Next Generation Quantum Based Molecular Dynamics

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Parameterization of the Approximate Density Functional Theory Method DFTB3 for Alkaline and Alkaline Earth Metals and Halogens

Density Functional Tight Binding

Optimized basis set :

$$\left[-\frac{1}{2}\nabla^2 + V^{\text{eff}}[\rho] + \left(\frac{r}{r_0}\right)^2\right]|\mu\rangle = \epsilon_\mu |\mu\rangle$$

Taylor series expansion of the DFT energy around a reference density:

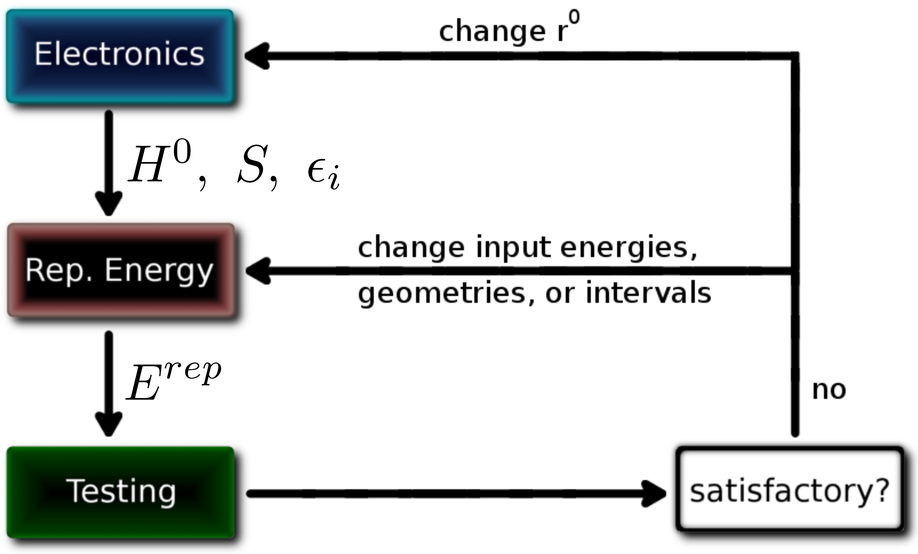
$$E^0 = \sum_{\mu\nu} c_\mu c_\nu H^0_{\mu\nu} + E^{2nd} + E^{3rd} + E^{rep}$$

Eigenvalue problem: $H^0 C = SC\epsilon$

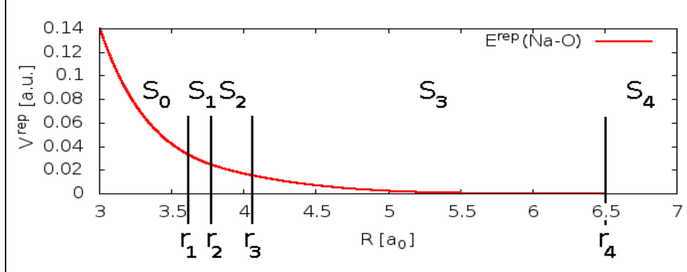
Tabulate H^0, S, ϵ_i and E^{rep}.

→ No evaluation of integrals at run-time!

Parameterization Scheme



Repulsive Energy



Repulsive potential, represented by a spline with several intervals S_i.

Fitting the spline with the training set: molecules with reference
- Atomization energies,
- Geometries and forces,
- Reaction equations.

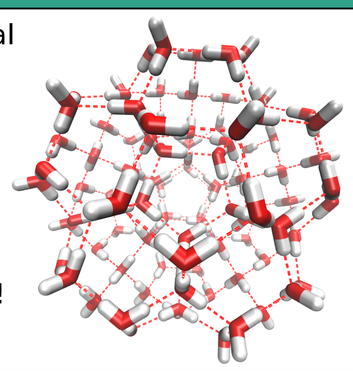
Timings: Performance of DFTB3

Theory	Basis	N_{bas}	t_{CPU}
B3LYP	def2-SVP	2400	18413.0
RI-PBE	def2-SVP	2400	2488.6
DFTB3	3OB	600	3.1

DFT calculations run with Turbomole 6.5
DFTB3 calculations run with DFTB+ 1.2
CPU: AMD Phenom™ II X6 1090T
RAM: 5 GB

Test: Icosahedral water cluster, 100 molecules

→ Up to 1000 times faster than DFT!

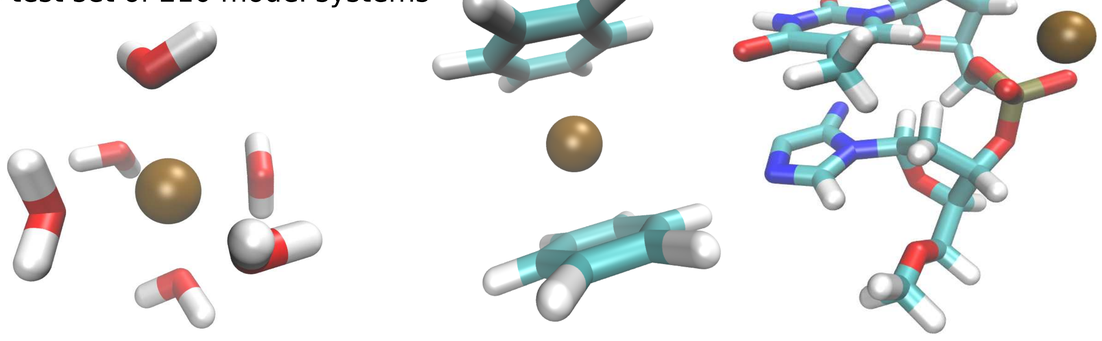


3OB: Parameterization for C, H, N, and O

Method	N	Ref.	DFTB2/MIO	DFTB3/3OB	PBE/6-31G(d)
E^{At} [kcal/mol]	65	G3B3	45.6	5.2	21.4
E^{reac} [kcal/mol]	49	G3B3	8.2	5.5	4.7
PA [kcal/mol]	23	G3B3	5.8	2.9	4.7
HB [kcal/mol]	22	G3B3	8.9	3.8	7.0
r [Å]	236	B3-LYP*	0.014	0.008	0.013
a [°]	196	B3-LYP*	0.9	0.8	0.4
$\nu^{stretch}$ [cm^{-1}]	15	B3-LYP*	159	94/25**	48

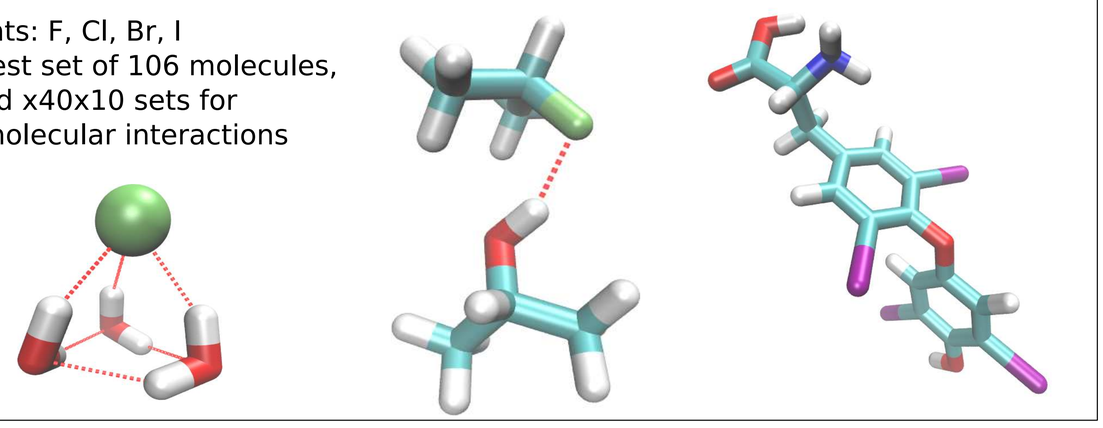
Parameterization of Alkaline and Alkaline Earth Metals

Elements: Ca, K, Na
BioMe test set of 210 model systems

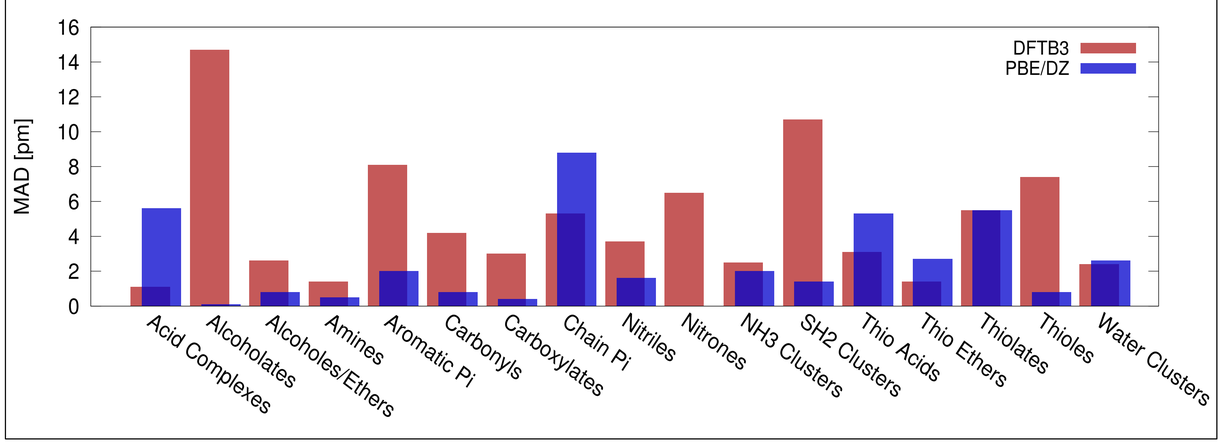


Parameterization of Halogens

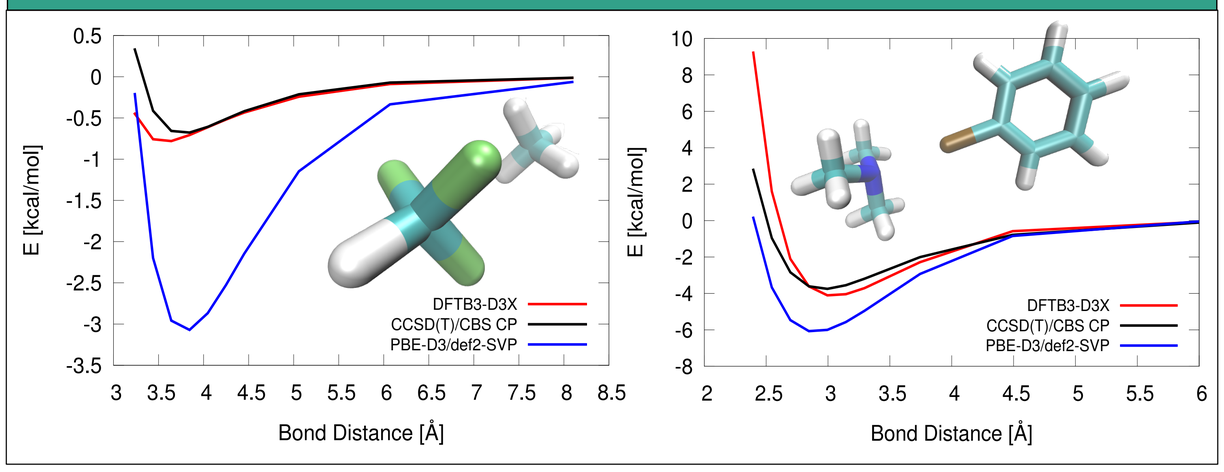
Elements: F, Cl, Br, I
OrgX test set of 106 molecules, x40 and x40x10 sets for supramolecular interactions



Example: Bond Distance Deviations of Calcium



x40x10 Set: Dissociation Curves



BioMe Set: Performance of Metal Parameters

Property	DFTB3/3OB Ca	DFTB3/3OB K	DFTB3/3OB Na	PBE/def2-SVP Ca	PBE/def2-SVP K	PBE/def2-SVP Na
Bond Distances [Å]	0.049	0.074	0.048	0.018	0.029	0.016
Bond Angles [°]	9.5	5.3	11.6	3.8	3.9	2.5
LBE[a] H_2O [kcal/mol]	2.5	1.0	0.7	9.2	6.2	5.0
LBE[a] NH_3 [kcal/mol]	2.2	4.5	1.5	6.8	5.3	1.8
LBE[a] H_2S [kcal/mol]	4.3	9.9	2.2	6.6	9.4	1.4

a) Incremental ligand binding energies.

OrgX Set: Performance of Halogen Parameters

Mean Absolute Deviations	DFTB3/3OB F	DFTB3/3OB Cl	DFTB3/3OB Br	DFTB3/3OB I	PBE/def2-SVP F	PBE/def2-SVP Cl	PBE/def2-SVP Br	PBE/def2-SVP I
Bonding Distances [Å]	0.011	0.007	0.013	0.034	0.005	0.006	0.007	0.019
Bonding Angles [°]	1.1	1.8	2.7	1.8	0.5	0.4	0.4	0.5
At. Energies [kcal/mol]	5.2	11.2	17.0	7.8	31.2	24.7	17.0	13.5
Vib. Frequencies [cm^{-1}]	45.9	46.6	108.4	25.3	43.3	15.6	11.3	3.1

References

M. Kubillus, T. Kubar, M. Gaus, J. Řezáč, and M. Elstner, JCTC **10**, 332 (2015).
M. Elstner, D. Porezag, G. Jungnickel, J. Elstner, M. Haugk, Th. Frauenheim, S. Suhai and G. Seifert, *PRB* **58**, 7260 (1998).
M. Gaus, A. Goez, and M. Elstner, *JCTC* **9**, 338 (2013).
M. Gaus, Xiya Lu, Marcus Elstner, and Qiang Cui, *JCTC* **10**, 518 (2014).

Learn more about DFTB

Parameters: http://www.dftb.org/
DFTB+ Code: http://www.dftb-plus.info/
Elstner Group: http://www.ipc.kit.edu/tcb/

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