Large Scale Simulations for Carbon Nanotubes

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CARBON NANOTUBE RESEARCH GROUP
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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 developing a new *ab-initio* method for treating finite-temperature systems. For the second one, we present the simulation results of the following three studies: (1) ability of CNT adsorbing Cesium in the environment, (2) CNT dynamics under pulse laser, and (3) simulation of Helium Ion Microscope of grapheme.

Keywords: Large scale simulation, *ab-initio* theory, Time-dependent DFT, Carbon Nanotube, Fullerenes, Graphene, 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 developing a new *ab-initio* method for treating finite-temperature systems. The second one contains the following three physical studies: (1) ability of adsorption of radioactive cesium on carbon-nanotube (CNT), (2) CNT dynamics under pulse laser, and (3) simulation of helium ion microscope of graphene.

2. Development of a model

The linear combination of atomic orbitals (LCAO) method is one of the most powerful theoretical methods for computing the electronic structure of materials. The conventional LCAO method, however, is formulated for ground-state systems with a fixed number of electrons. This makes it difficult to extract finite-temperature properties from those calculations. In the preceding year, we have extended the LCAO method to finite temperature with the Mermin functional and developed code to implement our method. The aim of the present study is to optimize the simulation code corresponding to two-electron repulsion integral which accounts for more than 90 percent of the total computation time. The procedure of the optimization is as follows: (i) The six-fold integral in two electron repulsion integral is transformed into five-fold summation and one-fold integral as shown in eq. (1). (ii) Dividing five-fold summation into two groups consisting of two-fold, and three-fold summation, we can perform effective calculation using vector processors. As a result, the computation time is reduced by about a third.

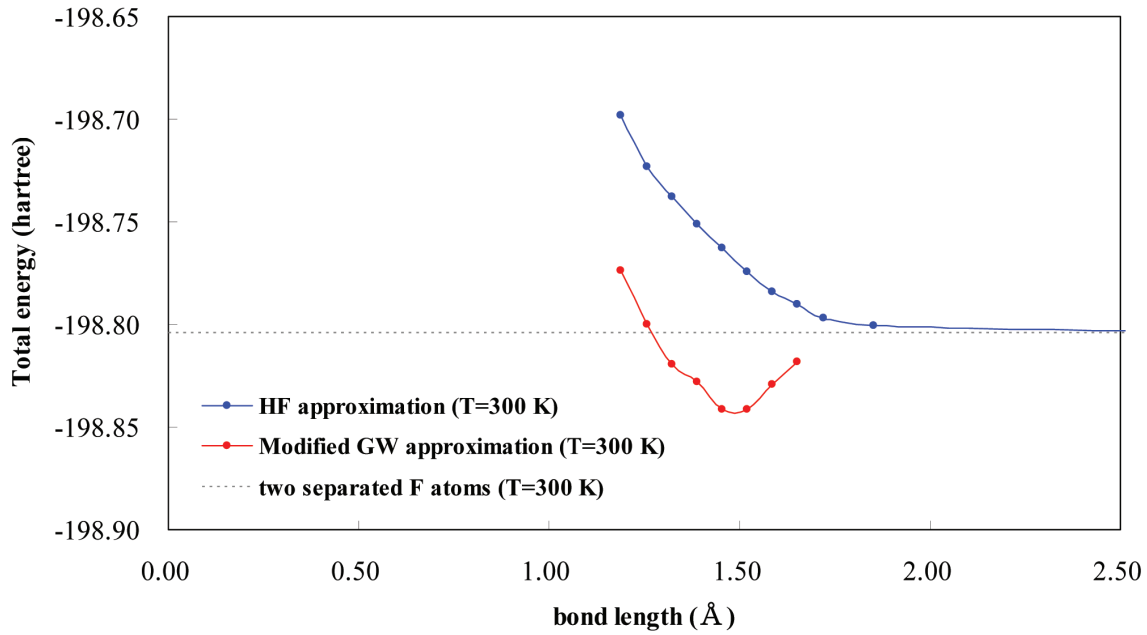

Fig. 1 Bond dissociation potential for F_2 molecule at T=300 K.

$$U_{\xi_a,\xi_b;\xi_c,\xi_d} = \int d\mathbf{r}_1 \int d\mathbf{r}_2 \chi_{\xi_a}(\mathbf{r}_1)\chi_{\xi_c}(\mathbf{r}_1)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\chi_{\xi_b}(\mathbf{r}_2)\chi_{\xi_d}(\mathbf{r}_2)$$
$$= \sum_{l_1=0}^{\infty}\sum_{m_1=-l_1}^{l_1}\sum_{l_2=0}^{\infty}\sum_{m_2=-l_2}^{l_2}\sum_{l=|l_1-l_2|}^{l_1+l_2} F_{l_1,l_2,l}^{m_1,m_2}\int Q_{l_1,l_2,l}^{m_1,m_2}(k)dk \quad (1)$$

As further development of the above method, we propose a new type of self-consistent scheme beyond the GW approximation, which we call modified GW approximation. As an example, Fig. 1 shows the bond dissociation potential for the F_2 molecule. According to the Hartree-Fock approximation, the F_2 molecule does not exist at all, whereas the fact is that it exists and is known. On the other hand, when the modified GW approximation is used, its bond dissociation potential has an energy minimum and provides a reasonable description of the F_2 molecule. This result indicates that our scheme includes the effects of electron correlation in an appropriate way.

3. Physical studies on nano carbon-based materials

3.1 The ability of CNT adsorbing Cesium in the environment

For investigating the applicability of nanocabons to the environmental remediation, CNT has been studied on the adsorption for Cesium (Cs) by the first principle calculation. Our simulations give results that there are no clear differences between a single or double walled CNT (SWCNT, DWCNT). But the adsorption becomes strong as the CNT radius decreases, or curvature increases. Furthermore, applicability of CNT is influenced in the environment. A metal or atomic state of Cs in vacuum space can be well adsorbed on CNT. A ionic state of Cs^+ as in water or seawater environments can be also well adsorbed on CNT. Figure 2 shows that Cs^+'s with three or four water molecules are well adsorbed on CNT. This implies that CNT adsorbs Cs^+ equilibrated with three or four water molecules rather than five ones. If Cs is Cs^+ in the mixture of AM^+'s as Na^+ and K^+, the effect of Na^+ or K^+ on CNT adsorbing Cs^+ is small. In Fig. 3, the Cs^+ cluster breaks a bond of with one of three water molecules and then CNT adsorbs the Cs^+ cluster. But the K^+ cluster stays in the initial position and is not adsorbed on CNT. The Cs reacting with water vapor in air becomes to the compound of CsOH. CNT cannot adsorb CsOH. It should be noted that CsOH is easily dissolved and ionized in water. Through adsorbing Cs^+ or the ionized state, CNTs such as SWCNT and DWCNT can be basically applicable for the environmental remediation of the radioactive products as in river, lakes, marshes and coasts.

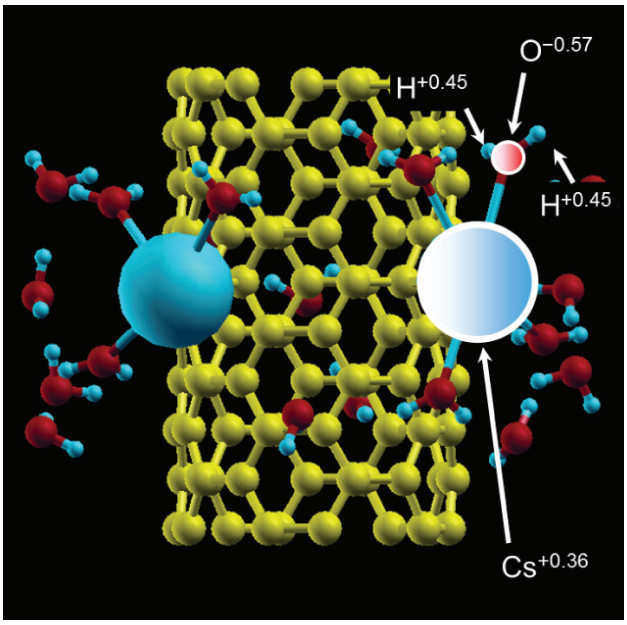

Fig. 2 Two Cs^+ adsorption with twenty water molecules. CNT adsorbs the Cs^+ equilibrated with three or four water molecules rather than five ones.

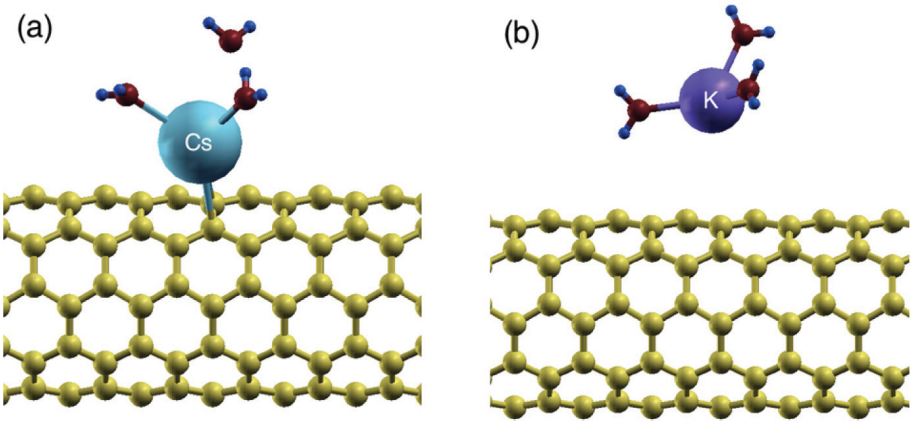

Fig. 3 In the Cs^+ case in (a), the Cs^+ cluster is leaving a water molecule and is adsorbed stably on CNT, taking with the rest of water molecules. On the other hand, K^+ in (b) shows that K^+ bonds easily with water molecules and becomes more stable structure than that adsorbed on CNT.

3.2 CNT dynamics under pulse laser

Last year we investigated the possibility of applying CNT as testing-tube of photochemical reactions of molecules inside CNT (Publications in PNAS, Vol. 109, 8861 in 2012, and PRL, Vol. 105, 248301 in 2011). This year, for practical purpose, we investigated the toughness of CNT against a strong pulse laser pulse According to the first-principles simulation, very short pulse can induce large radial deformation on semiconducting CNT, and interestingly, a larger diameter (14,0) CNT was found to be weaker than smaller diameter (8,0) tube as denoted by Fig. 4, which shows radial breathing motion of (8,0) and (14,0) CNTs under a pulse laser shot.

3.3 Simulation of Helium Ion Microscope of grapheme[1]

The Helium Ion Microscopy (HIM) is newly developed experimental technique, which has recently applied for imaging graphene devices. The imaging is made by counting secondary emitted electron upon impact of fast He ion on the sample as a function of impact position. We has performed electron-ion dynamics simulation to clarify the physical origin of electron emission and limit of resolution of HIM with a thin beam-size of He ion. (This work was published in PRL, Vol. 109, 265505 in 2012.) Figure 5 (a) shows intensity of secondary emitted electron as a function of He-impact point (white color means highest intensity and dark green means lowest intensity). Figure 5 (b) shows similarity of valence charge density of graphene to the HIM image. The current result shows feasibility of taking lattice image of graphene by HIM with narrower beam-size and recognition of presence of defects.

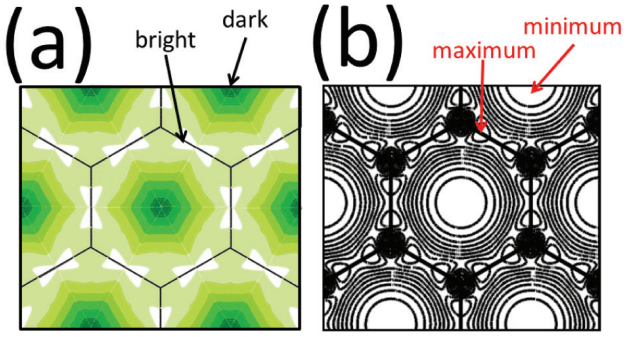

Fig. 5 (a) Simulated HIM image and (b) valence charge density of graphene.

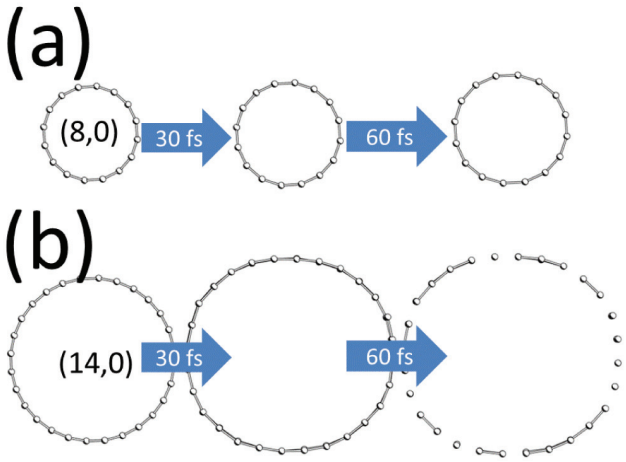

Fig. 4 Expansion of diameter of (a) (8,0) CNT and (b) (14,0) CNT upon applying ultra- short laser pulse with perpendicular polarization to tube axis.

4. Summary

We have developed a new computational scheme based on the preceding year's study. We also have performed large-scale simulations for nano materials by using large-scale simulation models, including *ab-initio* DFT model and time-dependent DFT model. Our achievements are summarized as follows:

(a) We optimized our simulation code to calculate free energy of systems at finite-temperature systems based on the LCAO method. Furthermore, we developed a new type of electron correlation technique for a more accurate calculation of the free energy.

(b) We performed the *ab-initio* simulation for the applicability of CNT to the environmental remediation. CNT was studied on the mechanism of adsorption and its ability for Cesium in the environment. It turned out that

CNT has applicability to environmental remediation.

(c) We are exploring the application of CNT as photochemical test-tube. The simulation tool for electron-ion dynamics were applied for testing stability of carbon nanotube (CNT) against strong laser field.

(d) We examined feasibility of measuring graphene by newly developed experimental technique (Helium Ion Microscopy), which will be powerful tool to characterize fabricated devices made of graphene.

References

[1] H. Zhang, Y. Miyamoto and A. Rubio, "*Ab initio* simulation of helium-ion microscopy images: The case of suspended grapheme", Phys. Rev. Lett. 109, 265505 (2012).

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

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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) 計算律速となる２電子積分計算のアルゴリズムを見直し、高精度化を図るとともに高速化を行った。原子数が多くなると、４つの分子軌道の組み合わせが増えるために、２電子積分の計算量は膨大となる。そこで２つの分子軌道から構成される項を事前に並列計算して配列に格納し、その配列を計算に用いることで、高速かつ効率良く２電子積分を計算することが可能になった。また強相関電子系の電子状態を適切に記述するために、電荷揺らぎに基づく電子相関を考慮したポスト - ハートリー - フォック法の開発を行った。

(2) ナノ炭素類の環境回復への利用の調査として、第一原理計算コードを用いて CNT のセシウム（Cs）吸着特性を調べた。吸着における CNT 特性の効果は、単層 CNT（SWCNT）、二層 CNT（DWCNT）のような構造間での明確な違いはないが、CNT の半径の減少もしくは曲率の増大に伴い CNT の Cs 吸着能力が強くなることが分かった。環境の効果については、Cs の状態が CNT の吸着能力評価の判断要因になることが分かった。Cs が真空中で金属状態もしくは原子状態にある場合、CNT は Cs を非常に良く吸着する。また Cs の状態がイオン状態（Cs^+）である水中もしくは海水中においても、CNT は Cs を吸着する。特に海水中では Cs^+ が他のアルカリ金属イオン（Na^+、K^+）と混在している海水中では、Na^+ と K^+ は CNT の Cs 吸着を妨げる大きな要因とはならないことが分かった。また Cs が水酸化セシウム（CsOH）等の化合物を生成する大気中では、CsOH は CNT に吸着しない結果となった。

(3) 昨年度は、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いれてレーザーパルスを照射した場合と、直接照射した場合との反応を比較した。本年度は、応用の限界を見極めるために、レーザーによる試験管たる CNT へのダメージの直径依存性を調べ、直径の細いチューブの方が耐性は高いという結果を得た。

(4) ヘリウムイオン顕微鏡（HIM）像を予測する計算技術を開発し、グラフェンの格子像を観測するために必要な HIM の解像度を求めた。シミュレーションを応用した結果、ヘリウムイオンのビーム径を小さくすることで高解像度のグラフェン格子像が観察できる可能性があることが判明した。

キーワード: 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, 光電材料