_{bond} \]

\[ U^{(TB)}_{prom} = -(E_{p\sigma} - E_s) \delta N_s^{(TB)} \]

\[ U^{(TB)}_{bond} = 2\beta_\sigma \Theta^{(TB)}_\sigma + 2\beta_\pi \Theta^{(TB)}_\pi \]

repulsion = overlap + core

True for all sp valent dimers
Systems composed of many atoms: Screened TB Parameters from DFT Eigenspectrum

DFT (TB-LMTO) screened bond integrals for Si

\[ \tilde{\beta}_{ij} = \beta_{ij} (1 - S_{ij}) \]

where \( S_{ij} \) is a screening function due to overlap

Nguyen-Manh, DGP, Vitek, PRL 84 (2000) 4136
Coarse Graining II: From TB to BOP

How does bond order depend on local environment?

BOP theory (Pettifor PRL (1989), Aoki PRL (1993)) derived Exact Many-Atom Expansion:

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

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

$$G_{ij} = \sum_{n=0}^{\infty} G_{0n}^2 \delta a_n + \sum_{n=1}^{\infty} 2 G_{0,n-1} G_{n0} \delta b_n$$

$$\delta a_0 = (\zeta_2)_{ij}, \quad \delta b_1 = \frac{1}{4\sqrt{\mu_2}} (\zeta_3)_{ij}, \quad \delta a_1 = \frac{1}{\mu_2} (\zeta_4)_{ij} - \frac{\mu_3}{\sqrt{\mu_2}} (\zeta_3)_{ij} - 2(\zeta_2)_{ij}, \ldots$$

Coarse grain electronic structure into moments about atoms and interference paths about bonds.

Conclusion: directional character of bond very important
Analytic BOP for group IV sp-valent elements:

**σ Bond**

Constrain poles of $G_{ij}$ to be the same as $\frac{1}{2}(G_{ii} + G_{jj})$

$$\Theta_{i,j,\sigma}^{\left(\frac{1}{2}\right)} = \frac{1}{\sqrt{1 + \frac{2\Phi_2 + \xi_4^{ring} + X(2+Y)}{(1+Y)^2}}}$$

$$X = \frac{\Phi_2^i \Phi_2^j}{\sqrt{\Delta \Phi_4 + \Phi_2^i \Phi_2^j}}$$

$$Y = \frac{\Delta \hat{\Phi}_4}{\sqrt{\Delta \Phi_4 + \Phi_2^i \Phi_2^j}}$$

$$\Delta \hat{\Phi}_4 = \Phi_4 - \frac{1}{2}(\Phi_2^i + \Phi_2^j)$$

2-hop contribution $1/\sqrt{1 + 2\Phi_2}$ looks like Tersoff. But require 4-hop for structural prediction.
Analytic BOP for group IV sp-valent elements:

**π Bond**

Use 2x2 matrix recursion with $p_x$ and $p_y$ orbitals treated on equal footing:

$$
\Theta_{ij, \pi}^{(1/2)} = \frac{1}{\sqrt{1 + \Phi_{2\pi} + \Phi_{4\pi}^{1/2}}} + \frac{1}{\sqrt{1 + \Phi_{2\pi} - \Phi_{4\pi}^{1/2}}} \quad \text{π bond order}
$$

**Two-hop contribution**

$$
\Phi_{2\pi} = \frac{1}{2} \sum_{k \neq i,j} \left[ \sin^2 \theta_{ijk} \hat{h}^2_\sigma (R_{ik}) + (1 + \cos^2 \theta_{ijk}) \hat{h}^2_\pi (R_{ik}) + (i \leftrightarrow j) \right]
$$

**Four-hop contribution**

$$
\Phi_{4\pi} = \frac{1}{4} \sum_{k,k' \neq i,j} \left[ \sin^2 \theta_{ijk} \sin^2 \theta_{ijk'} \hat{h}^2_\sigma \hat{h}^2_{jk} \hat{h}^2_{jk'} + \sin^2 \theta_{ijk} \sin^2 \theta_{ijk'} \hat{h}^2_\pi \hat{h}^2_{jk} \hat{h}^2_{jk'} + (i \leftrightarrow j) \right] \times \cos 2(\phi_k - \phi_k')
$$

Rotational Barrier under Torsion
Example: C-C Bond Orders

<table>
<thead>
<tr>
<th>System</th>
<th>$\Theta_{\sigma}$</th>
<th>$\Theta_{\pi^+}$</th>
<th>$\Theta_{\pi^-}$</th>
<th>$\Theta_{\text{tot}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2$</td>
<td>0.936</td>
<td>1.000</td>
<td>1.000</td>
<td>2.936</td>
</tr>
<tr>
<td>$C_2H_2$</td>
<td>0.974</td>
<td>1.000</td>
<td>1.000</td>
<td>2.974</td>
</tr>
<tr>
<td>$C_2H_4$</td>
<td>0.955</td>
<td>1.000</td>
<td>0.194</td>
<td>2.149</td>
</tr>
<tr>
<td>$C_6H_6$</td>
<td>0.953</td>
<td>0.577</td>
<td>0.141</td>
<td>1.671</td>
</tr>
<tr>
<td>$C_{Gr}$</td>
<td>0.951</td>
<td>0.477</td>
<td>0.121</td>
<td>1.520</td>
</tr>
<tr>
<td>$C_2H_5$</td>
<td>0.929</td>
<td>0.214</td>
<td>0.145</td>
<td>1.288</td>
</tr>
<tr>
<td>$C_2H_6$</td>
<td>0.917</td>
<td>0.149</td>
<td>0.149</td>
<td>1.214</td>
</tr>
<tr>
<td>$C_6$</td>
<td>0.915</td>
<td>0.126</td>
<td>0.126</td>
<td>1.167</td>
</tr>
</tbody>
</table>

Conclusion: Analytic BOP quantifies the concept of single, double, triple, conjugate and radical bonds

DGP and Oleinik, PRL 84 (2000) 4124
Band Filling dependence within TB

Input (from DFT)

Output (from TB)

TB bond integrals: $\beta_\sigma(R)$ × × $\beta_\pi(R)$

Well-known structural trends across periodic table are predicted in Tight Binding
Band Filling dependence of Analytic BOP

TB bond order

- $pp\sigma/sss\sigma = 2$, $pp\pi = 0$, $\delta = 0$

Analytic BOP bond order

- $pp\sigma/sss\sigma = 2$, $pp\pi = 0$, $\delta = 0$

- values at ½-full from analytic BOP
- other values interpolated using boundaries

Drautz, DGP et al., PRB (submitted)

k-space TB calculations using OXON
TB to BOP: Structural Trends

Conclusion: Analytic BOP predicts structural trends correctly
MD Growth of Films using BOP Prototype

Si (100)  

GaAs (100)  


Murdick, Zhou, Wadley (unpublished)
Conclusions

- DFT
  - development of robust TB scheme, involving screened bond integrals and screened overlap and core repulsion
  - applicable from dimers through to close-packed systems

- TB
  - predicted analytic form of interatomic many-body potentials by coarse graining TB electronic structure in terms of moments about atoms and interference paths about bonds

- BOP
  - applicable to growth behaviour of semiconductors
  - currently: including charge transfer and magnetism