Introduction to the Density-Functional Tight-Binding (DFTB) Method

Part II

Density-Functional Tight-Binding (DFTB) as fast approximate DFT method


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Density-Functional Tight-Binding

Part I

1. Tight-Binding
2. Density-Functional Tight-Binding (DFTB)

Part II

3. Bond Breaking in DFTB
4. Extensions
5. Performance and Applications

Density-Functional Tight-Binding

Part I

1. Tight-Binding
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Part II

3. **Bond Breaking in DFTB**
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5. Performance and Applications

SCC-DFTB and SDFTB Dissociation of H_2^+

$$E_{SDFTB} = \sum_{\sigma=\uparrow,\downarrow} \sum_{i}^{MO} n_{i\sigma} \langle \psi_{i\sigma} | \hat{H}[\rho_0] | \psi_{i\sigma} \rangle + \frac{1}{2} \sum_{\alpha\beta}^{N} \gamma_{\alpha\beta} \Delta q_\alpha \Delta q_\beta + \frac{1}{2} \sum_{\alpha}^{N} \sum_{l\in\alpha} \sum_{l'\in\alpha} p_{\alpha l} p_{\alpha l'} W_{\alpha l l'} + E_{rep}$$

H^+: (no electron):

$$E_{SDFTB} = 0 + \frac{1}{2} \gamma_{HH} \Delta q_H \Delta q_H + 0 + 0 = \frac{1}{2} 0.4195 * 1 * 1 = 0.20975\ h \neq 0$$

Energy without electrons in an electronic structure method

H: (one electron) (spin-polarized SCC-DFTB):

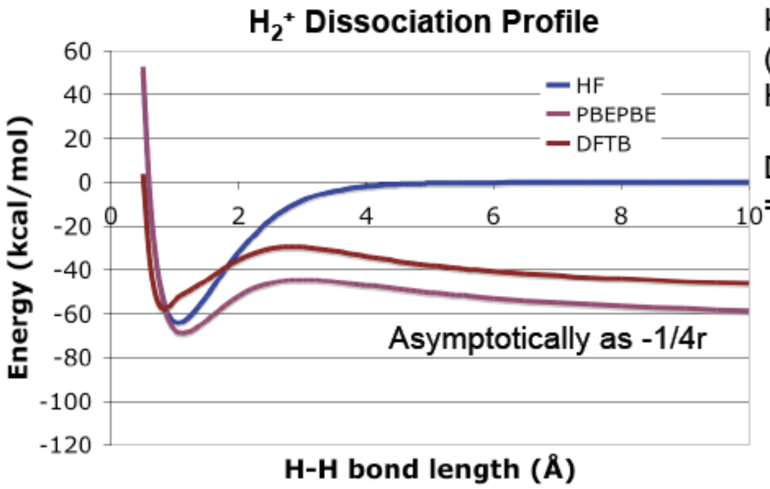
$$E_{SDFTB} = \varepsilon_i + \frac{1}{2} * 1 * 1 * W_{Hss} = -0.2386 + \frac{1}{2} * (-0.072) = -0.2746\ h$$

Ionization Potential of H (IP_H) = E(H+) - E(H) = 0.5 h

Spin-polarized SDFTB: IP_H = 0.4821 h (error of 11.2 kcal/mol)
SCC-DFTB: IP_H = 0.4461 h (error of 33.8 kcal/mol)

Spin-polarized SDFTB is qualitatively correct for H^+, H (and also H^-)

SCC-DFTB and SDFTB Dissociation of H_2^+



HF exact for 1-electron system (in basis set limit)
Here cc-pVTZ for HF and DFT

Dissociation limit = $E(H) + E(H^+)$
= Reference energy (0 kcal/mol)

Intrinsic dissociation error:
DFTB: ~54 kcal/mol
PBEPBE: ~67 kcal/mol
Artificial stabilization of $H^{0.5+} + H^{0.5+}$

In most DFT functionals, the electron unphysically interacts with its own density (i.e. self-interaction error - SIE). This error can contribute to:

- Incorrect dissociation limits for systems with unpaired electrons (e.g. H_2^+)
- Underestimation of transition state barriers (of simple organic reactions)
- Exaggerated delocalization in conjugated systems
- Too low energy of charge-transfer excitations

SCC-DFTB and SDFTB Dissociation of H_2^+

$$E_{SDFTB} = \sum_{\sigma=\uparrow\downarrow} \sum_{i}^{MO} n_{i\sigma} \langle \psi_{i\sigma} | \hat{H}[\rho_0] | \psi_{i\sigma} \rangle + \frac{1}{2} \sum_{\alpha\beta}^{N} \gamma_{\alpha\beta} \Delta q_\alpha \Delta q_\beta + \frac{1}{2} \sum_{\alpha}^{N} \sum_{l\in\alpha} \sum_{l'\in\alpha} p_{\alpha l} p_{\alpha l'} W_{\alpha l l'} + E_{rep}$$

Error in dissociation energy at infinite distance:

$$E_{SDFTB}(H + H^+) = \varepsilon_i + \frac{1}{2} W_{Hss} + \frac{1}{2} \gamma_{HH} \quad \text{(correct)}$$

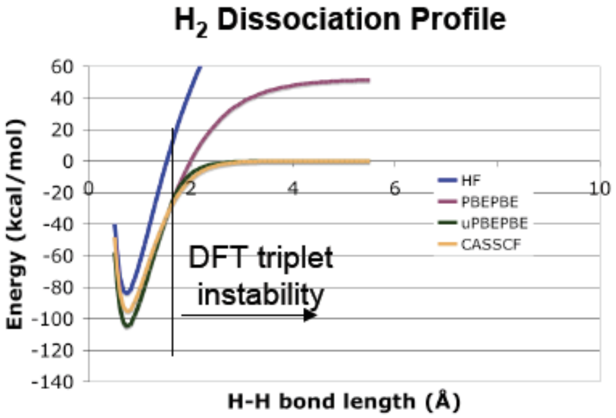
$$E_{SDFTB}(H^{0.5^+} + H^{0.5^+}) = \frac{1}{2} 2\varepsilon_i + \frac{1}{2} 0.5 * 0.5 W_{Hss} * 2 + \frac{1}{2} 0.5 * 0.5 \gamma_{HH} * 2 = \varepsilon_i + \frac{1}{4} W_{Hss} + \frac{1}{4} \gamma_{HH}$$

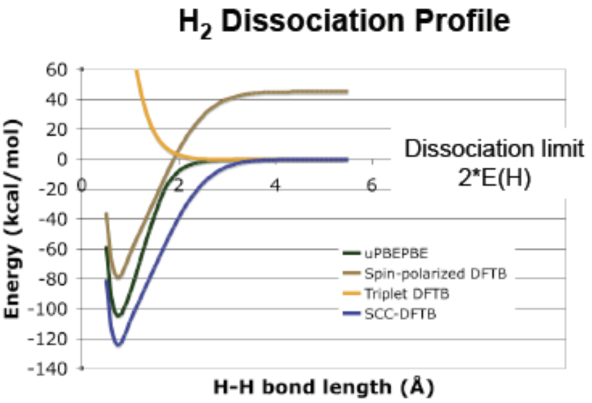
(wrong)

$$Error(SDFTB) = E_{SDFTB}(H + H^+) - E_{SDFTB}(H^{0.5^+} + H^{0.5^+}) = \frac{1}{4} W_{Hss} + \frac{1}{4} \gamma_{HH}$$

Error in dissociation energy of H_2^+
Spin-polarized DFTB: (0.4195/4-0.072/4)=0.086875 h = 54.5 kcal/mol
Normal SCC-DFTB: 0.4195/4 = -0.104875 = 65.8 kcal/mol

SCC-DFTB and SDFTB Dissociation of H_2





Triplets: αα ββ αβ+βα
Singlet = αβ-βα
UDFT singlet: αβ = 1/2[(αβ- βα) + (αβ+βα)]
Correct energy limit by triplet spin-contamination

Atoms are spin polarized, but H_2 (singlet) does not include spin-polarization at any distance. No UDFTB solution
SCC-DFTB energy is better but has α/2+ β/2 electrons at each nuclei.
No DFTB method can give qualitatively correct dissociation curve

M. Lundberg, Y. Nishimoto, SI, *Int. J. Quant. Chem.* **112**, 1701 (2012)

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4. **Extensions**
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Analytical Hessian for DFTB and SCC-DFTB

H. A. Witek, S. Irle, K. Morokuma, *J. Chem. Phys.* **121**, 5163 (2005)

$$G_{ab}^{\mathrm{DFTB}} = \frac{\partial^2 E_{\mathrm{rep}}}{\partial a \partial b} + 2\sum_{im}^{\mathrm{MO}} n_i \sum_{\mu\nu}^{\mathrm{AO}} U_{mi}^{b} c_{\mu m} c_{\nu i} \left[\frac{\partial H_{\mu\nu}^{0}}{\partial a} - \varepsilon_i \frac{\partial S_{\mu\nu}}{\partial a} \right] +$$

$$+ \sum_{i}^{\mathrm{MO}} n_i \sum_{\mu\nu}^{\mathrm{AO}} c_{\mu i} c_{\nu i} \left[\frac{\partial^2 H_{\mu\nu}^{0}}{\partial a \partial b} - \varepsilon_i \frac{\partial^2 S_{\mu\nu}}{\partial a \partial b} - \frac{\partial \varepsilon_i}{\partial b} \frac{\partial S_{\mu\nu}}{\partial a} \right]$$

$$G_{ab}^{\mathrm{SCC\text{-}DFTB}} = \frac{\partial^2 E_{\mathrm{rep}}}{\partial a \partial b} + 2\sum_{im}^{\mathrm{MO}} n_i \sum_{\mu\nu}^{\mathrm{AO}} U_{mi}^{b} c_{\mu m} c_{\nu i} \left[\frac{\partial H_{\mu\nu}^{0}}{\partial a} + \left(\frac{1}{2} \sum_{K}^{\mathrm{atoms}} (\gamma_{MK} + \gamma_{NK}) \Delta q_K - \varepsilon_i \right) \frac{\partial S_{\mu\nu}}{\partial a} \right] +$$

$$+ \sum_{i}^{\mathrm{MO}} n_i \sum_{\mu\nu}^{\mathrm{AO}} c_{\mu i} c_{\nu i} \left[\frac{\partial^2 H_{\mu\nu}^{0}}{\partial a \partial b} + \left(\frac{1}{2} \sum_{K}^{\mathrm{atoms}} (\gamma_{MK} + \gamma_{NK}) \Delta q_K - \varepsilon_i \right) \frac{\partial^2 S_{\mu\nu}}{\partial a \partial b} \right] -$$

$$- \sum_{i}^{\mathrm{MO}} n_i \sum_{\mu\nu}^{\mathrm{AO}} c_{\mu i} c_{\nu i} \left[\frac{\partial \varepsilon_i}{\partial b} - \frac{1}{2} \sum_{K}^{\mathrm{atoms}} \left(\frac{\partial \gamma_{MK}}{\partial b} + \frac{\partial \gamma_{NK}}{\partial b} \right) \Delta q_K - \frac{1}{2} \sum_{K}^{\mathrm{atoms}} (\gamma_{MK} + \gamma_{NK}) \frac{\partial \Delta q_K}{\partial b} \right] \frac{\partial S_{\mu\nu}}{\partial a} +$$

$$+ \sum_{K}^{\mathrm{atoms}} \frac{\partial^2 \gamma_{AK}}{\partial a \partial b} \Delta q_A \Delta q_K + \sum_{K}^{\mathrm{atoms}} \frac{\partial \gamma_{AK}}{\partial a} \frac{\partial \Delta q_A}{\partial b} \Delta q_K + \sum_{K}^{\mathrm{atoms}} \frac{\partial \gamma_{AK}}{\partial a} \Delta q_A \frac{\partial \Delta q_K}{\partial b}$$

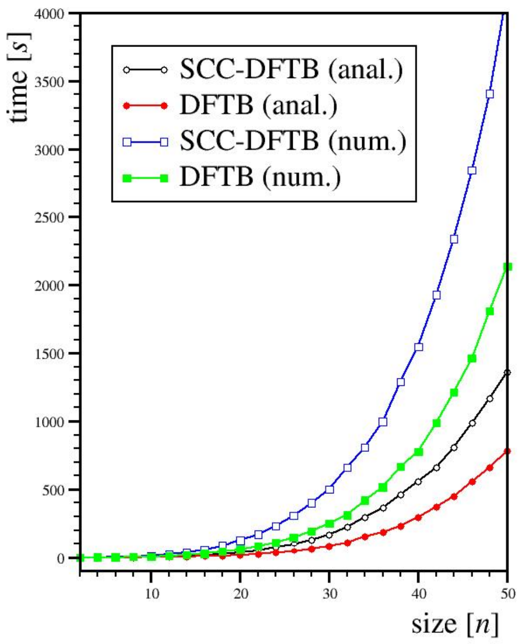
Coupled Perturbed SCC-DFTB Equations

- To determine response of molecular orbitals to nuclear perturbation, one has to solve a set of iterative coupled-perturbed SCC-DFTB equations

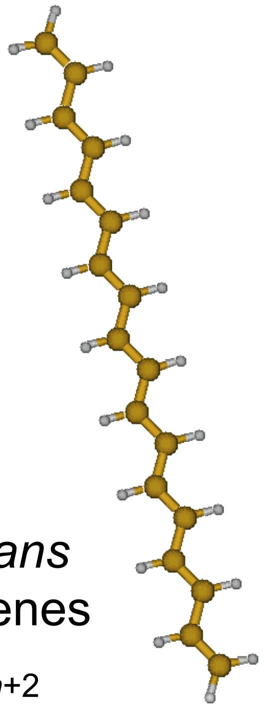
$$\begin{cases} U_{ij}^{b} = \dfrac{1}{\varepsilon_j - \varepsilon_i} \displaystyle\sum_{\mu\nu}^{\mathrm{AO}} c_{\mu i} c_{\nu j} \left[\frac{\partial H_{\mu\nu}^{0}}{\partial b} + \left(\frac{1}{2} \sum_{K}^{\mathrm{atoms}} (\gamma_{MK} + \gamma_{NK}) \Delta q_K - \varepsilon_i \right) \frac{\partial S_{\mu\nu}}{\partial b} + \right. \\ \qquad - \\ \qquad \left. + \dfrac{1}{2} S_{\mu\nu} \displaystyle\sum_{K}^{\mathrm{atoms}} \left(\frac{\partial \gamma_{MK}}{\partial b} + \frac{\partial \gamma_{NK}}{\partial b} \right) \Delta q_K + \frac{1}{2} S_{\mu\nu} \sum_{K}^{\mathrm{atoms}} (\gamma_{MK} + \gamma_{NK}) \frac{\partial \Delta q_K}{\partial b} \right] \\ \dfrac{\partial \Delta q_K}{\partial b} = \displaystyle\sum_{i}^{\mathrm{MO}} n_i \sum_{\mu \in K}^{\mathrm{AO}} \sum_{\nu} \left[c_{\mu i} c_{\nu i} \frac{\partial S_{\mu\nu}}{\partial b} + \sum_{m}^{\mathrm{MO}} U_{mi}^{b} \left(c_{\mu m} c_{\nu i} + c_{\mu i} c_{\nu m} \right) S_{\mu\nu} \right] \end{cases}$$

Frequency calculations

performance test



all-*trans* polyenes C_nH_{n+2}



How to treat van der Waals interactions cheaply?

Addition of empirical **London dispersion** term!

$$E_{tot} = E_{QM} - \Sigma_{\alpha\beta} f\,(R_{\alpha\beta})\ \ C_6^{\alpha\beta}\ \ /R^6_{\alpha\beta}\ (+1/R^8_{\alpha\beta}\text{ etc. terms})$$

$f\,(R_{\alpha\beta})$: damping function

Fritz London
$1/R^6$: 1922

- Ahlrichs *et al.,* Chem. Phys. **19**, 119 (1977): **HFD** (Hartree-Fock Dispersion), $\mathbf{C_i}$ parameters from **expt.**
- Mooij *et al.,* J. Phys. Chem. A **103**, 9872 (1999): PES with London dispersion, $\mathbf{C_6}$ parameters from **MP2** calculations
- Elstner *et al.,* J. Chem. Phys. **114**, 5149 (2001): **SCC-DFTB-D** (dispersion-augmented SCC-DFTB), C_6 parameters via Halgren,J. Am. Chem. Soc. **114**, 7872 (1992) from expt.
- Yang *et al.,* J. Chem. Phys. **116**, 515 (2002): **DFT+vdW** (DFT including van der Waals interactions), C_6 parameters from expt.
- Grimme, J. Comput. Chem. **25**, 1463 (2004): **DFT-D**, C_6 parameters from expt.
- … several more plus many reviews and benchmarks

London Dispersion

- No overlapping densities
- Interaction of two polarisable objects

$$E_{London} = -\frac{2}{3}\frac{I_1 I_2}{I_1 + I_2}\alpha_1 \alpha_2 \frac{1}{r^6}$$

London, F.; Z. Physik 1930, 63, 245.

Well-known application: Lennard-Jones potential:

$$E_{Lennard-Jones} = \boxed{\frac{C_{12}}{r^{12}}} - \boxed{\frac{C_6}{r^6}}$$

short-range repulsion long-range attraction

DFTB+Dispersion

Elstner *et al.*, JCP **114**, 5149 (2001)

$$E_{tot} = E_{DFTB} + \sum_{i<j} E_{dispersion}(i,j)$$

$$E_{dispersion}(i,j) = -\frac{1}{r_{ij}^{\;6}} f \;\; * C_6(i,j),$$

$$f = \left(1 - \exp\left(-3.0 * \left(\frac{r_{ij}}{R_{ij,vdw}}\right)^7\right)\right), \text{damping function}$$

$$R_{ij,vdw} = \frac{R_{i,vdw}^3 + R_{j,vdw}^3}{R_{i,vdw}^2 + R_{j,vdw}^2}, \text{ cubic mean rule}$$

$$C_6(i,j) = \frac{3}{2} * \frac{\alpha_i \alpha_j}{(\alpha_i / N_i)^{1/2} + (\alpha_j / N_j)^{1/2}}$$

α_i, α_j: atomic polarizability parameer

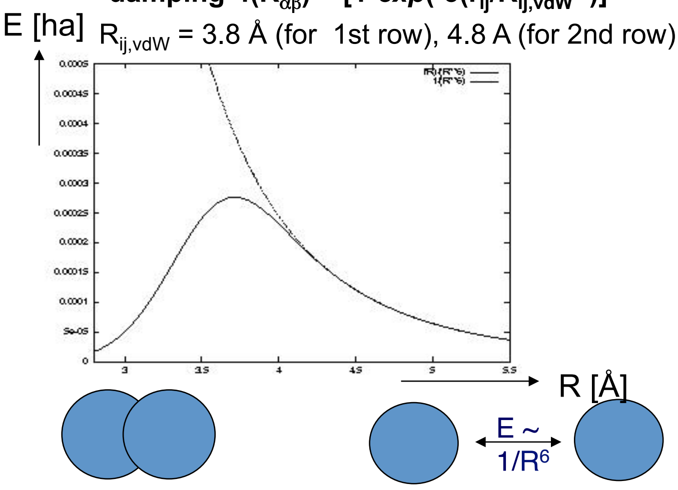
N_i, N_j: Slater Kirkwood effective number of electrons

DFTB+Dispersion

Elstner *et al.*, JCP **114**, 5149 (2001)

damping $f(R_{\alpha\beta}) = [1-exp(-3(r_{ij}/R_{ij,vdW})^7)]^3$

$R_{ij,vdW}$ = 3.8 Å (for 1st row), 4.8 A (for 2nd row)



DFTB-D choice of C_6 parameters:

- generally hybridization dependent (i.e. not simply atomic values)

- use “empirical” values for parameters to match BSSE-corrected MP2 interaction energies

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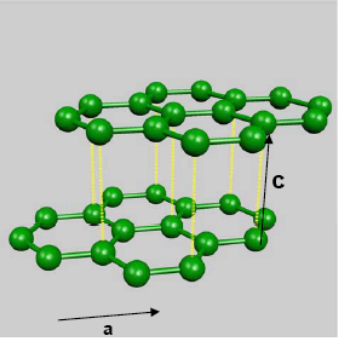
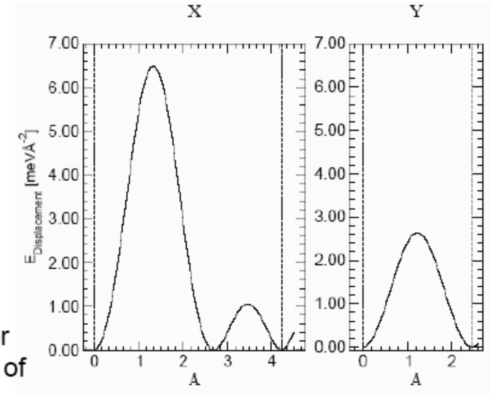
Application to Graphite



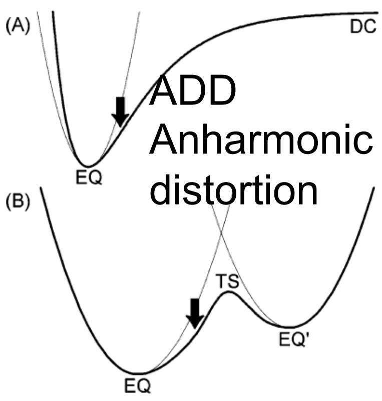
	DFTB-D	Experiment
a	2.45Å	2.45Å
c	3.38Å	3.35Å
bulk modulus	330 GPa	318 ±11GPa



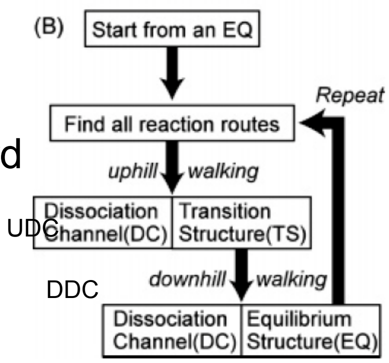
Energy change for lateral movement of graphite layers

GRRM with DFTB

Principles of GRRM



ADD
Anharmonic downward distortion

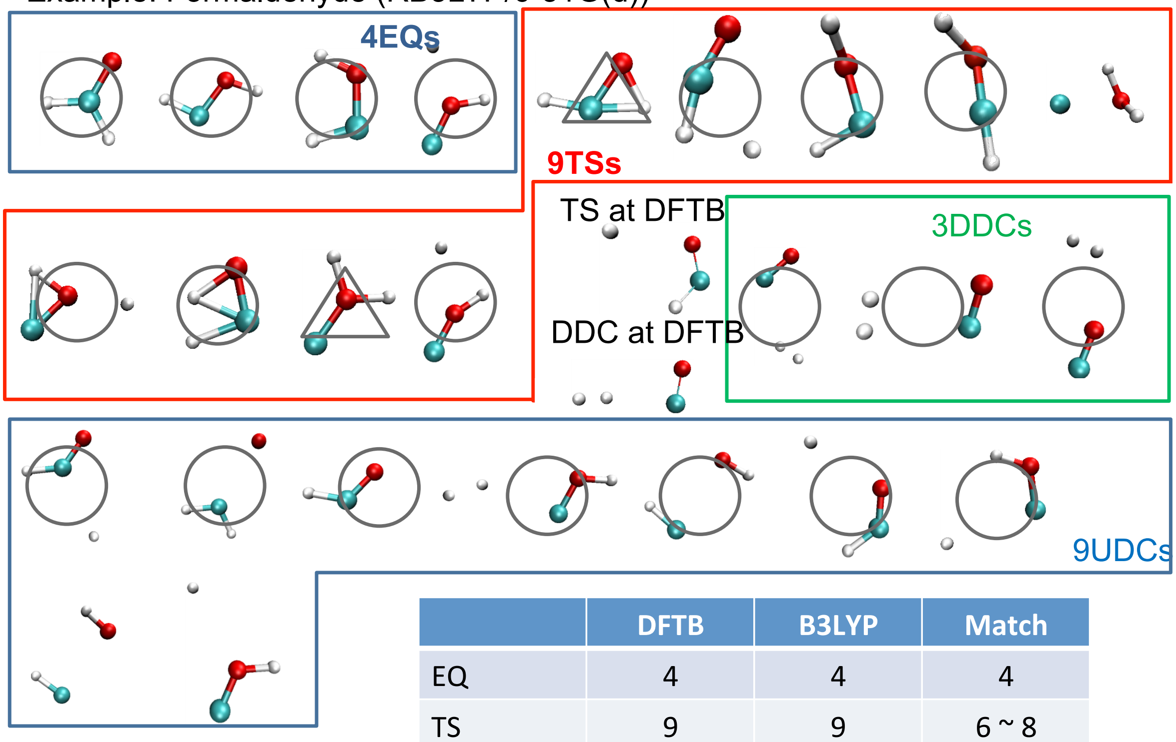


S. Maeda and K. Ohno, *J. Phys. Chem. A*, **2005**, *109*, 5742.

One of the most powerful and reliable methods to find reaction pathways.

Y. Nishimoto and S. Irle, in preparation

Example: Formaldehyde (RB3LYP/6-31G(d))



	DFTB	B3LYP	Match
EQ	4	4	4
TS	9	9	6 ~ 8
DDC	4	3	3
UDC	7	9	7

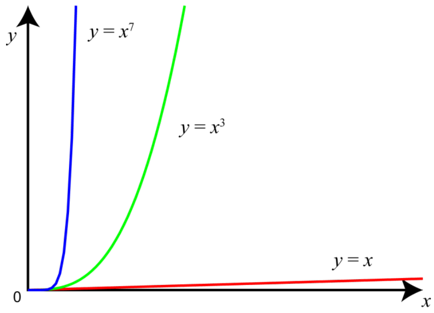
○ : Reproduced by DFTB
△ : Found

FMO-DFTB

Motivation

Want to perform quantum mechanical (QM) calculation of **large systems**

However, problem is the scaling of QM calculations … QM calculations scale $N^3 \sim N^7$



We need a method which scales **linearly** with **cheap** computational cost (yet QM)

What can we do?

1) Linear scaling method: fragment molecular orbital (FMO), divide-and-conquer (DC), generalized energy-based fragmentation (GEBF) …
2) Cheap QM method → semi-empirical QM
   MNDO, PM3, PM6, AM1, ZINDO, DFTB …

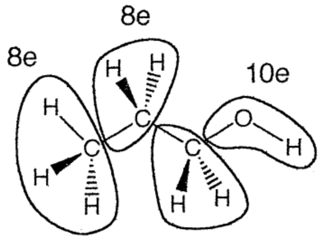
FMO-DFTB

Concept of FMO-DFTB

1) Divide a large system to a set of fragments

Fragment molecular orbital method (FMO)

Kitaura, K.; Ikeo, E.; Asada, T.; Nakano, T.; Uebayashi, M. *Chem. Phys. Lett.* **1999**, *313*, 701-706.



FMO-DFTB

2) Use a semi-empirical method

Density-functional tight-binding method (DFTB)

Elstner, M.; Porezag, D.; Jungnickel, G.; Elsner, J.; Haugk, M.; Frauenheim, T.; Suhai, S.; Seiferg, G. *Phys. Rev. B* **1998**, *58*, 7260-7268.

$$E^{\mathrm{SCC}} = \sum_i \sum_{\mu\nu} n_i c^*_{\mu i} c_{\nu i} H^0_{\mu\nu} + \sum_{A>B} E^{\mathrm{rep}}_{AB} + \frac{1}{2} \sum_{AB} \gamma_{AB} \Delta q_A \Delta q_B$$

FMO-DFTB Theory

Calculate the molecular energy by the sum of internal energies of monomers and dimers:

$$E = \sum_{I}^{N} E'_I + \sum_{I>J}^{N} (E'_{IJ} - E'_I - E'_J) + \sum_{I>J}^{N} \Delta E^V_{IJ} \qquad \text{(FMO2)}$$

where internal energy is defined by

$$E'_X = \sum_{i \in X} \sum_{\mu\nu \in X} n_i^X c_{\mu i}^{X*} c_{\nu i}^X H_{\mu\nu}^{0,X} + \sum_{A>B \in X} E_{AB}^{\mathrm{rep}} + \frac{1}{2} \sum_{AB \in X} \gamma_{AB} \Delta q_A^X \Delta q_B^X$$

Additionally, we need the coupling of the charge transfer to the embedding potential:

$$\Delta E^V_{IJ} = \sum_{A \in IJ} \sum_{K \notin I,J}^{N} \sum_{C \in K} \gamma_{AC} \Delta\Delta q_A^{IJ} \Delta q_C^K$$

FMO-DFTB Hamiltonian is defined by

$$H_{\mu\nu}^X = H_{\mu\nu}^{\mathrm{SCC},X} + V_{\mu\nu}^X + P_{\mu\nu}^X$$

where $V_{\rho\sigma}^X = \frac{1}{2} S_{\rho\sigma}^X \sum_{K \neq X}^{N} \sum_{D \in K} (\gamma_{AD} + \gamma_{BD}) \Delta q_D^K$, and $P_{\mu\nu}^X$ is the projection operator.

Nishimoto, Y.; Fedorov, D. G.; Irle, S. submitted.

FMO-DFTB ES-DIM

Electrostatic Dimer (ES-DIM)* Approximation

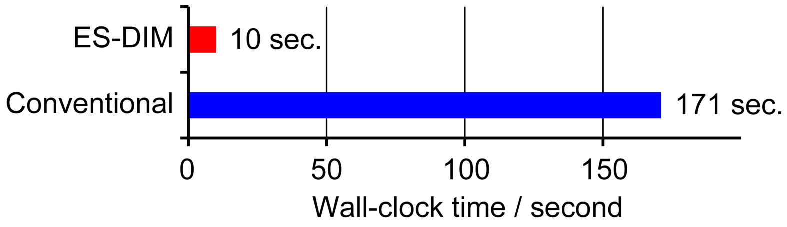
* Nakano, T. *et al. Chem. Phys. Lett.* **2002**, *351*, 475-480.

For separated pairs (dimers), we introduce the electrostatic dimer approximation:

$$E'_{IJ} \approx E'_I + E'_J + \sum_{A \in I} \sum_{B \in J} \gamma_{AB} \Delta q_A^I \Delta q_B^J \quad \longrightarrow$$

No SCF calculation

The loss of energy with ES-DIM approximation is only 1.02×10^{-3} kcal/mol for extended COMe-$(\mathrm{Ala})_{200}$-NHMe (2,012 atoms)



ES-DIM approximation saves computational cost dramatically without loss of accuracy.

FMO-DFTB

Orbital Projection

Projection operator works for DFTB too!

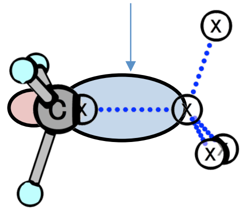
T. Nagata *et al. Chem. Phys. Lett.* **2010**, *492*, 302.

$$P_{\mu\nu} = B\sum_i \langle\mu|\theta_i\rangle\langle\theta_i|\nu\rangle$$

$$= \sum_i\sum_{\lambda\sigma} B\tilde{c}_{\lambda i}\langle\mu|\lambda\rangle\langle\sigma|\nu\rangle\tilde{c}^*_{\sigma i}$$

$$= B\sum_{\lambda\sigma}\tilde{D}_{\lambda\sigma}\underbrace{S_{\mu\lambda}S_{\sigma\nu}}_{\text{DFTB has overlap matrix parameters!}}$$

This (hybrid) p orbital should be removed



$\tilde{D}_{\lambda\sigma}$: weighted density matrix of hybrid orbital

↓

We need to prepare localized orbitals

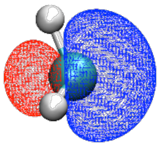
In DFTB, **Pipek-Mezey localization** is the logical choice.

Pipek-Mezey localization: maximize the sum of Mulliken charges

Pipek, J. *et al. J. Chem. Phys.* **1989**, *90*, 4916.

"projected out" orbital

$\psi_7{}^*$



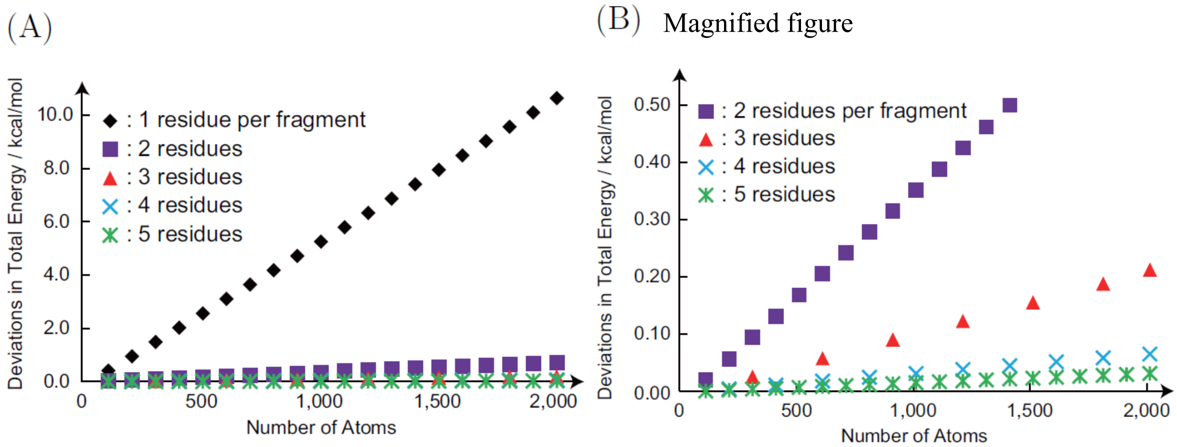
ε_7 = +2.721*10^7 eV ≈ "*B*" constant value

FMO-DFTB

Accuracy

Accuracy of FMO-DFTB: Energy

The energy difference between full SCC-DFTB and FMO-DFTB with extended poly-alanine

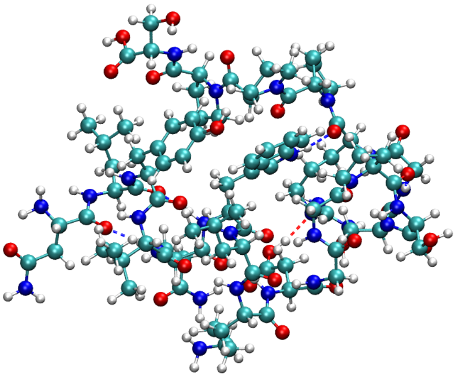


Error is less than 1 kcal/mol for 2,000 atom system (with more than 2 residues per fragment)

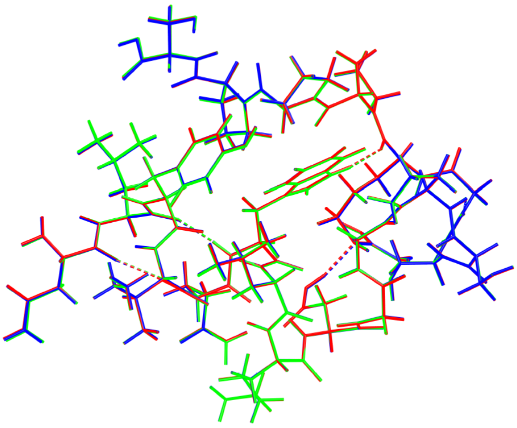
FMO-DFTB Accuracy

Accuracy of FMO-DFTB: Geometries

Geometry optimization of neutralized 1L2Y protein (Trp-cage / 20 residues)



Blue : Full calculation
Red : FMO-DFTB (1), RMSD = 0.067 Å
Green : FMO-DFTB (2), RMSD = 0.044 Å



FMO-DFTB (1) :: 1 residue per fragment
FMO-DFTB (2) :: 2 residues per fragment

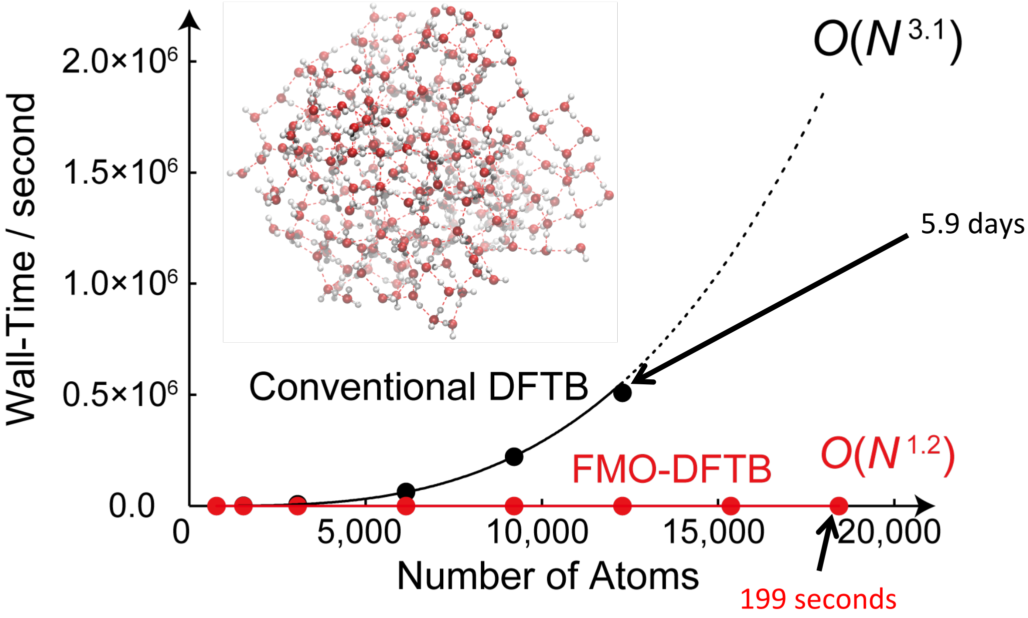
Error of total energy is 1.20 and 0.82 kcal/mol

FMO-DFTB well reproduced the optimized geometry of full calculation

FMO-DFTB Timing

Wall-clock time and scaling of FMO-DFTB vs. DFTB

Wall-clock time with 1 CPU core (Xeon E5-2650)

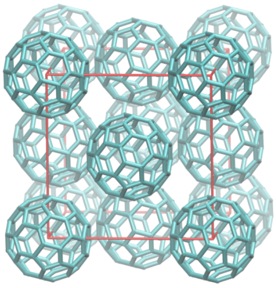


Scaling of FMO-DFTB (for 3D system) is close to linear

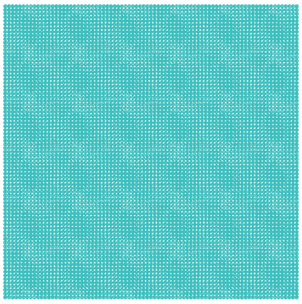
FMO-DFTB Parallelism

Inter-Node Parallel Calculation

FMO-DFTB is parallelized similar to conventional FMO with generalized distributed data interface (GDDI)



40 x 40 →



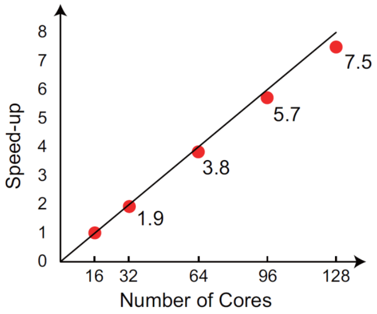
Face centered cubic (FCC)
a = 14.04 Å
Unit cell : $(C_{60})_{14}$ = 840 atoms

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

Calculation on 1 node (16 CPU cores) took **4.5** hours

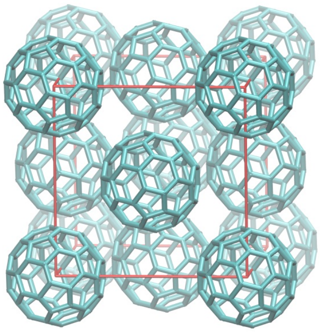
→ Finished in **0.6** hour with 8 nodes (128 CPUs)

Parallel efficiency (up to 8 nodes) = 93.8 %

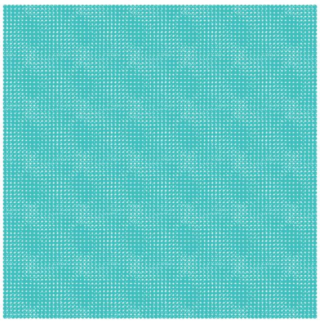


FMO-DFTB Application

Demonstration with FMO-DFTB



53 x 53 →



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

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

Geometry optimization at FMO-DFTB … Converged after 16 cycles in about 4 days

Total energy = -1772910.025319218 Hartree (1.8 million Hartree)

Geometry optimization at FMO-DFTB-D (+1.5 % wall time) … Converged after 60 cycles

Total energy = -1764778.120171755 Hartree (1.8 million Hartree)

Geometry optimization of million atom system is manageable

Nishimoto, Y.; Fedorov, D. G.; Irle, S. submitted.

FMO-DFTB

Summary

- Geometry optimization **of million atom system** is manageable
- FMO-DFTB for **MD simulations** with ~thousands of atoms becomes possible → prediction of reaction mechanism pathways, proton transfer channels, etc.
- FMO interaction energy decomposition allows the analysis **of ligand-protein interactions**
- Non-adiabatic **electron/hole transfer studies** following FMO-LCMO approach by Tsuneyuki *et al.* (CPL 476, 104 (2009)) becomes possible **for extended systems**

Special thanks to:

Dmitri G. Fedorov
(AIST)

Nishimoto, Y.; Fedorov, D. G.; Irle, S. submitted.

Density-Functional Tight-Binding

Part I

1. Tight-Binding
2. Density-Functional Tight-Binding (DFTB)

Part II

3. Bond Breaking in DFTB
4. Extensions
5. **Performance and Applications**

SCC-DFTB: general comparison with experiment

Performance for small organic molecules

(mean absolut deviations)

- Reaction energies: ~ 5 kcal/mole
- Bond-lenghts: ~ 0.014 A°
- Bond angles: ~ 2°
- Vib. Frequencies: ~6-7 %

Accuracy of DFTB Geometries and Energies for Fullerene Isomers

Fullerene Isomers **Geometries and Energies** vs B3LYP/6-31G(d)

- 102 Fullerene Isomers
- small cage non-IPR C_{20}-C_{36} (35), large cage IPR C_{70}-C_{86} (67)

G. Zheng, SI, M. Elstner, K. Morokuma, *Chem. Phys. Lett.* **412**, 210 (2005)

Geometries

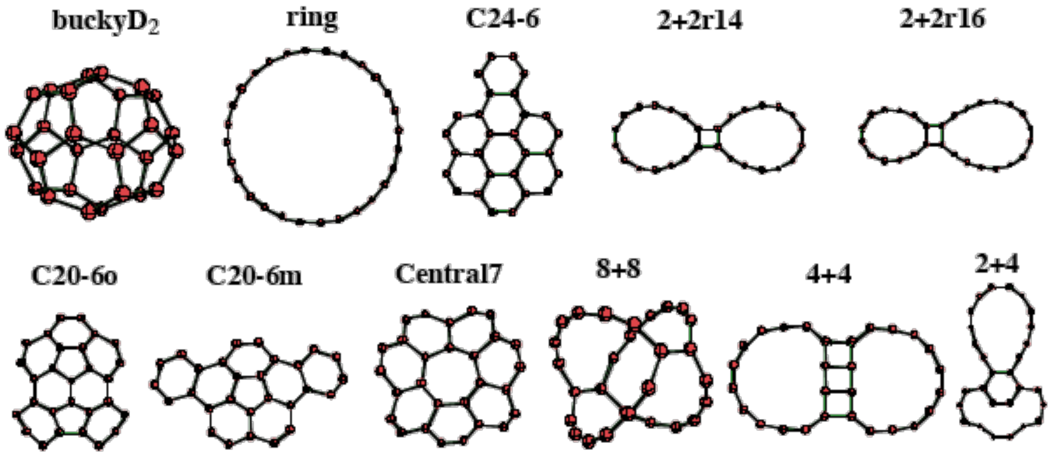
RMS [Å]	NCC-DFTB	SCC-DFTB	AM1	PM3
C20-C36	0.025	0.019	0.035	0.030
C60-C86	0.014	0.014	0.016	0.015

Energetics

R^2 (lin. reg.)	NCC-DFTB	SCC-DFTB	AM1	PM3
C20-C36	0.88	0.93	0.77	0.73
C60-C86	0.97	0.98	0.86	0.84

R^2: Energy linear regression between ΔE(Method) and ΔE(B3LYP)

What about non-cage carbon cluster structures? Some C_{28} isomers as example (from Scuseria, CPL 301, 98 (1999))



Structures of C_{28} used in the benchmark calculations presented in Table 1.

What about non-cage carbon cluster structures? Some C_{28} isomers as example *TACC'04 Symp. Proceedings*

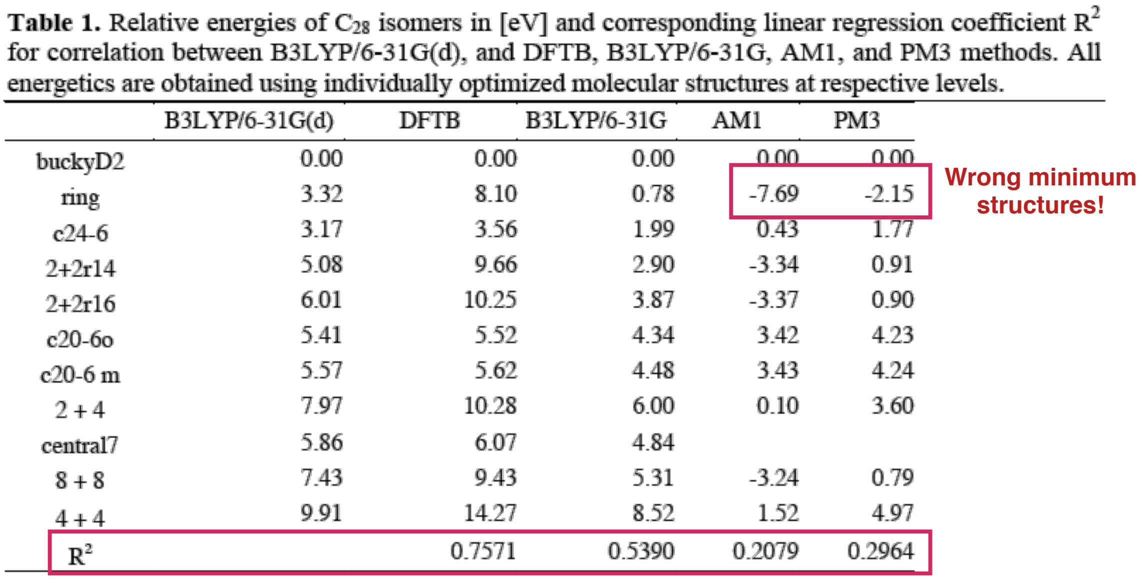


Table 1. Relative energies of C_{28} isomers in [eV] and corresponding linear regression coefficient R^2 for correlation between B3LYP/6-31G(d), and DFTB, B3LYP/6-31G, AM1, and PM3 methods. All energetics are obtained using individually optimized molecular structures at respective levels.

	B3LYP/6-31G(d)	DFTB	B3LYP/6-31G	AM1	PM3
buckyD2	0.00	0.00	0.00	0.00	0.00
ring	3.32	8.10	0.78	-7.69	-2.15
c24-6	3.17	3.56	1.99	0.43	1.77
2+2r14	5.08	9.66	2.90	-3.34	0.91
2+2r16	6.01	10.25	3.87	-3.37	0.90
c20-6o	5.41	5.52	4.34	3.42	4.23
c20-6 m	5.57	5.62	4.48	3.43	4.24
2 + 4	7.97	10.28	6.00	0.10	3.60
central7	5.86	6.07	4.84		
8 + 8	7.43	9.43	5.31	-3.24	0.79
4 + 4	9.91	14.27	8.52	1.52	4.97
R^2		0.7571	0.5390	0.2079	0.2964

Wrong minimum structures!

AM1 and PM3 are performing **very bad!**

DFTB includes effects of polarization functions through parameterization

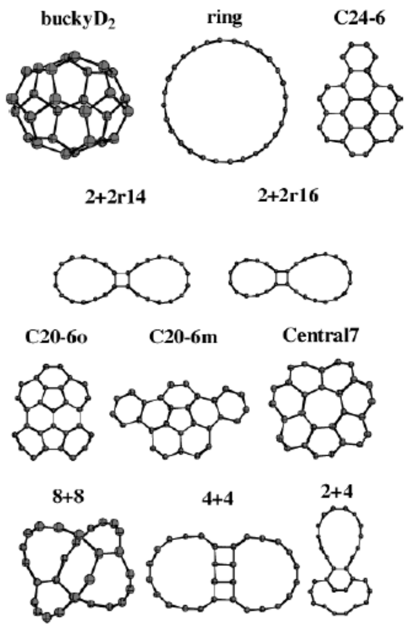
Accuracy of DFTB Geometries

Table 3. The relative energies (in eV) of 11 different isomeric singlet structures of C_{28} calculated with B3LYP/6-31G(d), and DFTB.

Structure [a]	**B3LYP/6-31G(d)**	**DFTB**	**B3LYP/6-31G(d) // DFTB**
buckyD2	0.00	0.00	0.00
ring	3.32	8.10	3.43
c24-6	3.17	3.56	3.66
2+2r14	5.08	9.66	5.22
2+2r16	6.01	10.25	6.13
c20-6o	5.41	5.52	5.96
c20-6 m	5.57	5.62	6.09
2 + 4	7.97	10.28	8.52
central7	5.86	6.07	6.47
8 + 8	7.43	9.43	7.41
4 + 4	9.91	14.27	10.20
R^2 [b]		**0.75**	**0.99**

[a] Structures illustrated below, with the labels taken from “Portmann, S.; Galbraith, J. M.; Schaefer, H. F.; Scuseria, G. E.; Lüthi, H. P. *Chem. Phys. Lett.* **1999**, *301*, 98-104.”

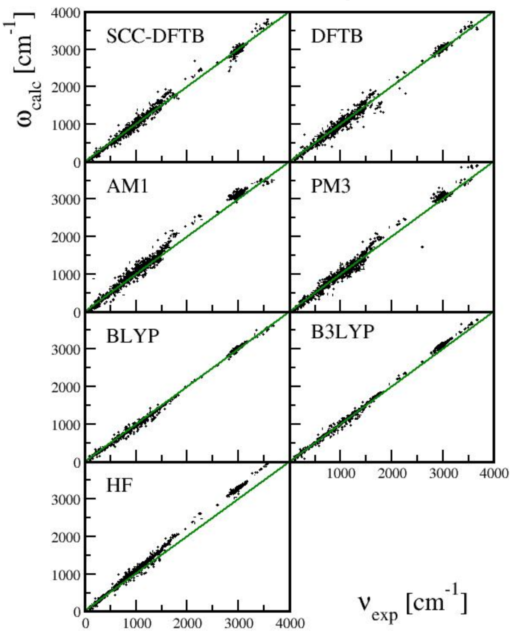
[b] Squared correlation coefficients R^2 in the linear regression analysis with B3LYP/6-31G(d) energies.



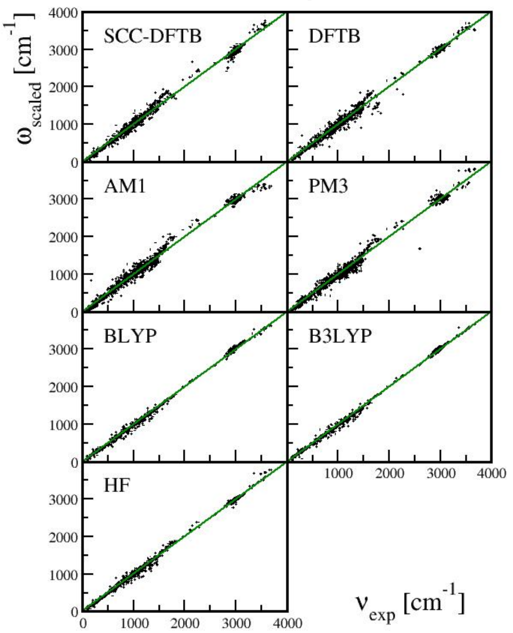
Accuracy of DFTB frequencies

Testing set of 66 molecules, 1304 distinct vibrational modes

calculated frequencies



scaled frequencies

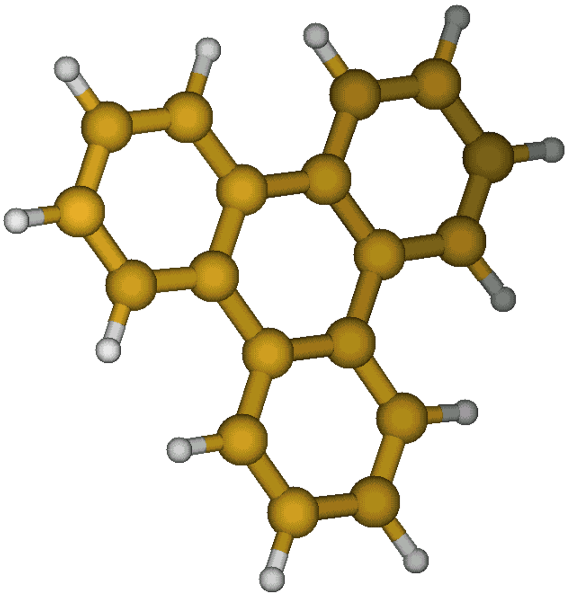


Accuracy of DFTB frequencies

Testing set of 66 molecules, 1304 distinct vibrational modes

	mean absolute deviation	standard deviation	maximal absolute deviation	scaling factor
SCC-DFTB	56 cm^{-1}	82 cm^{-1}	529 cm^{-1}	0.9933
DFTB	60 cm^{-1}	87 cm^{-1}	536 cm^{-1}	0.9917
AM1	69 cm^{-1}	95 cm^{-1}	670 cm^{-1}	0.9566
PM3	74 cm^{-1}	102 cm^{-1}	918 cm^{-1}	0.9762
HF/cc-pVDZ	30 cm^{-1}	49 cm^{-1}	348 cm^{-1}	0.9102
BLYP/cc-pVDZ	34 cm^{-1}	47 cm^{-1}	235 cm^{-1}	1.0043
B3LYP/cc-pVDZ	29 cm^{-1}	42 cm^{-1}	246 cm^{-1}	0.9704

Efficiency of DFTB frequencies



triphenylene

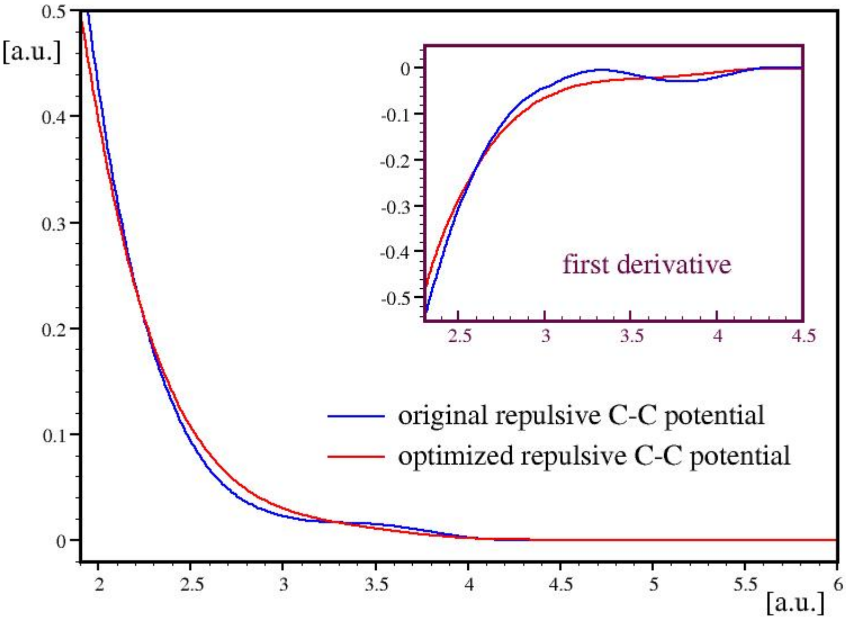
Energy, frequencies, and Raman and IR intensities calculations

DFT BLYP/cc-pVDZ
Linux 2.4GHz machine
32 hours

SCC-DFTB
Linux 333MHz machine
24 seconds

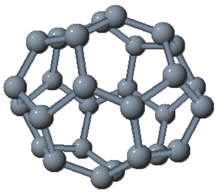
Improvement of DFTB E_{Rep}

H. A. Witek, et al, J. Theor. Comp. Chem. **4**, 639 (2005) and others

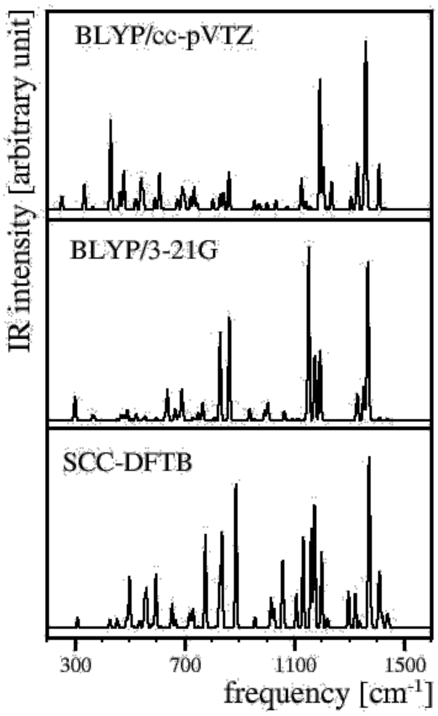


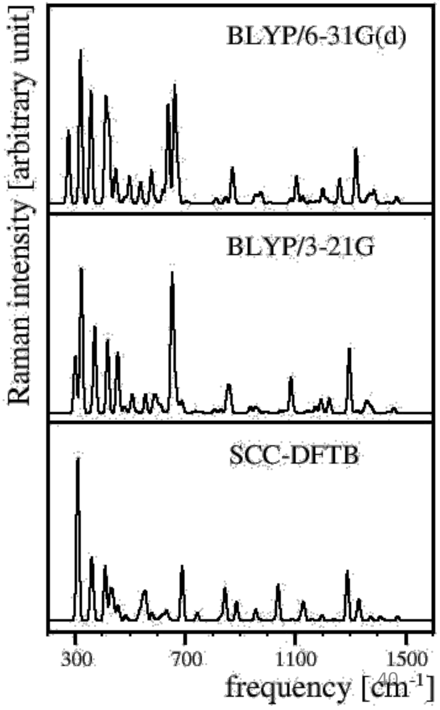
Harmonic IR and Raman Spectra of C_{28}

H. A. Witek, SI, G. Zheng, W. A. de Jong, K. Morokuma, *J. Chem. Phys.* **125**, 214706 (2005)



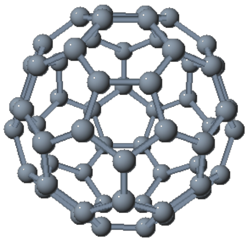
C_{28} D_2



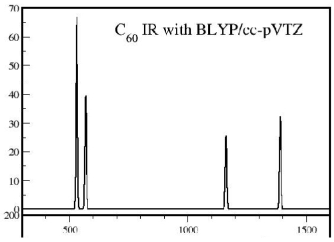


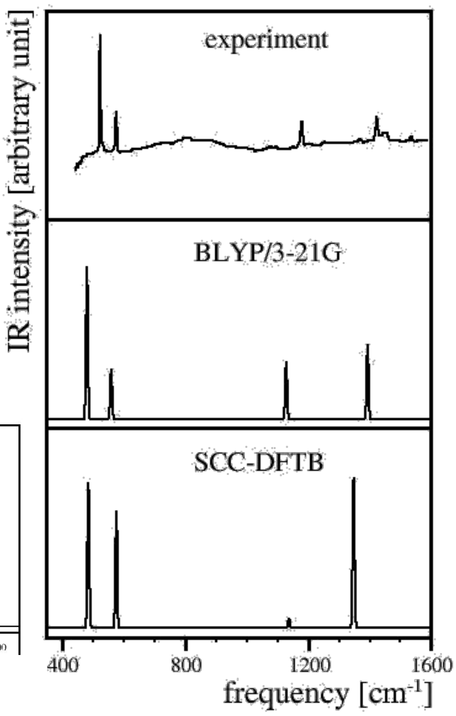
Harmonic IR and Raman Spectra of C_{60}

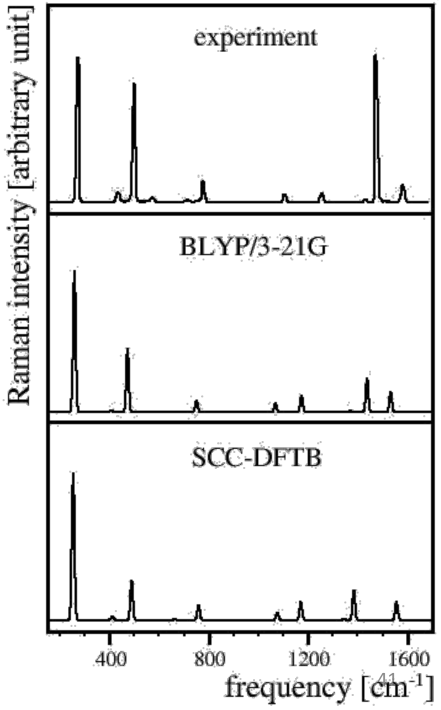
H. A. Witek, SI, G. Zheng, W. A. de Jong, K. Morokuma, *J. Chem. Phys.* **125**, 214706 (2005)



C_{60} D_{2h}~I_h

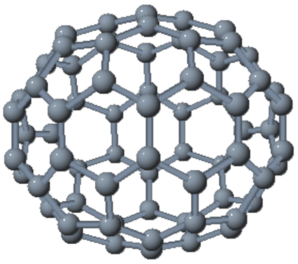




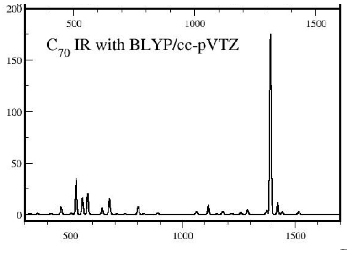


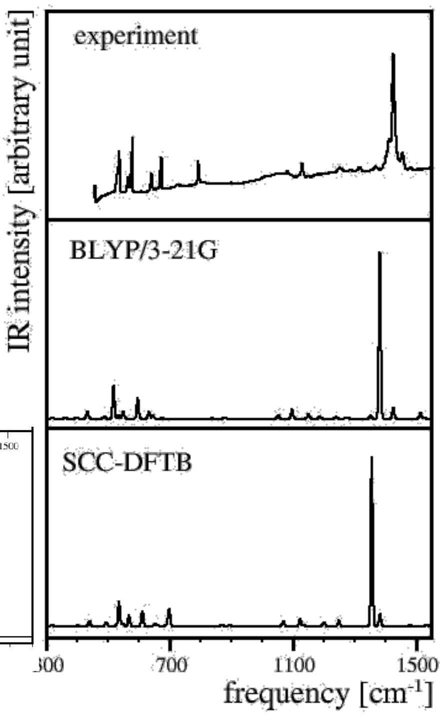
Harmonic IR and Raman Spectra of C_{70}

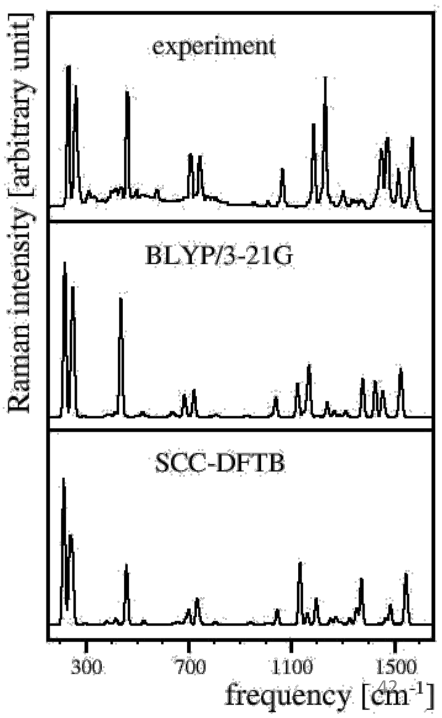
H. A. Witek, SI, G. Zheng, W. A. de Jong, K. Morokuma, *J. Chem. Phys.* **125**, 214706 (2005)



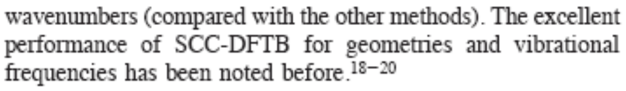
C_{70} D_{5h}







SCC-DFTB: Systematic comparison with other methods by Walter Thiel et al.



wavenumbers (compared with the other methods). The excellent performance of SCC-DFTB for geometries and vibrational frequencies has been noted before.[18−20]

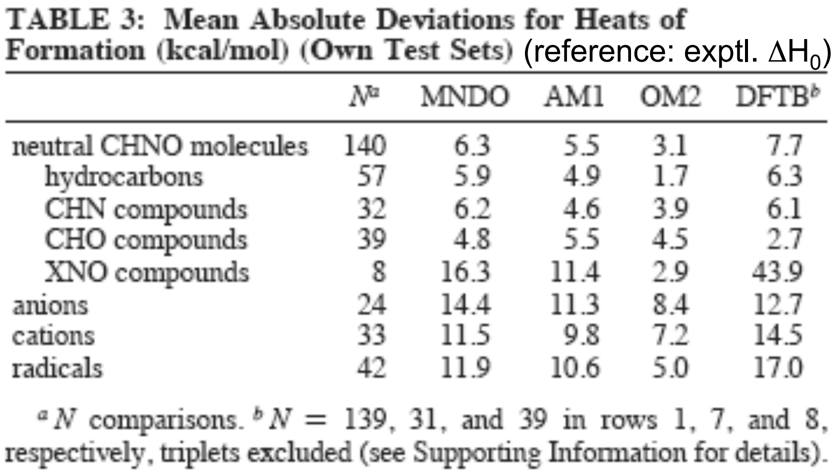


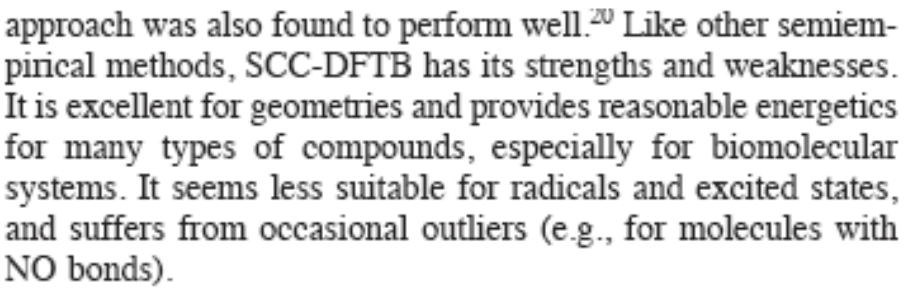
TABLE 3: Mean Absolute Deviations for Heats of Formation (kcal/mol) (Own Test Sets) (reference: exptl. ΔH_0)

	N[a]	MNDO	AM1	OM2	DFTB[b]
neutral CHNO molecules	140	6.3	5.5	3.1	7.7
hydrocarbons	57	5.9	4.9	1.7	6.3
CHN compounds	32	6.2	4.6	3.9	6.1
CHO compounds	39	4.8	5.5	4.5	2.7
XNO compounds	8	16.3	11.4	2.9	43.9
anions	24	14.4	11.3	8.4	12.7
cations	33	11.5	9.8	7.2	14.5
radicals	42	11.9	10.6	5.0	17.0

[a] *N* comparisons. [b] *N* = 139, 31, and 39 in rows 1, 7, and 8, respectively, triplets excluded (see Supporting Information for details).

Thiel and coworkers, *J. Phys. Chem. A* **111**, 5751 (2007)

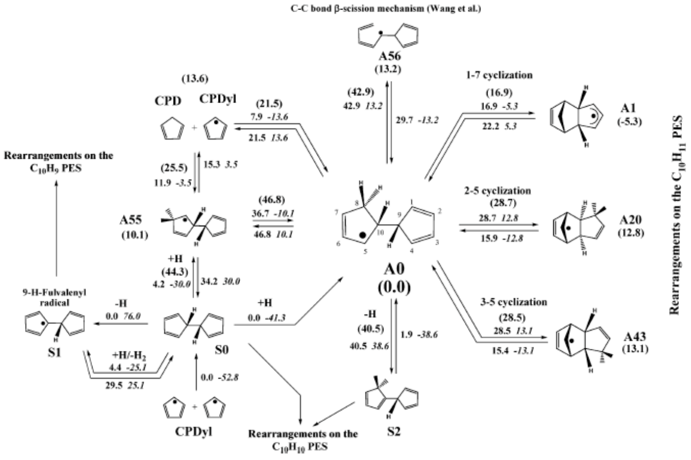
SCC-DFTB: Systematic comparison with other methods by Walter Thiel et al.



approach was also found to perform well.[20] Like other semiempirical methods, SCC-DFTB has its strengths and weaknesses. It is excellent for geometries and provides reasonable energetics for many types of compounds, especially for biomolecular systems. It seems less suitable for radicals and excited states, and suffers from occasional outliers (e.g., for molecules with NO bonds).

Thiel and coworkers, *J. Phys. Chem. A* **111**, 5751 (2007)

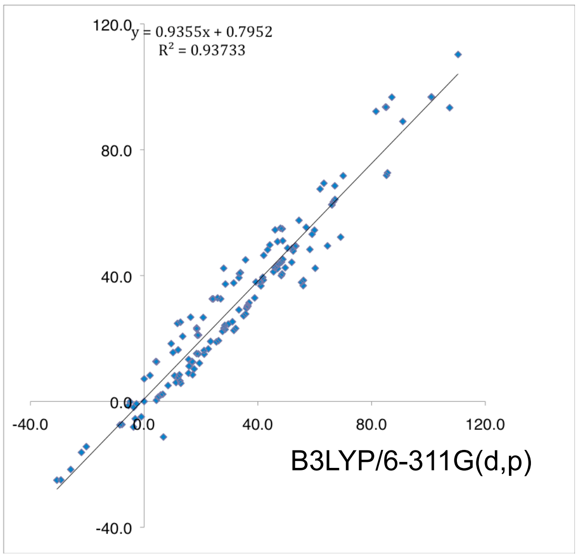
But: NCC- and SCC-DFTB for radicals: own comparison with B3LYP/6-311G**



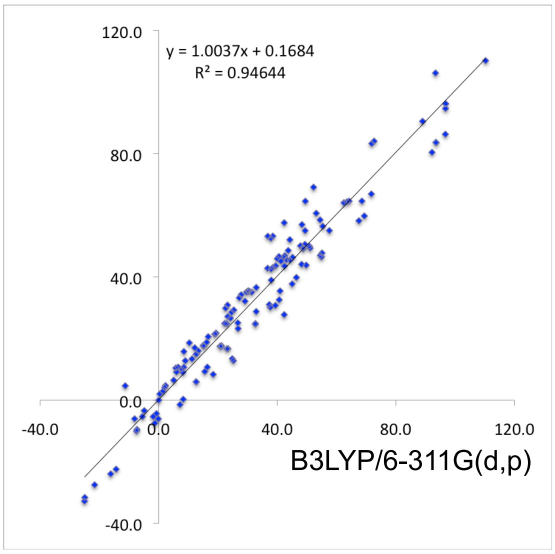
	NCC-DFTB	SCC-DFTB
Barrier heights	6.60	5.99
Rel. energies	7.96	7.31
Overall RMSD	7.17	6.55
Overall R^2	0.937	0.946

NCC- and SCC-DFTB for radicals: own comparison

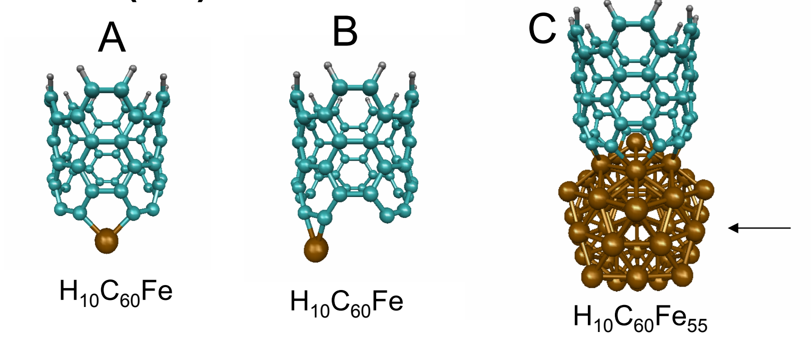
NCC-DFTB



SCC-DFTB



H-terminated **(5,5) armchair SWNT + Fe atom/cluster**



$H_{10}C_{60}Fe$ $H_{10}C_{60}Fe$ $H_{10}C_{60}Fe_{55}$

Fe_{55} icosahedron

Adhesion energies (eV/atom)

	A	B	C
DFT:PW91[1]	-6.24	-5.63	-1.82
SCC-DFTB[2]	-5.17	-4.68	-1.86

[1] Phys. Rev. B **75**, 115419 (2007) [2] Fermi broadening=0.13 eV

PW91: An ultrasoft pseudopotential with a plane-wave cutoff of 290 eV for the single metal and the projector augmented wave method with a plane-wave cutoff of 400 eV for the metal cluster

Fe-Fe and Fe-C DFTB parameters from: G. Zheng *et al., J. Chem. Theor. Comput*. **3**, 1349 (2007)

Acknowledgements

- Dmitri Fedorov
- Marcus Elstner
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- Marcus Lundberg
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- Some others