様式例：課程博士用

平成 20年 1月 11日

機能材料　工学専攻	学籍番号	003165
申請者氏名	仙石　康雄	

指導教員氏名	関野　秀男 栗田 典之

論　文　要　旨（博士）

論文題目	DNA電荷移動シミュレーション手法の開発と実践

（要旨 1,200字程度）

次世代ナノデバイスとして実用化が期待されるものの一つにDeoxyribo Nucleic Acid(DNA)がある。DNAは配列と環境によって構造を制御できる事が知られており、またこれを伝わる伝導が螺旋軸に沿って起こる事から、分子回路等のナノデバイスへの応用が期待されている。しかし、その伝導の仕組みに関しては不明な点が多く、これを制御し、デバイスとして実用化するには至っていない。

DNAの電荷移動は、近年実験・理論の両分野で多くの研究が行われており、これをメインテーマに置いたシンポジウムやワークショップが開かれる程注目を集めている。然るに未だ諸説紛々の様を呈している理由としては、まず微小であるが故の実験の難しさがある。また理論計算においては、DNAの非常に柔軟な構造と高精度計算を行うには些か大きな分子サイズがシミュレーションを困難にしている。そこで本研究では、DNAの電荷移動機構の解明に主眼を置き、新しいシミュレーション手法の開発とその実践を行った。

まず電荷平衡法を用いた、Step-wiseな電荷移動の再現を試みた。これは各塩基対上に電荷を拘束した系を連続して計算することにより、系の全エネルギーから電荷移動の起こり易さを見積もろうという試みである。電荷平衡法は少数のパラメータから系の電荷分布を高速に求める手法であり、これを利用して各塩基対上に電荷が存在する際の最適化構造とそのエネルギーを求める事で、ある塩基対上の電荷が次の塩基対上へと移る際に必要なエネルギーを擬似的に算出した。

しかし、本手法には依然いくつかの問題点があった事に加え、高性能PCクラスタの普及や高精度近似手法の開発など、研究を取り巻く環境の進化を考慮した結果、高精度第一原理計算によるシミュレーションを目指し、Fragment MO法とGreen関数理論を用いたLandauer理論による伝導計算手法の開発に取り組んだ。

Green関数による計算法は、対象とする系のHamiltonianとOverlapから効率的に伝達係数を算出できる手法である。また、Fragment MO法は分子を小断片に分割して計算する事で、通常の高精度第一原理計算法ではコストなどの問題から計算自体が不可能な巨大な分子を計算可能にする方法である。これで得られた情報からGreen関数を生成し、伝導計算を行う手法を考察した。

また、この過程において、Fragment MO法の開発とこれに対する分極率計算及びGradient計算機能の追加を行い、それぞれ成果を得た。またGreen関数を用いた伝導計算理論へのFragment MO法の適用の準備として、Extend Hückel法のパラメータを利用した伝導計算法を使い、分枝状化合物の伝導計算を行った。本論文中ではこれらについても言及する。

様式例：課程博士用

平成 20 年 1 月 11 日

機能材料　工学専攻	学籍番号	003165
申請者氏名	仙石　康雄	

指導教員氏名	関野　秀男

論　文　要　旨(博士)

論文題目	DNA電荷移動シミュレーション手法の開発と実践

(要旨 1,200字程度)

In the 21st century, the development of science and technology reached to the nano world. For example, some integrated circuits in our personal computer or other home electronics are created in nanometer processes. In such micro scale, we encounter new problems that have not appeared in macro systems and it is difficult to tackle the problem only by experiments. The target is too small and it is very difficult to observe all the occurring there. To solve the problem, simulations including quantum become be more important than ever.

Recently, Deoxiribo-Nucleic Acid (DNA) becomes one of the candidate materials for novel nano device. DNA is known to be very important molecule for lives. It brings our genes to next generation. There are so many studies on this molecule since early days because of its important function. At first, almost all studies targeted the expression of genes. But after the completion of the human genome project at 2003, DNA studies of nano device application evolve at rapid pace.

One of the reasons for this is that the characteristic of DNA is clarified by many researches. There are some demonstrations where nano-scale characters or pictures are created by DNA using its strong self-assembling ability. It is expected that this ability makes the processing for nano devices easy.

And the other reason is its mysterious conductivity. The conductivity of DNA is not clearly characterized and it is sometimes reported as metallic conductor and sometimes as insulator. Some researchers observed semiconducting or superconducting behavior in this molecule. We have not arrived at a decisive theory for charge transfer mechanism in DNA, despite the many experimental and theoretical works are performed around the world.

From the viewpoint of experiment, there are some technical and cost problems arising from the process of such micro scales. Especially it is hard to observe the geometry of DNA at the moment of electron transfer while this as well as the solvent effect must be very important for understanding such observations of various conductivities.

Theoretical determination of the geometry is expected to play an important role. Unfor tunately, the conductivity is very sensitive to the geometry, and exhaustive calculations with a variety of molecular trajectories are required in order to meaningful evaluation. But DNA is too large for such calculations especially with high accuracy first principle methods. Hence many scientists perform the conductance calculation using semi-empirical methods like Hückel Molecular Orbital theory. However, accuracy of these methods is n ot sufficient.

In this study, to solve these problems, we introduce 2 types of new approaches to esti mate the conductivity of DNA. 1) Charge transfer simulation for DNA using Charge-Equ ilibrium method (QEq), 2) Landauer formalism based upon Green's function theory using Fragment MO method (FMO).

In the former, we estimate step-wise charge transfers in mismatched DNA by optimizi ng its total energy under the constraint in its partial charge distribution. QEq can estim ate the energy of the system very efficiently using only a few parameters. We developed this method to apply for the system with constrained charge. We investigate the relativ e stability of 15 base- pair mismatched DNA by constraining the positive and negative c harges on different DNA base-pair positions in order to evaluate the electron mobility of different DNAs. This method provided qualitatively consistent results with the experime nt on the electron mobility of DNA.

In the latter, the FMO method is used for conductance calculation. The FMO is an ap proximate quantum chemical method for huge systems like biological macromolecules wit h sufficient precision compared with conventional first principle methods. It enables larg e system calculation by dividing the entire molecule into fragments. We implement this method into a quantum chemical program package NWChem, and performed some test c alculations. The results showed its total energies of test molecules with little error again st the values by ab initio computations without approximation.

Recently, the FMO is known to provide not only an accurate total energy but also pro perties of the system. In the present study, we report the spectroscopic properties such as dipole moment, polarizability and their derivatives computed by the FMO in order to examine the accuracy of the method in predicting IR and Raman spectroscopies of biolo gical macromolecules. The results obtained are promising for predicting such static molec ular properties.

Finally we extend our framework of the FMO to evaluate non-equilibrium properties s uch as conductance, using Green's function theory. Although Landauer formalism with G reen's function theory proposed by Datta and co-authors is excellent way to estimate the conductance of mesoscopic systems, it requires Hamiltonian and Overlap matrices of the entire system. It is still hard to apply the method to novel nano-materials like nanotub e or DNA. These are large systems, and we need add even larger contact part to them.

We solved this problem using the FMO formalism. In this study, we show that the F MO can provide highly reliable evaluation of the transmission probability. The results sh ow the promising features of the method as a theoretical tool for conductivity study of l arge molecules.