報 告 番 号	※ 甲　　第　　　　　号

主　論　文　の　要　旨

論 文 題 目　Evaluation, Improvement and Development of Density-Functional Tight-Binding Parameters for Simulations of Materials
（物質のシミュレーションのための密度汎関数強結合法のパラメータの評価、改良および開発）

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論　文　内　容　の　要　旨

　The thesis presents extensive results from the theoretical calculations using several quantum chemical methods, focusing on the density-functional tight-binding (DFTB) method. The main goal of the present work is to check the reliability and possibly to improve and develop the DFTB method for simulation of interesting and useful materials. DFTB is an efficient semi-empirical quantum chemical method with three orders of magnitudes faster than the standard density functional theory (DFT) method. Although in recent days the capacity of computer power and speed are growing rapidly, the simulation of materials with large (realistic) size and quantum mechanical (QM) treatment of the electrons are still not feasible. Therefore, DFTB can be the alternative method for the simulation of large-sized materials. Chapter 1 briefly explains the background and motivations for the present studies. Chapter 2 shows the theoretical background and methods employed in present works.

　Since DFTB is a semi-empirical method, the parameterizations are necessary. The parameters are derived from reliable quantum chemical calculations. The first part of the thesis deals mainly with the evaluations and benchmark of the available DFTB parameters. In Chapter 3, the reference data for the improvement of C-F DFTB parameters are presented. For the specific purpose, these parameters will be used for the further investigations of reaction between graphene surface and atomic fluorine. The　　 potential energy curves (PECs) of atomic fluorine

adsorption on coronene as a model for graphene or nanocarbon surfaces have been computed using a variety of quantum chemical methods. Various density functional theory (DFT) functionals, such as B3LYP, PBE, PBE0, CAM-B3LYP, LC-ωPBE; approximate DFT methods such as several levels of the DFTB method, as well as *ab initio* wave function theory (WFT) methods such as MP2, CCSD, CCSD(T), and G2MS extrapolations, were used to evaluate energies for B3LYP/cc-pVDZ PEC geometries. G2MS is an approximation to the highly accurate CCSD(T)/cc-pVTZ level of theory. In addition with the high-level WFT calculation results, we discovered that pure DFT functionals and their DFTB approximations fail to predict the correct dissociation limit due to the DFT-inherent self-interaction error (SIE) and various limitations in the DFTB approximation itself. From these results, we proposed improved C-F repulsive potentials by fitting the PECs of the high-level wave function theory.

Chapter 4 presents the interaction of coronene as graphene model with atomic oxygen and nitrogen as the continuation from the coronene-fluorine works by means of DFT and DFTB calculations. The trend of the type of atom with respect to the SIE has been elucidated. The fractional occupation number of the atomic orbitals in DFTB is one of the causes of the SIE in DFTB.

Second part of this thesis reports the development of repulsive potentials for materials simulations in periodic boundary condition (PBC). In chapter 5, a number of sets of DFTB2 repulsive potentials for $Zr - Zr$ element pair, namely the long-range and the short-range repulsive potentials, have been developed. The repulsive potentials were created from energy versus volume $(E - V)$ profiles of the bulk phases that had been generated from planewave DFT calculations using polynomial fitting and particle swarm optimization (PSO) algorithm. The potentials were tested to elucidate the properties of the experimental bulk phases of Zr, namely HCP, BCC and ω phase. The properties of the bulk phase, such as the equilibrium geometry, atomization energies, and the bulk modulus of the DFTB using the new parameters were tested and compared with the DFT reference data. By comparison for each potential's performance, the best potential that is suitable for the purpose of the simulationss has been deduced.

Finally, the summary and the future directions of the present project are presented in Chapter 6.