

## Refinement of DFTB Parameterization for Metal-Organic Frameworks

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### [Abstract]

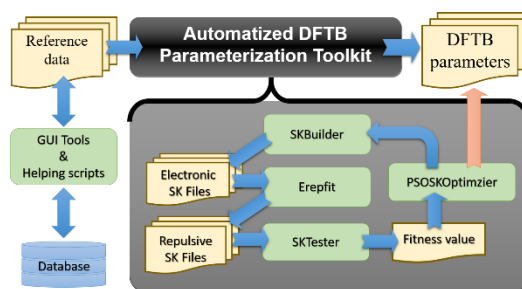
The DFTB parameters from the existing parameter set have been refined specially for describing the structure of the copper-containing metal-organic frameworks (MOFs). The refinement has been carried out using the previously developed automatized DFTB parameterization toolkit. The refinement processing includes cluster models of the secondary building units of MOFs. The mean absolute deviations of Cu-Cu and Cu-O bond lengths obtained using the refined DFTB parameters comparing to selected DFT optimized Cu-MOFs have been reduced from 0.258 to 0.016 Å, and 0.060 to 0.023 Å, respectively.

### [Introduction]

Metal-organic frameworks (MOFs) are a class of crystalline materials that exhibit high potential for many applications including the carbon capture and storage (CCS) technique. MOF crystals have coordination networks consisting of the metal-containing subunits, aka the secondary building units (SBU), connected by organic ligand linkers. Such large-scale systems might not be convenient studied with conventional quantum chemical methods. The density-functional tight-binding (DFTB) method[1] is an approximated density-functional theory (DFT) method with careful approximations. The DFTB method uses parameters that are pre-computed either directly from DFT or optimized from reference *ab initio* or DFT calculations, and stored in files, which makes the DFTB method in general three orders of magnitude faster than average DFT methods. Incorporating the divide-and-conquer (DC) technique[2], the time-complexity with respect to the number of atoms in DFTB can be reduced from cubic to nearly linear. The most widely used DFTB parameterization set 3ob[3] for organic and bio-organic systems has been extensively tested and successfully applied to many applications. Recently, the 3ob set has been extended to cover several metal elements[4–6]. However, the metal parameterization in the set was not applied to the MOFs. Benchmarks of those parameters on the geometry of DFT-optimized MOF structures show significant deviations and may not be suitable for MOF-related applications. The aim of this study is to refine the existing parameter set to have a better description of the MOFs. We expect that the new parameterization for MOFs will benefit the further studies on applications involving MOFs.

### [Methods]

The automatized DFTB parameterization toolkit named ADPT[7] provides a set of tool for optimizing DFTB parameterization in an automatic fashion. For the parameterization refining processes, additional reference geometry of SBUs of Cu-MOFs are included in the force equations to produce correct gradient of the Cu-Cu, Cu-N, and Cu-O repulsive potentials using the erepfit[8] code

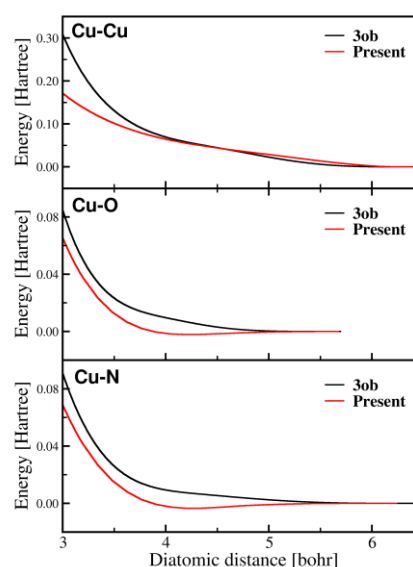


**Figure 1.** Architecture of the ADPT toolkit.

provided in the ADPT. The repulsive potential refining process also includes the reference geometries and energies data from the original parameterization paper[6] to retain the compatibility. All DFTB calculations, including the parameterization process and the benchmark have been carried using the DFTB+[9] package version 1.3.1. The reference SBU models have been computed at B3LYP-D3(BJ)/def2-TZVPP level of theory using the ORCA program system[10]. The full geometry relaxations including both the ion positions and the unit cell of the available DFT optimized Cu-MOFs, provided by the CoRE MOF database[11,12], have been carried using the refined and the existing parameters.

### [Results and Discussion]

Table 1 shows the benchmark results on the fully-relaxed DFTB geometries of selected Cu-MOFs to the reference DFT values. Owing to the additional force equations employed in the repulsive fitting process, the Cu-Cu and Cu-O bond lengths have been improved significantly, whereas the Cu-N bonds remain similar excellent quality. The refined repulsive potential of Cu-Cu, Cu-O, and Cu-N are shown in Figure 2, in comparison with those from the existing parameterization. The refined Cu-Cu repulsive potential has a smaller gradient at usual Cu-Cu bond distances in the Cu-MOFs around 5.0 bohr, preventing overestimating the Cu-Cu bonds; while the differences between repulsive potentials of the other two pairs are very small. The optimized unit cell volumes of all testing Cu-MOFs using existing and refined parameters show similar mean absolute deviations (MAD) of 3% comparing to the DFT-optimized volumes.



**Figure 2.** The refined repulsive potentials of Cu-Cu, Cu-O, and Cu-N, comparing to the existing 3ob ones.

**Table 1.** Mean absolute deviations of Cu-Cu, Cu-O, and Cu-N bond lengths (Å), and N-Cu-N, N-Cu-O, and O-Cu-O bond angles (degrees) computed using the existing 3ob and the refined DFTB parameterization comparing to the reference DFT-optimized MOF structures.

	R(Cu-Cu)	R(Cu-N)	R(Cu-O)	A(N-Cu-N)	A(N-Cu-O)	A(O-Cu-O)
3ob	0.258	0.043	0.060	4.0	3.0	2.0
Present	0.016	0.044	0.023	4.1	2.2	2.6

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