Quantum Dynamical Approach to Electron Transfers in DNA-Molecular Nanowires

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Abstract. We numerically investigate electron transfers in nanowires which consist of deoxyribonucleic acid (DNA) molecules (up to five base pairs for double-strands and seven bases for single-strands) by quantum dynamical calculations. DNA molecules are applied to organic nanodevices and the performance depends on electronic transfer properties. Combining quantum chemical molecular-orbital calculations and stochastic mechanics, we provide an analyzing method of quantum dynamical electron motions. From one-electron wavefunctions or molecular orbitals, we calculate some dynamical properties, such as mean-square displacement and self-diffusion coefficients relating with electron mobility. Our calculation suggests that the electron transfers through the double-strands of GC base pairs while the electrons are localized in the double-strands of AT base pairs nor the single-strands of G bases.

1. Introduction
Attempts to apply DNA molecules to nanodevices, such as DNA wiring between metal nanoparticles on a substrate have recently drawn attention while no dynamical mechanisms of electron transfers in the DNA nanowires are well understood. The electron transport of DNA is reported as a metallic conductor [1, 2] or as a semiconductor [3, 4] or as an insulator [5, 6]. In order to clarify the microscopic mechanism of the electron transfer, direct simulations of the quantum electron motion in pure DNA molecules are considered to be useful. In past theoretical studies, discussions of electron transfers are mostly based on transfer integrals. In this paper, we present the quantum dynamics simulation approach to the electron motion in DNA nanowires with stochastic mechanics and molecular orbital (MO) calculations. Quantum motion of the electron dominated by the Heisenberg uncertainty principle is treated as the stochastic process in the quantum dynamics. Position of the electron is determined probabilistically in every-time while motion of the electron is still uncertain. It has been shown that time development of the electron motion in the stochastic mechanics is identical to the time dependent Schrödinger equation.[7, 8] It also enables us to investigate electronic transfer in molecules from dynamical properties of electrons like Brownian motion.[9]

In the following section, we briefly introduce the quantum dynamics simulation associated with Nelson’s stochastic mechanics and MO calculations. Then, the quantum chemical results of one-electron states and the simulation results of electron transfers are discussed in the last section.
2. Formulation and Calculation

We consider motion of an electron which is affected by potential energy $V$. Because of a quantum fluctuation, the path of electron motion is in-differentiable in anywhere. The motion of electron should be treat as stochastic process then the time development of stochastic process $X(t)$ is given by Ito type stochastic differential equation,

$$dX(t) = v(X(t), t)dt + \sqrt{\frac{\hbar}{2m}}dW(t),$$

(1)

where $m$ is electron mass and $W(t)$ denotes the Wiener process. When the drift velocity $v$ is related to the wave function $\psi$ as

$$v = \frac{\hbar}{m} \left( \Re \frac{\nabla \psi}{\psi} + \Im \frac{\nabla \psi}{\psi} \right),$$

(2)

the Newton-Nelson’s equation of motion (the extension of the Newton’s equation of motion to the stochastic process) is identical to the Schrödinger equation,

$$i\hbar \frac{\partial \psi}{\partial t} = \left( -\frac{\hbar^2}{2m} \nabla^2 + V \right) \psi$$

(3)

by coupling with the Wiener process and its time reverse process.[7]

When the wave function or the molecular orbital $\psi$ is obtained as the solution of the Schrödinger equation, time development of the quantum electron motion is calculated with Eq. (1) and Eq. (2) step by step. We call this successive procedure a quantum dynamics simulation.

We perform the quantum dynamics simulations of DNA molecules, double strands of guanine-cytosine (GC) base pairs, double strands of adenine-thymine (AT) base pairs, and single strands of G bases. The structure of the molecules is the same as the B-type DNA and the both ends are terminated by hydrogen atoms. The number of the base pairs is up to five for the double strands and the number of the bases is up to seven for the single strands. Estimating the electron transfer in the molecules, mean square displacement (MSD) of an electron is calculated from the time evolution of the electron motion. MSD is connected with self diffusion constant $D$ as $\text{MSD} \sim 6Dt$ for long time $t$. The electron mobility $\mu$ is estimated by Einstein’s relation, $\mu \propto D$, for the condition of constant temperature.

**Figure 1.** Level energy in DNA double strands of GC base pairs.  
**Figure 2.** Level energy in DNA single strands of G bases.
Figure 3. Molecular orbitals of HOMO and LUMO: (a) 5-GC base pairs. (b) 5-AT base pairs. (c) DNA single strand of 7-G bases. All atoms are hidden and the absolute value of the wavefunction surface is 0.01.
Table 1. Upper bounds of self-diffusion coefficients of HOMO and LUMO electrons at Time= 0. [nm²/ps]

|           | 2-GC | 3-GC | 4-GC | 5-GC | 3-G | 5-G | 7-G |
|-----------|------|------|------|------|-----|-----|-----|
| LUMO      | 10.1 | 11.9 | 13.1 | 14.7 | 12.0| 13.9| 13.6|
| HOMO      | 10.3 | 11.9 | 13.7 | 14.5 | 10.9| 13.1| 13.4|

Although the time dependent wave functions of many body systems are required for the stochastic mechanical simulations, we use quantum chemical molecular orbitals as the wave function for simplicity. Quantum chemical calculation is performed by GAMESS. We chose the minimal basis set STO-3G and restricted Hartree-Fock method because the molecular orbital is used just for drift field and no energetic exactitude is required. The time dependency of wave function is neglected because the statistical average of electron motion is corresponding to the static wave function. In the mean field approximation, electron-electron and electron-atom interaction are involved in the wave functions, and the electron is forced by just the wave function as the drift field.

We chose time step $dt = 0.01 \text{ a.u.}$ and perform each simulation for 41,350,000 steps. This time scale is equivalent to 10 ps ($10 \times 10^{-12} \text{ sec}$).

3. Results and Discussion

In Fig. 1 and Fig. 2, we show level energies around the HOMO-LUMO gap in the double strands of GC base pairs and in the single strands of G bases, respectively. Although the one-electron states become denser with the increase of the base number, the HOMO-LUMO gaps are fairly constant in these molecular sizes, $\sim 1 \text{eV}$ for the double strands and $\sim 2 \text{eV}$ for the single strands.
The energy gap value, 1eV, is close to order of magnitude of an intrinsic semiconductor band gap.

Evaluating the one-electron wavefunctions of HOMO and LUMO, we find the wavefunctions are widely distributed in the 5-GC DNA strand (Fig. 3(a)). The electron transfers whole length of the molecules along the MO. Note the wavefunctions are distributed both on the \( \pi \)-conjugated stacking of G bases and on the nucleotide backbone. On the other hand, the wavefunctions in the 5-AT DNA strand (Fig. 3(b)) and in the 7-G DNA single strand (Fig. 3(c)) are localized. The MO is distributed on the nucleotide part in the 5-AT strand, and in the 7-G single strand, the MO is on the G base but still localized on a few bases. No contribution to electronic current is expected for the localized wavefunction since the electron hopping to the other state beyond 1eV energy gap is considered to be occasional.

The quantum dynamics simulations at HOMO and LUMO levels are performed in the GC double strands and G single strands, and the time dependences of the MSDs evaluated from the simulation results are shown in Fig. 4 and Fig. 5, respectively. Since the gradient of the MSD curve gives the self-diffusion coefficient of the electron, it is shown that no diffusion occurs at larger time steps for the DNA single strands. Considering the lower values of MSDs at time= 0.1[ps], no electron transfers from end to end in the single strands. The electrons in the double strands still transfer for self-diffusion coefficients is finite at time= 0.1[ps]. These results are consistent with the quantum chemical inspections.

The supremum of the self-diffusion coefficient is estimated from the gradient value at time= 0 (table 1) because the MSD is a monotonically decreasing function. The upper bound of the self-diffusion coefficient in the GC double strand depends on the MO size. This can be understood by considering Eq. (2); As the wavefunction \( \psi \rightarrow 0 \), then the drift velocity \( v \rightarrow \infty \). The MO of larger DNA molecule is more complicated then the MO has more nodes in comparison with the smaller molecules. The motion of the electron becomes faster in the vicinity of the nodes. The fact also means that the electron whose wavefunction is broadened to whole molecule has possibility of contribution to electron current even if the distribution of the wavefunction is sparse.

Finally, we point out some results and merits of quantum dynamics approaches; By quantum dynamics simulations, it is supported that the electron transfers through the DNA double-strands of GC base pairs. Stochastic mechanics coupling with quantum chemical calculation enable us to simulate electron dynamics directly. The path of the electron as the stochastic process corresponds to the molecular orbital. This means that the dynamical analysis of stochastic mechanics is reasonable as conventional analysis based on transfer integrals. For the drift velocity of the electron depends on the wave function according to Eq. (2), the nodes of the molecular orbital accelerate the electron motion. It is shown that not only the extensity of the electron distribution but also the shape of the molecular orbital plays the important role of the electron transfer. Our dynamical approach is efficient and practical, and especially important for electronic analyses of molecular or nanoscale devices.

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