

Density-Functional Tight-Binding Automated Parameterization of Zr-Zr and Zr-O Repulsive Potentials

A. S. Hutama¹, C. A. J. Fisher², C. Hettich³, B. Aradi³, Th. Frauenheim³, S. Irle¹

¹WPI-Institute of Transformative Bio-Molecules (ITbM) & Department of Chemistry, Nagoya University, Nagoya, 464-0814, Japan

²Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya 456-8587, Japan

³Bremen Centre for Computational Material Science, University of Bremen, 28359, Bremen, Germany

Zirconia (ZrO_2) is an important ceramic material with an increasing range of applications. The bulk phase is commonly used for ceramic materials and refractory materials, while surface applications such as thin film coatings and catalysis are proliferating. Recently, ZrO_2 nanotube structures have also been synthesized [1] which may allow ZrO_2 to be used in electronic devices in the future.

The density-functional tight-binding (DFTB) method is an efficient quantum mechanical simulation technique which depends on introducing a number of approximations. As an approximate method, its reliability depends on comparison with quantum mechanical results, e.g. from density functional theory (DFT) wherever possible. The DFTB method can be used for molecular and crystalline systems.

The DFTB method uses sets of binary parameters for pairs of elements. These parameters contain two parts, an electronic component and a repulsive component. Electronic parameters can be automatically obtained by fitting the DFTB band structure to a DFT reference band structure [2], while repulsive parameters are obtained by taking the difference between a DFT reference energy and the DFTB electronic energy.

In this work, we describe the development of Zr-Zr and Zr-O repulsive potentials. The automatic repulsive parameter toolkit developed by Bodrog *et al.* [3] was applied to different systems, i.e., different molecular structures or solid phases containing Zr and O to develop a reliable parameter set.

For Zr-Zr fitting was done using the Zr bulk *hcp* structure. Paths were created by uniformly changing the lattice parameter a from 2.5 Å to 4.0 Å with a constant c/a ratio of 1.592. Zr-O parameters were fitted using ZrO_2 in its tetragonal and cubic forms. In the case of the cubic phase, the lattice parameter was varied uniformly from 4.0 Å to 6.0 Å, while for the tetragonal phase the a parameter was varied from 4.0 Å to 6.0 Å with a constant c/a value of 1.436. We used energy targets for both fittings with different weights for cubic and tetragonal phases. We used the *mio* parameter set for O-O parameters [4]. All DFT references were calculated with VASP code at the PBE-PAW level theory. The generated Zr-Zr and Zr-O repulsive potential, as well as the electronic parameters, were used for test system containing cubic and tetragonal ZrO_2 phases. We optimized the geometry for both phases and calculate the energy difference between tetragonal and cubic and the Zr-O bond length. We compared our geometry-optimized DFTB result with DFT results.

FIG. 1 and FIG. 2. show the Zr-Zr and Zr-O repulsive energies, respectively, for the 1:4 fit for cubic and tetragonal phases. We chose a cutoff of 4.5 Å for Zr-Zr and 4.4 Å for Zr-O repulsive energy. We note that the Zr-Zr repulsive energy contains a value below zero between 3.3 and 4.4 Å. Nevertheless, these parameters are still valid because

the “working” range for Zr-Zr does not exceed 2.7 Å. DFTB geometry optimization results show that Zr-O bond lengths of 2.208 Å agree well with those from DFT, 2.219 Å, for the cubic phase. In the tetragonal phase, there are two bond lengths, Zr-O and Zr-O', which were also found to be in good agreement with DFT results. The Zr-Zr and Zr-O parameters generated are now being used for further simulations, such as surfaces of ZrO₂ and molecular dynamics simulations.

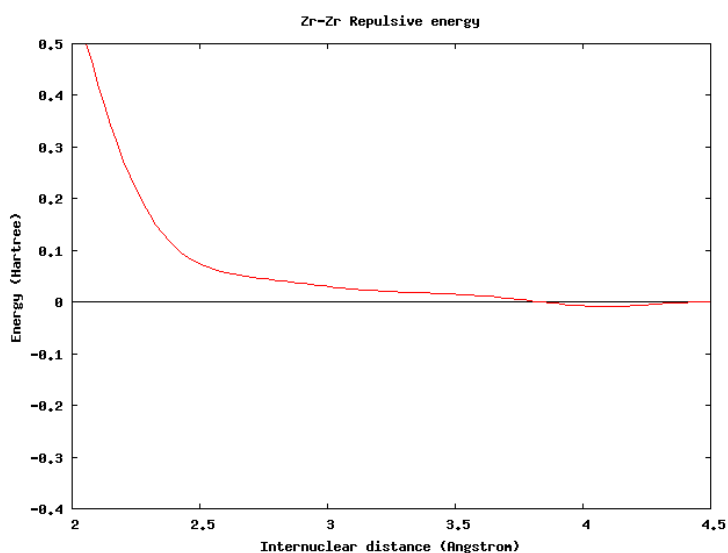


FIG. 1 Zr-Zr repulsive energy as a function of internuclear distance.

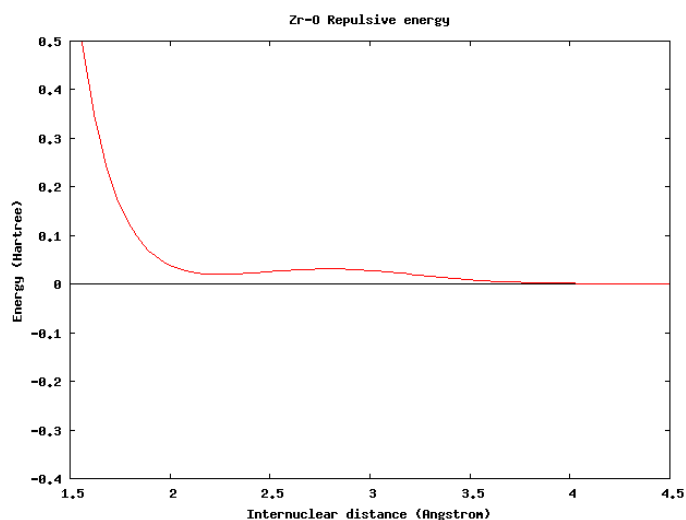


FIG. 2 Zr-O repulsive energy as a function of internuclear distance.

References

- [1] H. Tsuchiya et al., Chem. Phys. Lett. 410 (2005) 188.
- [2] Y. Nishimura, PhD Thesis. Nagoya University (2013).
- [3] Z. Bodrog et al., J. Chem. Theor. Comput. 7 (2011) 2654.
- [4] T. Krüger et al., J. Chem. Phys. 122 (2005) 114110.