

Progress towards accurate quantum chemical molecular dynamics simulations of plasma interactions with beryllium surfaces

Stephan Irle
Nagoya University

Toyoda Auditorium
Nagoya University

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Vienna, Austria, August 19, 2014

Overview

Motivation

DFTB Method

DFTB Parameterization of Be-H/D/T chemical interactions

Accelerating DFTB calculations

Overview

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DFTB Method

DFTB Parameterization of Be-H/D/T chemical interactions

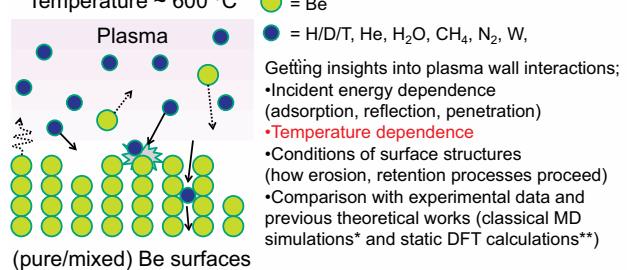
Accelerating DFTB calculations

Chemical Sputtering on Be

Motivation

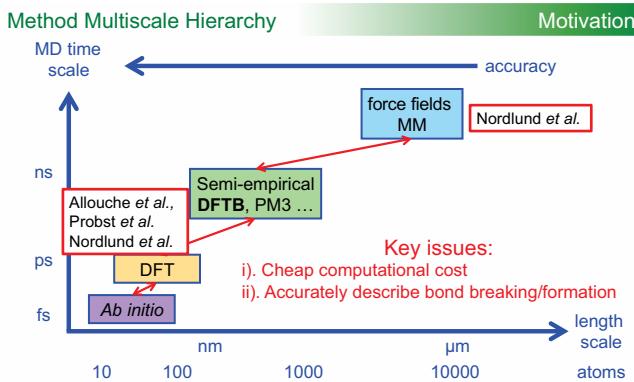
- Little is known about the plasma wall processes on Be surface
- Performing accurate molecular dynamics (MD) simulations is important to extend our knowledge at the atomistic level

Temperature ~ 600 °C



*Bjorkas, C. et al., *New. J. Phys.*, **11**, 123017, (2009).; Ueda, S. et al., *J. Nucl. Mater.*, **258-263**, 713, (1998); Ueda, S. et al., *J. Nucl. Mater.*, **283-287**, 1100, (2000).

Allouche, A. et al., *J. Phys. Chem. C*, **114, 3588, (2010).



➤ DFTB (density-functional tight-binding) is a well established **approximate DFT method** but there are *no available Be-X parameters*. Therefore, we started to develop Be-Be and Be-H parameters.

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Introduction

DFTB Method

Fast QM Method: Approximate DFT Density-Functional Tight-Binding (DFTB)

Tight Binding (extended-Hückel-like) method with parameters from DFT

Eschrig, Seifert (1980's):
• 2-center approximation
• Minimum basis set



$$E^{(NCC-)DFTB} = \sum_i^{\text{valence orbitals}} n_i \epsilon_i + \frac{1}{2} \sum_{A,B}^{\text{atoms}} F_{AB}^{ep}$$

$$E^{(SCC-)DFTB} = E^{(NCC-)DFTB} + \frac{1}{2} \sum_{A,B}^{\text{atoms}} \gamma_{AB} \Delta q_A \Delta q_B$$

$$E^{(spin-polarized)DFTB} = E^{(SCC-)DFTB} + \frac{1}{2} \sum_A^{\text{atoms}} \sum_{I \in A / I \in A} p_{AI} P_{AI} W_{AI}$$

Christof Köhler

No integrals, DFTB is roughly **1000 times faster** than DFT!

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DFTB

DFTB Method

Ref.: Oliviera, Seifert, Heine, Duarte, *J. Braz. Chem. Soc.* **20**, 1193-1205 (2009)



Thomas Heine



Hélio Duarte

J. Braz. Chem. Soc., Vol. 20, No. 7, 1193-1205, 2009
Printed in Brazil - ©2009 Sociedade Brasileira de Química
0101 - 5033 \$6.00+0.00

Density-Functional Based Tight-Binding: an Approximate DFT Method

Augusto F. Oliviera,^{a,b} Gotthard Seifert,^b Thomas Heine^c and Hélio A. Duarte^{a,b}

^aDepartamento de Química, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Av. Antonio Carlos, 6627-901 Belo Horizonte-MG, Brazil

^bPhysikalische Chemie, Technische Universität Dresden, Mommsenstr. 13, D-01062 Dresden, Germany

^cSchool of Engineering and Sciences, Jacobs University, P.O. Box 750 561, 28725 Bremen, Germany

...open access

Self-consistent-charge density-functional tight-binding (SCC-DFTB)

M. Elstner et al., Phys. Rev. B 58 7260 (1998)

Second order Taylor-expansion of DFT energy in terms of reference density ρ_0 and charge fluctuation $\delta\rho$ ($\rho \approx \rho_0 + \delta\rho$) yields:

$$\begin{aligned} E[\rho_0 + \delta\rho] = & \underbrace{\sum_i n_i \langle \phi_i | \hat{H}[\rho_0] | \phi_i \rangle}_{\text{valence orbitals}} + \underbrace{\sum_i n_i \langle \phi_i | \hat{H}[\rho_0] | \phi_i \rangle}_{\text{core orbitals}} \\ & + \underbrace{E_{xc}[\rho_0]}_{3} - \underbrace{\frac{1}{2} \int_{\mathbf{R}^3} \rho_0 V_H[\rho_0] - \int_{\mathbf{R}^3} \rho_0 V_{xc}[\rho_0] + E_{\text{nucl}}}_{4-6} \\ & + \underbrace{\frac{1}{2} \int_{\mathbf{R}^3} \delta\rho V_H[\delta\rho]}_{7} + \underbrace{\frac{1}{2} \iint_{\mathbf{R}^3} \frac{\partial^2 E_{xc}}{\partial \delta\rho^2} |_{\rho_0} \delta\rho^2}_{8} + o(3) \end{aligned}$$

Density-functional tight-binding (DFTB) method is derived from terms 1-6
SCC-DFTB method is derived from terms 1-8

Fouckes + Haydock Ansatz
Phys. Rev. B, 39, 12520 (1989)

DFTB and SCC-DFTB methods

$$E^{\text{DFTB}} = \underbrace{\sum_i n_i \epsilon_i}_{\text{term 1}} + \underbrace{\frac{1}{2} \sum_{A \neq B} E_{\text{rep}}^{AB}}_{\text{terms 2-6}}$$

$$E^{\text{SCC-DFTB}} = \underbrace{\sum_i n_i \epsilon_i}_{\text{term 1}} + \underbrace{\frac{1}{2} \sum_{A,B} \gamma_{AB} \Delta q_A \Delta q_B}_{\text{terms 7-8}} + \underbrace{\frac{1}{2} \sum_{A \neq B} E_{\text{rep}}^{AB}}_{\text{terms 2-6}}$$

where

n_i and ϵ_i — occupation and orbital energy of the i^{th} Kohn-Sham eigenstate

E_{rep} — distance-dependent diatomic repulsive potentials

Δq_A — induced charge on atom A

γ_{AB} — distance-dependent charge-charge interaction functional; obtained from chemical hardness (IP – EA)

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DFTB method

❖ Repulsive diatomic potentials replace usual nuclear repulsion energy

❖ Reference density ρ_0 is constructed from atomic densities

$$\rho_0 = \sum_A \rho_0^A$$

❖ Kohn-Sham eigenstates ϕ_i are expanded in Slater basis of valence pseudoatomic orbitals χ_i

$$\phi_i = \sum_{\alpha} c_{i\alpha} \chi_{i\alpha}$$

❖ The DFTB energy is obtained by solving a generalized DFTB eigenvalue problem with \mathbf{H}^0 computed by atomic and diatomic DFT

$$\begin{aligned} \mathbf{H}^0 \mathbf{C} = \mathbf{S} \mathbf{C} \epsilon & \quad \text{with} \quad S_{\alpha\beta} = \langle \chi_{i\alpha} | \chi_{i\beta} \rangle \\ H_{\alpha\beta}^0 &= \langle \chi_{i\alpha} | \hat{H}[\rho_0^M, \rho_0^N] | \chi_{i\beta} \rangle \end{aligned}$$

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SCC-DFTB method

❖ Additional induced-charges term allows for a proper description of charge-transfer phenomena

❖ Induced charge Δq_A on atom A is determined from Mulliken population analysis

$$\Delta q_A = \sum_i^{\text{MO}} n_i \sum_{B \neq A}^{\text{AO}} c_{iB}^* c_{iA} S_{iB} - q_A^0$$

❖ Kohn-Sham eigenenergies are obtained from a generalized, self-consistent SCC-DFTB eigenvalue problem

$$\mathbf{H} \mathbf{C} = \mathbf{S} \mathbf{C} \epsilon \quad \text{with} \quad S_{\alpha\beta} = \langle \chi_{i\alpha} | \chi_{i\beta} \rangle \quad \text{and}$$

$$H_{\alpha\beta} = \langle \chi_{i\alpha} | \hat{H}[\rho_0^M, \rho_0^N] | \chi_{i\beta} \rangle + \frac{1}{2} S_{\alpha\beta} \sum_K^{\text{atoms}} (\gamma_{MK} + \gamma_{NK}) \Delta q_K$$

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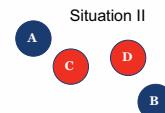
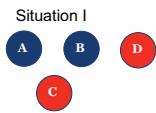
Approximations in the DFTB Hamiltonian

Traditional DFTB concept: Hamiltonian matrix elements are approximated to two-center terms. The same types of approximations are done to E_{rep} :

$$H_{\mu\nu}^0 = \begin{cases} \epsilon_{\mu}^{\text{neutral free atom}} & \text{if } \mu = \nu \\ \langle \varphi_{\mu}^{\alpha} | \hat{T} + V_{\alpha}^{\alpha} + V_{\beta}^{\beta} | \varphi_{\nu}^{\beta} \rangle & \text{if } \alpha \neq \beta \\ 0 & \text{otherwise.} \end{cases}$$

$$\begin{aligned} V_{\text{eff}}[\rho_0] &\approx V_{\text{eff}}[\rho_A + \rho_B] && \text{(Density superposition)} \\ V_{\text{eff}}[\rho_0] &\approx V_{\text{eff}}[\rho_A] + V_{\text{eff}}[\rho_B] && \text{(Potential superposition)} \end{aligned}$$

Both approximations are justified by the screening argument: Far away, neutral atoms have no Coulomb contribution.



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$$\begin{aligned} \text{LCAO ansatz of wave function} \quad \Psi_i &= \sum_{\alpha} c_{i\alpha} \phi_{\alpha}(\mathbf{r} - \mathbf{R}_a) & \xrightarrow{\text{variational principle}} & \text{secular equations} \\ & \text{pseudoatomic orbital} & & \sum_{\alpha} c_{i\alpha}^* (H_{\alpha\alpha} - \epsilon_i S_{\alpha\alpha}) = 0 & \uparrow & \text{Hamiltonian} & \text{Overlap} \end{aligned}$$

pre-computed parameter

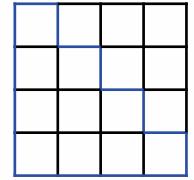
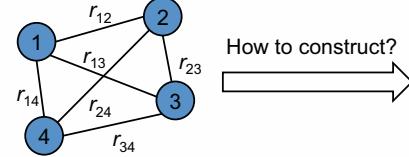
- Reference Hamiltonian H^0
- Overlap integral $S_{\alpha\beta}$

✓ two-center approximation

✓ nearest neighbor off-diagonal elements only

✓ (minimum basis set)

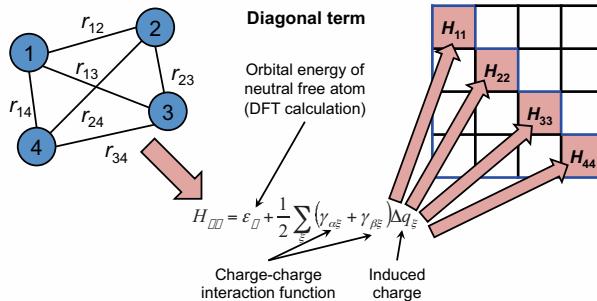
Example: X4: Atom 1 – 4 are the same atom & have only s shell



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$$\begin{aligned} \text{LCAO ansatz of wave function} \quad \Psi_i &= \sum_{\alpha} c_{i\alpha} \phi_{\alpha}(\mathbf{r} - \mathbf{R}_a) & \xrightarrow{\text{variational principle}} & \text{secular equations} \\ & \text{pseudoatomic orbital} & & \sum_{\alpha} c_{i\alpha}^* (H_{\alpha\alpha} - \epsilon_i S_{\alpha\alpha}) = 0 & \uparrow & \text{Hamiltonian} & \text{Overlap} \end{aligned}$$

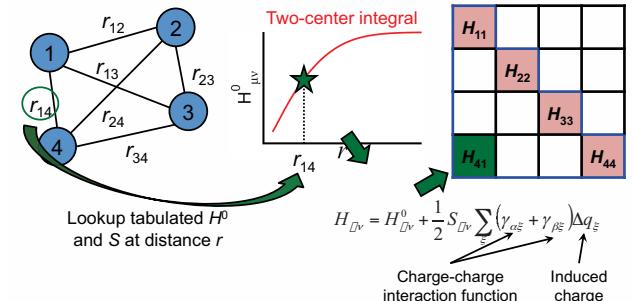
Atom 1 – 4 are the same atom & have only s shell



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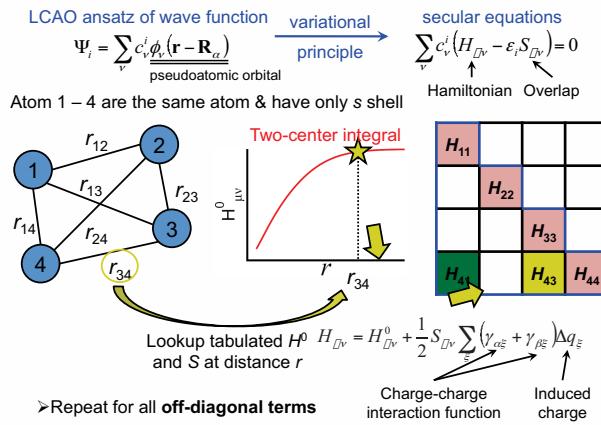
$$\begin{aligned} \text{LCAO ansatz of wave function} \quad \Psi_i &= \sum_{\alpha} c_{i\alpha} \phi_{\alpha}(\mathbf{r} - \mathbf{R}_a) & \xrightarrow{\text{variational principle}} & \text{secular equations} \\ & \text{pseudoatomic orbital} & & \sum_{\alpha} c_{i\alpha}^* (H_{\alpha\alpha} - \epsilon_i S_{\alpha\alpha}) = 0 & \uparrow & \text{Hamiltonian} & \text{Overlap} \end{aligned}$$

Atom 1 – 4 are the same atom & have only s shell



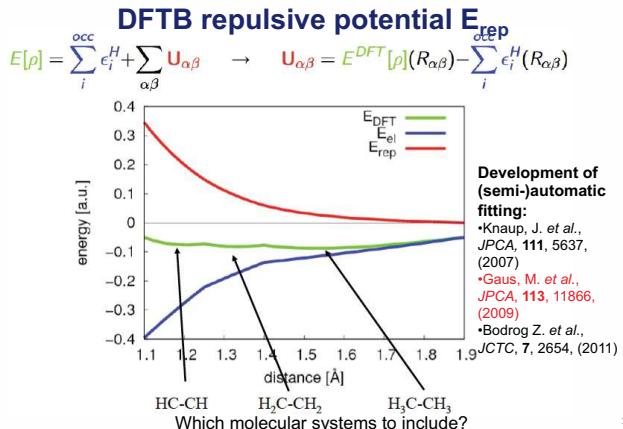
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DFTB



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DFTB repulsive potentials



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DFTB gradients

DFTB Method

Gradient for the DFTB methods

The DFTB force formula

$$F_a = - \sum_i^{MO} n_i \sum_{\nu}^{AO} c_{i\nu} c_{i\nu}^* \left[\frac{\partial H_{i\nu}^0}{\partial a} - \epsilon_i \frac{\partial S_{i\nu}}{\partial a} \right] - \frac{\partial E_{rep}}{\partial a}$$

The SCC-DFTB force formula

$$F_a = - \sum_i^{MO} n_i \sum_{\nu}^{AO} c_{i\nu} c_{i\nu}^* \left[\frac{\partial H_{i\nu}^0}{\partial a} - \left(\epsilon_i - \frac{1}{2} \sum_k^{atoms} (\gamma_{MK} + \gamma_{NK}) \Delta q_k \right) \frac{\partial S_{i\nu}}{\partial a} \right] - \Delta q_A \sum_k^{atoms} \frac{\partial \gamma_{AK}}{\partial a} \Delta q_k - \frac{\partial E_{rep}}{\partial a}$$

computational effort: energy calculation 90%
 gradient calculation 10%

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New Electronic Parameters

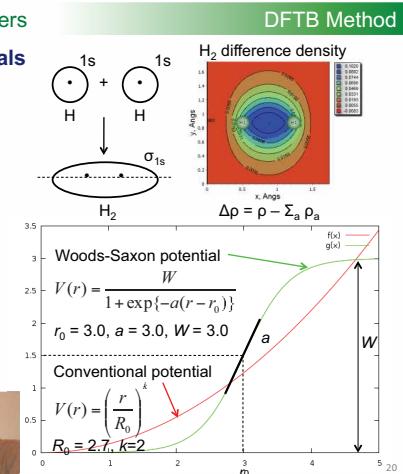
DFTB Method

New Confining Potentials

Typically, electron density contracts under covalent bond formation.

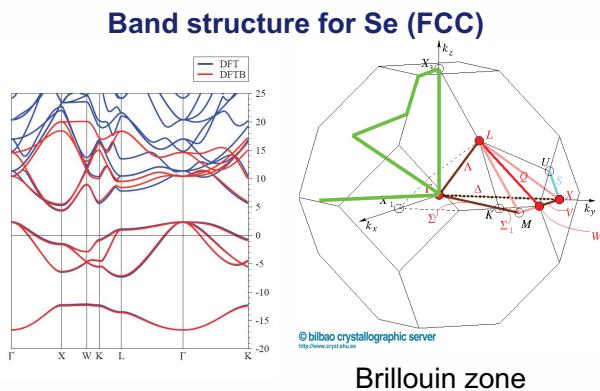
In standard *ab initio* methods, this problem can be remedied by including more basis functions.

DFTB uses minimal valence basis set: the confining potential is adopted to mimic contraction



New Electronic Parameters

DFTB Method

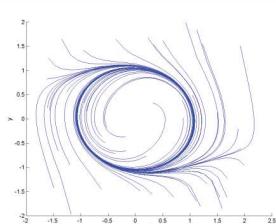


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New Electronic Parameters

DFTB Method

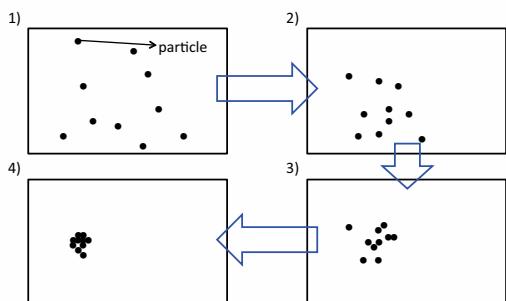
Particle swarm optimization (PSO)



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Particle Swarm Optimization

DFTB Method

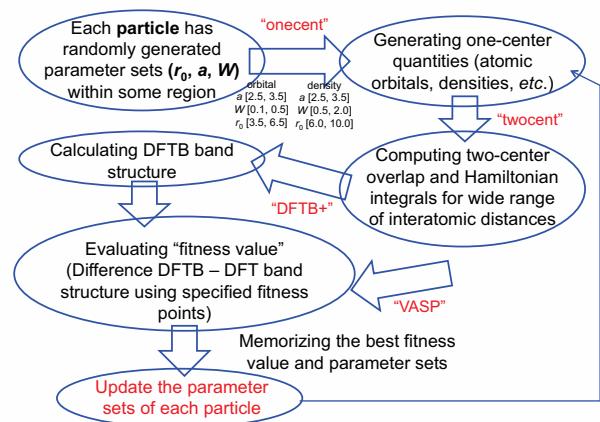


- 1) Particles (=candidate of a solution) are randomly placed initially in a target space.
- 2) – 3) Position and velocity of particles are updated based on the exchange of information between particles and particles try to find the best solution.
- 4) Particles converges to the place which gives the best solution after a number of iterations.

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Particle Swarm Optimization

DFTB Method



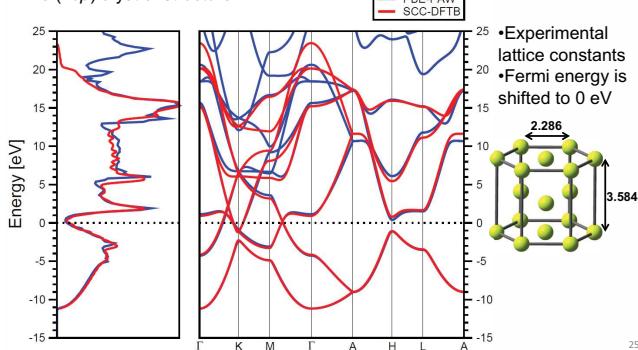
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Electronic Parameters

DFTB Method

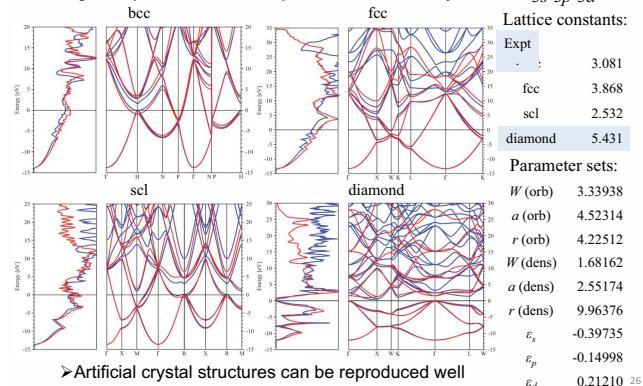
Example: Be, HCP crystal structure

Total density of states (left) and band structure (right) of Be (hcp) crystal structure



Transferability of optimum parameter for different structures

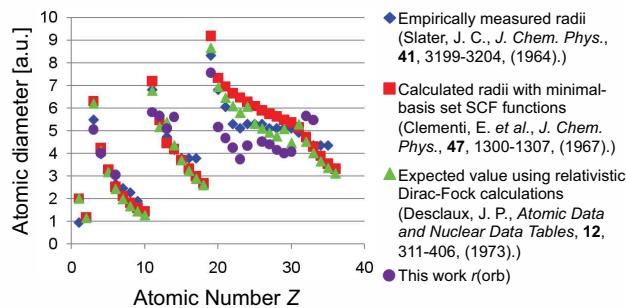
e.g.: Si, parameters were optimized with bcc only



Electronic Parameters

DFTB Method

Correlation of $r(\text{orb})$ vs. atomic diameter

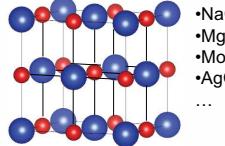


In particular for main group elements, there seems to be a correlation between $r(\text{orb})$ and atomic diameter.

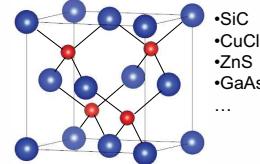
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Binary Systems

Rocksalt (space group No. 225)

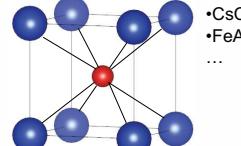


Zincblende (space group No. 216)



DFTB Method

B2 (space group No. 221)



Others

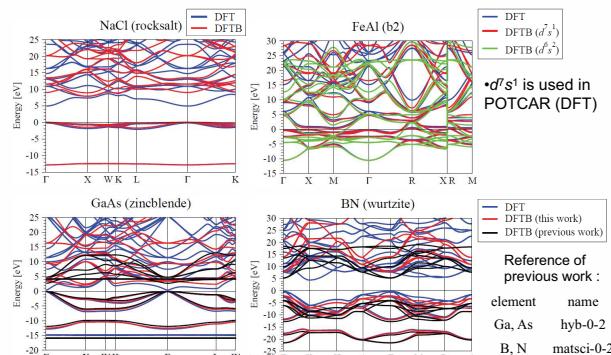
- Wurtzite (BeO, AlO, ZnO, GaN, ...)
- Hexagonal (BN, WC)
- Rhombohedral (ABCABC stacking sequence, BN)

more than 100 pairs tested

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Binary Systems

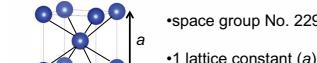
DFTB Method



Further improvement can be performed for specific purpose but this preliminary sets will work as good starting points

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BCC elements



Group Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	
2	3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne										
3	11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar										
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Ta	43 W	44 Re	45 Os	46 Ru	47 Pd	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Au	79 Ho	80 Tl	81 Pb	82 Bi	83 Po	84 At	85 Rn	
7	87 Fr	88 Ra	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uuu	114 Uup	115 Uuh	116 Uus	117 Uuo	118 Uus
*Lanthanoids	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb				
**Actinoids	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No				

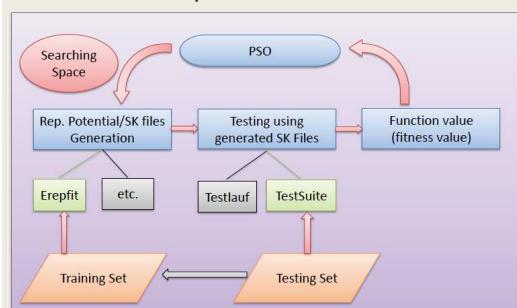
DFTB Method

Erepfit



DFTB Method

Workflow of PSO Optimization for DFTB Repulsive Potential



Overview

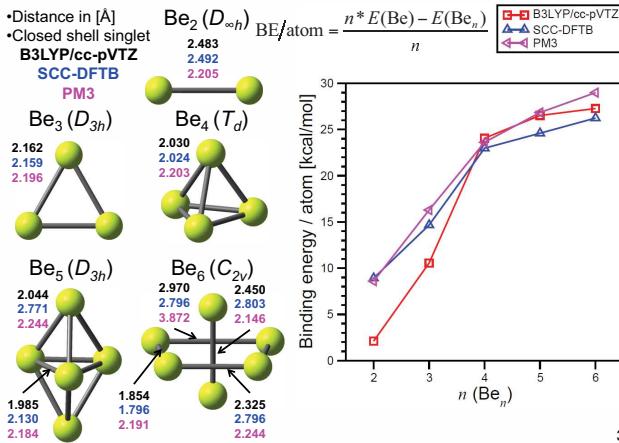
Motivation

DFTB Method

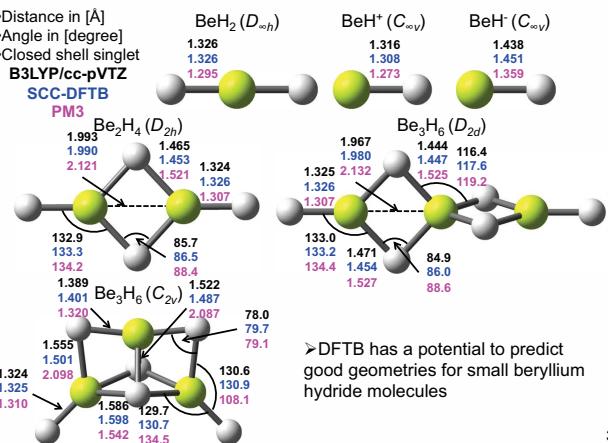
DFTB Parameterization of Be-H/D/T chemical interactions

Accelerating DFTB calculations

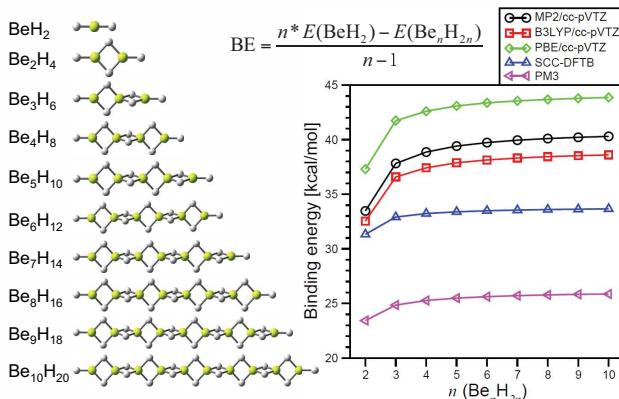
Description of small neutral beryllium clusters



Geometries of beryllium hydride molecules



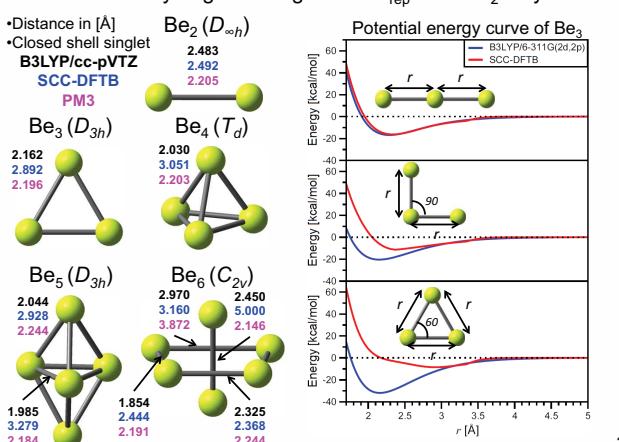
Binding energy of beryllium hydride oligomers



Scaling factor approach

> Discrepancy of DFTB binding energy from DFT or MP2 is reduced compared with other semi-empirical methods (PM3)

Difficulty of generating Be-Be E_{rep} from Be_2 only



Difficulty of generating Be-Be E_{rep} from Be_2 only

- When Be-Be E_{rep} is generated from Be_2 only, it is difficult to describe (even small) neutral beryllium clusters
- Potential curve of Be_3 with different angle indicates that the many body interaction cannot be negligible to form energetically stable clusters

To overcome this issue, two strategies were tested

Strategy1: Taking Be_3 and Be_4 as the reference molecule to yield E_{rep} (results correspond to slide 6-8)

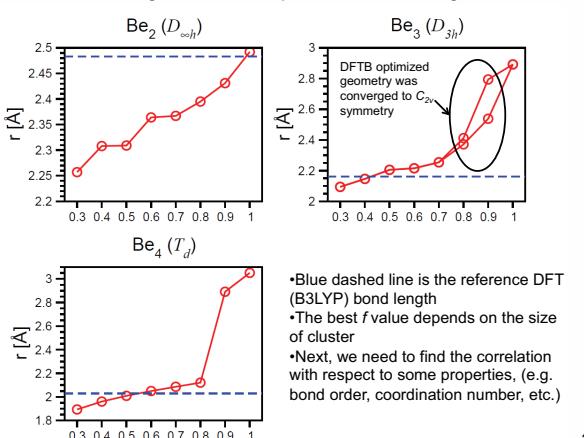
Strategy2: Multiplying scaling factor f to Be_2 E_{rep}

The first question of strategy 2 is;

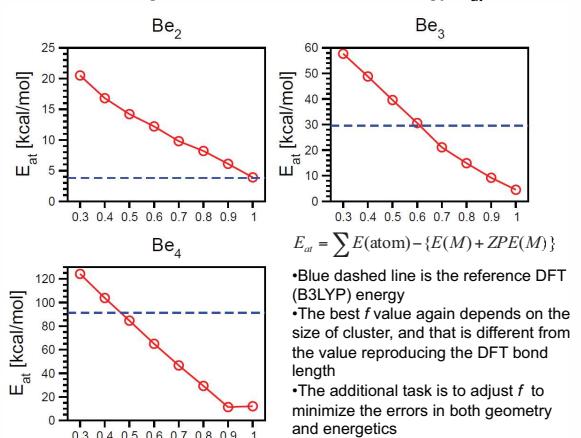
"What is the best value to be multiplied to reproduce DFT geometries and energetics?"

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Scaling factor f vs. optimized bond length



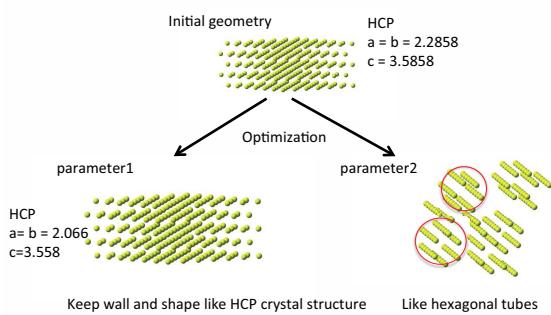
Scaling factor f vs. atomization energy E_{at}



Benchmark

DFTB Application

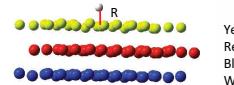
DFTB Application



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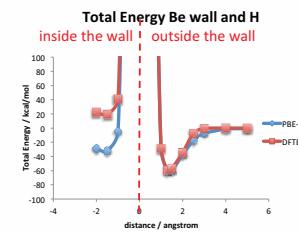
Beryllium wall/Hydrogen system w/ parameter 1

...Checking the potential energy surface of Be wall/H system



Number of beryllium atoms : 75
(5x5x3)
Geometry : hcp $a=b=2.066\text{\AA}$
 $c=3.558\text{\AA}$
K points = 3x3x1

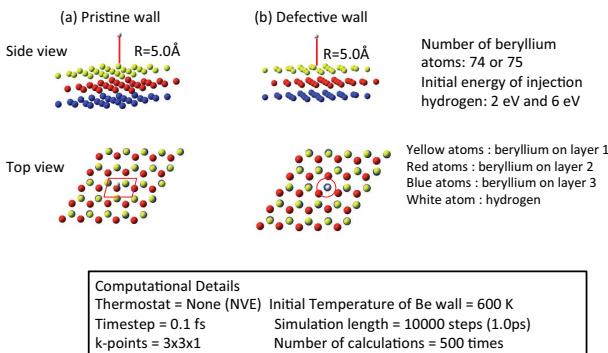
Differences between
DFTB and DFT are up to
2 eV, small compared to
plasma energies(100 eV).



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MD simulations

DFTB Application

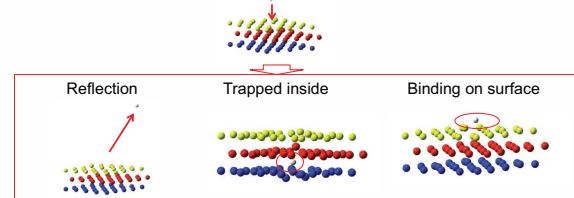


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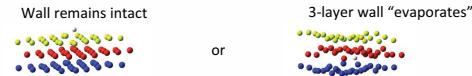
MD simulations

DFTB Application

Three different events concerning H atom occurred:



Two different wall behaviors for each of these three H events:

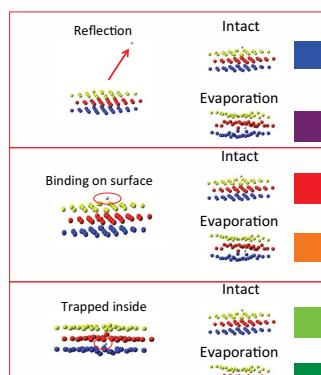
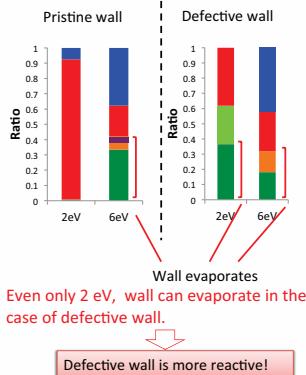


Thus, there are 6 categories of results.

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MD simulations

DFTB Application



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Summary

DFTB Application

- In the case of surface vacancy defects, the wall becomes more reactive and even at 2 eV, the wall can evaporate.

Future Plan

- To use this simulation for Be/D or T system.
- Compare results of SCC-DFTB method with that of non-SCC-DFTB method.

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Overview

Motivation

DFTB Method

DFTB Parameterization of Be-H/D/T chemical interactions

Accelerating DFTB calculations

Faster O(N) DFTB

Recent DFTB Developments

What is Fragment Molecular Orbital (FMO)?



FMO is a fragment-based MO method for large molecules.

Several fragment-based methods have been proposed. A brief review is given in Fedorov & Kitaura, Chapter 1 in "Modern Methods for Theoretical Physical Chemistry of Biopolymers", E. Starikov J. Lewis S. Tanaka, Eds, Elsevier (2006).

D. Fedorov
(AIST)

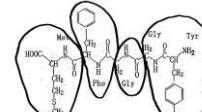


K. Kitaura
(AICS)

- A molecule is divided into N fragments and *ab initio* MO calculations on the fragments (monomers) and fragment pairs (dimers) are performed under electrostatic potential from other monomers.

- The total energy of a molecule (E) is calculated using the energies of the monomer (E_i) and dimer (E_{ij});

$$E = \sum E_i + \sum (E_{ij} - E_i - E_j)$$



Advantage of the method:

- reproduces *ab initio* properties with good accuracy,
- is efficient on massively parallel computers.

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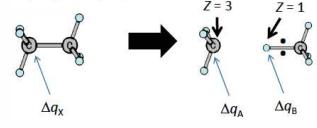
Faster O(N) DFTB

Recent DFTB Developments

Implementation of FMO-DFTB



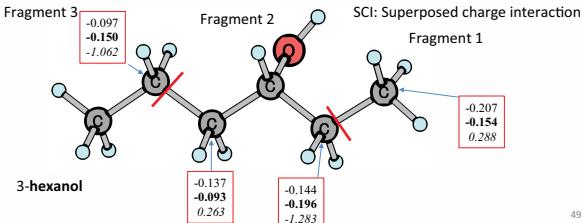
D. Fedorov (AIST)
Y. Nishimoto



Full SCC-DFTB (reference) : -18.9190503342 H
FMO-DFTB with SCI : -18.9190404398 H (+0.006 kcal/mol error)

FMO-DFTB without SCI : -18.9169093952 H (+1.34 kcal/mol error)

SCI: Superposed charge interaction

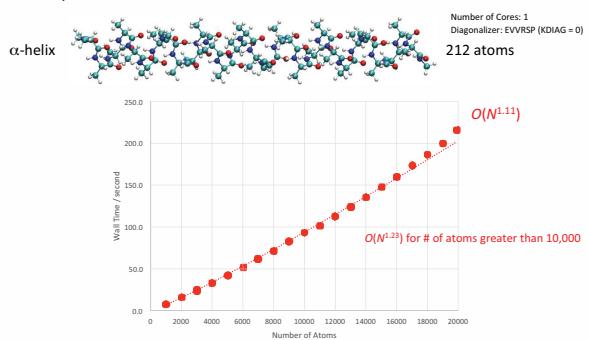


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Faster O(N) DFTB

Recent DFTB Developments

Not only for molecular clusters

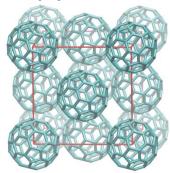


One core calculations worked (scaled) reasonably linear.

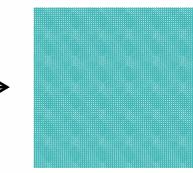
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Faster O(N) DFTB

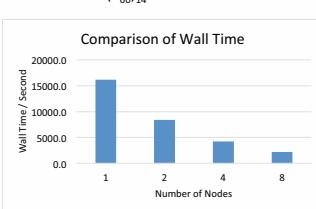
Recent DFTB Developments



Face centered cubic (FCC)
 $a = 14.04 \text{ \AA}$
Unit cell : $(C_{60})_{14} = 840 \text{ atoms}$



2 dimensional 40x40 fullerite
 $(C_{60})_{9842} = 590,520 \text{ atoms}$

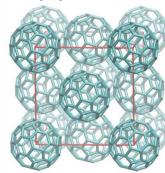


* 8 node calculation is 7.5 times faster than 1 node calculation

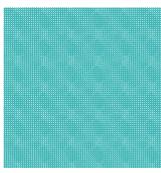
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Faster O(N) DFTB

Recent DFTB Developments



Face centered cubic (FCC)
 $a = 14.04 \text{ \AA}$
Unit cell : $(C_{60})_{14} = 840 \text{ atoms}$



2 dimensional 53x53 fullerite
 $(C_{60})_{17174} = 1,030,440 \text{ atoms}$

-1772909.858261038 Hartree

Single point with 8 nodes :: 4,993 seconds
Single point + gradient with 8 nodes :: 14,301 seconds
Geometry optimization possible.

One million atom calculation is manageable.

Summary

- Inter-node parallel calculations were done
- Achieved 7.5 times speed-up with 8 nodes
- One million atom calculation is manageable.

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Excited States ΔDFTB

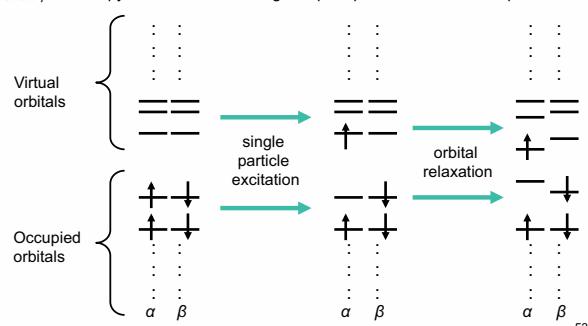
Recent DFTB Developments



Tim Kowalczyk

Prelude to ΔDFTB: review of the ΔSCF concept

Solve the SCF equations – Hartree-Fock or Kohn-Sham – but always occupy the orbitals according to a pre-specified **non-Aufbau** pattern:



Excited States ΔDFTB

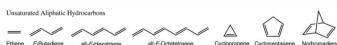
Recent DFTB Developments

Performance of ΔDFTB: S₁ states of small dyes

Excited States ΔDFTB

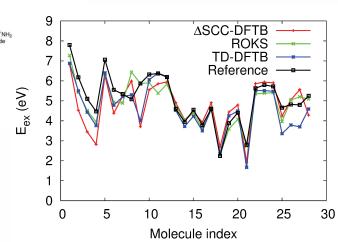
Recent DFTB Developments

Performance of ΔDFTB: S₁ states of small dyes



28 small-molecule test set of Thiel and co-workers

Silva-Junior et al. (2008) J. Chem. Phys. 129, 104103



- Worst performance is for polyenes
- Major improvement over TD-DFTB for 3 of 4 nucleobases

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Excited States ΔDFTB

Recent DFTB Developments

Performance of ΔDFTB: S₁ states of small dyes

Method	Mean Error	Mean Abs Error	RMSD
ROKS	-0.23	0.40	0.50
TD-DFT	-0.02	0.25	0.37
TD-DFTB	-0.47	0.52	0.70
ΔDFTB	-0.33	0.67	0.87
ΔSCF	-0.15	0.75	0.95

... ΔSCF worse than ΔDFTB? We are probably landing on some wrong states!

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