These are preliminary parameters (Version: rc4, date 2014 Oct 31st) for the DFTB3 3OB parameterization for organic and biomolecules. Please use with caution and report any problems to kubillus@kit.edu.

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1 Abstract

We present an extension to the recent 3OB parameterization of the Density Functional Tight Binding Model DFTB3[**?**, **?**]. Parameters for the halogens F, Cl, Br, and I have been created for use in covalently bound systems and benchmarked on a test set of 106 molecules (the 'OrgX' set), using bonding distances, bonding angles, atomization energies, and vibrational frequencies to assess the performance of the parameters. Additional testing has been done with the X40 set of 40 supramolecular systems containing halogens[**?**], adding a simple correction for the halogen bonds which are strongly overbound in DFTB3. Furthermore, parameters for Ca, K, and Na as counterions in biological systems have been created. To benchmark geometries as well as ligand binding energies a test set 'BioMe' of 210 molecules has been created covering coordination to various functional groups frequently occurring in biological systems.

The new DFTB3/3OB parameter set surpasses DFT calculations with a double-zeta basis set in terms of energies, whereas geometries suffer from the minimal basis set effects.

2 Definition of the Parameters

Table 1: Electronic parameters for all atoms parameterized in this work (in atomic units where not dimensionless). Parameters a_i, E^{spin}, n_{max}, U, U^{der} and ϵ_i are not subject to optimizations. All of the values r_i and σ are fitted to reproduce the reference data. The calculated parameters were obtained with the procedures described in our previous work.[**?**, **?**]

Parameter	Ca	K	Na	F	Cl	Br	I
Definition of the Basis Set							
l_{max}	1	1	1	1	2	2	2
n_{max}	2	2	1	2	2	2	2
a_0	0.50	0.50	0.50	0.50	0.50	0.50	0.50
a_1	1.26	7.65	1.08	1.03	1.21	1.45	1.60
a_2	3.16	3.08	2.35	2.12	2.92	4.18	5.15
a_3	7.95	1.24	5.08	4.37	7.04	12.10	16.52
a_4	20.00	19.00	11.00	9.00	17.00	35.00	53.00
r^s	6.4	7.0	4.4	2.8	4.3	6.0	6.3
C¿p8ex r^p	9.9	7.9	4.4	2.8	4.3	6.0	6.3
r^d	–	–	–	–	5.7	6.0	7.8
r^{dens}	12.0	12.0	8.6	5.0	13.0	10.0	11.0
σ	13.6	15.8	2.0	2.0	9.0	6.4	2.0
Calculated Parameters							
ϵ_s	−0.1379	−0.0852	−0.1007	−1.0958	−0.7544	−0.7394	−0.6382
ϵ_p	−0.0521	+0.0148	−0.0274	−0.4087	−0.3164	−0.2888	−0.2606
ϵ_d	–	–	–	–	+0.0222	+0.0243	+0.0223
E^{spin}	−0.0236	−0.0056	−0.0081	−0.0146	−0.0080	−0.0069	−0.0057
U	+0.1764	+0.1356	+0.1651	+0.5584	+0.3668	+0.3277	+0.2842
U^{der}	−0.0340	−0.0339	−0.0454	−0.1623	−0.0697	−0.0573	−0.0433

Table 2: Training sets for the parameterization of repulsive potentials using molecular geometries and reactions. All of the remaining data needed to reproduce the repulsive potentials are given in the Supporting Information.

Atom	Molecules	Reactions
Ca	Ca_2H_2, CaH_2, $HCaCH_3$, $Ca(NH_2)_2$, $Ca(OH)_2$, $HCa(SH)$, $HCa(PH_2)$, $Ca(HPO_4)$, $[Ca(NH_3)]^{2+}$, $[Ca(OH_2)]^{2+}$, $[Ca(OH_2)_4]^{2+}$, $[Ca(SH_2)]^{2+}$, $[Ca(SH_2)_4]^{2+}$, $[Ca(SH_2)_6]^{2+}$, CaMg, CaZn, HCaK, HCaNa	$Ca^{2+} + H_2O \longrightarrow [Ca(OH_2)]^{2+}$ $Ca^{2+} + NH_3 \longrightarrow [Ca(NH_3)]^{2+}$ $Ca^{2+} + H_2S \longrightarrow [Ca(SH_2)]^{2+}$
K	K_2, KH, $K(OH)_{lin}$, $[K(NH_3)]^+$, $K(CH_3)$, $K(PH_2)$, K(SH), HMgK, HZnK, KNa	$K^+ + H_2O \longrightarrow [K(OH_2)]^+$ $K^+ + NH_3 \longrightarrow [K(NH_3)]^+$ $K^+ + H_2S \longrightarrow [K(SH_2)]^+$
Na	Na_2, NaH, $Na(OH)_{lin}$, $Na(NH_2)$, $Na(CH_3)$, $Na(PH_2)$, $[Na(SH_2)]^+$, NaMgH, NaZnH	$Na^+ + H_2O \longrightarrow [Na(OH_2)]^+$ $Na^+ + NH_3 \longrightarrow [Na(NH_3)]^+$ $Na^+ + H_2S \longrightarrow [Na(SH_2)]^+$
F	F_2, HF, CH_3F, NH_2F, OHF, PH_2F, SHF, NaF, MgF, KF, CaHF, ZnHF	
Cl	Cl_2, HCl, CH_3Cl, C_2HCl, CCl_4, NH_2Cl, ClOH, $HClO_4$, ClO_4^-, PH_2Cl, ClSH, NaCl, ClMgH, ClF, KCl, ZnHCl, CaHCl	$HClO_4 + H_2 \longrightarrow HClO_3 + H_2O$
Br	Br_2, HBr, CH_3Br, NH_2Br, BrOH, BrO^-, BrO_4^-, PH_2Br, BrSH, NaBr, MgHBr, BrF, BrCl, KBr, ZnHBr, CaHBr	
I	I_2, HI, CH_3I, C_2HI NH_2I, IOH, IO^-, PH_2I, SHI, NaI, MgHI, IF, ICl, IBr, KI, ZnHI, CaHI	

3 Benchmarking and Performance

Table 3: Performance of the new DFTB3/3OB parameters for Na, K and Ca. Errors are presented as mean absolute deviations (MAD) from the results of reference calculations. Equivalent data for the PBE functional with a double-zeta basis set are presented for comparison. For the particular absolute values, types of reference data and the numbers of test systems, see the Supporting Information.
[a] Incremental Ligand Binding Energies.

		DFTB3/3OB			PBE/def2-SVP		
	Property	Ca	K	Na	Ca	K	Na
C¿p6ex	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]	18.3	9.9	2.2	20.4	9.4	1.4

Table 4: Performance of the current parameterization of halogens expressed as mean absolute deviations (MAD) from reference data. The particular absolute values, types of references and numbers of test systems can be found in the Supporting Information.

		DFTB3/3OB				PBE/def2-SVP			
	Property	F	Cl	Br	I	F	Cl	Br	I
C¿p6ex	Bond Distances [Å]	0.011	0.007	0.013	0.034	0.005	0.006	0.007	0.019
	Bond Angles [°]	1.1	1.8	2.7	1.8	0.5	0.4	0.4	0.5
	At. Energies [$\frac{\text{kcal}}{\text{mol}}$]	5.2	11.2	17.0	14.6	31.2	24.7	17.0	8.5
	Vib. Freq. [cm^{-1}]	45.9	46.6	108.4	25.3	43.3	15.6	11.3	3.1