Electric conductance of DNA molecules with adjustable number itinerant electrons

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Abstract. Electric transport of DNA is closely related to the itinerant π-electrons due to the soft characteristic of DNA molecules. We suggest a model with adjustable number itinerant electrons (ANIE). The density of states (DOS), the transmission coefficient and the electric conductance were studied. It was found that the conductance depends sensitively upon the number of the itinerant electrons. Resistivity of Poly(dG)-Poly(dC) was obtained, which is well consistent with the experimental data.

1. INTRODUCTION

Deoxyribonucleic Acid (DNA) has attracted the attention of physical scientists as its potential application as a molecular wire. Electric conductance of DNA in different states has been investigated widely. However, the results are inconsistent and even contradict as for DNA being a conductor[1,2,3,4], a semiconductor[5~9] or an insulator[10], even a superconductor[11]. All these investigations reveal the complexity and particularity of DNA.

Theoretically, the Hükel model[12,13], the density functional theory[14-16], Green function[17] and the tight binding model including the electrodes[18,19] were employed to study the conductance of a DNA molecule. Effect of the fluctuating base-base coupling on the electrical transport was also studied[20]. However, all the present investigations did not give a satisfying explanation on the density of carriers in DNA. Yoo et al. have found that poly(dA)-poly(dT) behaves as a n-type semiconductor, whereas poly(dG)-poly(dC) behaves as a p-type semiconductor by the gate-voltage dependent transport measurements. This suggest that the number of itinerant electrons is influenced by the structure of DNA.[2]. Conwell et al. supposed that a DNA molecule has no free carriers in its thermal equilibrium state and the molecule orbitals have been fully occupied[21]. By photoexcitation, they obtained that the carrier may be not a simple electron or hole but a self-trapping state called a polaron such as that in organic conducting polymers. Photoexcitation experiments have demonstrated that charge excitations could be promoted from a donor metallointercalator to the DNA-bridge states, preferentially injected through the guanine highest occupied molecular orbital (G-HOMO), and transmitted to a tethered acceptor[22]. It was shown that the density of carriers in DNA could be adjustable and the carrier appears in a state of a charged excitation. Due to the strong electron-lattice interaction, the electronic states and the conductance of DNA will closely related to the density of carriers. In this paper we suggested a model of ANIE and studied the conductance of Poly(dG)-Poly(dC), which is composed of homogeneous (G/C) base pairs, as the representative of periodic chain, has been investigated widely in experiment and theory. In the next section, the Hamiltonian is given and the formulae are derived for a DNA molecule chain. The transmission coefficient, density of states...
(DOS) and the resistivity of Poly(dG)-Poly(dC) are calculated in section 3. Finally in section 4, a summary is made.

2. MODEL AND FORMULAE

A DNA molecule is a double helix: two strands of genetic material spiraled around each other according to Watson-Crick complementary base pair (bp). Each strand contains a sequence of bases (nucleotides), which is denoted as A, T, C and G. Electronic transporting through DNA proceeds along a quasi-one-dimensional pathway constituted by the overlap between π orbitals in neighboring base pairs. In our work the DNA chain is assumed to be connected to two semi-infinite electrodes.

As a DNA molecule has a soft structure, which depends upon the strong electron-lattice interaction, in the framework of tight binding approach, the Hamiltonian can be written as[21]:

\[
H = \sum_{n=1}^{N} \Delta_n c_{n,s}^+ c_{n,s} - \sum_{n=1}^{N} t_n (c_{n,s}^+ c_{n+1,s} + c_{n+1,s}^+ c_{n,s}) + \sum_{n=1}^{N} K \frac{1}{2} (u_{n+1} - u_n)^2
\]

(1)

Where the bp has been treated as a single site. \(\Delta_n\) is the on-site energy. \(c_{n,s}^+ (c_{n,s})\) is the electron creation (annihilation) operator with spin \(s\) on the \(n\)th bp. \(K\) is the elastic constant between adjacent bps. The transfer integral of the itinerant electrons is dependent upon the bond length and has been expended up to the linear term of displacement \(u_n\) of the \(n\)th bp as \(t_n = t_0 - \alpha (u_{n+1} - u_n)\). Quantity \(\alpha\) describes the strength of the electron-phonon coupling.

From Hamiltonian (1), we can obtain self-consistent circulated equations, which includes the eigenequation and the equilibrium condition (the subscript \(s\) has been neglected),

\[
E_\mu z_{\mu,n} = \Delta_n z_{\mu,n} - [t_0 - \alpha u_{n+1}] z_{\mu,n+1} - [t_0 - \alpha u_n] z_{\mu,n-1}
\]

(2)

\[
y_n = -\frac{2\alpha}{K} \sum_{\mu} z_{\mu,n}^* z_{\mu,n+1} + \frac{2\alpha}{(N-1)K} \sum_{m=1}^{N-1} z_{\mu,m}^* z_{\mu,m+1}
\]

(3)

where \(y_n = u_{n+1} - u_n\). The prime means a sum over the occupied states. Because the ends of the DNA molecule are fixed by the electrodes, a fixed-end boundary condition \(u_1 = u_N = 0\) is adopted.

DOS of DNA molecule is calculated by Gauss expansion,

\[
DOS(E) = \sum_{\mu} \frac{n_\mu}{(2\pi\sigma)^{1/2}} \exp\left[-\frac{(E - E_\mu)^2}{2\sigma^2}\right]
\]

(4)

where \(n_\mu\) denotes the degenerate degree of the state \(\mu\), \(\sigma\) is the coefficient of expanding width.

The electrodes are also described by tight binding model with site energy \(\Delta_d\) and hopping integral \(t_d\). Such choices for modeling the external leads allow us to scan the transmission profile of a given DNA sequence over spectrum with width \([-2t_d + \Delta_d, \ 2t_d + \Delta_d]\).

Transmission coefficient \(T(E)\) with energy \(E\) is calculated from a standard transfer matrix formalism[23],

\[
T(E) = \frac{4 - \frac{(E - \Delta_d)}{t_d^2}}{2 + \sum_{i,j=1,2} \rho_{ij}^2 \frac{(E - \Delta_d)}{t_d^2} \left(P_{11} - P_{22}\right) \left(P_{12} - P_{21}\right) - \frac{(E - \Delta_d)^2}{t_d^2} \left(P_{12} P_{21} + 1\right)}
\]

(5)

with

\[
\rho = \prod_{n=N}^{1} M_n, \quad M_n = \begin{pmatrix}
\frac{-(E - \Delta_n)}{t_{n+1}} & -t_n \\
\frac{1}{t_{n+1}} & 0
\end{pmatrix}
\]
The intrinsic resistivity corresponding to the state with energy $E$ can be calculated by the following formula\[20\]:

$$
\rho(E) = \frac{h}{2e^2} \frac{1 - T(E)}{T(E)} \frac{S_{DNA}}{L_{DNA}}
$$

with $L_{DNA}$ the length of the molecule, $S_{DNA} = 3 \times 10^{-18}$ m$^2$ the average cross section, and $h/2e^2 = 13k\Omega$ the quantum resistance.

In the condition of the linear response, the resistivity of DNA chain can be roughly estimated by (7).

$$
\rho = \frac{h}{2e^2} \frac{1 - \overline{T}}{\overline{T}} \frac{S_{DNA}}{L_{DNA}}
$$

Where $\overline{T}$ is the average of $T(E)$.

3. RESULTS AND DISCUSSION

The calculations were carried out in Poly(dG)-Poly(dC) with the number of base pairs $N=30$, which has been given by experiments\[9\]. Setting parameters as: $\Delta_{G/C} = 0.0$ eV, $\Delta_{C/G} = 0.3$ eV, $\Delta_{T/A} = 0.5$ eV, $\Delta_{A/T} = 0.65$ eV, $\alpha = 6 eVnm^{-1}$ and $K = 85 eVnm^{-2}$, $\Delta_d = 0.0$ eV, $t_0 = 0.4$ eV \[21\]. The absolute value $\eta = \frac{t_0}{t_d}$, expressing the contact between the electrode and the molecule. Indeed, if $t_d = t_0$ the potential barrier at the contact interface is small, allowing for a better investigation of intrinsic scattering properties inside the DNA, whereas for $\eta << 1$, strong backscattering at the interface might dominate the behavior of the transmission coefficient and screen its intrinsic features (such as the typical resistivity). This motivates our choice to consider $t_d = t_0$.

The dependence of the resistivity of Poly(dG)-Poly(dC) on ANIE are shown in Figure 1. The resistivity of Poly(dG)-Poly(dC) changes nonlinearly within the range $cm \Omega^{-10,10}$ and has a central symmetry at the half filling state. When the itinerant electron filling rate is low or high Poly(dG)-Poly(dC) represents good conductivity with the resistivity nearly $cm \Omega^{-3}$. Specially at half filling rate the resistivity of Poly(dG)-Poly(dC) is in the order of $10^{-2} \Omega cm$. This is consistent with the experiment result\[12\]. From this we infer that the itinerant electrons are half filled in its thermal equilibrium state but the filling number of itinerant electrons may have a departure from its thermal equilibrium state influenced by preparation condition.

![Figure 1](image1.png)

**Figure 1.** The dependence of the resistivity of Poly(dG)-Poly(dC) on ANIE.

![Figure 2](image2.png)

**Figure 2.** The transmission coefficient and DOS of Poly(dG)-Poly(dC) with half filling itinerant electrons, (a) the transmission coefficient, (b) DOS.
The transmission coefficient and DOS of Poly(dG)-Poly(dC) with half filling itinerant electrons is shown in Figure 2. Porath et al. have supposed that the charge carries are transported by band resonant in Poly(dG)-Poly(dC) [9]. Our calculation illuminates that the energy band is split into two parts, with an energy band gap about 1.0 eV, caused by dimerizing owing to the electron-phonon interaction (see Figure 2). When the itinerant electrons are half filled the molecule is a semiconductor. When the filling rate has a small departure from its thermal equilibrium state, some localized energy levels, which do not favor for charge transport in DNA molecule, appearing at the energy band-side, the resistivity of Poly(dG)-Poly(dC) becomes larger.

While the filling rate departs the half filling state over 10%, the energy band-side states delocalized, some empty energy levels existing in the energy band, the molecule shows a good conductivity with the resistivity nearly $10^{-3} \, \text{Ωcm}$. The calculation also suggests that the conductance of Poly(dG)-Poly(dC) can be improved by photoexcitation or doping to change the number of itinerant electrons.

4. Conclusion

DNA molecule is a large complex soft biomolecule. The preparation condition, doping and photo excitation all can cause the variety of itinerant electrons. In this paper, an ANIE model, which represents that the itinerant electron number of DNA sample varies with the preparation condition and the experiment condition, is put forward. We suppose that the itinerant electrons cause the lattice distortion of a DNA molecule, which result in a dependence of the conductance on ANIE. In the frame work of one dimensional tight binding model, with a standard transfer matrix formalism [23], the transmission coefficients, DOS and the resistivity of Poly(dG)-Poly(dC) were calculated. The calculation represents that the resistivity of Poly(dG)-Poly(dC) with half filled itinerant electrons is in the order of $10^{-2} \, \text{Ωcm}$. This is consistent with the experiment result [9]. From this we infer that the itinerant electrons should be half filled in its thermal equilibrium state, but the filling rate may have a departure from its thermal equilibrium state influenced by preparation condition. The calculation also shows that Poly(dG)-Poly(dC) has good conductivity as the filling rate is low or high. That suggests we can improve the conductivity of Poly(dG)-Poly(dC) by photoexcitation or doping in experiment.

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