

Large Scale Simulations for Carbon Nanotubes

Project Representative

Syogo Tejima

Research Organization for Information Science & Technology

Authors

Syogo Tejima^{*1}, Satoshi Nakamura^{*1}, Yoshiyuki Miyamoto^{*2} and Hisashi Nakamura^{*1}

*1 Research Organization for Information Science & Technology (RIST)

*2 National Institute of Advanced Industrial Science and Technology (AIST)

Nanosystem Research Institute (NRI)

CARBON NANOTUBE RESEARCH GROUP

Morinobu Endo, Eiji Osawa, Atushi Oshiyama, Yasumasa Kanada, Susumu Saito, Riichiro Saito, Hisanori Shinohara, David Tomanek, Tsuneo Hirano, Shigeo Maruyama, Kazuyuki Watanabe, Takahisa Ohno, Yutaka Maniwa, Yoshikazu Fujisawa, Yoshiyuki Miyamoto, Hisashi Nakamura

Our study consists of two parts: development of a model and application of different models that had been optimized by our group for the Earth Simulator. The first one is extending a linear combination of atomic orbitals model to finite temperature case. For the second one, we present the simulation results of the following four studies: (1) controllable gap of Mackey crystal for a solar cell material, (2) ability of adsorption of cesium on carbon-nanotube, (3) electron transport properties of grapheme for electric device, and (4) collective motion of molecular dimer of acetylene molecules inside carbon-nanotube.

Keywords: Large scale simulation, TB theory, ab initio theory, Time-dependent DFT, Carbon Nanotube, Fullerenes, Graphene, Mackay crystal, solar cell, Green energy, quantum electronic transport, photoelectric material

1. Introduction

Nano-carbon materials such as nanotube, fullerene and graphene have potential for applications to the advanced industries. For nano-carbon materials, it has been recognized that large-scale simulation is a powerful and efficient tool to find and create novel functional nano-carbon materials.

Our aim is to investigate fundamental properties of nano-scale phenomena and to design nanostructure materials, using Earth Simulator. To this end, so far we have developed different large-scale simulation models, including tight-binding molecular dynamics model, *ab-initio* density functional theory (DFT) model, and time-dependent DFT model.

Our subjects in the current year are classified into two categories: development of a model and application of different models that had been optimized by our group for the Earth Simulator. The first one is extending a linear combination of atomic orbitals model to finite temperature case. The second one contains the following four physical studies: (1) controllable band gap of Mackey crystal for a solar cell material, (2) ability of adsorption of radioactive cesium and strontium on carbon-nanotube, (3) electron transport properties of grapheme for electric device, and (4) collective motion of molecular dimer of acetylene molecules inside carbon-nanotube (CNT).

2. Development of a model

2.1 Finite-temperature LCAO method using Slater-type basis functions

Linear combination of atomic orbitals (LCAO) methods have made a great success in the study of electronic structures of atoms, molecules, and solids. The conventional LCAO methods, however, are formulated for ground-state systems. This makes it difficult to extract finite-temperature properties from those calculations.

The aim of our study is to propose an approach for extending the conventional LCAO methods to finite-temperature case. As an application of our approach, we have developed a code named MORIS, which calculates finite-temperature electronic structure within the unrestricted Hartree-Fock approximation.

In the implementation of most LCAO methods, the true atomic orbitals are not used, but approximate atomic orbitals are used instead. They are called basis functions. Among the basis functions, Gaussian-type orbitals (GTOs) and Slater-type orbitals (STOs) are extensively used in literature. We adopt STOs, since they resemble the true atomic orbitals more closely than GTOs.

Figure 1 shows the Helmholtz free energy for a hydrogen fluoride (HF) molecule at $T=300\text{[K]}$ within the unrestricted

Hartree-Fock approximation with STOs. The orbital exponents without optimization are set to the values of isolated H and F atoms.

As seen from Fig. 1, when the optimization of the orbital exponents is not performed, the calculated values of the bond length and dissociation energy are 0.99[Å] and 2.28[eV], respectively. On the other hand, when the optimization of the orbital exponents is performed, the calculated values of the bond length and dissociation energy are 0.93[Å] and 3.25[eV], respectively. Since the experimental values of the bond length and dissociation energy for a HF molecule are 0.92[Å] and 5.84[eV], respectively, we find that the optimization of the orbital exponents makes a significant modification of the bond length and dissociation energy. Figure 2 shows the optimized values of the orbital exponents as a function of the bond length. We can see that the values of the orbital exponents for a HF molecule are considerably different from those for separated hydrogen and fluorine atoms. This indicates that using the orbital exponents for isolated atoms is not appropriate in the case of molecules. In the conventional LCAO methods, the orbital exponents are determined to be the best for the electronic structure not of the entire molecule but of each atom; therefore the feature of our LCAO method consists in being able to

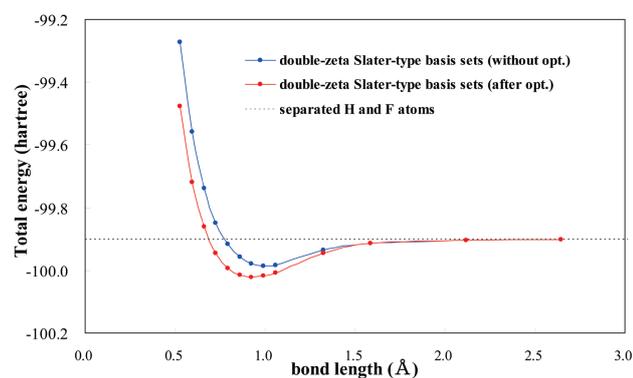


Fig. 1 The Helmholtz free energy for a HF molecule at $T=300$ [K]. The blue and red lines represent the simulation results without and after optimization of orbital exponents, respectively. The orbital exponents without optimization are set to the values of isolated H and F atoms.

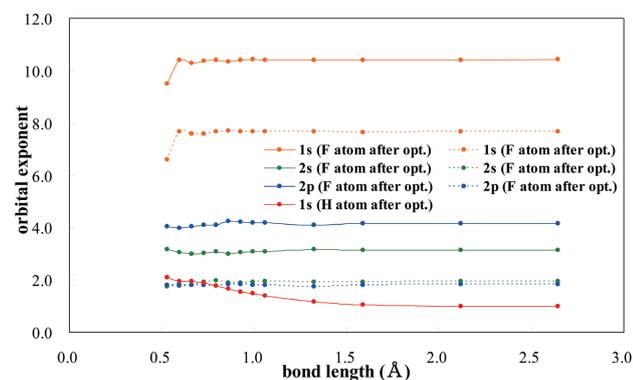


Fig. 2 The optimized values of the orbital exponents for a HF molecule at $T=300$ [K].

optimize the orbital exponents as well as in being able to calculate the electronic structure at finite temperature.

3. Physical studies on nano carbon-based materials

3.1 Controllable band gap of Mackay crystal for a solar cell material

We have been carrying out the whole simulations on the Mackay crystals using GSW method to find synthesis process and DFT approximation to obtain mechanical and electrical properties. These simulations showed the band gap for Mackay crystals are ranged from 0.05 eV to 0.94 eV in the different sizes, P48, P144 and P192, respectively. On the basis of this prediction, we proposed a tandem-type solar cell designed by stacking Mackay crystal films with the different band gap. Such a solar cell would be able to absorb the sun light with spread spectrum.

In this year, the possibility whether the band gap can be controlled by putting pressure and distorting the lattice, besides by using the different sizes, is investigated. Figures 3 and 4 show the effect of crystal strain on band gap. Where Fig. 3 is for zigzag type, Fig. 4 armchair and the top figure represents total energy vs. lattice constant, bottom figure band gap vs. lattice constant. The lattice constant of a steady Mackay crystal with the minimum value in terms of total energy is shown by the arrow in the figure.

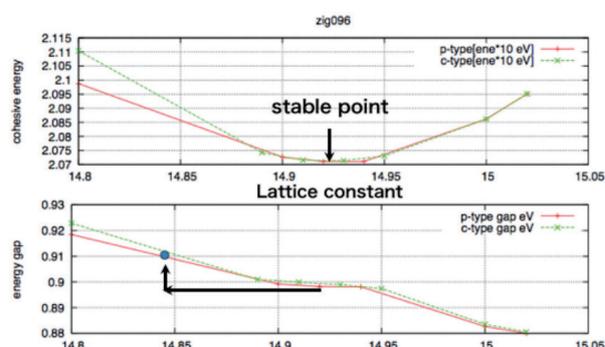


Fig. 3 For zigzag type, top figure represents total energy vs. lattice constant, bottom figure band gap vs. lattice constant. The band gap increases with decreasing the lattice constant.

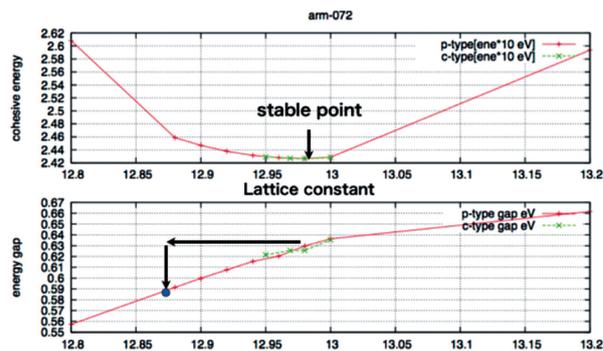


Fig. 4 For armchair type, top figure represents total energy vs. lattice constant, bottom figure band gap vs. lattice constant. The band gap decreases with decreasing the lattice constant.

In general, if the lattice constant decreases, then the wave function of atomic orbitals may overlap each other. Thus the crystal becomes metallic and the band gap decreases or disappears. This scenario agrees with the result of armchair type. Conversely, in the case of zigzag type, the band gap extends if lattice constant decrease. Such a interested band mechanism is unknown yet.

By compression of crystal (lattice constant becomes to decrease), one type of crystal extends band gap and the other type of crystal narrow. The band gap is controllable by compressing the lattice constant. We expect the high efficient tandem-type solar cell consisting of different band gap of Mackay crystal.

3.2 The ability of adsorption of cesium on CNT^[1]

The remediation of environment contaminated by the falling radioactive species as cesium and strontium, is one of the urgent technical targets of our society. It is required to develop the new materials having features as effective absorbent, low cost, abundant supplies and incineration or so for the practical cleaning operation and deployment. In this context, we have studied the ability of carbon nanotubes to adsorb the radioactive cesium atoms.

From the view point of atomic binding energy, we have investigated the adsorption process of cesium atoms on CNT through simulation. As first stage we modeled that both cesium and carbon of nanotube exist only in the atmosphere.

Simulations showed that when the isolated three cesium atoms form a cluster, the total energy decrease by the formation energy, about 0.7 eV per atom. The cluster state is then stable than the isolated. Furthermore, when a cesium cluster is

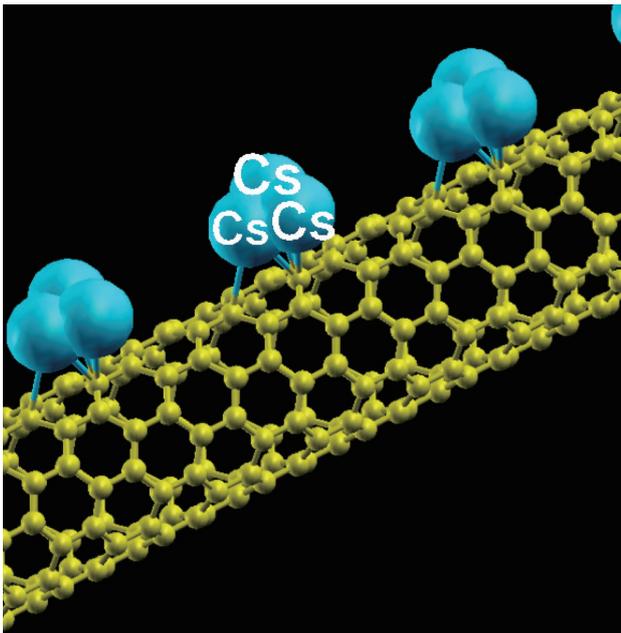


Fig. 5 Cesium clusters adsorb on the surface of CNT. CNT would be candidate for materials to remedying the radioactive Cesium atoms from environment.

adsorbed on the surface of carbon nanotube shown as in Fig. 5, the total energy additionally decreases by 1.5 eV. As for cesium, simulation on different four elements shows, as in Fig. 6, that the cesium cluster is most easily adsorbed on the surface of CNT among the four elements.

The mechanism of adsorption of cesium on the surface of CNT is considered from atomic charge movement. Figure 7 shows the number of electrons filling the atomic orbital. It shows the atomic binding changes the number of the electrons occupied, between before- and after- absorption.

We understand that the cesium atoms interact with another

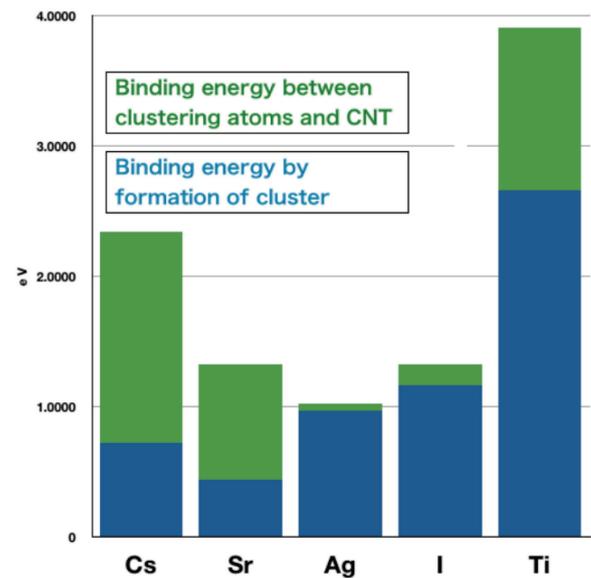


Fig. 6 Binding energy for five elements. The blue means the binding energy between three isolated atoms and their cluster and the green binding energy of cluster on the surface of CNT.

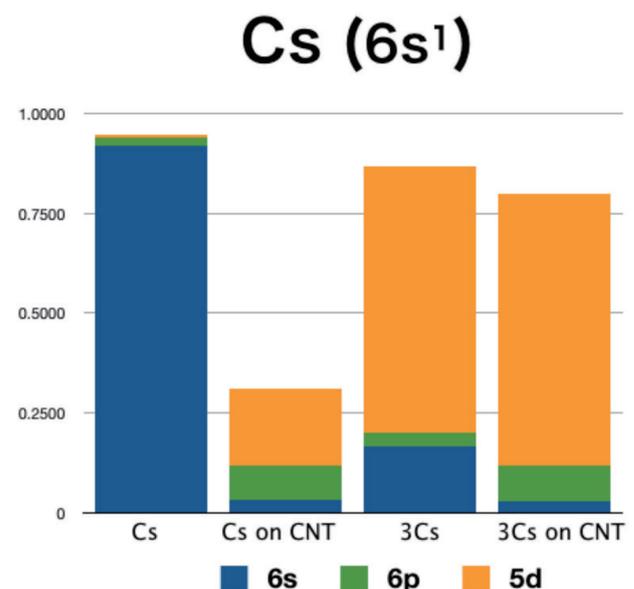


Fig. 7 Atomic orbitals are full with electrons. The isolated cesium atom consists of almost all 6s electrons of 0.9 e. On the surface of CNT, the number of electrons on cesium atom decreases. The cluster of three atoms fills with electrons of 5d-orbital.

cesium atoms and CNT by moving the electron from 6s-orbital to empty 5d-orbital. The π -orbital of CNT plays important role in the adsorption of cesium.

3.3 Electronic Transport properties of graphene for electronics device^[2]

On the basis of a tight-binding (TB) theory, we have developed a simulation program to investigate the electron transport characteristics of graphene for both basic properties and applicability for 'nano-carbon conductor.' The effect of contact between nano-carbons conductor and metallic electrodes are studied through simulations. It is our assumption that the electric transport be controlled by wave function overlap between nano-carbon structure and metal rather than by intrinsic properties of nano-carbons.

Last year we simulated an electron transport under the parameter of a hopping integral t_α coupling between electrodes and α -orbital of CNT. The results strongly depend on choice of orbitals α . The electron transport is strongly

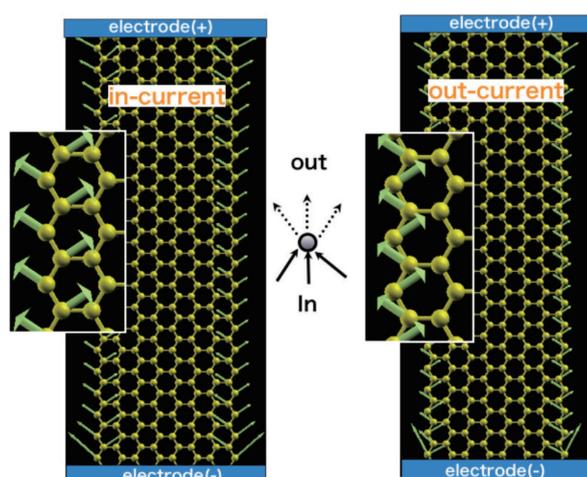


Fig. 8 The arrow shows the direction of in or out electron flow for zigzag ribbon graphene.

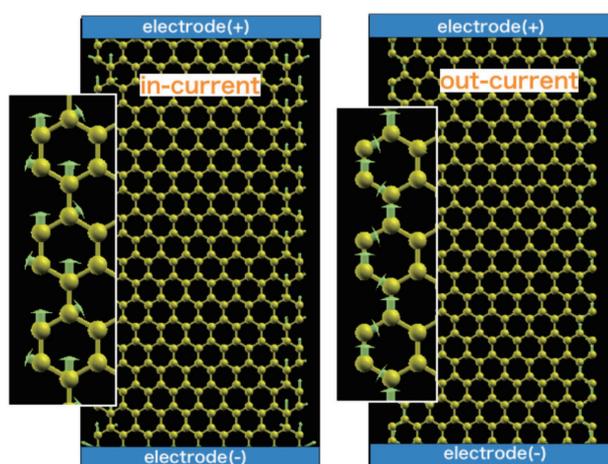


Fig. 9 The arrow shows the direction of in or out electron flow for armchair ribbon graphene.

dominated by coupling through the σ - or π -orbital. The π -orbital coupling, rather than σ -orbital coupling, of CNT allows better conductance.

This year we applied the simulation model to graphene sheets. Figure 8 shows the direction of electron flow on each atom for zigzag edge. The electrons flow almost at both edges. The graphene for armchair edge is shown in Fig. 9. It is expected that the electronic conduction becomes excellent even if graphene have a narrow width. As for electronic transport, the π -orbital coupling of graphene allows better conductance. As a result, it is considered that, as the π orbital is located vertically at the surface, the electrode can be connected with the π -orbital directly, even if graphene is sandwiched in between electrodes. Such behavior of graphene is one of promising features for highly efficient electronic conductor device.

3.4 Collective motion of molecular dimer of acetylene molecules inside CNT

Following 2010, investigation of molecular dynamics under irradiation with the femtosecond laser was continued. Last year, we proved laser-induced disintegration of HCl molecules inside (8,0) CNT, and that result was published in Phys. Rev. Lett (2010). We further tested collective motion of molecular dimer of acetylene (C_2H_2) molecules in larger diameter (14,0) CNT. Acetylene is important gas for fuel and source of higher organic molecules, and nano-space reaction inside CNT has attracted high attentions. We performed electron-ion dynamics under presence of pulse laser with alternating electric field mimicking the laser pulse by solving time-dependent Kohn-Sham equation

$$i\hbar \frac{d\Psi_n(r, t)}{dt} = \{H_{KS}(r, t) + V_{ext}(r, t)\} \Psi_n(r, t),$$

which includes scalar potential mimicking optical field.

Two acetylene molecules were investigated and the stable orientation of them was found to be perpendicular with respect to tube axis shown in Fig. 10. Laser pulse with wavelength

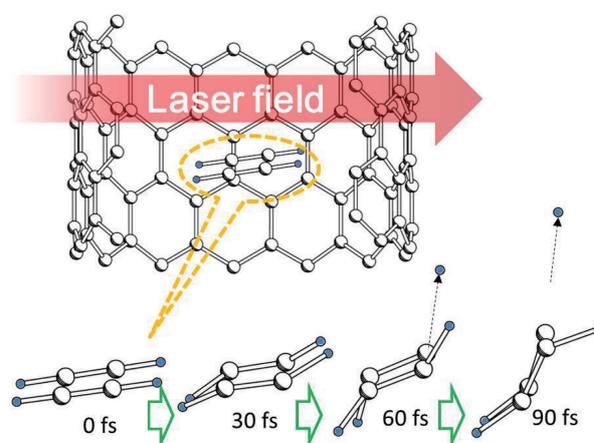


Fig. 10 Two acetylene dynamics inside (14,0) CNT upon laser irradiation. The display showing the dynamics of two acetylene molecules omits the atomic positions of (14,0) CNT for easy viewing.

800 nm with full-width of half maximum 2 fs was applied with maximum intensity of laser field $E_{\max} = 12 \text{ V/\AA}$. Interestingly, after giving ultra-short laser pulse, these two molecules start to rotate with synchronized manner, while C-H vibrations inside molecules were not synchronized.

Emission of hydrogen atom from one of the two acetylene molecules were seen but not shown in weaker intensity of pulse ($E_{\max}=10 \text{ V/\AA}$). This result was compared to isolated single acetylene molecule and artificially located two acetylene dimers under impulse of ultra-short laser. Inter-molecular interaction during the photo-excited dynamics and modulation of the laser field by CNT wall were recognized by comparing the simulation results. We believe that this kind of simulation would be useful for designing new chemical pathway forming new material with use of CNT as nano-test tube. This simulation has just accepted for the publication in Proceedings of the National Academy of Science of the United States of America (PNAS) in 2012.

4. Summary

We have developed a new computer code named MORIS from scratch. We also have performed large-scale simulations for nano materials by using large-scale simulation models, including tight-binding molecular dynamics model, *ab-initio* DFT model, and time-dependent DFT model. These models allowed us to simulate the nano material properties with excellent performance on the Earth Simulator. Our large-scale simulations can provide valuable information on physical phenomena, method of materials design, and method of development of novel functionality of nano carbon-based materials.

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カーボンナノチューブの特性に関する大規模シミュレーション

プロジェクト責任者

手島 正吾 高度情報科学技術研究機構

著者

手島 正吾^{*1}, 中村 賢^{*1}, 宮本 良之^{*2}, 中村 壽^{*1}

*1 高度情報科学技術研究機構

*2 産業技術総合研究所 ナノシステム研究部門

1. 研究目的

優れた物性が予想されたナノテクノロジーの基本材料であるナノ炭素類（カーボンナノチューブ（CNT）、フラーレン、グラフェン）を対象として、熱伝導、機械特性、新奇な物質であるマッカーイ構造体の生成パス、次世代CPUのCNT配線における電磁作用の影響など、実験では得がたい物理現象、新物質創成法、新機能発現法を大規模な第一原理・強結合近似分子動力学シミュレーションによって明らかにし、その成果を学界、先端産業へ提供するとともに、地球シミュレータの性能を実証する。加えて、ナノ炭素類の新奇特性を人類的課題である温暖化対策としての環境技術・新エネルギー開発に役立てる大規模シミュレーション研究を実施する。

2. 成果

本研究により産業応用、学術応用、計算科学に係わる以下のような成果をあげることができた。

- (1) 有限温度における物理量を予言できる形へLCAO法を拡張した第一原理計算コードを作成した。実装にはスレーター型軌道を用いて、少ない数の基底関数で高い精度の計算を可能にした。また有限温度下にある分子のさまざまな状態において、スレーター型軌道の軌道指数を自動的に最適化することができるため、従来のLCAO法よりも物理量が基底関数の取り方に依存しないシミュレーションを可能にした。テスト計算として、27°Cでのフッ化水素のシミュレーションを実施し、軌道指数の最適化により計算結果が大幅に改善することを示した。
- (2) マッカーイ結晶の太陽電池への応用の観点から、第一原理計算法によるマッカーイ結晶の電子状態計算を実施し、その格子定数依存性を調べた。昨年度までの研究では、マッカーイ結晶はそのサイズによりバンドギャップが異なることから積層マッカーイ結晶からなる多接合型太陽電池を提案した。本年度は、安定状態の近傍で結晶を歪ませ格子定数を変化させたときのバンドギャップの変化を調べた。格子定数を小さくすれば電子軌道が重なりバンドギャップは小さくなると予想されるが、あるサイズのマッカーイ結晶では逆に大きくなる結果を得た。外力によりバンドギャップを抑制することが期待できる。そのメカニズムを今後明らかにする。
- (3) 大気中、地層、海水に拡散した放射性元素を回収する技術は社会的急務である。その材料として、安価で、豊富で、安全で、処理が容易な新素材を開発することが望まれており、本研究ではカーボンナノチューブによるセシウム元素回収の可能性を調査した。結合エネルギーの観点から、CNTへの吸着のし易さを調べた結果、孤立した3原子セシウムは結合してクラスターになり易く、さらにこのクラスターがCNTに結合し易いことが明らかになった。比較のために、4つの元素について、同様の計算をしたが、クラスター化したセシウムが最もCNTと結合し易い事が明らかになった。吸着のし易さを、電荷移動の観点から考察した結果、セシウムはCNTへ移動させ電子を減少させ、さらに6s軌道から空の5d軌道へ電子を移動させ、CNTや他のセシウムと強い結合をたもっていることが分かった。特に、CNTの π 軌道と5d軌道が強い結合をする。
- (4) 拡張した強結合近似分子動力学法により、グラフェンの高精度化した量子伝導計算を実施した。昨年度は、グラフェンの側面の影響を無視できるように電極を両端中央に小さく付け、グラフェンの電気伝導を調べた。本年度は、グラフェンの側面がジグザグ型とアームチェア型のときの影響を調べるために電極をすべてに付け、グラフェンの電気伝導を調べた。微視的に各原子位置での電子の流れを調べると、電子はグラフェンの内部ではなく端を流れやすいことが明らかになった。またジグザグ型とアームチェア型の端のバンド構造の違いによる電気伝導への影響は小さかった。CNTの場合と同様に、グラフェンの π 軌道を介した電極との接合が電気伝導を良好にすることが判った。グラフェンの電気伝導では、電子がグラフェンの端を流れることから、幅の狭いグラフェンでも良好な電気伝導が期待できる。
- (5) CNTをナノ試験管として内部にアセチレン分子ダイマーを入れてレーザーパルス照射した場合とアセチレン分子ダイマーに直接レーザーパルス照射した場合との反応を比較した。直接照射の場合、ダイナミックに分子間干渉が生じた。CNT内部での照射の場合、CNTによる光電場変調により直接照射の場合とは反対方向に水素分子は運動

し、CNTの大きな伸縮運動にともなって2個のアセチレン分子の協調的な回転運動が始まる。この運動は重合などの反応に有利に働くと期待できる。

キーワード: TB理論, 第一原理手法, 時間依存DFT, カーボンナノチューブ, フラーレン, グラフェン, マッカーイ結晶, 太陽電池, グリーンエネルギー, 量子電子伝導, 光電材料