Large Scale Simulations for Carbon Nanotubes

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CARBON NANOTUBE RESEARCH GROUP
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Nano carbon materials as nanotube, fullerene and graphen have a potential for applications to the advanced industries. For nano carbon materials, it has been recognized as large-scale simulation is a powerful and efficient tool to find and create new functional nano carbon materials.

Aiming at conducting the productive simulation for nano-materials, we have developed the large-scale simulation models such as tight-binding molecular dynamic model, *ab-initio* density functional theory (DFT), and time-dependent DFT model.

In this term, by utilizing these models effectively, we have studied various physical properties of nano-carbon and applications such as (1) application of novel functions of Mackay Crystal to solar cell, (2) Large-scale Simulation on Electron Conduction in Carbon Nanotubes at Finite Temperature, (3) applications of time-dependent density functional theory for photo-chemical reaction of molecules inside CNTs. Along these works, we have realized as the Earth Simulator is a very powerful tool for large-scale nano-material simulations.

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 have been expected to bring breakthrough to material science and nanotechnology. A lot of potential applications of nanotube and fullerene to electronic devices have been attracted to scientists and engineers.

In the present days, large-scale numerical simulation by using supercomputer's computational performance has turned to be a very efficient tool and leverage for investigating their novel material properties. It now allows us to simulate complex nano-structures with more than ten thousand atom of carbon

Aiming at using large-scale simulations on the Earth Simulator, we have developed an application package of *ab initio* DFT theory and parameterized tight-binding (TB) models. Especially, the TB model shows that it is very suitable for the very large systems even if it has a lack of symmetrical arrangement.

In this term, we have carried out simulation studies, in which there are three primary objectives as (1) design of innovative nonmaterial with the required properties; (2) obtain fundamental properties in nano-scale matter, and (3) develop new applications.

2. Physical studies on nano materials

2.1 Application of Novel Functions of Mackay Crystal to Solar Cell [1]

We have carried out the extensive simulation on the Mackay crystals using GSW method to find synthesis process and DFT approximation to obtain mechanical and electrical properties. In 2009, from the investigation on electronic properties of Mackay crystals, it was indicated that the band gap of Mackay crystals of P48, P144 and P192 are ranged from 0.05eV to 0.94 eV. On the basis of this prediction, we proposed that a tandem-type solar cell could be conceptually designed by stacking Mackey crystal films with the different size. This solar cell would be able to

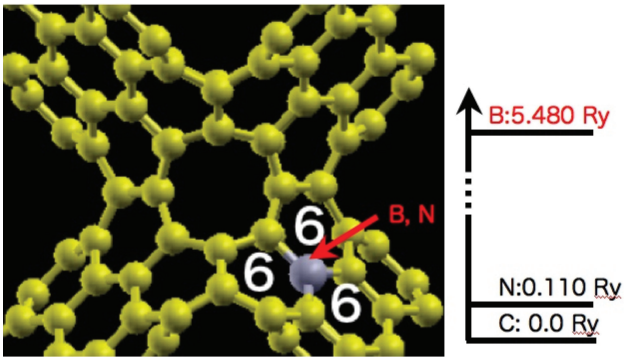


Fig. 1 A carbon surrounded only hexagon is replaced by Boron and Nitrogen atom. Replaced energy is described at the right side.

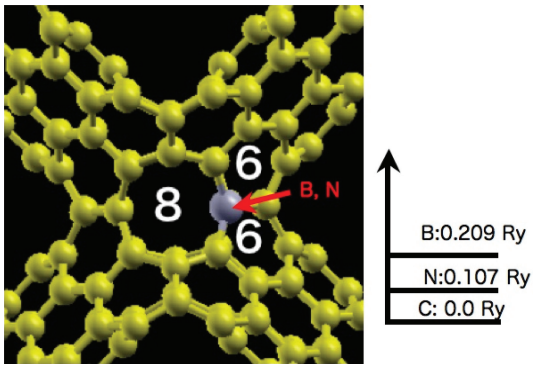


Fig. 2 A carbon surrounded two hexagons and a octagon are replaced by Boron and Nitrogen atoms. Replaced energy is described at the right side.

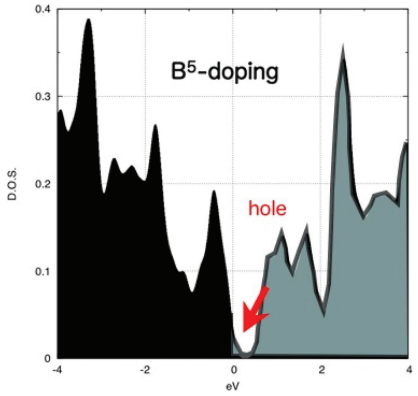


Fig. 3 The N-doping leads to injection of electron in the energy band.

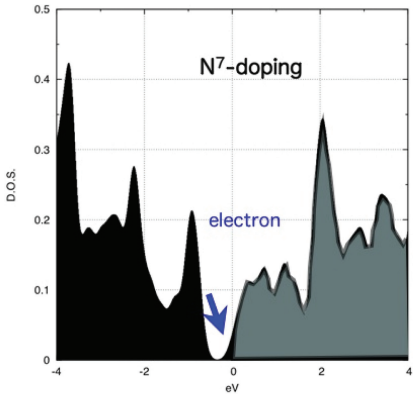


Fig. 4 The B-doping leads to injection of hole in the energy band.

absorb the sun light with near infrared light.

The electrical energy is converted from photon energy of solar cell. In order to derive electrical energy from the Mackay crystal, we have to set p-n semi-conductance junction. In this year, we have simulated the electronic structure of Mackay crystals with Nitrogen and Boron as the doping material for producing p-n Mackay junction. Nitrogen and Boron inject electrons and holes into the crystal as the carrier mobility, respectively, into the crystal. Figures 1 and 2 show the energy-dependence of doping materials inserted to different atomic sites. From these figures, it is clear that the doped atomic site is surrounded by only hexagons and by two hexagon and octagon in fig. 3, respectively. The replaced energy measured from pure crystal is also exhibited at the right side in Figs. 1 and 2. The simulation has revealed the doping of Nitrogen and Boron are more stable at octagonal than hexagonal one.

Figures 3 and 4 show the electrical density of state for Nitrogen and Boron doping to the octagonal site. The N-doping (B-doping) leads to the injection of holes (electrons) as shown in Fig. 3 (Fig. 5). Such as band structure indicates N- and B-doping to Mackay crystal can lead to a carrier of hole and electrons in the crystal.

As the next step, from valence-conduction band transition probability, we plan to simulate the photon energy absorption efficiency. Mackay crystals are expected to be a highly efficient photoelectric material for solar cell.

2.2 Large-scale simulation on electron conduction of carbon-nanotubes in finite-temperature environments [2]

The rapid development of integrated circuit technology is primarily achieved due to the sustained downscaling in the metal-oxide-semiconductor field effect transistor (MOSFET). Moore's law is a phenomenological observation that the number of transistors on integrated circuits doubles every two years. Silicon-based MOS technology, however, is considered to face technical and economical limits as soon as at the end of this decade. Therefore, new types of nanoscale devices are being investigated aggressively. In this context, a lot of attention is paid to integrated circuits made of carbon-nanotubes (CNTs). In nano-scale systems, the macroscopic Ohm's law breaks down due to the various effects caused by finite size effects. Here one needs to study the transport behavior of CNTs using a quantum mechanical description.

Our group has been developing an order-*N* code for simulating electron conduction. Our approach is based on the non-equilibrium Green's function (NEGF) formalism which is the method of choice to evaluate electron conductance in nanostructure.

$$J_{j_1\to j_2}=\frac{2e}{h}\sum_{\xi_1\xi_2} t_{j_2\xi_2 j_1\xi_1}(\{R\})\int\{f(\varepsilon-\mu_R)-f(\varepsilon-\mu_L)\}$$
$$\times\sum_{\sigma}\mathrm{Re}\left[\hat{G}^r_{CC}(\varepsilon)\{-\mathrm{i}\hat{\Gamma}_{LL}(\varepsilon)\}\hat{G}^a_{CC}(\varepsilon)\right]_{(j_1,\xi_1,\sigma)(j_2,\xi_2,\sigma)}d\varepsilon ,$$

where the retarded and advanced NEGFs are defined as follow:

$$\hat{G}^r_{CC}(\varepsilon) = = \frac{\hat{I}_{CC}}{(\varepsilon+\mathrm{i}\gamma)\hat{I}_{CC}-\hat{H}_{CC}-\hat{\Sigma}^r_{LL}(\varepsilon)-\hat{\Sigma}^r_{RR}(\varepsilon)} ,$$

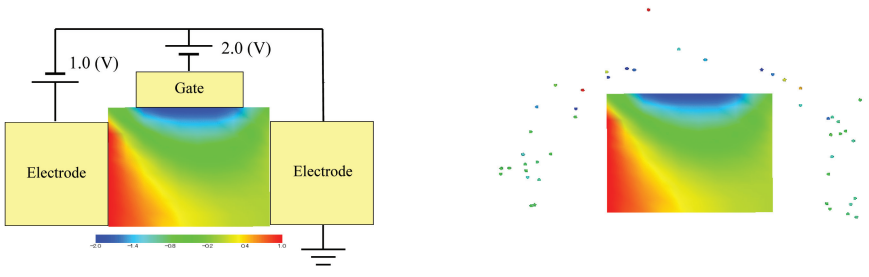
$$\hat{G}^a_{CC}(\varepsilon) = = \frac{\hat{I}_{CC}}{(\varepsilon+\mathrm{i}\gamma)\hat{I}_{CC}-\hat{H}_{CC}-\hat{\Sigma}^a_{LL}(\varepsilon)-\hat{\Sigma}^a_{RR}(\varepsilon)} .$$

The true electron conduction is obtained by taking the limit as g tends to positive zero. In order to calculate the NEGFs in the above equations, we have adopted the embedding potential method which works well on treating quasi-one-dimensional systems such as carbon-nanotubes. This method provides an algorithm of the order-N, indicating the possibility of performing high-performance computation in large-scale models. The NEGF formalism can also be applied to CNTs of arbitrary chirality or CNTs with defects.

Moreover, by solving self-consistently the coupled NEGF and three-dimensional Poisson equations, we can obtain the electrostatic potential distribution in carbon-nanotubes. In this case, we need to solve the Poisson equation as fast as possible. A promising method for this is to use the substitute charge method. However, since the conventional substitute charge method determines the values of the charges on the basis of empirically-predicted charge distribution, this method has the problem that its calculation accuracy depends on how to select the substitute charge distribution. Therefore, we have developed a new method by changing not only the values of the charges but also their positions. Our method allows us to impose the Dirichlet boundary conditions on three-dimensional surfaces with arbitrary shape and to treat even problems with incomplete boundary conditions. In addition, once the substitute charge distribution is determined, there is no need to repeat this procedure any more. This makes efficient and stable calculation possible. As an application of our substitute charge method, we consider the system consisting of one gate and two electrodes as shown in Fig.5 (a), where the gate voltage is 2.0 eV and the bias applied between two electrodes is 1.0 eV. Then, the effect of the gate and electrodes is represented by the substitute charges as shown in Fig. 5 (b).

Now, in order to simulate microscopic electron conduction at atomic scale using our method, we need to calculate NEGFs of which number is equal to the number of mesh points used in numerical integration with respect to energy. On the one hand, the accuracy of calculation increases with the increase of the number of mesh points; on the other hand, the number of mesh points needed to obtain reliable estimates of the electron conduction increases inversely proportionally with the strength of nanotube-electrode junction. As a result, when the strength of the junction is comparatively small, it takes enormous computing time to simulate the electron conduction. To overcome this difficulty, we have developed a method for computing the NEGFs with high accuracy and high speed by applying analytic continuation via the Pade approximants. An example of our method is shown in Fig. 6. We first have simulated NEGFs at g = 0.00094278 eV through the embedding potential method and computed the electron current indicated by the green circle. Using these NEGFs as input data of the Pade approximants, we obtained the electron currents represented by the blue triangles. Finally, applying the Pade approximants again to the values of the electron current corresponding to different values of g, we obtained the ideal results which are obtained in the limit as g tends to positive zero (the red lozenge in Fig. 6).

According to the simulation results using 80 nodes (640 processors) on the Earth Simulator, it took about 1,800 sec to compute all the NEGFs with out method. On the other hand, when all the NEGF is computed directly without the Pade approximants, it took about 5,100 sec to perform the same simulations. Hence, our method is about 2.8 more effective than that without the Pade approximants.



(a) (b)

Fig. 5 (a) Schematic view of the system consisting one gate and two electrodes; (b) the different color dots represent different values of the substitute charge.

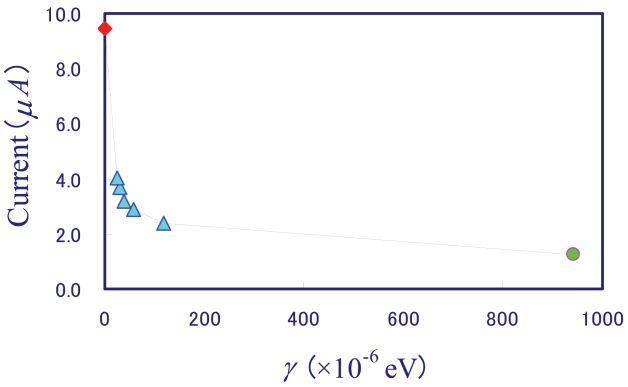


Fig. 6 The green circle was calculated via the embedding potential method. The blue triangles were evaluated from the Pade approximants of which input data are the NEGFs at g = 0.00094278 eV. The red lozenge is estimated using the value of the blue triangles as input data of the Pade approximants.

2.3 Application of time-dependent density functional theory for photo-chemical reaction of molecules inside CNTs [3]

Following 2009, application of femto-second laser was investigated for photo-chemical reaction of molecules inside CNTs. Since molecules in gas phase are dilute and thus has low cross-section of photo-irradiation, confining molecules into nano-space was expected effective to increase the cross-section. A question here is whether there is proper material which can confine molecules in narrow space and can penetrate optical field. We tested semiconducting (8,0) CNT, and discovered this CNT works as nano-test-tube. We performed electron-ion dynamics under present of pulse laser with alternating electric field mimicking the laser pulse by solving time-dependent Kohn-Sham equation

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

which includes scalar potential mimicking optical field.

An HCl molecule was chosen as our case study, which is historically studied as a subject of photo-induced disintegration. When this is encapsulated inside (8,0) nanotube exothermically, this molecule can be disintegrated as following figure with ultra-short femto-second laser pulse with corresponding power is 1.91×10^{15}W/cm^2.

This result will stimulate experimental work in nanotube community and been published in Physical Review Letters in 2010, as well as the last year's product (laser-induced graphene exfoliation). Because of the mass difference, only H atom obtained high kinetic energy which is enough to move outside from the open-end of the CNT into the vacuum. We expect that pulse laser can extract from any molecule that contains H atom being encapsulated by CNT.

This year, we are exploring more complex situation, i.e., a molecular dimer of acetylene which never exists in natural gas phase but can exist in CNT. Pulse-induced synchronized motion of two molecules inside CNT is monitored by the simulation. We expect that further time-simulation will reveal a new path of chemical reaction of these molecules.

3. SUMMARY

Large-scale simulations have been carried out on nonmaterial by using *ab initio* density functional theory and the parameterized tight-binding models. These optimized models allowed us to simulate the nano maretial properties with excellent performance on the Earth Simulator. It enables us to come across discoveries of novel phenomena in nano scale and to find out some useful materials for clean energies and nano device.

References

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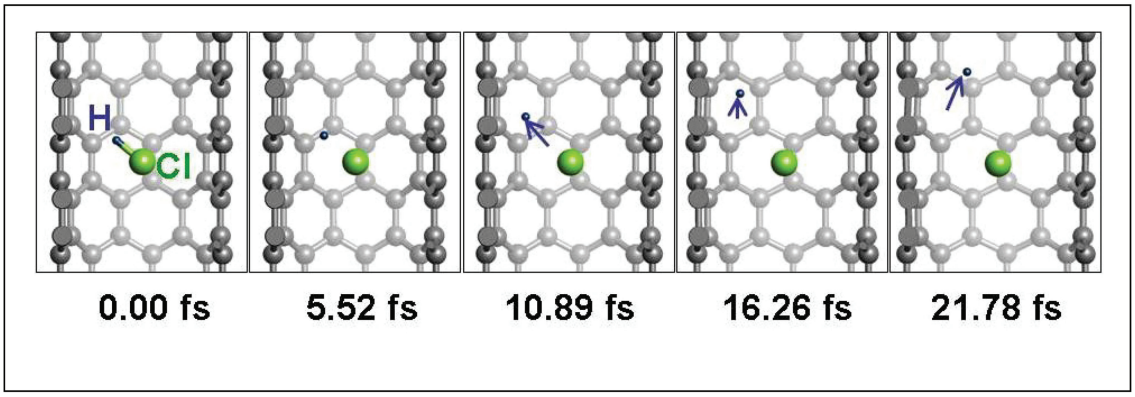

Fig. 7 Dynamics of an HCl inside (8,0) CNT.

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ナノテクの基本材であるナノ炭素類（カーボンナノチューブ（CNT)、フラーレン、グラフェン）の電子・機械特性を従来不可能だった大規模シミュレーションにより推定し、科学技術及び産業界に提供すると共に、応用として特性の優れた新構造を発見し、基本材の拡充に寄与する目的で実施された。

2. 成果

これまで、我が国のナノチューブ研究で当面する課題解決に向けた応用シミュレーションを実施した。本年度さらに、グリーンエネルギーに関するシミュレーションを推進した。得られた結果を以下に示す。

(1) これまでマッカイ結晶の包括的な特性把握のために、合成法、機械特性などのシミュレーションを実施してきた。昨年度は、電子構造特性のシミュレーションにより、マッカイ結晶が太陽電池材料としての可能性があることが示せた。本年度は、光電変換で生じた電気エネルギーを外部に取り出す為に、キャリアを持つを p-n 半導体を作りその特性を調べた。ホールと電子のキャリアを挿入するためのドーピング元素としてホウ素と窒素を選んだ。全エネルギー計算の結果､ドーピング元素がマッカイ結晶の８員環の原子の一部を置換し易いことが明らかになった｡また、置換された結晶の電子状態密度から、ホウ素置換では価電子帯にホールが、窒素置換では伝導体に電子がそれぞれ出現することが明らかになった。キャリアが導入されことにより、太陽電池として n-p 型半導体ジャンクションを利用して電流を外部に導く機能を得る事ができた。積層半導体マッカイ結晶は、応用として、広範囲の波長の光吸収を可能とする、高効率太陽が期待される。

(2) 本研究では、非平衡グリーン関数（NEGF）法を用いた伝導特性計算において、CNT のような擬 1 次元系で威力を発揮する埋め込みポテンシャル法を用いたアルゴリズムを採用し、オーダー N 法の量子伝導シミュレーションコードを開発している。NEGF 法では､ポテンシャル分布を求める際にポアソン方程式を高速に解く必要がある。そこで、電荷の値だけでなく電荷の位置も変化させることができる新たな電荷代用法を開発し、これにより高速で安定した計算を可能にした。これらの手法を用いて原子スケールでの微視的な電流をシミュレーションするには､エネルギーに関する数値積分での分点の数だけ NEGF を計算する必要がある。高速化を目的に、パデ近似による解析接続を用いて NEGF を高い精度で高速に求める計算手法を開発し、計算時間を 3 分の 1 程度に減らすことに成功した。

(3) ナノチューブ内分子分解反応の第一原理時間発展計算によるシミュレーション実施した。フェムト秒レーザショットの強さを制御するとナノチューブ内部で HCl 分子は自然に分解する現象が生じた。この結果は、カーボンナノチューブを使って分子の光化学反応の過程が進行する事を示している。

キーワード:大規模シミュレーション, タイトバインディング理論, 時間依存密度汎関数法, カーボンナノチューブ, グラフェン, マッカイ結晶, 太陽電池, グリーンエネルギー , 量子伝導, 光電材料, 光化学反応